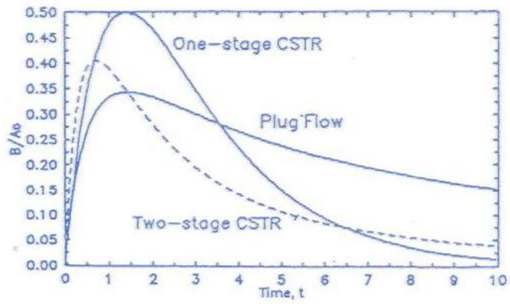
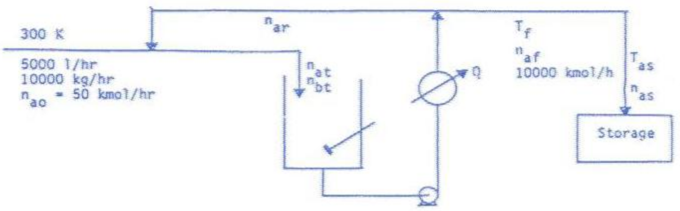
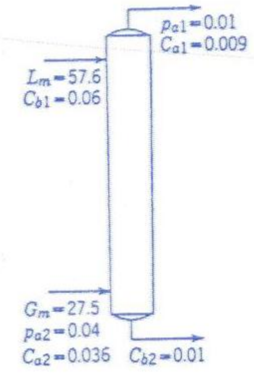
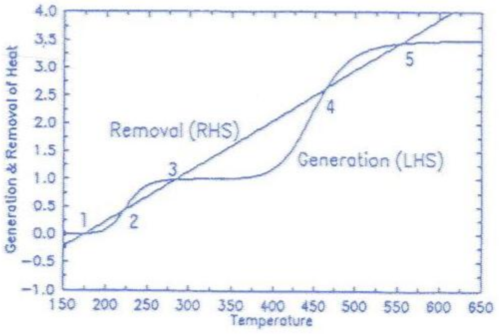
CHEMICAL REACTION ENGINEERING HANDBOOK OF SOLVED PROBLEMS

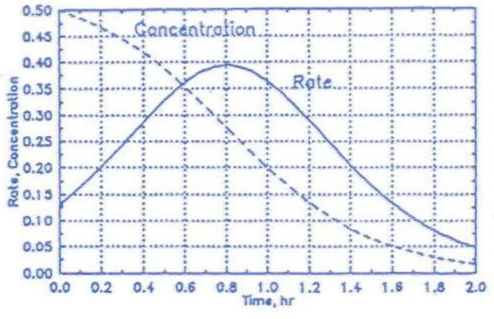
STANLEY M. WALAS

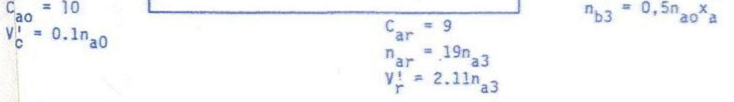


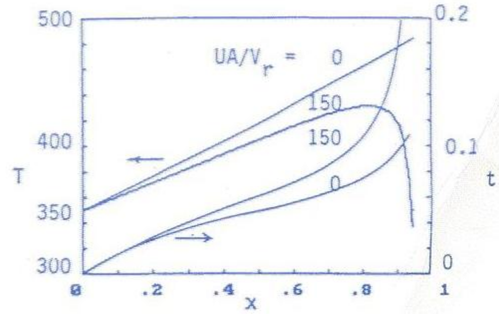












Gordon and Breach Publishers

Chemical Reaction Engineering
Handbook of Solved Problems

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CONTENTS

PROBLEMS P2.00.00

THEORY

PROBLEMS P3.00.00

THEORY

PROBLEMS P4.00.00

THEORY

PROBLEMS P5.00.00

THEORY

PREFACE

This book is a collection of solved problems in elementary chemical reaction kinetics from an engineer's point of view. Brief statements of definitions and theory begin each chapter, but detailed derivations of major formulas largely are left as problems to be solved. Some of the problems are original to the extent that "originality" is possible in an area that has been worked over for so many years. Those taken from the literature and textbooks often are modified and provided with solutions when they are not in the original, which is usually the case. The List of Sources of Some Problems may be consulted for additional problems, although solutions usually are not provided in these references. Standard textbooks also should be consulted for systematic parallel or fuller treatment of some of the theory covered by this collection.

For the most part, the problems are quite short. The object has been to present a large variety of problems and exercises, including some replication for purposes of drill. Accordingly, comprehensive design-type problems largely have been avoided—those requiring detailed knowledge and data of other areas of engineering such as mass transfer or fluid dynamics or economics. The topics included are identified by chapter headings and subheadings. Briefly, they cover rate equations, analysis of rate data, sizes and performance of ideal reactors, residence time distributions and non-ideal models, solid catalyzed reactions, behavior of porous catalysts, and reactions involving mutliple phases.

Solutions are presented in the form of equations, tables, and graphs—most often the last. Serious numerical results generally have to be obtained with computers or powerful calculators. The introductory chapter describes the numerical procedures that are required. Inexpensive software has been used here for integration, differentiation, nonlinear equations, simultaneous equations, systems of differential equations, data regression, curve fitting, and graphing.

Students, other beginners in chemical engineering kinetics, and possibly experienced engineers who may wish to review their rusty knowledge should be able to profit from the opportunites of "learning by doing" provided by this collection.

Reactors are of course the basic equipment in any chemical plant. The large variety of substances that have been used in the research cited in the problems emphasize this point. Also cited are the many different kinds of equipment, analytical techniques, and methods of data analysis that have been used. The Indexes of Substances and Subjects are the keys to this information.

Inspiration for the material in this book was provided by several generations of students; I hope that the current generation may find it of value. The word processor ChiWriter of Horstmann Software, Inc. was used. I appreciate the interest shown by Dr. Reza Shams and Professor Bala Subramaniam during the often tedious course of preparation of the manuscript. My parents Stanislaus and Apolonia and my wife Suzy Belle were with me in spirit.

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SYMBOLS

A, B, C, . . .	names of substances, or their concentrations
$A^{\cdot}$	free radical, as $CH_3^{\cdot}$
C_a	concentration of substance A
C°	initial mean concentration in vessel, p. 506, 508
C_p	heat capacity
CSTR	Continuous Stirred Tank Reactor
D, D_e, D_x	dispersion coefficient, p. 500, 617, 629
D_{eff}	effective diffusivity, p. 721
D_K	Knudsen diffusivity, p. 721
$E(t)$	residence time distribution, p. 507, 508
$E(t_r)$	normalized residence time distribution, p. 508
f_a	$= C_a/C_{aO}$ or n_a/n_{aO}, fraction of A remaining unconverted
$F(t)$	Age Function of tracer, p. 506, 508
ΔG	Gibbs energy change, p. 249
Ha	Hatta number, p. 828, 829
ΔH_r	heat of reaction
K, K_e, K_y, K_ϕ	chemical equilibrium constant, p. 248
k, k_c, k_p	specific rate of reaction, p. 35, 103
L	length of path in reactor
n	parameter of Erlang or Gamma distribution, or number of stages in a CSTR battery, p. 497
n_a	number of mols of A present
n'_a	number of mols flowing per unit time, the prime (') may be omitted when context is clear
n_t	total number of mols

o	subscript designating initial or inlet conditions, as in C_{ao}, n_{ao}, V'_o, . . .
p_a	partial pressure of substance A
Pe	Peclet number for dispersion, p. 617
PFR	Plug Flow Reactor
Q	heat transfer rate
r	radial position
r_a	rate of reaction of A per unit volume, p. 34
R	radius of cylindrical vessel
Re	Reynolds number, p. 627, 717
Sc	Schmidt number, p. 627, 717
t	time
$\bar{t}$	mean residence time, p. 506, 508
t_r	$= t/\bar{t}$, reduced time
TFR	Tubular Flow Reactor
u	linear velocity
u(t)	unit step input, p. 492
V	volume of reactor contents
V'	volumetric flow rate
V_r	volume of reactor
x	axial position in a reactor
x_a	$= 1 - f_a = 1 - C_a/C_{ao}$ or $1 - n_a$, n_{ao}, fraction of A converted
z	$= x/L$, normalized axial position
β	$= r/R$, normalized radial position, p. 410
$\gamma^3(t)$	skewness of distribution, p. 507, 508
$\delta(t)$	unit impulse input, Dirac function, p. 492
ε	fraction void space in a packed bed
ϑ	$= t/\bar{t}$, reduced time
η	effectiveness of porous catalyst, p. 724
$\Lambda(t)$	intensity function, p. 492, 508
μ	viscosity

ν	$= \mu/\rho$, kinematic viscosity
π	total pressure
ρ	density
ρ	$= r/R$, normalized radial position in a pore, p. 723
$\sigma^2(t)$	variance, p. 507, 508
$\sigma^2(t_r)$	normalized variance, p. 507, 508
τ	$= t/\bar{t}$, reduced time
τ	tortuosity, p. 722
ϕ	Thiele modulus, p. 723
ϕ_m	modified Thiele modulus, p. 731

CHAPTER 1
MATHEMATICAL AND NUMERICAL METHODS

THEORY

PROBLEMS

The problems of this collection require numerical or graphical or sometimes analytical methods of solution. There is a large number of books and software on these topics. An outline with examples of these methods is the aim of this chapter. It is expected that the student will have access to some equivalents of the software used here for the solved problems and listed subsequently. Some of the work can be done with a programmable calculator, but not as easily as on a PC.

1.1. SOFTWARE

Of the following list, the first six items are the principal ones used here. All but TableCurve are currently available at reduced prices to students, but most of the required curvefitting also can be done with POLYMATH or AXUM. The last three items do analytical as well as numerical work.

1. POLYMATH. AIChE Cache Corp, P O Box 7939, Austin TX 78713-7939. Polynomial and cubic spline curvefitting, multiple linear regression, simultaneous ODEs, simultaneous linear and nonlinear algebraic equations, matrix manipulations, integration and differentiation of tabular data by way of curve fit of the data.

2. CONSTANTINIDES, Applied Numerical Methods with Personal Computers, McGraw-Hill, 1987. Nonlinear regression, partial differential equations, matrix manipulations, and a more flexible program for simultaneous ODEs.

3. CHAPRA & CANALE, Numerical Methods for Engineers, McGraw-Hill, 1988. Explains the methods but the diskette is limited. It does have the trapezoidal

rule for data in tabular or equation form.

4. SEQS simultaneous equation solver. CET, PO Box 2029, Norman OK 73070. Twenty simultaneous equations can be solved. The program seems to be superior to the one in POLYMATH.

5. AXUM. Trimetrix Inc, 444 NE Ravenna Blvd, Seattle WA 98115. High quality graphics and data analysis, including nonlinear regression.

6. TableCurve. Jandel Scientific, 65 Koch Road, Corte Madera CA 94925. Automatically fits 3000 different xy relations with statistical criteria.

7. MathCad Numerical Supplement. MathSoft 201 Broadway, Cambridge MASS 02139

8. Maple V. Brooks/Cole Publishing Company, Pacific Grove CA 93950.

9. Mathematica. Wolfram Research, 100 Trade Center Drive, Champaign ILLINOIS 61820-9910.

1.2. PLOTTING AND CURVE FITTING

Graphical representation and corresponding equations of tabular data are of value for interpolation, for revealing behavior patterns, and other purposes. The most complete software for this purpose is TableCurve. More limited but adequate for the present book are POLYMATH and MathCad. All spreadsheet software, for instance QuattroPro, can make plots of all kinds. In this book the most used software for making plots of tabular data and equations is AXUM which is also capable of fitting polynomials and nonlinear equations to tabular data. All of these commercial packages have tutorials and user friendly instructions.

1.3. REGRESSION OF TABULAR DATA

Regression is a process of representing tabular data, say (C,t), in equation form. The purpose may be

..For interpolation of intermediate values of C or t

..To obtain an equation, $C = f(t)$, that can be handled readily in a computer program

..To facilitate repeated differentiation or integration of the data.

The form of the equation is specified in advance, and the best correspnding values of any constants are found by least squares. The goodness of fit of several assumed equations are compared by statistical criteria such as the correlation coefficient or the F-test. When the number of sets of data equals the number of unknown constants in the equation, the constants are found by simultaneous solution. Otherwise a least squares regression is used.

Linearity refers to the unknown constants. The following are linear in this sense,

$$y = a+bx+cx^2 \text{ and } \ln y = a+b \ln x + c/x^2$$

but not

$$y = a + \frac{b}{x+c} \text{ and } y = \exp(a+\frac{b}{x})\ x^c$$

although the last can be linearized as

$$\ln y = a + \frac{b}{x} + c \ln x$$

There are four main classes of data regression.

1. Polynomial, $y = a_0 + a_1x + a_2x^2 + \dots$. Linear regression is a special case.

2. Multilinear, $y = a_0 + a_1x_1 + a_2x_2 + \dots$, where x_1, x_2, ... are independent variables or functions.

3. Nonlinear, say of two variables, x and y,

$$y_i = f(x_i;\ a_0,\ a_1,\ a_2, \ldots)$$

and the derivatives

$$\frac{\partial\Sigma}{\partial a_0} = \frac{\partial\Sigma}{\partial a_1} = \frac{\partial\Sigma}{\partial a_2} = \ldots = 0$$

of the least squares condition,

$$\Sigma[y_i - f(x_i;a_0,\ a_1,\ a_2,\ \ldots)]^2 \Rightarrow \text{Minimum}$$

are not linear in the unknown constants a_i.

4. Periodic data, using the Fast Fourier Transform.

These topics are explained in specialist books and briefly by CHAPRA & CANALE. Polynomial and multilinear regression programs are in POLYMATH and AXUM, nonlinear in CONSTANTINIDES and AXUM. No periodic data are regressed in the present collection.

Examples: Polynomial regression is applied in problem P1.03.02. Several examples of POLYMATH multilinear regression are in sections P3.06, P3.08 and P3.10. A non-linear regression is worked out in P1.02.07.

1.4. ROOTS OF NUMERICAL EQUATIONS

Methods for finding roots of numerical nonlinear equations first involve making estimates and subsequently improving them by some systematic procedure, ideal problems for implementation on computers. Many scientific calculators also have built-in capability for finding roots of single equations, for instance the HP-15C or HP-32SII.

1.4.1 SINGLE EQUATIONS

The Newton-Raphson method is based on the truncated Taylor expansion. If x_0 is an estimate for $f(x) = 0$, an improved value is

$$x = x_0 - kf(x_0)/f'(x_0)$$

where $f'(x) = df/dx$ and k is a positive fraction that is selected arbitrarily to speed convergence; $k = 1$ often is acceptable. When the derivative is awkward to find analytically, a finite difference equivalent can be used, for instance,

$$f'(x) = \frac{f(1.0001x)-f(x)}{0.0001x}$$

Then,

$$x = x_0 - k\,\frac{0.0001x_0f(x_0)}{f(1.0001x_0)-f(x_0)}$$

The factor 1.0001 is arbitrary and can be changed to improve convergence or accuracy.

Wegstein method. This does not require a derivative and usually converges more rapidly than the Newton-Raphson. The equation is put in the form

$$x = f(x)$$

When x_0 is the estimated value of the root and $x_1 = f(x_0)$, an improved value is

$$x = \frac{x_0f(x_1)-f(x_0)^2}{x_0+f(x_1)-2f(x_0)} = \frac{x_0f(x_1)-x_1^2}{x_0+f(x_1)-2x_1}$$

The process is repeated with the improved estimate as a start.

Polynomials, $a_0\ a_1x\ a_2x^2 + a_3x^3 + \ldots = 0$. Procedures for finding all real and complex roots are on the diskettes of CONSTANTINIDES and Al-Khafaji & Tooley (Computerized Numerical Analysis, 1986). For instance the roots of

$$x^6 - 3x^5 - 4x^4 - 9x^3 + 10x^2 + 2x + 3 = 0$$

are

$$x = -0.1438 \pm 0.1610j,\ -1.000 \pm 1.414j,\ 4.288,\ 1.000$$

1.4.2. SIMULTANEOUS LINEAR EQUATIONS

These are solved by matrix manipulations. Programs are in POLYMATH, CONSTANTINIDES AND CHAPRA & CANALE. When the number of equations is not large, a manual procedure can be used to eliminate one variable at a time by reduction of the leading coefficients to unity and appropriate additions and subtractions of the equations.

1.4.3. SIMULTANEOUS NONLINEAR EQUATIONS

The Newton-Raphson method for multiple equations also starts with truncated Taylor expansions. For the system

$$f(x,y,z) = 0,\ g(x,y,z) = 0,\ h(x,y,z) = 0$$

the corrections to initial estimates x_0, y_0, z_0 are a, b and c found from the linear system

$$f_0 + af_x + bf_y + xf_z = 0$$
$$g_0 + ag_x + bg_y + cg_z = 0$$
$$h_0 + ah_x + bh_y + ch_z = 0$$

where the functions and all the derivatives, for instance $f_x = \partial f/\partial x$, are evaluated at (x_0,y_0,z_0). Programs are on the diskettes of POLYMATH and SEQS. The speed of convergence and even the possibility of convergence depend on how close the estimates are to the correct values. It is of course possible that there may not be a solution in the range of interest, or there may be several solutions.

1.5. INTEGRATION & DIFFERENTIATION

Only a comparatively few forms of integrals are encountered in reaction kinetics. Some of the more complex ones are reducible with partial fractions. Table 1.1 of indefinite integrals and partial fractions supplies most needs.

When integrating between numerical limits it may be more convenient to proceed directly with a numerical integration rather than through an analytical integration, particularly when the coefficients and integration limits are long numbers, for example, the integral

$$\int_{1.27}^{10.93} \frac{x}{2.1x^2-3.78x+5.86}\,dx = 1.2811,\ \text{50 trapezoidal steps}$$

$$1.2815,\ \text{200 trapezoidal steps}$$

by CHAPRA & CANALE which takes a very simple input. Such a result may well be more reliable than the laborious evaluation of the analytical integral by way of item 11 of Table 1.1.

Softwares for numerical integration of equations include the calculator HP-32SII, POLYMATH, CONSTANTINIDES AND CHAPRA & CANALE. The last of these also can handle tabular data with variable spacing. POLYMATH fits a polynomial to the tabular data and then integrates. A comparison is made in problem P1.03.03 of the integration of an equation by the trapezoidal and Runge-Kutta rules. One hundred intervals with the trapezoidal rule takes little time and the result is usually accurate enough, so it is often convenient to standardize on this number.

For manual integration of tabular data, the trapezoidal or Simpson's rules usually are adequate. Between two points the trapezoidal rule is

$$\int_{x_1}^{x_2} y\,dx = 0.5(x_2-x_1)(y_1+y_2)$$

and between n points spaced equally with $\Delta x = x_n - x_{n-1}$ as interval,

$$\int_{x_0}^{x_n} ydx = \Delta x\left(\frac{y_0+y_n}{2} + y_1+y_2+\ldots+y_{n-1}\right)$$

Simpson's rule for three equally spaced points is

$$\int_{x_0}^{x_2} ydx = \frac{x_1-x_0}{3} (y_0+4y_1+y_2).$$

Differentiation. The main application of numerical differentiation in this book is to find a rate, dC/dt, from tabular data (C, t). In view of the availability of computer routines for fitting of polynomials and other equations to tabular data, this is the way to go, differentiating the curve fit equation analytically. POLYMATH can provide direct numerical values of derivatives and integrals from the curvefit result.

Numerical differentiation may be quite sensitive to the correlating equation. In problem P1.03.01, the results with four different curvefits do not agree well although the curvefits themselves are statistically satisfactory. In problem P1.0302, however, the agreement between the higher polynomial fits is more nearly acceptable.

1.6. ORDINARY DIFFERENTIAL EQUATIONS

Differential equations arise in reaction kinetics through application of two main fundamental rate laws, which are

1. The rate of reaction is proportional to the concentrations of the participants. Law of mass action.
2. The rate of transfer of mass (or heat) is proportional to the concentration gradient. Fick's law (or Newton-Fourier law).

1.6.1. FORMULATION

As a basis, a differential element of volume, dV_r = dxdydz, or time, dt, is identified. In cylindrical geometry, the element of volume may be a thin disk, Adz, if changes occur only in an axial direction, or a ring $2\pi rdrdz$, if changes occur both radially and axially.

To this element of space the conservation law is applied in the form

Inputs + Sources = Outputs + Sinks + Accumulations

where each of these terms may be a quantity or a rate. Inputs and Outputs are accomplished by crossing the boundary of the reference volume. In case of mass transfer this occurs by bulk flow and diffusion. Sources and Sinks are accretions and depletions of a species without crossing the boundaries. In a mass and energy balance, sinks are the rate of reaction, rdV_r, or a rate of enthalpy change, $-\Delta H_r \rho dC$. Accumulation is the time derivative of the content of the species within the reference volume, for example, $(\partial C/\partial t)dV_r$ or $C_p(\partial T/\partial t)\rho dV_r$.

Conversion of the differential balance to a differential equation follows after division throughout by the differentials of space and time. Boundary and initial conditions are specified to complete the physical description of the problem. With ordinary differential equations the number of such conditions is the same as the order of the equation. With partial differential equations, the safest rule to follow is that the problem be completely defined in a physical sense. For example, the condition of every entering and/or leaving stream must be defined, the initial state of the vessel must be known (or a final state if the initial is to be found), symmetry conditions (such as radial symmetry) must be recognized if they exist in the particular problem, and conditions at the boundary such as rate of heat transfer or rate of reaction or rate of diffusion must be formulated mathematically.

A detailed application of the conservation principle to the derivation of a second order equation is in problem P5.08.01.

1.6.2. INTEGRATION

Differential equations of the first order arise with application of the law of mass action under either steady or unsteady conditions, and second order with Fick's or Newton-Fourier laws. A particular problem may be represented by one equation or several that must be solved simultaneously.

Solutions of the commonest first order equations are listed in Table 1.2. Variables separable and first order linear are most often encountered. Exercises dealing with first order equations are in problem P1.05.05.

Sometimes an equation out of this classification can be altered to fit by change of variable. The equations with separable variables are solved with a table of integrals or by numerical means. Higher order linear equations with constant coefficients are solvable with the aid of Laplace Transforms. Some complex equations may be solvable by series expansions or in terms of higher functions, for instance the Bessel equation encountered in problem P7.02.07, or the equations of problem P2.02.17. In most cases a numerical solution is possible.

1.6.3. THE SECOND ORDER LINEAR ODE

Some problems with diffusion or dispersion give rise to the second order linear equation with constant coefficients,

$$\frac{d^2y}{dt^2} + 2k\omega\frac{dy}{dt} + \omega^2 y = f(t)$$

When $f(t) = 0$, the equation is called <u>homogeneous</u>. The general solution is the sum of the solution of the homogeneous equation and a complementary function which can be found by several means. The form of the homogeneous solution depends on the value of the <u>discriminant</u>, $D = k^2-1$, as tabulated.

Discriminant	Solution
Positive	$y = C_1\exp(\lambda_1 t)+C_2\exp(\lambda_2 t)$
Zero	$y = (C_1+C_2 t)\exp(-k\omega t)$
Negative	$y = \exp(-k\omega t)[C_1\cos(\omega t\sqrt{1-k^2})+C_2\sin(\omega t\sqrt{1-k^2})]$ $y = C\exp(-k\omega t)\cos(\omega t\sqrt{1-k^2}-\phi)$ $y = C\exp(-k\omega t)\sin(\omega t\sqrt{1-k^2}+\phi)$

where $\lambda_1,\lambda_2 = \omega(-k\mp\sqrt{D})$, $C = \sqrt{C_1^2+C_2^2}$, $\phi = \arctan(C_2/C_1)$

The complete solution of the non-homogeneous equation can be found directly in some cases by Laplace Transform, as the problems of section P1.04 show.

Several examples of second order equations are in problem section P5.08

1.6.4. LAPLACE TRANSFORM METHOD

The Laplace Transform of a function f(t) is defined as

$$L\{f(t)\} = f(s) = \bar{f} = \int_0^\infty f(t)\exp(-st)\,dt$$

Several notations are in use, as indicated. Tables 1.3 and 1.4 summarize various operations and provide some pairs of functions and their transforms.

Transformation replaces a differential equation with independent variable, t, to an algebraic equation in variable, s. The latter relation can be solved algebraically for the transform f(s). Then f(t) is found by inversion with Table 1.4. Problems P1.04.01 ff are examples. Cases of multiple reactions are treated this way in problems P2.02.08 and P2.02.10.

<u>Step and impulse inputs.</u> These discontinuous functions are used particularly in Chapter 5. Their definitions and transforms are:

Step: $H(t-a) = 0, \ t \le a$
$\qquad 1, \ t \ge a$

$$\mathcal{L}\{H(t-a)\} = \frac{1}{s}\exp(-as)$$

Impulse: $\delta(t-a) = 0, \ t \ne a$
$\qquad 1, \ t = a$

$$\mathcal{L}\{\delta(t-a)\} = \exp(-as)$$

The inverse of a transform with exp(-as) as one of the factors is

$$\mathcal{L}^{-1}\{f(s)\exp(-as)\} = f(t-a)\,H(t-a)$$
$$f(t-a), \ t \ge a$$
$$0, \ t \le a$$

<u>Example.</u> For the equation with a step input,

$$\frac{d^2f}{dt^2} + \omega^2 f = H(t-a)$$

$$f(s) = \frac{\exp(-as)}{s(s^2+\omega^2)}$$

and the solution is

$$f(t) = \frac{1}{\omega^2}\{1 - \cos[\omega(t-a)]\ H(t-a)$$

$$\frac{1}{\omega^2}\{1 - \cos[\omega(t-a)]\}, \ t \ge a$$

$$0, \ t \le a$$

With an impulse input,

$$\frac{d^2f}{dt^2} + \omega^2 f = \delta(t-a)$$

$$f(s) = \frac{\exp(-as)}{s^2+\omega^2}$$

$$f(t) = \frac{1}{\omega}\sin[\omega(t-a)]\ H(t-a)$$

$$\frac{1}{\omega}\sin[\omega(t-a)], \ t \ge a$$

$$0, \ t \le a$$

Problem P1.04.03 has a square pulse.

1.7. NUMERICAL SOLUTION OF ODEs

For numerical processing, a first order ODE is arranged explicitly for the derivative,

$$y' = \frac{dy}{dx} = f(x,y)$$

A procedure based on the truncated Taylor series is named after Euler. With increment h = Δx, successive values of y are

$$y_{i+1} = y_i + h\, f(x_i,y_i)$$

A substantial improvement employs the following iteration,

$$y^{(k+1)}_{i+1} = y_i^{(k)} + 0.5h[f(x_i,y_i)^{(k)} + f(x_{i+1},y_{i+1})^{(k)}]$$

where the superscript denotes a trial number at a particular value of i. This is called the Modified Euler Method.

Both POLYMATH and CONSTANTINIDES use this method and also a fourth order Runge-Kutta method. Other methods are available in other software, but these two are adequate for the present book.

Higher order ODEs are reduced to a set of first order equations for solution by these softwares. Thus the third order equation,

$$\frac{d^3y}{dx^3} = f(x,y, \frac{dy}{dx}, \frac{d^2y}{dx^2})$$

becomes the set

$$\frac{dy}{dx} = y', \quad \frac{dy'}{dx} = y'', \quad \frac{dy''}{dx} = y''' = f(x,y,y',y'')$$

The independent variable is x and the dependent variables are y, y', y'' and y'''.

Integration is started with known values of the dependent variables at one value of the independent variable, except when the "shooting method" is needed. Auxiliary algebraic equations can be entered to the program along with the differential equations and the boundary conditions.

1.7.1. POLYMATH PROGRAM

A variable name may have any combination of up to ten lower case letters and numbers. A typical equation entry is

$\frac{dx}{dt} = \frac{xy}{0.2+y} - 0.4z$	d(x)/d(t) = c-0.4*x*z
$\frac{dy}{dt} = - \frac{-2xy}{0.2+y}$	d(y)/d(t) = -2*c
$\frac{dz}{dt} = \frac{0.1xy}{0.2+y}$	d(z)/d(t) = 0.1*c
	c = x*y/(0.2+y)

with intial values t = 0, x_0 = 0.1, y_0 = 10, z_0 =0.

Note the parentheses in the derivatives. There is no choice of the number of integration intervals; it is supposedly adjusted to obtain a good precision. The output can be a graph or a table with 20 divisions of the independent variable. The scale of the ordinate is selected automatically to fit the range of the abscissa.

1.7.2. CONSTANTINIDES PROGRAM

The independent variable is always designated x and the dependent variables y(1), y(2), ... The derivative is designated

$$G(i) = \frac{dy(i)}{dx} = f[x, y(1), y(2),..., C(1), C(2),...)$$

where the C(i) are constants that are entered during the course of the solution and can be changed to obtain a range of solutions. In this nomenclature the equations of the POLYMATH example become,

$$G(1) = \frac{x*y(2)}{0.2+y(2)} - 0.4x*y(3) = c - 0.4*x*y(3)$$

$$G(2) = -\frac{0.2*x*y(2)}{0.2+y(2)} = -2*c$$

$$G(3) = \frac{0.1*x*y(2)}{0.2+y(2)} = 0.1*c$$

$$c = \frac{x*y(2)}{0.2+y(2)}$$

with initial values $x_0 = 0$, $y(1)_0 = 0.1$, $y(2)_0 = 10$, $y(3)_0 = 0$.

This program permits any number of intervals with a printout at each interval, and the ranges on the axes of the graph can be controlled.

1.7.3. SECOND ORDER EQUATIONS WITH TWO-POINT BOUNDARY CONDITIONS

Second order equations or a pair of first order equations require two conditions. When these are at the same value of x, say y_0 and $(dy/dx)_0$ at x_0, a numerical integration can be started. When one condition is y_0 at x_0 and the other is $(dy/dx)_L$ at x_L the shooting method can be applied. This consists of several steps:

1. Assume a value of $(dy/dx)_0$ at x_0.
2. Do the integration from x_0 to x_L. That result will provide both y_L and $(dy/dx)_L$.
3. The correct integration will be attained when the specified and calculated values of $(dy/dx)_L$ agree. This procedure also is described in Section 5.8.2. Numerical examples are problems P1.05.02 and P5.08.23 , as well as P5.08.02, P5.08.03, P5.08.11 and P5.08.12.

1.8. PARTIAL DIFFERENTIAL EQUATIONS

Common situations in reactors are when the conditions can vary with time and position as independent variables. Partial derivatives of dependent variables such as concentration and temperature with respect to each of the independent variables then are involved. Such an equation, for unsteady state dispersion in a cylindrical reactor, was derived in problem 5.08.01, namely

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + \frac{D_r}{r}\frac{\partial}{\partial r}(r\frac{\partial C}{\partial r}) - u\frac{\partial C}{\partial x} - kC^n$$

In this book PDEs appear primarily in Section 8.1 and problem section P8.01. Some simpler methods of solution are mentioned there: Separation of variables, application of finite differences and method of lines. Analytical solutions can be made of some idealized cases, usually in terms of infinite series, but the main emphasis in this area is on numerical procedures. Beyond the brief statements in Chapter 8, this material is outside the range of this book. Further examples are treated by WALAS (*Modeling with Differential Equations in Chemical Engineering*, 1991).

Table 1.1. Integrals and Partial Fractions

1. $$\int (ax + b)^n \, dx = \frac{1}{a(n+1)} (ax + b)^{n+1}. \quad (n \neq -1)$$

2. $$\int \frac{dx}{ax + b} = \frac{1}{a} \ln (ax + b).$$

3. $$\int \frac{x \, dx}{ax + b} = \frac{x}{a} - \frac{b}{a^2} \ln (ax + b).$$

4. $$\int \frac{x \, dx}{(ax + b)^2} = \frac{b}{a^2(ax + b)} + \frac{1}{a^2} \ln (ax + b).$$

5. $$\int \frac{dx}{x(ax + b)} = \frac{1}{b} \ln \frac{x}{ax + b}.$$

6. $$\int \frac{dx}{x^2(ax + b)} = -\frac{1}{bx} + \frac{a}{b^2} \ln \frac{ax + b}{x}.$$

7. $$\int \frac{dx}{(ax + b)(px + q)} = \frac{1}{bp - aq} \ln \frac{px + q}{ax + b}. \quad (bp - aq \neq 0)$$

8. $$\int \frac{x \, dx}{(ax+b)(px+q)} = \frac{1}{bp - aq} \left[\frac{b}{a} \ln (ax + b) - \frac{q}{p} \ln (px + q) \right]. \quad (bp - aq \neq 0)$$

9. $$\int \frac{dx}{ax^2 + bx + c} = \frac{1}{\sqrt{b^2 - 4ac}} \ln \frac{2ax + b - \sqrt{b^2 - 4ac}}{2ax + b + \sqrt{b^2 - 4ac}}. \quad (b^2 > 4ac)$$

10. $$\int \frac{dx}{ax^2 + bx + c} = -\frac{2}{2ax + b}. \quad (b^2 = 4ac)$$

11. $$\int \frac{x \, dx}{ax^2 + bx + c} = \frac{1}{2a} \ln (ax^2 + bx + c) - \frac{b}{2a} \int \frac{dx}{ax^2 + bx + c}.$$

12. $$\frac{1}{(x + a)(x + b)(x + c)} \equiv \frac{A}{x + a} + \frac{B}{x + b} + \frac{C}{x + c},$$

where $A = \dfrac{1}{(b - a)(c - a)}$, $B = \dfrac{1}{(a - b)(c - b)}$, $C = \dfrac{1}{(a - c)(b - c)}$

13. $$\frac{1}{(x + a)(x + b)(x + c)(x + d)} \equiv \frac{A}{x + a} + \frac{B}{x + b} + \frac{C}{x + c} + \frac{D}{x + d},$$

where $A = \dfrac{1}{(b - a)(c - a)(d - a)}$, $B = \dfrac{1}{(a - b)(c - b)(d - b)}$ etc.

14. $$\frac{1}{(a + bx^2)(f + gx^2)} \equiv \frac{1}{fb - ag} \left(\frac{b}{a + bx^2} - \frac{g}{f + gx^2} \right).$$

Table 1.2. Solutions of Ordinary Differential Equations of the First Order

1. *Variables separable.* The differential equation $f_1(x)g_1(y)\,dx + f_2(x)g_2(y)\,dy = 0$ has the solution

$$\int \frac{f_1(x)}{f_2(x)}\,dx + \int \frac{g_2(y)}{g_1(y)}\,dy = C$$

2. *Homogeneous equation.* The equation $dy/dx = f(y/x)$ has the solution

$$\ln x = \int \frac{dv}{f(v) - v} + C, \quad \text{where } v = \frac{y}{x}$$

3. *The linear equation* $dy/dx + f_1(x)y = g_2(x)$ has the solution

$$y = e^{-z}\left[\int f_2(x)e^{z}\,dx + C\right], \quad \text{where } z = \int f_1(x)\,dx$$

4. *Total or exact differential equation.* The equation $f_1(x, y)\,dx + f_2(x, y)\,dy = 0$ is exact when $\partial f_1/\partial y = \partial f_2/\partial x$. The solution is

$$\int f_1\,dx + \int \left[f_2 - \frac{\partial}{\partial y}\int f_1\,dx\right] dy = C$$

where y is constant when integrating with respect to x, and x is constant when integrating with respect to y. It may be possible to find an *integrating factor* μ that will make $\partial(\mu f_1)/\partial y = \partial(\mu f_2)/\partial x$.

5. *Explicitly solvable for one of the variables* in $F(x, y, p) = 0$.
   (a) *Solvable for p.* $F(x, y, p) = [p - f_1(x, y)][p - f_2(x, y)] \cdots = 0$. One integral is obtained for each factor $dy/dx - f_i(x, y) = 0$.
   (b) *Solvable for y.* $F(x, y, p) = [y - f_1(x, p)][y - f_2(x, p)] \cdots = 0$. Eliminate y from each factor by differentiation:

$$p = \frac{dy}{dx} = \frac{\partial f_i}{\partial x} + \frac{\partial f_i}{\partial p}\frac{dp}{dx}$$

   The solution will be $G(x, p, C) = 0$. It will be possible to eliminate the parameter p between the integral and the original differential equation. The final results will be $g_i(x, y, C) = 0$.
   (c) *Solvable for x.* $F(x, y, p) = [x - f_1(y, p)][x - f_2(x, p)] \cdots = 0$. Eliminate x from each factor by differentiation:

$$\frac{dx}{dy} = \frac{1}{p} = \frac{\partial f_i}{\partial y} + \frac{\partial f_i}{\partial p}\frac{dp}{dy}$$

   The solution will be $G(y, p, C) = 0$. It will be possible to eliminate the parameter p between the integral and the original differential equation. The final result will be $g_i(x, y, C) = 0$.

6. *Simultaneous linear differential equations with constant coefficients.* Take the pair

$$\frac{dx_1}{dt} = A_1x_1 + B_1x_2 + f_1(t) \qquad \text{and} \qquad \frac{dx_2}{dt} = A_2x_1 + B_2x_2 + f_2(t)$$

Apply the Laplace transform to each with $L(dx_i/dt) = s\bar{x}_i - x_{i0}$. Solve the resulting pair of linear algebraic equations for $\bar{x}_1 = g_1(s)$ and $\bar{x}_2 = g_2(s)$; then invert to $x_1 = h_1(t)$ and $x_2 = h_2(t)$ with the aid of a table of transforms.

TABLE 1.3. Laplace Transform Operations

$f(t)$	$F(s) \equiv \bar{f}(s)$
1. $f(t)$	$\int_0^\infty e^{-st} f(t)\, dt$
2. $\dfrac{df}{dt} = f'(t)$	$sF(s) - f(0)$
3. $\dfrac{d^2f}{dt^2} = f''(t)$	$s^2F(s) - f'(0) - sf(0)$
4. $f^{(n)}(t)$	$s^n F(s) - \sum_{k=0}^{n-1} s^k f^{(n-1-k)}(0)$
5. $f(t-a)$; $f(t) = 0, t < 0$.	$e^{-as} F(s)$
6. $t^n f(t)$	$(-1)^n F^{(n)}(s)$
7. $\int_0^t f(u)\, du$	$\dfrac{1}{s} F(s)$
8. $\int_0^t f(\theta) g(t-\theta)\, d\theta$	$F(s)G(s)$ (convolution theorem)
9. $\dfrac{\partial f(x,t)}{\partial x}$	$\dfrac{\partial F(x,s)}{\partial x}$
10. $\dfrac{\partial f(x,t)}{\partial t}$	$sF(x,s) - f(x,0)$
11. $\dfrac{\partial^2 f}{\partial x^2}$	$\dfrac{\partial^2 F(x,s)}{\partial x^2}$
12. $\dfrac{\partial^2 f}{\partial x\, \partial t}$	$s\dfrac{\partial F(x,s)}{\partial x} - \dfrac{\partial f(x,0)}{\partial x}$
13. $\dfrac{\partial^2 f}{\partial t^2}$	$s^2F(x,s) - sf(x,0) - \dfrac{\partial f(x,0)}{\partial t}$
14. Initial value theorem.	$\lim_{t\to 0} = \lim_{s\to\infty} sF(s)$
15. Final value theorem:	$\lim_{t\to\infty} = \lim_{s\to 0} sF(s)$

Table 1.4. Laplace Transform Pairs

$F(s)$	$f(t)$, $0 \le t$
1. 1	$\delta(t)$ unit impulse at $t = 0$
2. $\frac{1}{s}$	1 or $H(t)$ unit step starting at $t = 0$
3. $\frac{1}{s^2}$	$tH(t)$ ramp function
4. $\frac{1}{s^n}$	$\frac{1}{(n-1)!}t^{n-1}$ n = positive integer
5. $\frac{1}{s}e^{-as}$	$H(t-a)$ unit step starting at $t = a$
6. $\frac{1}{s}(1-e^{-as})$	$H(t) - H(t-a)$ rectangular pulse
7. $\frac{1}{s+a}$	e^{-at} exponential decay
8. $\frac{1}{(s+a)^n}$	$\frac{1}{(n-1)!}t^{n-1}e^{-at}$ n = positive integer
9. $\frac{1}{s(s+a)}$	$\frac{1}{a}(1-e^{-at})$
10. $\frac{1}{s(s+a)(s+b)}$	$\frac{1}{ab}\left(1 - \frac{b}{b-a}e^{-at} + \frac{a}{b-a}e^{-bt}\right)$
11. $\frac{s+\alpha}{s(s+a)(s+b)}$	$\frac{1}{ab}\left[\alpha - \frac{b(\alpha-a)}{b-a}e^{-at} + \frac{a(\alpha-b)}{b-a}e^{-bt}\right]$
12. $\frac{1}{(s+a)(s+b)}$	$\frac{1}{b-a}(e^{-at} - e^{-bt})$
13. $\frac{s}{(s+a)(s+b)}$	$\frac{1}{a-b}(ae^{-at} - be^{-bt})$
14. $\frac{s+\alpha}{(s+a)(s+b)}$	$\frac{1}{b-a}[(\alpha-a)e^{-at} - (\alpha-b)e^{-bt}]$
15. $\frac{1}{(s+a)(s+b)(s+c)}$	$\frac{e^{-at}}{(b-a)(c-a)} + \frac{e^{-bt}}{(c-b)(a-b)} + \frac{e^{-ct}}{(a-c)(b-c)}$
16. $\frac{s+\alpha}{(s+a)(s+b)(s+c)}$	$\frac{(\alpha-a)e^{-at}}{(b-a)(c-a)} + \frac{(\alpha-b)e^{-bt}}{(c-b)(a-b)} + \frac{(\alpha-c)e^{-ct}}{(a-c)(b-c)}$
17. $\frac{\omega}{s^2+\omega^2}$	$\sin \omega t$
18. $\frac{s}{s^2+\omega^2}$	$\cos \omega t$
19. $\frac{s+\alpha}{s^2+\omega^2}$	$\frac{\sqrt{\alpha^2+\omega^2}}{\omega}\sin(\omega t + \phi)$, $\phi = \arctan\frac{\omega}{\alpha}$
20. $\frac{s\sin\theta + \omega\cos\theta}{s^2+\omega^2}$	$\sin(\omega t + \theta)$
21. $\frac{1}{s(s^2+\omega^2)}$	$\frac{1}{\omega^2}(1-\cos\omega t)$
22. $\frac{s+\alpha}{s(s^2+\omega^2)}$	$\frac{\alpha}{\omega^2} - \frac{\sqrt{\alpha^2+\omega^2}}{\omega^2}\cos(\omega t + \phi)$; $\phi = \arctan\frac{\omega}{\alpha}$
23. $\frac{1}{(s+a)(s^2+\omega^2)}$	$\frac{e^{-at}}{a^2+\omega^2} + \frac{1}{\omega\sqrt{a^2+\omega^2}}\sin(\omega t - \phi)$; $\phi = \arctan\frac{\omega}{a}$
24. $\frac{1}{(s+a)^2+b^2}$	$\frac{1}{b}e^{-at}\sin bt$
24a. $\frac{1}{s^2+2\zeta\omega_n s+\omega_n^2}$	$\frac{1}{\omega_n\sqrt{1-\zeta^2}}e^{-\zeta\omega_n t}\sin \omega_n\sqrt{1-\zeta^2}\,t$
25. $\frac{s+a}{(s+a)^2+b^2}$	$e^{-at}\cos bt$

Table 1.4 (continued)

26.	$\dfrac{s+\alpha}{(s+a)^2+b^2}$	$\dfrac{\sqrt{(\alpha-a)^2+b^2}}{b}e^{-at}\sin(bt+\phi);\quad \phi=\arctan\dfrac{b}{\alpha-a}$
27.	$\dfrac{1}{s[(s+a)^2+b^2]}$	$\dfrac{1}{a^2+b^2}+\dfrac{1}{b\sqrt{a^2+b^2}}e^{-at}\sin(bt-\phi);\quad \phi=\arctan\dfrac{b}{-a}$
27a.	$\dfrac{1}{s(s^2+2\zeta\omega_n s+\omega_n^2)}$	$\dfrac{1}{\omega_n^2}-\dfrac{1}{\omega_n^2\sqrt{1-\zeta^2}}e^{-\zeta\omega_n t}\sin(\omega_n\sqrt{1-\zeta^2}\,t+\phi);\quad \phi=\arccos\zeta$
28.	$\dfrac{s+\alpha}{s[(s+a)^2+b^2]}$	$\dfrac{\alpha}{a^2+b^2}+\dfrac{1}{b}\sqrt{\dfrac{(\alpha-a)^2+b^2}{a^2+b^2}}e^{-at}\sin(bt+\phi);\quad \phi=\arctan\dfrac{b}{\alpha-a}-\arctan\dfrac{b}{-a}$
29.	$\dfrac{1}{(s+c)[(s+a)^2+b^2]}$	$\dfrac{e^{-ct}}{(c-a)^2+b^2}+\dfrac{e^{-at}\sin(bt-\phi)}{b\sqrt{(c-a)^2+b^2}};\quad \phi=\arctan\dfrac{b}{c-a}$
30.	$\dfrac{1}{s(s+c)[(s+a)^2+b^2]}$	$\dfrac{1}{c(a^2+b^2)}-\dfrac{e^{-ct}}{c[(c-a)^2+b^2]}+\dfrac{e^{-at}\sin(bt-\phi)}{b\sqrt{a^2+b^2}\sqrt{(c-a)^2+b^2}};$ $\phi=\arctan\dfrac{b}{-a}+\arctan\dfrac{b}{c-a}$
31.	$\dfrac{s+\alpha}{s(s+c)[(s+a)^2+b^2]}$	$\dfrac{\alpha}{c(a^2+b^2)}+\dfrac{(c-\alpha)e^{-ct}}{c[(c-a)^2+b^2]}+\dfrac{\sqrt{(\alpha-a)^2+b^2}}{b\sqrt{a^2+b^2}\sqrt{(c-a)^2+b^2}}e^{-at}\sin(bt+\phi);$ $\phi=\arctan\dfrac{b}{\alpha-a}-\arctan\dfrac{b}{-a}-\arctan\dfrac{b}{c-a}$
32.	$\dfrac{1}{s^2(s+a)}$	$\dfrac{1}{a^2}(at-1+e^{-at})$
33.	$\dfrac{1}{s(s+a)^2}$	$\dfrac{1}{a^2}(1-e^{-at}-ate^{-at})$
34.	$\dfrac{s+\alpha}{s(s+a)^2}$	$\dfrac{1}{a^2}[\alpha-\alpha e^{-at}+a(a-\alpha)te^{-at}]$
35.	$\dfrac{s^2+\alpha_1 s+\alpha_0}{s(s+a)(s+b)}$	$\dfrac{\alpha_0}{ab}+\dfrac{a^2-\alpha_1 a+\alpha_0}{a(a-b)}e^{-at}-\dfrac{b^2-\alpha_1 b+\alpha_0}{b(a-b)}e^{-bt}$
36.	$\dfrac{s^2+\alpha_1 s+\alpha_0}{s[(s+a)^2+b^2]}$	$\dfrac{\alpha_0}{c^2}+\dfrac{1}{bc}[(a^2-b^2-\alpha_1 a+\alpha_0)^2+b^2(\alpha_1-2a)^2]^{1/2}e^{-at}\sin(bt+\phi);$ $\phi=\arctan\dfrac{b(\alpha_1-2a)}{a^2-b^2-\alpha_1 a+\alpha_0}-\arctan\dfrac{b}{-a};\quad c^2=a^2+b^2$

P1.01.01. CURVE FIT OF ORIGINAL AND LINEARIZED DATA

Vapor pressure data of toluene, in °C and Torr, are

T	-26.7	-4.4	6.4	18.4	31.8	40.3	51.9	69.5	89.5	110.6
p	1	5	10	20	40	60	100	200	400	760

The Antoine equation is fitted to the data in the original and linearized forms,

$$p = \exp\left(a + \frac{b}{T+273.2}\right) \text{ and } \ln p = a + \frac{b}{T+273.2}.$$

The two TableCurve plots show that the constants are a = 18.62 and b = -4570, exactly the same in the two cases.

The modified Antoine equation, however,

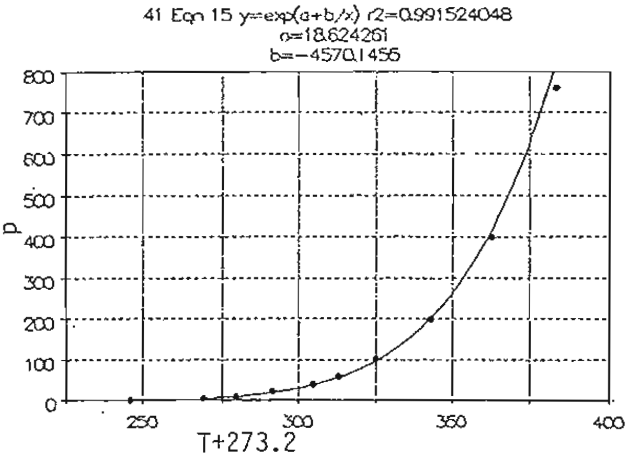
$$\ln p = A - \frac{B}{T+D}$$

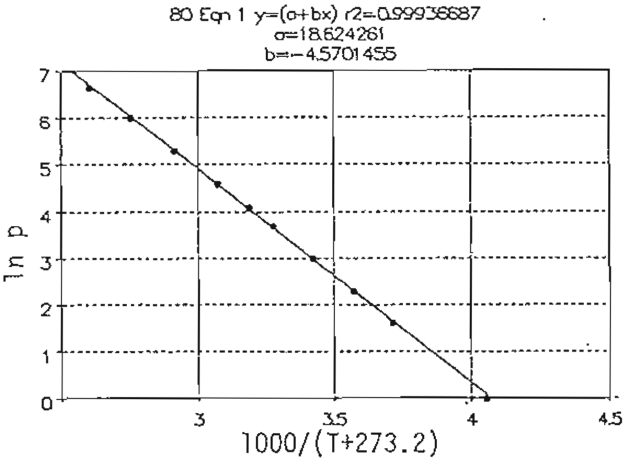
cannot be linearized. Although this form is not in the TableCurve repertory, the following relation can be used,

$$y = \frac{a+cx}{1+bx} = A - \frac{B}{x+D}$$

where

$$A = c/b,\ D = 1/b,\ B = D(A-a)$$





P1.01.02. POLYNOMIAL REGRESSION

A quadratic equation will be fitted to N sets of data, (x_i, y_i), by least squares.

$$y = a_0 + a_1x + a_2x^2$$

$$\Sigma[y_i - (a_0+a_1x+a_2x^2)]^2 \Rightarrow \text{Minimum}$$

On setting

$$\frac{\partial\Sigma}{\partial a_0} = \frac{\partial\Sigma}{\partial a_1} = \frac{\partial\Sigma}{\partial a_2} = 0,$$

the resulting "normal equations" are

$$a_0N + a_1\Sigma x_i + a_2\Sigma x_i^2 = \Sigma y_i$$

$$a_0\Sigma x_i + a_1\Sigma x_i^2 + a_2\Sigma x_i^3 = \Sigma x_iy_i$$

$$a_0\Sigma x_i^2 + a_1\Sigma x_i^3 + a_2\Sigma x_i^4 = \Sigma x_i^2 y_i$$

The various sums are tabulated below so the normal equations become

$$11a_0 + 6.01a_1 + 4.6545a_2 = 5.905$$
$$6.01a_0 + 4.6545a_1 + 4.1150a_2 = 2.1839$$
$$4.6545a_0 + 4.1150a_1 + 3.9161a_2 = 1.3357$$

and the correlation becomes

$$y = 0.998 - 1.018x + 0.225x^2$$

x_i	0.05	0.11	0.15	0.31	0.46	0.52	0.70	0.74	0.82	0.98	1.17
Y_i	0.956	0.890	0.832	0.717	0.571	0.539	0.378	0.370	0.306	0.242	0.104

$\sum x_i = 6.01$

$\sum x_i^2 = 4.6545$

$\sum x_i^3 = 4.1150$

$\sum x_i^4 = 3.9161$

$N = 11$

$\sum Y_i = 5.905$

$\sum x_i Y_i = 2.1839$

$\sum x_i^2 Y_i = 1.3357$

P1.01.03. MULTILINEAR REGRESSION

The data of the first three columns of the table are to be fitted to the equation

$$y = a_0 + a_1x_1 + a_2x_2$$

The least squares criterion is

$$\Sigma[y_i - (a_0+a_1x_1+a_2x_2)]^2 \Rightarrow \text{Minimum}$$

Applying

$$\frac{\partial\Sigma}{\partial a_0} = \frac{\partial\Sigma}{\partial a_1} = \frac{\partial\Sigma}{\partial a_2} = 0$$

makes the normal equations

$$a_0N + a_1\Sigma x_{1i} + a_2\Sigma x_{2i} = \Sigma y_i$$
$$a_0\Sigma x_{1i} + a_1\Sigma x_{1i}^2 + a_2\Sigma x_{1i}x_{2i} = \Sigma x_{1i}y_i$$
$$a_0\Sigma x_{2i} + a_1\Sigma x_{1i}x_{2i} + a_2\Sigma x_{2i}^2 = \Sigma x_{2i}y_i.$$

On substituting the various summations from the table, the equations are

$$6a_0 + 16.5a_1 + 14a_2 = 54$$
$$16.5a_0 + 76.25a_1 + 48a_2 = 243.5$$
$$14a_0 + 48a_1 + 54a_2 = 100$$

The solution is

$$y = 5 + 4x_1 - 3x_2.$$

	y	x_1	x_2	x_1^2	x_2^2	x_1x_2	x_1y	x_2y
	5	0	0	0	0	0	0	0
	10	2	1	4	1	2	20	10
	9	2.5	2	6.25	4	5	22.5	18
	0	1	3	1	9	3	0	0
	3	4	6	16	36	24	12	18
	27	7	2	49	4	14	189	54
Σ	54	16.5	14	76.25	54	48	243.5	100

P1.01.04. NONLINEAR REGRESSION

The normal equations will be written for the least squares regression of the nonlinear equation for N sets of data, (x_i, y_i),

$$y = a + \frac{b}{x+c}$$

The least squares criterion is

$$\Sigma\ [y_i - (a+\frac{b}{x_i+c})]^2 \Rightarrow \text{Minimum}$$

$$\frac{\partial\Sigma}{\partial a} = \frac{\partial\Sigma}{\partial b} = \frac{\partial\Sigma}{\partial c} = 0$$

$$\frac{\partial\Sigma}{\partial a} = 2[\Sigma(y_i - a - \frac{b}{x+c})] = 0$$

$$aN + b\Sigma\ \frac{1}{x_i+c} = \Sigma y_i \qquad (1)$$

$$\frac{\partial\Sigma}{\partial b} = 2[\Sigma(y_i - a - \frac{b}{x+c})(-\ \frac{1}{x_i+c})] = 0$$

$$a\Sigma\ \frac{1}{x_i+c} + b\Sigma(\frac{1}{x_i+c)})^2 = \Sigma\ \frac{y_i}{x_i+c} \qquad (2)$$

$$\frac{\partial\Sigma}{\partial c} = 2[\Sigma(y_i - a - \frac{b}{x_i+c})(\frac{b}{(x_i+c)^2})] = 0$$

$$a\Sigma(\frac{1}{x+c})^2 + b\Sigma(\frac{1}{x_i+c})^3 = \Sigma\ \frac{y_i}{(x_i+c)^2} \qquad (3)$$

Equations 1, 2, and 3 are nonlinear in a, b and c. In principle they could be solved simultaneously, but an improved technique is explained in problem P1.01.05.

P1.01.05. NONLINEAR REGRESSION BY THE NEWTON-GAUSS METHOD

Take the case of a function of one variable and two constants,

$y_i = f(x_i;\ a,\ b)$.

Estimates of the values of the constants are made. For the j-th iteration they will be called a_j and b_j and corrected values will be

$$a_{j+1} = a_j + \Delta a,\ b_{j+1} = b_j + \Delta b \qquad (1)$$

Represent the function by the truncated Taylor series,

$$f(x_i)_{j+1} = f(x_i)_j + (\frac{\partial f(x_i)}{\partial a})_j\ \Delta a + (\frac{\partial f(x_i)}{\partial b})_j\ \Delta b$$

$$= f + f_a\Delta a + f_b\Delta b \qquad (2)$$

The least squares criterion is

$$\Sigma[y_i - f(x_i)_{j+1}]^2 = \Sigma[y_i - (f+f_a\Delta a+f_b\Delta b)]^2 \Rightarrow \text{Minimum}$$

The function and the derivatives are evaluated at the trial values a_j and b_j of the constants. On placing

$$\frac{\partial\Sigma}{\partial a} = \frac{\partial\Sigma}{\partial b} = 0$$

the normal equations become

$$\Sigma[(y_i-f-f_a\Delta a-f_b\Delta b)(-f_a)] = 0$$
$$\Sigma[(y_i-f-f_a\Delta a-f_b\Delta b)(-f_b)] = 0$$

or

$$\Delta a\Sigma f_a^2 + \Delta b\Sigma f_a f_b = \Sigma(y_i-f)f_a \qquad (3)$$

$$\Delta a\Sigma f_a f_b + \Delta b\Sigma f_b^2 = \Sigma(y_i - f)f_b \quad (4)$$

where

$$f = f(x_i)_j,\ f_a = \left(\frac{\partial f(x_i)}{\partial a}\right)_j,\quad f_b = \left(\frac{\partial f(x_i)}{\partial b}\right)_j \quad (5)$$

Solve for Δa and Δb from (3) and (4), substitute into (1) and repeat the procedure. Continue until values of Δa and Δb are near enough to zero.

P1.01.06. NEWTON-GAUSS METHOD. NUMERICAL EXAMPLE

Data of the first two columns of the table are to be fitted to the equation

$$y = f(x) = \exp\left(a+\frac{b}{x+c}\right)$$

Trial values of the constants are

$$a_j = 18.6,\ b_j = -4.57$$

The derivatives are

$$f_a = \frac{\partial f}{\partial a} = \exp(a+b/x_i)$$

$$f_b = \frac{\partial f}{\partial b} = \left(\frac{1}{x_i}\right)\exp(a+ b/x_i)$$

Corresponding values of the function and the derivatives are tabulated. The various summations are

$$\Sigma f_a^2 = 0.61(10^6),\ \Sigma f_b^2 = 4.26(10^6),\ \Sigma f_a f_b = 1.61(10^6),$$
$$\Sigma(y-f)f_a = 5720,\ \Sigma(y-f)f_b = 15624$$

Eqs (3) and (4) of problem P1.01.05 become

$$0.61\Delta a + 1.61\Delta b = 5720(10^{-6}) \quad (3)$$

$$1.61\Delta a + 4.26\Delta b = 15624(10^{-6}) \quad (4)$$

Accordingly

$$\Delta a = -0.1084,\ \Delta b = 0.04498$$

and corrected trial values of the constants are

$$a = 18.6-0.1084 = 18.492,\ b = -4.57+0.045 = -4.525$$

1/x	y	f	f_a	f_b
3.72	5	4.95	4.95	18.42
3.43	20	18.63	18.63	63.91
3.19	60	55.8	55.8	178.0
2.92	200	191.6	191.6	559.5
2.62	760	754.9	754.9	1978.0

P1.02.01. ROOTS OF A SINGLE EQUATION

The equation is

$$y = -1 + 0.7x\exp[0.5(1-x)^2] + 1.2(1-x)\exp(.5x^2) = 0$$

or

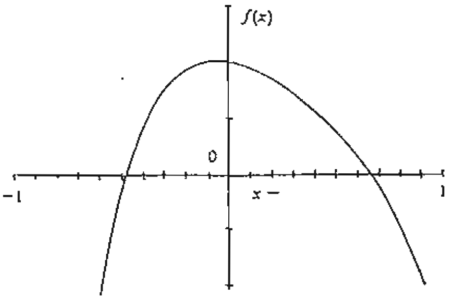
$$x = \frac{1 - 1.2(1-x)\exp(.5x^2)}{0.7\exp[.5(1-x)^2]}$$

The derivative is

$$\frac{dy}{dx} = (x^2 - x + 1)\{0.7\exp[0.5(1-x)^2] - 1.2\exp(0.5x^2)\}$$

The plot shows that the roots are approximately -0.47 and +0.65. However, to test the Newton-Raphson and Wegstein methods, starting values were assumed -1 and +1. The successive evaluations are tabulated. Wegstein is a little faster for the negative root but a little slower for the positive one.

Trial	NR	NR	Weg	Weg
0	-1	1	-1	1
1	-0.7687857	0.76534	-0.495743	0.85931
2	-0.4971118	0.66673	-0.470811	0.73556
3	-0.4721097	0.65458	-0.470626	0.66884
4	-0.4706308	0.65442		0.65492
5	-0.4706259	0.65442		0.65442
6	-0.4706259			



P1.02.02. PROGRAMS FOR ROOTS OF SINGLE EQUATIONS

Programs are written in QUICKBASIC for the Newton-Raphson method with analytical or numerical derivatives and the Wegstein method. The particular equation is entered following line 30. The one used here is from problem P1.02.01.

```
   ! N-R SOLUTION OF Y=F(X)=0 WITH
   ANALYTICAL DERIVATIVE
   SHORT X
   INPUT X
   PRINT X
10 GOSUB 30
   H=Y/Y1
   X=X-H
   PRINT X
   IF ABS(H/X)<=.0001 THEN 20
   GOTO 10
20 END
30 ! SR FOR Y AND Y1
   Y=-1+.7*X*EXP(.5*(1-X)^2)+1.2*(1-X)*EXP
   (.5*X^2)
   Y1=(X^2-X+1)*(.7*EXP(.5*(1-X)^2)-1.2*
   EXP(.5*X^2))
   RETURN
```

```
   ! N-R SOLUTION OF Y=F(X)=0 WITH
   NUMERICAL DERIVATIVE
   SHORT X
   INPUT X
   PRINT X
10 GOSUB 30
   Y1=Y
   X=1.0001*X
   GOSUB 30
   Y2=Y
   H=.0001*X*Y1/(Y2-Y1)
   X=X/1.0001-H
   PRINT X
   IF ABS(H/X)<=.0001 THEN 20
   GOTO 10
20 END
30 ! SR FOR Y=F(X)
   Y=-1+.7*X*EXP(.5*(1-X)^2)+1.2*(1-X)*EXP
   (.5*X^2)
   RETURN
```

```
   ! WEGSTEIN SOL'N OF X=F(X)
   SHORT X
   INPUT X1
   PRINT X1
   X=X1
10 X2=X
   GOSUB30
   X=Y1
   GOSUB30
   X=(X2*Y1-X^2)/(X1+Y1-2*X)
   IF ABS((X-Y1)/(X+Y1))≤=.0001 THEN 20
   PRINT X
   X1=X
   GOTO 10
20 END
30 ! SR FOR Y1=X=F(X)
   Y1=(1-1.2*(1-X)*EXP(.5*X^2))/.7/EXP(.5*
   (1-X)^2)
   RETURN
```

P1.02.03. MULTIPLE LINEAR EQUATIONS

A set of linear equations can be solved by a variety of procedures. In principle the method of determinants is applicable to any number of equations but for large systems other methods require much less numerical effort. The method of Gauss illustrated here eliminates one variable at a time, ends up with a single variable and finds all the roots by a reverse procedure.

In the example, each of the four equations are divided by the leading coefficient, 2.0, of the first equation. By appropriate additions and subtractions the variable x_1 is eliminated from the second, third and fourth equations. Similarly x_2 is eliminated from the third and fourth equations, and so on. The second group of equations is the result. By a reverse procedure, all variables are evaluated by the third group of equations.

$$\left.\begin{aligned} 2.0x_1+1.0x_2-0.1x_3+1.0x_4&=2.7,\\ 0.4x_1+0.5x_2+4.0x_3-8.5x_4&=21.9,\\ 0.3x_1-1.0x_2+1.0x_3+5.2x_4&=-3.9,\\ 1.0x_1+0.2x_2+2.5x_3-1.0x_4&=9.9. \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} x_1+0.5x_2-0.05x_3+0.5x_4 &=1.35,\\ x_2+13.40x_3-29.00x_4 &=71.20,\\ x_3-1.72298x_4&=4.72298,\\ 1.11998x_4&=-1.11998. \end{aligned}\right\} \quad (2)$$

$$\left.\begin{aligned} x_4&=-1.00000,\\ x_3&=4.72298-1.72298=3.00000,\\ x_2&=71.20-13.40\cdot 3+29.0=2.00000,\\ x_1&=1.35-0.5\cdot 2+0.05\cdot 3+0.5=1.00000. \end{aligned}\right\} \quad (3)$$

P1.02.04. SOLUTION AFTER LINEARIZATION

For the rate equation

$$r = kC_a^{\alpha}C_b^{\beta}$$

data are

C_a	C_b	r
0.7	0.2	0.4567
0.9	0.3	1.0707
1.6	0.2	2.5917

Linearize the equation and substitute data.

$$\ln 0.4567 = \ln k + \alpha \ln 0.7 + \beta \ln 0.2$$
$$\ln 1.0707 = \ln k + \alpha \ln 0.9 + \beta \ln 0.3$$
$$\ln 2.5917 = \ln k + \alpha \ln 1.6 + \beta \ln 0.2$$

The solution by determinants is

$$r = 3.5C_a^{2.1}C_b^{0.8}$$

P1.02.05. A LINEAR RELATION WITH THREE CONSTANTS

Data of the first three columns of the table are to be used to find the constants of the rate equation

$$r = kC_a^pC_b^q$$

In the linearized form,

$$\ln r = \ln k + p \ln C_a + q \ln C_b$$

or in the simplified notation,

$$y = w + \alpha p + \beta q$$

POLYMATH multilinear regression could be used to find the constants w, p and q but the problem will be solved directly.

The least squares condition is

$$\Sigma(w + \alpha_i p + \beta_i q - y_i)^2 \Rightarrow \text{Minimum}$$

Apply

$$\frac{\partial\Sigma}{\partial w} = \frac{\partial\Sigma}{\partial p} = \frac{\partial\Sigma}{\partial q} = 0$$

to obtain the normal equations

$$Nw + p\Sigma\alpha_i + q\Sigma\beta_i = \Sigma y_i \qquad (1)$$

$$w\Sigma\alpha_i + p\Sigma\alpha_i^2 + q\Sigma\alpha_i\beta_i = \Sigma\alpha_i y_i \qquad (2)$$

$$w\Sigma\beta_i + p\Sigma\alpha_i\beta_i + q\Sigma\beta_i^2 = \Sigma\beta_i y_i \qquad (3)$$

The various summations are evaluated from the data of the table and substituted into (1), (2) and (3). The following groups of equations are for successive eliminations of the variables w, p and q. The coefficients are listed.

w	p	q	RHS
5	3.1135	4.3663	11.349
3.1135	2.6914	2.1611	7.9345
4.3663	2.1611	4.2609	9.3730
1	0.6227	0.8727	2.2870
0	0.7526	-0.5560	0.8139
0	-0.5578	0.4504	-0.6127
	1	-0.7388	1.0815
	0	0.8625	-1.2160

From the last line, $q = -1.2160/0.8625 = -1.4098$. Then $p = 1.0815+0.7388(-1.4098) = 0.03994$. Finally,

$w = \ln k = 3.492$, and $k = 32.85$

so the rate equation is

$$r = 32.85C_a^{0.04}C_b^{-1.41}$$

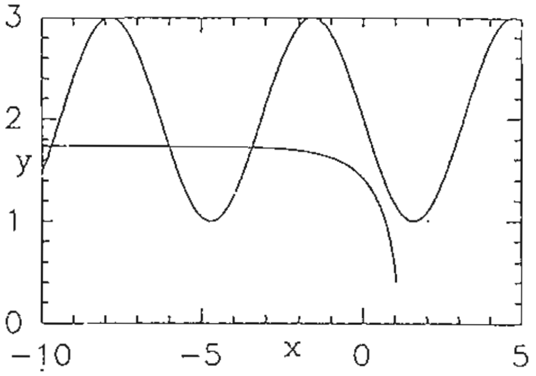
Values from this equation are listed in the last column of the table. The agreement is only fair.

C_a	C_b	r_{data}	r_{calc}
3	1.5	15.91	19.37
2.5	2.0	13.98	12.82
2	2.5	11.18	9.28
1.5	3.0	7.955	7.09
1.0	3.5	4.677	5.61

P1.02.06. A CASE OF MULTIPLE SOLUTIONS

The pair of equations $\sin x + y = 2$ and $\exp x + y^2 = 3$ are plotted to estimate the solution. SEQS is used to obtain accurate values of the roots.

Trial		
x	*y*	Converged Values
−2	1.7	Does not converge
−4	1	−3.42267, 1.72261
−4.5	1	−3.42267, 1.72261
−5	1	−9.69606, 1.73203
−5	1.7	−6.01119, 1.73134
−6	1	−6.01119, 1.73134
−10	1	−9.69606, 1.73203



Which roots are found apparently depends on the prior estimated values.

P1.02.07. TWO NONLINEAR EQUATIONS

In Newton's method for a set of nonlinear equations, each equation is expanded in a truncated Taylor series. The result is a set of linear equations in corrections to previous estimates. Repetition of the process ultimately may converge to correct roots provided initial estimates are sufficiently close.

Suppose the equations are

$$F(x,y) = 0,\quad G(x,y) = 0 \tag{1}$$

and estimates of the roots are x_n and y_n. The successive approximations then are computed by the following formulas.

$$\left.\begin{aligned} x_{n+1} &= x_n - \frac{1}{J(x_n,\ y_n)}\begin{vmatrix} F(x_n,\ y_n) & F'_y(x_n,\ y_n) \\ G(x_n,\ y_n) & G'_y(x_n,\ y_n)\end{vmatrix} = x_n - \frac{\Delta_x^{(n)}}{J(x_n,\ y_n)}, \\ y_{n+1} &= y_n - \frac{1}{J(x_n,\ y_n)}\begin{vmatrix} F'_x(x_n,\ y_n) & F(x_n,\ y_n) \\ G'_x(x_n,\ y_n) & G(x_n,\ y_n)\end{vmatrix} = y_n - \frac{\Delta_y^{(n)}}{J(x_n,\ y_n)}, \end{aligned}\right\} \tag{2}$$

where

$$\Delta_x^{(n)} = \begin{vmatrix} F(x_n,\ y_n) & F'_y(x_n,\ y_n) \\ G(x_n,\ y_n) & G'_y(x_n,\ y_n)\end{vmatrix}, \qquad \Delta_y^{(n)} = \begin{vmatrix} F'_x(x_n,\ y_n) & F(x_n,\ y_n) \\ G'_x(x_n,\ y_n) & G(x_n,\ y_n)\end{vmatrix},$$

and the Jacobian

$$J(x,\ y) = \begin{vmatrix} F'_x(x,\ y) & F'_y(x,\ y) \\ G'_x(x,\ y) & G'_y(x,\ y)\end{vmatrix} \neq 0.$$

Example 1. Find the real roots of the system

$$F(x,\ y) \equiv 2x^3 - y^2 - 1 = 0,$$
$$G(x,\ y) \equiv xy^3 - y - 4 = 0.$$

Solution. Find graphically the approximate values $x_0 = 1.2$ and $y_0 = 1.7$. Computing the Jacobian at the point (1.2; 1.7), we have

$$J(x,\ y) = \begin{vmatrix} 6x^2 & -2y \\ y^3 & 3xy^3 - 1\end{vmatrix},$$

$$J(1.2;\ 1.7) = \begin{vmatrix} 8.64 & -3.40 \\ 4.91 & 9.40\end{vmatrix} = 97.910.$$

From formulas (2) we get

$$x_1 = 1.2 - \frac{1}{97.910}\begin{vmatrix} -0.434 & -3.40 \\ 0.1956 & 9.40\end{vmatrix} = 1.2 + 0.0349 = 1.2349,$$

$$y_1 = 1.7 - \frac{1}{97.910}\begin{vmatrix} 8.64 & -0.434 \\ 4.91 & 0.1956\end{vmatrix} = 1.7 - 0.0390 = 1.6610.$$

Continuing this process with the obtained values x_1 and y_1 we get

$x_2 = 1.2343$, $y_2 = 1.6615$ and so forth.

P1.03.01. DIFFERENTIATION OF FITTED EQUATIONS

Four different equations are fitted by TableCurve to the data of the table. They all have correlation coefficients > 0.995. The derivatives are evaluated at selected points, and mostly do not agree closely. Presumably the derivatives from the equation with four constants are the best.

$$y'_{10} = 2(a+bx+cx^2+dx^3)(b+2cx+3dx^2)$$

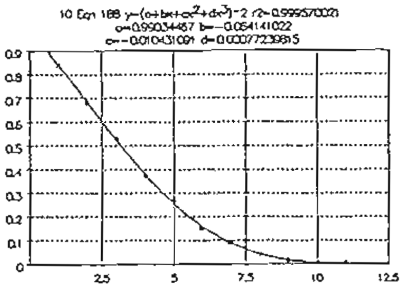
$$y'_{31} = b+2cx$$

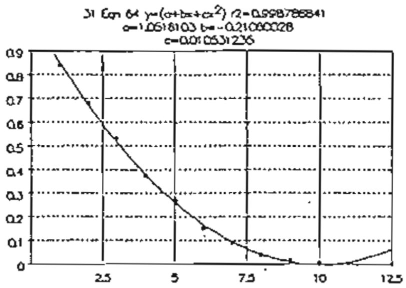
$$y'_{47} = \exp(a+bx+cx^2)(b+2cx)$$

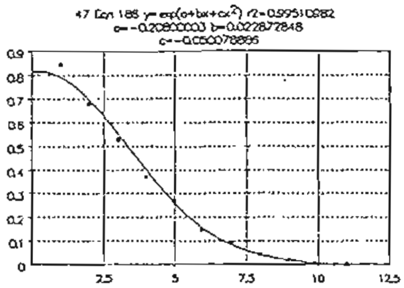
$$y'_{48} = \frac{2(a+cx)[c(1+bx)-b(a+cx)]}{(1+bx)^3}$$

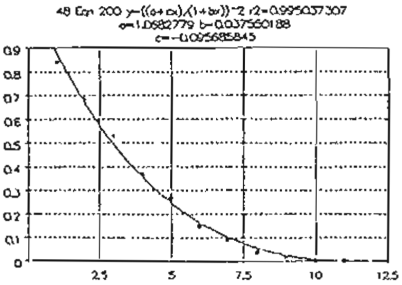
Eqn	r^2	$-y'$ x=1	x=5	x=10
10	0.99957	0.1516	0.1117	0.0064
31	0.99879	0.1895	0.1053	$1.1(10^{-8})$
47	0.99511	0.0610	0.1244	0.0067
48	0.99504	0.2365	0.0956	0.0116

x	y
1	0.841
2	0.679
3	0.532
4	0.371
5	0.268
6	0.149
7	0.0895
8	0.0406
9	0.0182
10	0.0061
11	0.0025





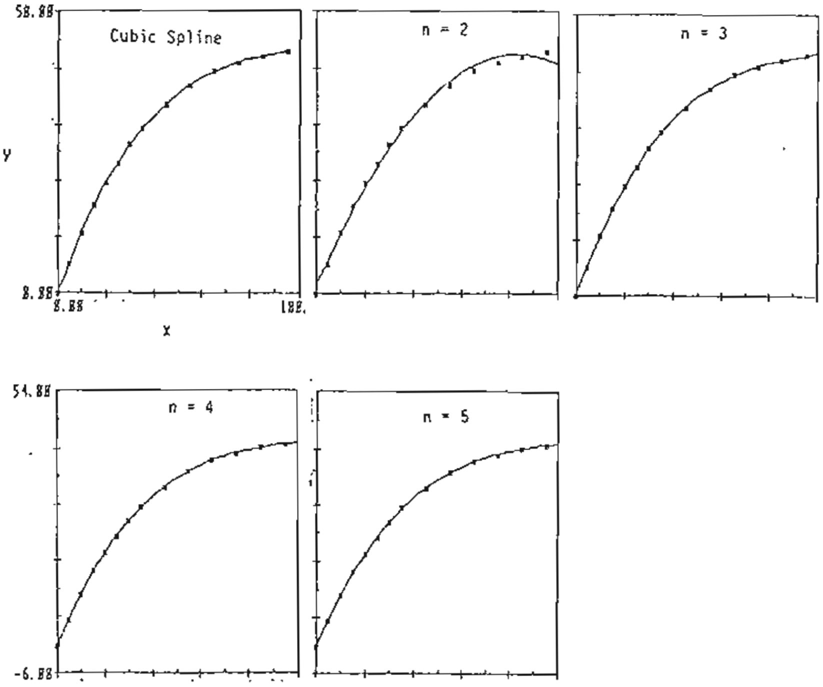




P1.03.02. OXIDATION OF CARBON MONOXIDE

Catalytic oxidation of carbon monoxide is studied in problem P3.07.06. The change in pressure is given as a function of the time in the first two columns of the table. Polynomials of several degrees are fitted to the data and the derivatives, -dP/dt, are found at selected points by POLYMATH. Values derived from degrees 3, 4 and 5 agree fairly well.

t	-ΔP	-dP/dt CuSpl	n=2	n=3	n=4	n=5
0	0	1.0510	0.9968	1.2099	1.2448	1.2502
5	5.4					
10	11.1					
15	15.8					
20	19.9	0.7297	0.7555	0.7789	0.7722	0.7710
25	23.2					
30	26.5					
35	29.4					
45	33.7	0.3820	0.4539	0.3864	0.3854	0.3865
55	37.2					
65	39.5					
75	41.1					
85	42.3					
95	43.0	0.0587	-0.1494	0.0889	0.0511	0.0570



P1.03.03. TRAPEZOIDAL AND RUNGE-KUTTA INTEGRATION

The trapezoidal program of CHAPRA & CANALE and the Runge-Kutta routine of CONTANTINIDES are compared for the integral

$$y = \int_0^5 \frac{x}{\sqrt{x^3-2x^2+7x+20}}\,dx$$

with several intervals as tabulated. The Runge-Kutta is superior.

Intervals	Trap.	R-K
2	1.5287	1.6488
10	1.6448	1.6498
50	1.6496	1.6498
100	1.6497	1.6498
1000	1.64976	1.6498

P1.03.04. ANALYTICAL AND NUMERICAL INTEGRATION

The integral to be evaluated is

$$y = \int_{1.3}^{23.2} \frac{1}{(x+1.2)(x+2.5)(x+5.0)(x+0.5)}\,dx$$

The integrand is transformed into partial fractions by item 13 of Table 1.1.

$$y = \int_{1.3}^{23.2} \left(-\frac{0.2892}{x+1.2} + \frac{0.1538}{x+2.5} - \frac{0.02339}{x+5.0} + \frac{0.1587}{x+0.5}\right) dx$$

= 0.009326, by analytic evaluation

0.009377, by trapezoidal rule with 100 intervals

With the aid of the computer, the numerical evaluation is much less laborious.

P.04.01. ANALYTICAL SOLUTION OF FIRST ORDER EQUATIONS

A. Separable Variables

(a) $x^2y'\cos y + 1 = 0, \quad y \to \frac{16}{3}\pi, \quad x \to +\infty$
(b) $x^2y' + \cos 2y = 1, \quad y \to \frac{10}{3}\pi, \quad x \to +\infty$
(c) $x^3y' - \sin y = 1, \quad y \to 5\pi, \quad x \to \infty$
(d) $(1 + x^2)y' - \frac{1}{2}\cos^2 2y = 0, \quad y \to \frac{7}{2}\pi, \quad x \to -\infty$
(e) $e^y = e^{4y}y' + 1$, y being bounded when $x \to +\infty$
(f) $(x + 1)y' = y - 1$, y being bounded when $x \to +\infty$
(g) $y' = 2x(\pi + y)$, y being bounded when $x \to \infty$
(h) $x^2y' + \sin 2y = 1, \quad y \to \frac{11}{4}\pi, \quad x \to +\infty$

Answers

(a) $y = \arcsin\left(\frac{\sqrt{3}}{2} - \frac{1}{x}\right) + 5\pi$

(b) $y = 2\,\mathrm{arccot}\left(\frac{2}{x} + \frac{1}{\sqrt{3}}\right) + 3\pi$

(c) $y = 2\arctan\left(1 - \frac{1}{2x^2}\right) + \frac{9\pi}{2}$

(d) $y = \frac{1}{2}\arctan\left(\frac{\pi}{2} + \arctan x\right) + \frac{7\pi}{2}$

(e) $y = 0$
(f) $y = 1$
(g) $y = -\pi$

(h) $y = \mathrm{arccot}\,\frac{1}{2x} + \frac{9}{4}\pi$

B. Homogeneous

(a) $2xy\,dx + (x^2 + y^2)\,dy = 0$
(b) $(x + \sqrt{y^2 - xy})\,dy - y\,dx = 0$
(c) $(x + y)\,dx - (x - y)\,dy = 0$
(d) $xy' - y - x\sin(y/x) = 0$
(e) $(2x^2y + y^3)\,dx + (xy^2 - 2x^3)\,dy = 0$
(f) $y^2\,dx + (x\sqrt{y^2 - x^2} - xy)\,dy = 0$
(g) $\frac{y}{x}\cos\frac{y}{x}\,dx - \left(\frac{x}{y}\sin\frac{y}{x} + \cos\frac{y}{x}\right)dy = 0$

Answers

(a) $3x^2y + y^3 = c$.
(b) $y = ce^{-2\sqrt{1-x/y}}, y > 0, x < y; y = ce^{2\sqrt{1-x/y}}$,
$y < 0, x > y$.
(c) $\mathrm{Arctan}(y/x) - \frac{1}{2}\log(x^2 + y^2) = c$.
(d) $y = 2x\,\mathrm{Arctan}\,cx$.
(e) $x/y^2 + \log xy = c, \ x \neq 0, \ y \neq 0$.
(f) $y^2 - cx = y\sqrt{y^2 - x^2}$, or equivalently, $c(y + \sqrt{y^2 - x^2}$
$= xy, y^2 > x^2$.
(g) $y\sin(y/x) = c$.

C. Linear

(a) $x^2 = xy' = y; \ y|_{x=1} = 0$
(b) $y' - 2xy = 2xe^{-x^2}$
(c) $y' + 2xy = e^{-x^2}$
(d) $y'\cos x - y\sin x = 2x; \ y|_{x=0} = 0$
(e) $xy' - 2y = x^3\cos x$
(f) $y' - y\tan x = \frac{1}{\cos^3 x}; \ y|_{x=0} = 0$
(g) $y'x\ln x - y = 3x^3\ln^2 x$
(h) $(2x - y^2)\,y' = 2y$
(i) $y' + y\cos x = \cos x; \ y|_{x=0} = 1$

Answers
(a) $y = x - x^2$.
(b) $y = (C + x^2)e^{x^2}$.
(c) $y = (C + x)e^{-x^2}$.
(d) $y = x^2/(\cos x)$.
(e) $y = Cx^2 + x^2\sin x$.
(f) $y = (\sin x)/(\cos^2 x)$.
(g) $y = (C + x^3)\ln x$.
(h) $x = Cy - y^2/2$.
(i) $y = 1$.

D. Simultaneous

(a) $\frac{dx}{dt} = -x^2; \qquad \frac{dy}{dt} = -y.$
(b) $\frac{dx}{dt} = 3e^{-t}, \qquad \frac{dy}{dt} = x + y.$
(c) $\frac{dx}{dt} = x^2t, \qquad \frac{dy}{dt} = yt^2.$
(d) $\frac{dx}{dt} = 2t, \qquad \frac{dy}{dt} = 3x + 2t, \qquad \frac{dz}{dt} = x + 4y + t.$
(e) $\frac{dx}{dt} = e^t, \quad \frac{dy}{dt} = \frac{x - y}{t}.$
(f) $\frac{dx}{dt} = x + \sin t, \qquad \frac{dy}{dt} = t - y.$

Answers
(a) $x^{-1} = t + c_1; \ y = c_2e^{-t}$
(b) $x = -3e^{-t} + c_1; \ y = \frac{3}{2}e^{-t} - c_1 + c_2e^t$
(c) $x^{-1} = -\frac{1}{2}(t^2 + c_1); y = c_2e^{t^3/3}$
(d) $x = t^2 + c_1; \ y = t^3 + t^2 + 3c_1t + c_2;$
$z = t^4 + \frac{5}{3}t^3 + (6c_1 + \frac{1}{2})t^2 + (c_1 + 4c_2)t + c_3$
(e) $x = e^t + c_1; \ y = t^{-1}e^t + c_1 + c_2t^{-1}$
(f) $x = c_1e^t - \frac{1}{2}(\sin t + \cos t); \ y = t - 1 + c_2e^{-t}$

P1.04.02. LT SOLUTION WITH INITIAL VALUES UNKNOWN

Transforms of the first two derivatives are

$$L\left(\frac{dy}{dt}\right) = s\bar{y} - y_0, \qquad L\left(\frac{d^2y}{dt^2}\right) = s^2\bar{y} - sy_0 - y_0'$$

The initial values, y_0 and y_0', can be made part of the integration constants.

The equation is $y'' + 3y' + 2y = 4t$, and its transform is

$$s^2\bar{y} - sy_0 - y_0' + 3(s\bar{y} - y_0) + 2\bar{y} = \frac{4}{s^2}$$

Isolating the transform,

$$\bar{y} = \frac{1}{(s+1)(s+2)}\left(\frac{4}{s^2} + (s+3)y_0 + y_0'\right)$$

Invert with the data of Table 1.4

$$\begin{aligned} y &= 4e^{-t} - e^{-2t} + 2t - 3 + (2e^{-t} - e^{-2t})y_0 + (e^{-t} - e^{-2t})y_0' \\ &= (4 + 2y_0 + y_0')\,e^{-t} - (1 + y_0 + y_0')e^{-2t} + 2t - 3 \\ &- C_1e^{-t} + C_2e^{-2t} + 2t - 3 \end{aligned}$$

This solution also is found readily by the method of undetermined coefficients.

When the conditions are $y(1) = 1$ and $y(2) = 2$, the integration constants are found from

$$\begin{aligned} 1 &= 0.3670C_1 + 0.1353C_2 + 2 - 3 \\ 2 &= 0.1353C_1 + 0.0183C_2 + 4 - 3 \end{aligned}$$

as

$$\begin{aligned} C_1 &= 4 + 2y_0 + y_0' = 8.5281 \\ C_2 &= -(1 + y_0 + y_0') = -8.4071 \end{aligned}$$

The initial conditions are found from these equations as

$$y_0 = -2.879, \qquad y_0' = 10.2861$$

P.04.03. LT SOLUTION WITH CONDITIONS AT TWO POINTS

The equation is $d^2y/dt^2 + 0.25\,y = 0$, with conditions $y(0) = 0$, $y(\pi) = 0.5$. The transform is

$$s^2\bar{y} - sy_0 - y_0' + 0.25\bar{y} = 0$$

$$\bar{y} = \frac{1}{s^2 + 0.25}y_0', \qquad \text{with } y_0 = 0$$

Inverting,

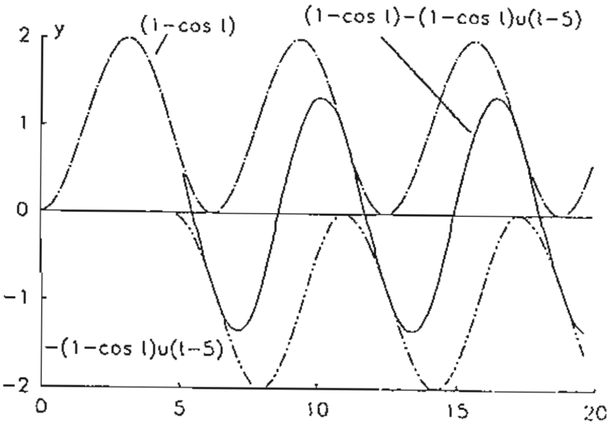
$$y = 2y_0' \sin 0.5t$$

Since $y(\pi) = 0.5 = 2y_0' \sin(\pi/2) = 2y_0'$, $y_0' = 0.25$, and the solution is

$$y = 0.5 \sin 0.5t$$

P1.04.04. LT SOLUTION WITH SQUARE PULSE INPUT

$$\frac{d^2y}{dt^2} + w^2y = u(t) - u(t-a)$$



The transform is

$$s^2\bar{y} - sy_0 - y_0' + w^2\bar{y} = \frac{1-e^{-as}}{s}$$

With the initial conditions $y_0 = y_0' = 0$,

$$\bar{y} = \frac{1}{s(s^2+w^2)} - \frac{1}{s(s^2+w^2)}e^{-as}$$

The second term corresponds to a delayed response. The inverse is

$$y = \frac{1}{w^2}(1-\cos t) - \frac{1}{w^2}(1-\cos t)\,u(t-a)$$

The two contributions of the response and the net response are plotted for $w = 1$ and $a = 5$.

P1.04.05. IMPULSE AND STEP INPUTS

The solutions of second order equations with impulse or step inputs are to be found.

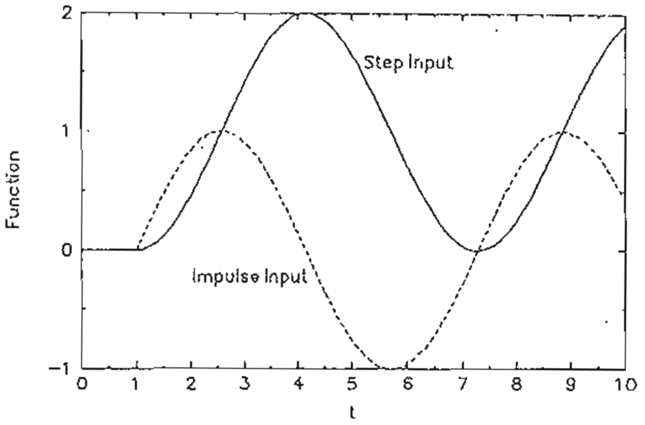
$$y'' + y = \delta(t-a), \text{ with } y''(0) = y'(0) = 0 \qquad (1)$$

$$z'' + z = H(t-a), \text{ with } z(0) = z'(0) = 0 \qquad (2)$$

The transforms are

$$\bar{y} = \frac{1}{s^2+1}\exp(-as)$$

$$\bar{z} = \frac{1}{s(s^2+1)}\exp(-as)$$



The inverses are found from Table 1.4,

$$y(t) = \sin(t-a)\,u(t-a)$$
$$\sin(t-a),\ t \ge a$$
$$0,\ t \le a$$
$$z(t) = 1 - \cos(t-a)\,u(t-a)$$
$$1 - \cos(t-a),\ t \ge a$$
$$0,\ t \le a$$

The plots with the two inputs are shown for $a = 1$.

P1.04.06. USE OF THE CONVOLUTION THEOREM

The convolution theorem, item 8 of Table 1.3, is of value when the transform is a product of two factors whose inverses are known individually. Take the case of the equation,

$$y'' + 3y' + 2y = f(t) = \exp(-3t), \text{ with } y(0) = y'(0) = 0$$

The transform is

$$(s^2 + 3s + 2)\,\bar{y} = f(s) = \frac{1}{s+3}$$

or

$$y(s) = f(s)\,\frac{1}{(s+1)(s+2)} = f(s)g(s)$$

where

$$g(s) = \frac{1}{(s+1)(s+2)}$$

$$g(t) = \exp(-t) - \exp(-2t)$$

Also

$$g(t-\vartheta) = \exp[-(t-\vartheta)] - \exp[-2(t-\vartheta)]$$

Since $f(\vartheta) = \exp(-3\vartheta)$, application of the convolution theorem gives

$$y(t) = \int_0^t f(\vartheta)g(t-\vartheta)d\vartheta$$

$$= \int_0^t \exp(-3\vartheta)\{\exp[-(t-\vartheta)]-\exp[-2(t-\vartheta)]\}d\vartheta$$

$$= 0.5\exp(-t) -\exp(-2t) + 0.5\exp(-3t)$$

This can be checked by finding the inverse of

$$y(s) = \frac{1}{(s+1)(s+2)(s+3)}$$

with item 29 of Table 1.4.

P1.05.01. POLYMATH AND CONSTANTINIDES

Three simultaneous ODEs are to be solved.

$$\frac{dy}{dt} = t^2+y,\ \frac{dz}{dt} = 5(y-z),\ \frac{dw}{dt} = 3+t+z$$

with

$$t_0 = 0,\ t_1 = 1,\ y_0 = 1,\ z_0 = w_0 = 0.$$

The POLYMATH input is

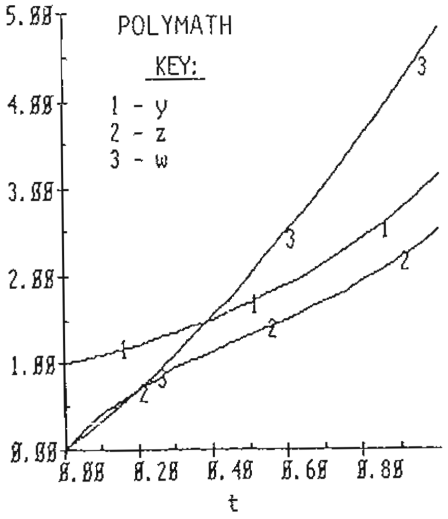
$$\frac{d(y)}{d(t)} = t{*}{*}2+y,\ \frac{d(z)}{d(t)} = 5{*}(y-z),\ \frac{d(w)}{d(t)} = 3+t+z$$

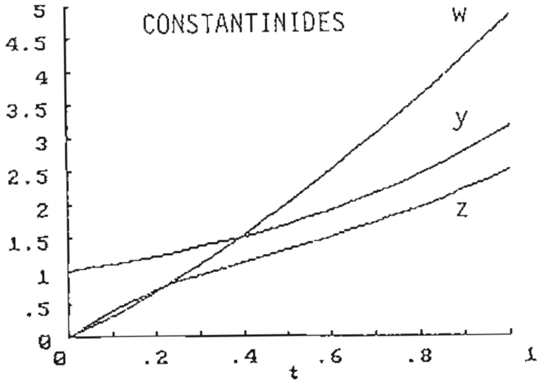
Note the parentheses around the variables in the derivative. The CONSTANTINIDES input is

$$G(1) = x^2+y(1),\ G(2) = 5{*}(y(1)-y(2)),\ G(3) = 3+x+y(2)$$

Note that the independent variable is always designated x in this program.

The two graphs agree.





P1.05.02. SHOOTING METHOD FOR EQUATIONS WITH TWO-POINT BOUNDARY CONDITIONS

The higher order ODEs are reduced to systems of first-order equations and solved by the Runge-Kutta method. The missing condition at the initial point is estimated until the condition at the other end is satisfied. After two trials, linear interpolation is applied; after three or more, Lagrange interpolation is applied.

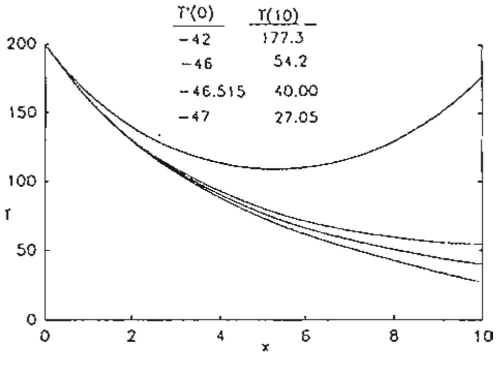
(a) Fluid enters an immersed cooling coil 10 m long at 200° and is required to leave at 40°. The cooling medium is at 20°. The heat balance is

$$\frac{d^2T}{dx^2} = 0.01(T-20)^{1.4}, \qquad \text{with } T(0) = 200;\ T(10) = 40$$

which is equivalent to the pair of equations

$$\frac{dT}{dx} = z, \qquad \frac{dz}{dx} = 0.01(T-20)^{1.4}$$

The table and the graph show that the exit point condition is satisfied when $T'(0) = -46.515$.



(a)

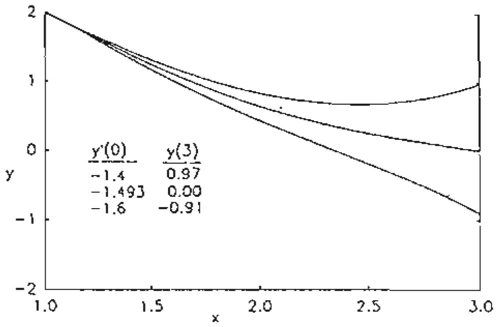
(b) The equation

$$y'' = xy + (1-0.2x)yy' \qquad \text{with } y(1) = 2;\ y(3) = 0$$

is equivalent to the system

$$\frac{dy}{dx} = z, \qquad \frac{dz}{dx} = xy + (1-0.2x)yz$$

The value $y'(0) = -1.493$ makes the solution satisfy the condition $y(3) = 0$. The xy plot for that condition is the middle one.



(b)

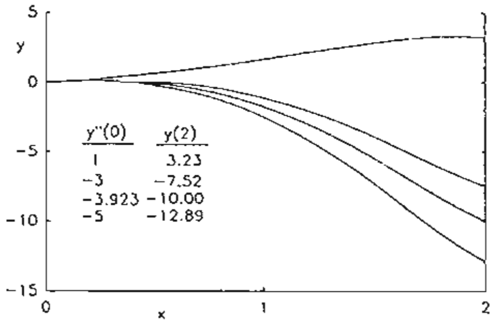
(c) The third-order equation

$$y''' = y'' - xy' - x^2y, \qquad \text{with } y(0) = 0;\ y'(0) = 1;$$
$$y(2) = -10$$

is solved as the system

$$y' = w, \qquad y'' = \frac{dw}{dx} = z, \qquad \frac{dz}{dx} = z - xw - x^2y$$

The curves and the tabulation show that $y(2) = -10$ is satisfied with the assumption $Y'''(0) = -3.923$.

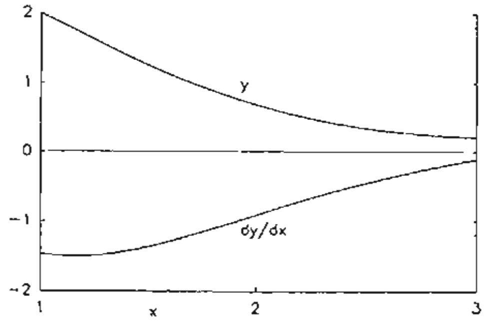


(c)

(d) The equation of part (b) is solved for the terminal condition, $y(3) + 2y'(3) = 0$. The results of several trials are

$y'(1)$	$y(3)$	$y'(3)$	$y(3) + 2y'(3)$
−2	−3.15	−4.16	−11.47
−1.5	−0.07	−0.57	−1.21
−1.4708	0.2139	−0.1084	−0.003
−1.4	0.97	1.26	3.49

Graphs of $y(x)$ and $y'(x)$ are shown for the correct value, $y'(1) = -1.4708$.



(d)

P1.05.03. DIRECT AND LAPLACE TRANSFORM SOLUTIONS

(a) A pair of consecutive reactions,

Reactions:

$$A \xrightarrow{k_1} B, \qquad B \xrightarrow{k_2} C$$

Rate equations:

$$\frac{dn_a}{dt} = -k_1 n_a$$

$$\frac{dn_b}{dt} = k_1 n_a - k_2 n_b$$

Material balance:

$$n_{a0} + n_{b0} + n_{c0} = n_a + n_b + n_c$$

The solution of the first rate equation is direct:

$$n_a = n_{a0} e^{-k_1 t}$$

Substitution into the other rate equation results in a linear differential equation of the first order:

$$\frac{dn_b}{dt} + k_2 n_b = k_1 n_{a0} e^{-k_1 t}$$

of which the solution is

$$n_b = n_{b0} e^{-k_2 t} + \frac{k_1 n_{a0}}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

Also,

$$\begin{aligned} n_c &= n_{a0} + n_{b0} + n_{c0} - n_a - n_b \\ &= n_{a0} + n_{b0} + n_{c0} - n_{a0} e^{-k_1 t} - n_{b0} e^{-k_2 t} \\ &\quad - \frac{k_1 n_{a0}}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \end{aligned}$$

(b) Solution of part (a) by Laplace transformation.

$$s\bar{n}_a - n_{a0} = -k_1 \bar{n}_a$$

$$s\bar{n}_b - n_{b0} = k_1 \bar{n}_a - k_2 \bar{n}_b$$

$$\bar{n}_a = \frac{n_{a0}}{k_1 + s}$$

$$\bar{n}_b = \frac{n_{b0} + k_1 \bar{n}_a}{k_2 + s} = \frac{n_{b0}}{k_2 + s} + \frac{k_1 n_{a0}}{(k_1 + s)(k_2 + s)}$$

The inverse transforms are found in Table 1.4. and give the same results as part (a).

P1.05.04. LAPLACE TRANSFORM AND NUMERICAL SOLUTIONS

A set of reversible-consecutive reactions, $A \underset{k_3}{\overset{k_1}{\Leftrightarrow}} B \overset{k_2}{\Rightarrow} C$, has the rate equations

$$\frac{dA}{dt} = -k_1A + k_3B$$

$$\frac{dB}{dt} = k_1A - (k_2+k_3)B$$

$$\frac{dC}{dt} = k_2B$$

Laplace transformations are made and rearranged to

$$(s+k_1)\bar{A} - k_3\bar{B} = A_0 \tag{1}$$

$$-k_1\bar{A} + (s+k_2+k_3)\bar{B} = B_0 \tag{2}$$

$$-k_2\bar{B}+s\bar{C} = C_0 \tag{3}$$

These linear equations are solved for the transforms as

$$D = s^2 + (k_1+k_2+k_3)s + k_1k_2 \tag{4}$$

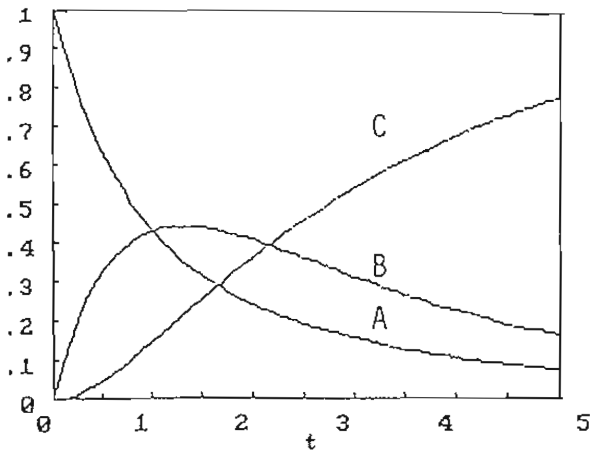
$$\bar{A} = \frac{A_0s+(k_2+k_3)A_0+k_3B_0}{D} \tag{5}$$

$$\bar{B} = \frac{B_0s+k_1(A_0+B_0)}{D} \tag{6}$$

$$\bar{C} = \frac{k_2\bar{B}+C_0}{s} \tag{7}$$

Formulas 24a and 27a of Table 1.4 can be used for inversion of these transforms to obtain A, B and C as functions of t.

A numerical solution is found, alternately, by application of the CONSTANTINIDES program for these values of the constants: $k_1 = 1$, $k_2 = 0.5$, $k_3 = 0.3$, $A_0 = 1$, $B_0 = C_0 = 0$.



CHAPTER 2
REACTION RATES AND OPERATING MODES

THEORY

PROBLEMS

INDEX OF REACTIONS IN SECTION 2

1. qA ⇒ Products at constant V or constant P
2. A ⇔ B
3. A + B ⇔ C + D
4. A + B ⇔ C + D, in terms of equilibrium conversion
5. aA + bB ⇔ cC + dD, at constant P
6. A + B + C ⇒ Products
7. A ⇒ B, B ⇒ C
8. A ⇒ B ⇒ C ⇒ D
9. Hydrogenation of cottonseed oil
10. A ⇔ B ⇒ C
11. A ⇔ B ⇔ C
12. 2A ⇒ B ⇒ C
13. A ⇒ B, A + B ⇒ C
14. A + B ⇒ C, B + C ⇒ D
15. A + B ⇒ C + E, A + C ⇒ D + E
16. A + B ⇒ 2C, A + C ⇒ D, Numerical
17. A ⇒ B, 2B ⇒ C; 2A ⇒ B ⇒ C; 2A ⇒ B, 2B ⇒ C. Analytical

INDEX OF MECHANISMS IN SECTION 3

1. Diffusion and n-th order reaction
2. Enzyme kinetics. Michaelis-Menten equation

3. Enzyme kinetics with reversible decomposition
4. Cell growth rate. Monod equation
5. Solid catalyzed reaction. Langmuir-Hinshelwood mechanism
6. Chain polymerization
7. Rice-Herzfeld mechanisms of thermal decompositions
8. $A+3B \Rightarrow C+D$ by a three step process
9. ABCD from the components by a three step process
10. $A+2B \Rightarrow C+2D$ by a two step sequence
11. Acetaldehyde thermal decomposition
12. Pyrolysis of ethyl nitrate. Data from a CSTR
13. Decomposition of ethane
14. Nitrogen peroxide decomposition
15. Hydrogen and bromine reaction
16. Phosgene from CO and Cl_2
17. Photochemical oxidation of phosgene
18. Decomposition of ozone catalyzed by chlorine
19. Ozone decomposition
20. Decomposition of diethyl ether
21. Chlorination of n-heptane
22. Decomposition of nitrous oxide
23. Phosphorous acid
24. Acetone decomposition
25. Thermal cracking of propane
26. A kinetic reforming model

This chapter deals with rate equations of chemical reactions carried out under batch or flow conditions. The applications are to identifying mechanisms of reactions, to sizing equipment, and to evaluating its performance. Tables 2.1 to 2.6 are an overview of the substance of this chapter.

The participant A is identified by subscript a. Thus the concentration is C_a, the number of mols is n_a, the fractional conversion is x_a, the partial pressure is p_a, the rate of decomposition is r_a. The capital letter A also is used on occasion instead of C_a. The flow rate in terms of mols is n_a' but the prime (') is left off when the meaning is clear, The volumetric flow rate is V', reactor volume is V_r or simply V of batch reactors, the total pressure is π.

2.1. RATE OF REACTION

The term "rate of reaction" means the rate of decomposition per unit volume,

$$r_a = -\frac{1}{V}\frac{dn_a}{dt}, \text{ mols/(unit time)(unit volume)} \tag{2.1}$$

$$= \frac{n_{a0}}{V}\frac{dx_a}{dt}, \quad n_a = n_{a0}(1-x_a) \tag{2.2}$$

where x_a is the fractional conversion of substance A. A rate of formation will have the opposite sign. The negative sign is required for the rate of decomposition to be a positive number. When the volume is constant,

$$r_a = -\frac{dC_a}{dt}, \text{ only at constant volume} \tag{2.3}$$

Law of mass action. The effect of concentrations on the rate is isolated as

$$r_a = kf(C_a,\ C_b, \ldots) \qquad (2.4)$$

where the specific rate, k, is independent of concentrations but does depend on temperature, catalysts and other factors. The law of mass action states that the rate is proportional to the concentrations. For the reaction

$$aA + bB + cC + \ldots \Rightarrow lL + mM + \ldots \qquad (2.5)$$

the rate equation is

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = k\left(\frac{n_a}{V}\right)^p\left(\frac{n_b}{V}\right)^q\left(\frac{n_c}{V}\right)^r\ldots \qquad (2.6)$$

$$= k_c C_a^p C_b^q C_c^r\ldots, \text{ at constant volume} \qquad (2.7)$$

The exponents p, q, r, ... are empirical, but they are identical with the stoichiometric coefficients a, b, c, ... when the stoichiometric equation truly represents the mechanism of reaction. The first group of exponents identify the order of the reaction, the second group the molecularity.

Effect of temperature. The Arrhenius equation relates the specific rate to the absolute temperature,

$$k = k_0\exp(-E/RT) \qquad (2.8)$$

$$= \exp(A-B/T) \qquad (2.9)$$

$$\ln k = A - \frac{B}{T} \qquad (2.10)$$

E is called the energy of activation and k_0 the preexponential factor. From experimental data, the constants are found with the linearized plot, Eq 2.10.

2.2. CONCENTRATION, MOLS, PARTIAL PRESSURE, MOL FRACTION

Any property of a reacting system that changes regularly as the reaction proceeds can be formulated as a rate equation which should be convertible to the fundamental form, Eq 2.6. Examples are rate of change of electrical conductivity or of pH, or of optical rotation. The commonest other variables are partial pressure p_i and mol fraction N_i. The relations between these units are,

$$n_i = VC_i = n_tN_i = \frac{n_tp_i}{\pi} \qquad (2.11)$$

where subscript t denotes total and π the total pressure. For ideal gases,

$$n_i = \frac{n_tRT}{\pi}C_i = \frac{n_i}{n_t}p_i = \frac{V}{RT}p_i = \frac{\pi V}{RT}N_i \qquad (2.12)$$

Other volume explicit equations of state are sometimes necessary, such as the compressibility factor equation, $V = zRT/P$, or the truncated virial equation, $V = \frac{RT}{P}(1+B)$. The quantities z and B are not constants so some kind of averaging may be required. More accurate equations of state are even more difficult to use but are not often justified for kinetic work.

Designate δ_a as the increase in the number of mols per mol decrease of substance A according to stoichiometric Eq 2.5,

$$\delta_a = \frac{(l+m+\ldots)-(a+b+c+\ldots)}{a} \qquad (2.13)$$

The total number of mols present is

$$n_t = n_{t0}+\delta_a(n_{a0}-n_a) = n_{t0}+\delta_ax_a = n_{t0}+\delta_bx_b = \ldots \qquad (2.14)$$

It then follows that

$$-\frac{dn_i}{dt} = \delta_a\frac{dn_a}{dt} = \delta_b\frac{dn_b}{dt} = \delta_c\frac{dn_c}{dt} = \ldots \qquad (2.15)$$

At constant volume,

$$\frac{dn_i}{dt} = V\frac{dC_i}{dt} = \frac{V}{RT}\frac{dp_i}{dt} = n_i\frac{dN_i}{dt} + N_i\frac{dn_i}{dt} \tag{2.16}$$

At constant pressure

$$\frac{dn_i}{dt} = \frac{RT}{\pi}(n_i\frac{dC_i}{dt} + C_i\frac{dn_i}{dt}) = \frac{n_i(dC_i/dt)}{\pi/RT+\delta_iC_i} \tag{2.17}$$

$$\frac{dn_i}{dt} = \frac{1}{\pi}(n_i\frac{dp_i}{dt} + p_i\frac{dn_i}{dt}) = \frac{n_i(dp_i/dt)}{\pi+\delta_ip_i} \tag{2.18}$$

$$\frac{dn_i}{dt} = n_t\frac{dN_i}{dt} + N_i\frac{dn_i}{dt}) = \frac{n_t(dN_i/dt)}{1+\delta_iN_i} \tag{2.19}$$

An equation like Eq 2.7 can be written in terms of partial pressures and mol fraction as

$$r_a = k_cC^n = k_pp_a^n = k_NN_a^n \tag{2.20}$$

The relation between the specific rates is

$$k_c = (RT)^nk_p = (\frac{RT}{\pi})^nk_N \tag{2.21}$$

Typical units of a first order reaction in terms of different variables are:

Variable	Rate equation	Typical units of k
Concentration	$r = k_cC$	sec^{-1}
Partial pressure	$r = k_pp$	mols/(liter)(sec)(atm)
Mol fraction	$r = k_NN$	mols/(liter)(sec)

2.3. REACTION TIME

Flow reactors usually operate more nearly at constant pressure, thus at variable volume with gases. An apparent residence time is defined as the ratio of the reactor volume to the inlet volumetric rate,

$$\bar{t}_{app} = V_r/V'_0 \tag{2.22}$$

The true residence time is found by integration of the rate equation,

$$\bar{t} = \int dV_r/V' = \int dn/rV' \tag{2.23}$$

Both the reaction rate, r, and the volumetric flow rate, V', must be known in terms of the number of mols, n, of the reference component. The apparent residence time is popularly used to indicate the loading of a reactor.

A related concept is that of space velocity which is the ratio of a flow rate at STP (usually 60 F, 1 atm) to the size of the reactor. The most common versions in typical units are,

GHSV (gas hourly space velocity) = (volumes of feed as gas at STP/hr)/(volume of the reactor or its content of catalyst) = SCFH gas feed/cuft.

LHSV (liquid hourly space velocity) = (Volume of liquid feed at 60 F/hr)/cuft= SCFH liquid feed/cuft.

WHSV (weight hourly space velocity) -= (lb of feed/hr)/(lb of catalyst).

2.4 CONSTANTS OF THE RATE EQUATION

The problem is to find the constants of rate equations such as

$$r = -\frac{dC}{dt} = kC^n \tag{2.24}$$

or

$$r = -\frac{dC}{dt} = k\ \exp(A-B/T)\ C^n \qquad (2.25)$$

or

$$r_a = kC_a^m C_b^n\ldots \qquad (2.26)$$

Experimental data that are most easily obtained are of (C, t), (p,t), (r,t) or (C,T,t). Values of the rate are obtainable directly from measurements on a continuous stirred tank reactor (CSTR), or they may be obtained from (C,t) data by curve fitting and then differentiating. Several methods are commonly used to find the constants.

(i) Linear regression of the rate data. Take logarithms of Eq 2.25.

$$\ln r = \ln k + A - B/T + n \ln C \qquad (2.27)$$

The linear variables are ln r, 1/T and ln C. The term (ln k + A) is a single constant. A multilinear regression program can be used to find the constants, or only three sets of data can be used and the constants found by simultaneous solution of three linear equations. For a linearized Eq 2.26 the linear variables are the logarithms of r, C_a, C_b,....The logarithmic form of Eq 2.24 has only two constants so the data can be plotted and the constants read off from the slope and intercept of the best straight line.

(ii). From the integrated equations. The integral of Eq 2.24 is

$$k = \frac{1}{t-t_0} \ln \frac{C}{C_0}, \quad \text{when } n = 1 \qquad (2.28)$$

$$\frac{C_0^{n-1}}{(t-t_0)(n-1)}[(C_0/C)^{n-1} - 1), \quad \text{when } n \neq 1 \qquad (2.29)$$

A value of n is assumed and values of k are calculated from the data. The correct value of n has been chosen when the values of k are nearly constant.

Integrals of some common rate equations are summarized in Table 2.2. Others are developed in problem Section 2 of this chapter.

(iii). Plots of the data. The integrals are rearranged as

$$\ln(C/C_0) = k(t-t_0), \quad \text{when } n = 1 \qquad (2.30)$$

$$(1/C)^{n-1} = (1/C_o)^{n-1} + k(n-1)(t-t_0), \quad \text{when } n \neq 1 \qquad (2.31)$$

A value of n is assumed and values of the left hand side are plotted against $(t-t_0)$. The correct value of n has been found when the data are collinear. The correct value of k is found from the slope of the best straight line.

2.5. MULTIPLE REACTIONS AND STOICHIOMETRIC BALANCES.

Before an expression such as Eq 2.26 can be integrated, the RHS must be expressed in terms of the single variable C_a. From the stoichiometric Eq 2.5,

$$\frac{x}{a} = \frac{n_{a0}-n_a}{a} = \frac{n_{b0}-n_b}{b} = \ldots = -\frac{n_{l0}-n_l}{l} = -\frac{n_{m0}-n_m}{m} = \ldots \qquad (2.32)$$

$$C_a = \frac{n_a}{V} = \frac{n_{a0}-x}{V}$$

$$C_b = \frac{n_{b0}-bx/a}{V}$$

$$C_c = \frac{n_{c0}-cx/a}{V} \qquad (2.33)$$

Also,

$$C_b = C_{bo} - \frac{b}{a}(C_{ao}-C_a)$$

$$C_c = C_{co} - \frac{c}{a}(C_{ao}-C_a) \qquad (2.34)$$

Thus the rate equation becomes

$$r_a = \frac{1}{V}\frac{dx}{dt} = -\frac{1}{V}\frac{dn_a}{dt}$$

$$= k\left(\frac{n_{ao}-x}{V}\right)^p\left(\frac{n_{bo}-bx/a}{V}\right)^q\left(\frac{n_{co}-cx/a}{V}\right)^r\ldots \qquad (2.35)$$

In terms of concentrations,

$$r_a = -\frac{dC_a}{dt} = kC_a^pC_b^qC_c^r\ldots$$

$$= kC_a^p[C_{bo}-\frac{b}{a}(C_{ao}-C_a)]^q[C_{co}-\frac{c}{a}(C_{ao}-C_a)]^r\ldots \qquad (2.36)$$

2.5.1. Multiple reactions.

When a substance participates in several reactions at the same time, its net rate of decomposition is the algebraic sum of its rates in the individual reactions. The rates of the individual steps are identified with subscripts: $(dC/dt)_1$, $(dC/dt)_2$,.... Take this group of reactions:

$$A + B \overset{1}{\Rightarrow} C$$

$$A + C \overset{2}{\Rightarrow} D + E$$

$$D + E \overset{3}{\Rightarrow} A + C$$

The overall rates of the several participants are

$$r_a = r_{a1} + r_{a2} + r_{a3} = -k_1C_aC_b - k_2C_aC_c + k_3C_dC_e \qquad (2.37)$$

$$r_b = -k_1C_aC_b$$

$$r_c = k_1C_aC_b - k_2C_aC_c + k_3C_dC_e$$

$$r_d = r_e = k_2C_aC_e - k_3C_dC_e$$

The number of independent rate equations is the same as the number of independent stoichiometric relations. In the present example, reactions 2 and 3 are reversible and are not independent.

Some reactions apparently represented by single stoichiometric equations are in reality the result of a number of other reactions, often involving short lived intermediates such as free radicals. After a set of such elementary reactions is postulated by experience, intuition and exercise of judgement, a rate equation is deduced and checked against rate data. Problem Secion 3 of this chapter has a number of real examples.

2.5.2. Stoichiometric balances.

The amounts of all participants of a group of reactions can be expressed in terms of a number of key components equal to the number of independent stoichiometric relations. The independent rate equations then will involve only the key components and can be integrated. Problem Section 1 of this chapter develops several examples.

Eq 2.32 relates changes of the particpants of a reaction. For multiple reactions, the procedure for finding the end concentrations of all participants starts by assuming that the reactions occur consecutively. Key components are identified. Intermediate concentrations are identified by subscripts. The resulting concentration from a particular reaction is the starting concentration for the next reaction in series. The intermediate concentrations are eliminated algebraically.The compositions of the excess components then will be expressible in terms of the key components.

Example. Take the three reactions

$$A + 2B \overset{1}{\Rightarrow} 3C$$

$$A + C \overset{2}{\Rightarrow} 2D$$

$$C + D \overset{3}{\Rightarrow} 2E$$

with A, B and C as the key components. Eq 2.32 becomes

$$A_0-A_1 = \frac{B_0-B}{2} = \frac{C_1-C_0}{3}$$

$$A_1-A_2 = C_1-C_2 = \frac{D_2-D_0}{2}$$

$$C_2-C = D_2-D = \frac{E-E_0}{2} \qquad (2.38)$$

Elimination of the concentrations with subscripts 1 and 2 will find D and E in terms of A, B and C, as in the following.

An alternative procedure is called the xyz method. The amount of change by the first reaction is x, by the second it is y and by the third it is z. For the same Example,

$$A = A_0-x-y$$
$$B = B_0-2x$$
$$C = C_0+3x-y-z$$
$$D = D_0+2y-z$$
$$E = E_0 + 2z \qquad (2.39)$$

Elimination of x, y and z gives for the excess components,

$$D_0-D = -3(A_0-A) + 3(B_0-B)$$
$$E_0-E = 2(A_0-A)-4(B_0-B)-2(C_0-C) \qquad (2.40)$$

The differential equations for the three key components are,

$$\frac{dA}{dt} =-k_1AB^2-k_2AC$$

$$\frac{dB}{dt} = -2k_1AB^2$$

$$\frac{dC}{dt} = 3k_1AB^2-k_2AC-k_3CD$$

$$= 3k_1AB^2 -C\{[k_1A +k_3[D_0+3(A_0-A)-3(B_0-B)]\} \qquad (2.41)$$

These rate equations are numerically integrable for A, B and C. Then D and E are found by algebra.

Alternatively, five differential equations can be written and solved simultaneously for the five participants as functions of time, thus avoiding the making of the stoichiometric balances.

2.6. REACTOR OPERATING MODES

Two limiting modes of operating chemical reactors employ (a) a vessel so well stirred that the composition and temperature are the same throughout; (b) a vessel typified by a tube without mixing in which all molecules have the same residence time, and in which gradients of composition and temperature exist. Material and heat balances on these devices utilize the conservation law,

Input + Source = Output + Sink + Accumulation (2.42)

Various such balances will be made. They also are summarized in Tables 2.3 to

2.6.1. The stirred vessel, material balance.

The balances are written in terms of volumetric flow rates, concentrations and a power law rate equation, $r_c = kC^n$. The sink term is r_cV_r, the rate of reaction in a reference volume. V_r is the instantaneous volume occupied by the fluid in the vessel and V_{rt} is the capacity of the vessel.

$$V'_0C_0 = V'C + kV_rC^n + \frac{d(V_rC)}{dt} \qquad (2.43)$$

When starting empty, $V_r = (V'_0-V')t$. A number of special cases can be recognized:

(i). A filling operation. There is no effluent and $V_r = V'_0t$.

$$C_0 = ktC^n + \frac{d(tC)}{dt}$$

$$\frac{dC}{dt} = \frac{C_0-C}{t} - kC^n, \quad t \le V_r/V' \qquad (2.44)$$

(ii). An emptying operation. When starting with a full vessel, $V_r = V_{rt}-V't$,

$$0 = V'C + k(V_{rt}-V't)C^n + \frac{d[(V_{rt}-V't)C]}{dt}$$

$$\frac{dC}{dt} = -kC^n \qquad (2.45)$$

(iii). A batch operation. $V'_0 = V'$,

$$\frac{dC}{dt} = -kC^n \qquad (2.46)$$

(iv). A steady state operation (CSTR), $dC/dt = 0$,

$$V'_0C_0 - V'C = kV_rC^n \qquad (2.47)$$

and when the volumetric flow rate is constant,

$$r_c = kC^n = \frac{C_0-C}{\bar{t}}, \quad \bar{t} = V_r/V' \qquad (2.48)$$

The last equation indicates a way of measuring a rate of reaction by relatively simple means.

2.6.2. The stirred vessel heat balance.

In a batch reactor,

Heat input, say $Q = UA(T_{source}-T)$ (2.49)

Sink $= V_rr_c\Delta H_r$

Accumulation $= \rho V_rC_p\frac{dT}{dt}$

Altogether,

$$\frac{dT}{dt} = \frac{1}{\rho V_rC_p}(Q - V_rr_c\Delta H_r) \qquad (2.50)$$

This may be solved together with Q , the material balance and the rate equation

$$-\frac{dC}{dt} = r_c = \exp(A-B/T)\ C^n \qquad (2.51)$$

to find T and C as functions of time.

A more detailed heat balance is summarized in Table 2.3.

In a CSTR, sensible heat gain = heat generated by reaction, so that

$$V'\rho C_p(T-T_0) = -\Delta H_r V_r (C_0-C)$$

or

$$T-T_0 = \frac{-\Delta H_r \bar{t}}{\rho C_p}(C_0-C) \qquad (2.52)$$

A more detailed heat balance is summarized in Table 2.4.

2.6.3. Tubular flow reactor.

n' is the mol flow rate of a reactant. Over a differential volume dV_r of the vessel,

$$-dn' = n_0'dx = -V'dC = r_c dV_r = kC^n dV_r = k(n'/V')^n dV_r$$

$$\frac{V_r}{n_0'} = \int \frac{dn'}{k(n'/V')^n} \qquad (2.53)$$

When there is no chance of confusion, for simplicity n is written for n'. The term on the left of Eq 2.53 is the reciprocal of a form of space velocity. Flow reactors usually are operated at nearly constant pressure, so for gases particularly V' will depend on temperature and extent of conversion along the reactor.

The heat balances with heat exchange and under adiabatic conditions are summarized in Table 2.5.

2.6.4. Packed bed catalytic reactor.

The material and energy balances of a tubular vessel are based on the conservation law, Eq 2.42, applied to a differential ring between r and r+dr and z and z+dz. A material balance is derived, for example, in problem P5.08.01, and is quoted in Table 2.6 along with the heat balance. The result is a pair of second order partial differential equations, usually nonlinear, that must be solved numerically. Table 2.6 indicates one possible procedure, but computer software is plentiful.

Some attention is devoted to these problems in the last chapter.

2.7. Heterogeneous reactions. Rates of diffusion.

Reactions do occur between participants that are primarily in different phases. Gases may react with liquids or solids, primarily immiscible liquids with each other, and liquids with solids. In all such cases a rate of chemical reaction exists in series with a rate of mass transfer. At steady state these rates are equal.

The simplest mechanism postulated for transfer between phases is that a concentration gradient exists only across a stagnant film between phases. Then the rate of transfer is proportional to the interfacial area and a difference of concentrations across the film. For a power law chemical rate, at steady state,

$$r = r_d = r_c$$

or

$$r = k_d a(C-C_i) = k_v C^n \qquad (2.54)$$

where C is the concentration in the source phase, C_i that at the interface, and a is the interfacial area per unit volume.

Elimination of the interfacial concentration from this equation results in

$$r = k_v\left(C - \frac{r}{k_d a}\right)^n \qquad (2.55)$$

Many correlations exist for the mass transfer coefficient, k_da, so it is not usually necessary to evaluate it during a kinetic investigation.

Given data of (C, t) or of (r, C) and a correlation for k_da, the other constants can be found as for single reactions. All three constants also can be found by nonlinear regression or by the solution of three simultaneous equations.

Although the rate r may not be known explicitly from Eq 2.55, that does not prevent its utility in any numerical applications.

Some processes involve chemical reaction and more than one simultaneous physical step. These occur, for instance, when solid catalysts are employed and are discussed in Chapter 6. Examples of processes that involve several chemical steps are in problem Section 3 of this chapter.

TABLE 2.1. Basic Rate Equations

(Tables 2.1-2.6 are from WALAS, *Chemical Process Equipment Selection and Design*, Butterworth-Heinemann, 1990).

1. *The reference reaction* is

$$\nu_a A + \nu_b B + \cdots \rightarrow \nu_r R + \nu_s S + \cdots$$
$$\Delta\nu = \nu_r + \nu_s + \cdots - (\nu_a + \nu_b + \cdots)$$

2. *Stoichiometric balance* for any component *i*,

$$n_i = n_{i0} \pm (\nu_i/\nu_a)(n_{a0} - n_a)$$
$$\begin{cases} + \text{ for product (right-hand side, RHS)} \\ - \text{ for reactant (left-hand side, LHS)} \end{cases}$$
$$C_i = C_{i0} \pm (\nu_i/\nu_a)(C_{a0} - C_a), \quad \text{at constant } T \text{ and } V \text{ only}$$
$$n_t = n_{t0} + (\Delta\nu/\nu_a)(n_{a0} - n_a)$$

3. *Law of mass action*

$$r_a = -\frac{1}{V_r}\frac{dn_a}{dt} = kC_a^{\nu_a}C_b^{\nu_b}\cdots$$
$$= kC_a^{\nu_a}[C_{b0} - (\nu_b/\nu_a)(C_{a0} - C_a)]^{\nu_b}\cdots$$
$$r_a = kC_a^{\alpha}[C_{b0} - (\nu_b/\nu_a)(C_{a0} - C_a)]^{\beta}\cdots$$

where it is not necessarily true that $\alpha = \nu_a$, $\beta = \nu_b, \cdots$

4. *At constant volume*, $C_a = n_a/V_r$

$$kt = \int_{C_a}^{C_{a0}} \frac{1}{C_a^{\alpha}[C_{b0} - (\nu_b/\nu_a)(C_{a0} - C_a)]^{\beta}\cdots} dC_a$$
$$kt = \int_{n_a}^{n_{a0}} \frac{V_{\cdots}^{-1+\alpha+\beta}}{n_a^{\alpha}[n_{b0} + (\nu_b/\nu_a)(n_{a0} - n_a)]^{\beta}\cdots} dn_a$$

Completed integrals for some values of α and β are in Table 2.2

5. *Ideal gases at constant pressure:*

$$V_r = \frac{n_t RT}{P} = \frac{RT}{P}\left[n_{t0} + \frac{\Delta\nu}{\nu_a}(n_{a0} - n_a)\right]$$
$$r_a = kC_a^{\alpha}$$
$$kt = \left(\frac{RT}{P}\right)^{\alpha-1}\int_{n_a}^{n_{a0}} \frac{[n_{t0} + (\Delta\nu/\nu_a)(n_{a0} - n_a)]^{\alpha-1}}{n_a^{\alpha}} dn_a$$

6. *Temperature effect* on the specific rate:

$$k = k_{\infty}\exp(-E/RT) = \exp(a' - b'/T)$$
$$E = \text{energy of activation}$$

7. *Simultaneous reactions:* The overall rate is the algebraic sum of the rates of the individual reactions. For example, take the three reactions:

1. $A + B \xrightarrow{k_1} C + D.$ [illegible]
2. $C + D \xrightarrow{k_2} A + B.$
3. $A + C \xrightarrow{k_3} E.$

The rates are related by:

$$r_a = r_{a1} + r_{a2} + r_{a3} = k_1C_aC_b - k_2C_cC_d + k_3C_aC_c$$
$$r_b = -r_d = k_1C_aC_b - k_2C_cC_d$$
$$r_c = -k_1C_aC_b + k_2C_cC_d + k_3C_aC_c$$
$$r_e = -k_3C_aC_c$$

The number of independent rate equations is the same as the number of independent stoichiometric relations. In the present example, reactions 1 and 2 are a reversible reaction and are not independent. Accordingly, C_c and C_d, for example, can be eliminated from the equations for r_a and r_b which then become an integrable system.

TABLE 2.1 (continued)

8. *Mass transfer resistance:*

C_{ai} = interfacial concentration of reactant A

$$r_a = -\frac{dC_a}{dt} = k_d(C_a - C_{ai}) = kC_{ai}^{\alpha} = k\left(C_a - \frac{r_a}{k_d}\right)^{\alpha}$$

$$kt = \int_{C_a}^{C_{a0}} \frac{1}{(C_a - r_a/k_d)^{\alpha}}\, dC_a$$

The relation between r_a and C_a must be established (numerically if need be) from the second line before the integration can be completed

9. Solid catalyzed reactions. These involve simultaneous diffusion, adsorption and surface reaction. See Chapter 6.

10. *A continuous stirred tank reactor battery* (*CSTR*)

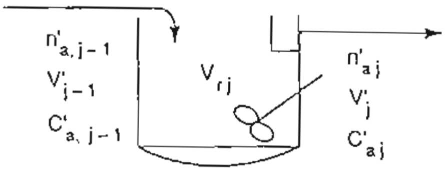
Material balances:

$$n'_{a0} = n'_a + r_{a1}V_{r1}$$
$$\vdots$$
$$n'_{a,j-1} = n'_{aj} + r_{aj}V_{rj}, \quad \text{for the } j\text{th stage}$$

For a first order reaction, with $r_a = kC_a$,

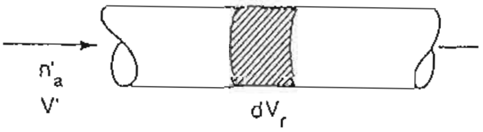
$$\frac{C_{aj}}{C_{a0}} = \frac{1}{(1+k_1\bar{t}_1)(1+k_2\bar{t}_2)\cdots(1+k_j\bar{t}_j)}$$
$$= \frac{1}{(1+k\bar{t}_i)^j},$$

for j tanks in series with the same temperatures and residence times $\bar{t}_i = V_{ri}/V'_i$, where V' is the volumetric flow rate



11. *Plug flow reactor* (PFR):

$$r_a = -\frac{dn'_a}{dV_r} = kC_a^{\alpha}C_b^{\beta}\cdots$$
$$= k(n'_a/V')^{\alpha}(n'_b/V')^{\beta}\cdots$$



12. *Material and energy balances* for batch, CSTR and PFR are in Tables 2.3, 2.4 and 2.5

13. *Notation*

A, B, R, S are participants in the reaction; the letters also are used to represent concentrations

$C_i = n_i/V_r$ or n'_i/V', concentration

n_i = mols of component i in the reactor

n'_i = molal flow rate of component i

V_r = volume of reactor

V' = volumetric flow rate

ν_i = stoichiometric coefficient

r_i = rate of reaction of substance i [mol/(unit time)(unit volume)]

α, β = empirical exponents in a rate equation

TABLE 2.2. Some Isothermal Rate Equations and their Integrals

1. *$A \rightarrow$ products:*

$$-\frac{dA}{dt} = kA^q$$

$$A/A_0 = \begin{cases} \exp[-k(t-t_0)], & q = 1 \\ \left[\dfrac{1}{1+(q-1)kA_0^{q-1}(t-t_0)}\right]^{1/(q-1)}, & q \neq 1 \end{cases}$$

2. *$A + B \rightarrow$ products:*

$$-\frac{dA}{dt} = kAB = kA(A + B_0 - A_0)$$

$$k(t - t_0) = \frac{1}{B_0 - A_0} \ln \frac{A_0(A + B_0 - A_0)}{AB_0}$$

3. *Reversible reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$:*

$$-\frac{dA}{dt} = k_1A - k_2(A_0 + B_0 - A) = (k_1 + k_2)A - k_2(A_0 + B_0)$$

$$(k_1 + k_2)(t - t_0) = \ln \frac{k_1A_0 - k_2B_0}{(k_1 + k_2)A - k_2(A_0 + B_0)}$$

4. *Reversible reaction, second order, $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$*

$$\begin{aligned} -\frac{dA}{dt} &= k_1AB - k_2RS = k_1A(A + B_0 - A_0) \\ &\quad - k_2(A_0 + R_0 - A)(A_0 + S_0 - A) \\ &= \alpha A^2 + \beta A - \gamma \end{aligned}$$

$$\alpha = k_1 - k_2$$

$$\beta = k_1(B_0 - A_0) + k_2(2A_0 + R_0 + S_0)$$

$$\gamma = k_2(A_0 + R_0)(A_0 + S_0)$$

$$q = \sqrt{\beta^2 + 4\alpha\gamma}$$

$$k(t - t_0) = \begin{cases} \dfrac{2\alpha A_0 + \beta}{2\alpha A + \beta}, & q = 0 \\ \dfrac{1}{q}\ln\left[\left(\dfrac{2\alpha A_0 + \beta - q}{2\alpha A_0 + \beta + q}\right)\left(\dfrac{2\alpha A + \beta + q}{2\alpha A + \beta - q}\right)\right], & q \neq 0 \end{cases}$$

5. *The reaction $\nu_aA + \nu_bB \rightarrow \nu_rR + \nu_sS$ between ideal gases at constant T and P*

$$-\frac{dn_a}{dt} = \frac{kn_a^\alpha}{V^{\alpha-1}}$$

$$V = n_t\frac{RT}{P} = \left[n_{t0} + \frac{\Delta\nu}{\nu_a}(n_{a0} - n_a)\right]\frac{RT}{P}$$

$$k(t - t_0) = \begin{cases} \displaystyle\int_{n_a}^{n_{a0}} \frac{V^{\alpha-1}}{n_a^\alpha}\,dn_a, \text{ in general} \\ \dfrac{RT}{P}\left[n_{b0} + \dfrac{\Delta\nu}{\nu_a}\left(\dfrac{1}{n_a} - \dfrac{1}{n_{a0}}\right) \right. \\ \qquad \left. - \dfrac{\Delta\nu}{\nu_a}\ln\left(\dfrac{n_{a0}}{n_a}\right)\right], \quad \text{when } \alpha = 2 \end{cases}$$

TABLE 2.3. Material and Energy Balances of Nonflow Reactions

Rate equations:

$$r_a = -\frac{1}{V_r}\frac{dn_a}{d\theta} = kC_a^\alpha = k\left(\frac{n_a}{V_r}\right)^\alpha \tag{1}$$

$$k = \exp(a' - b'/T) \tag{2}$$

Heat of reaction:

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p \, dT \tag{3}$$

Rate of heat transfer:

$$Q' = UA(T_s - T) \tag{4}$$

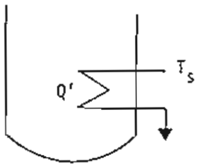
(the simplest case is when UA and T_s are constant)
Enthalpy balance:

$$\frac{dT}{dn_a} = \frac{1}{\rho V_r \bar{C}_p}\left[\Delta H_r + \frac{UA(T_s - T)}{V_r k (n_a/V_r)^\alpha}\right] \tag{5}$$

$$\frac{dT}{dC_a} = \frac{1}{\rho \bar{C}_p}\left[\Delta H_r + \frac{UA(T_s - T)}{V_r k C_a^\alpha}\right] \tag{6}$$

$$T = T_0 \quad \text{when} \quad C_a = C_{a0} \tag{7}$$

$$\bar{C}_p = \frac{1}{\rho V_r}\sum n_i C_{pi} \tag{8}$$



Solve Eq. (6) to find $T = f(C_a)$; combine Eqs. (1) and (2) and integrate as

$$\theta = \int_{C_a}^{C_{a0}} \frac{1}{C_a^\alpha \exp[a' - b'/f(C_a)]} \, dC_a \tag{9}$$

Temperature and time as a function of composition are shown for two values of UA/V_r for a particular case represented by

$$\frac{dT}{dC_a} = \frac{1}{50}\left[-5000 - 5T + \frac{UA(300 - T)}{V_r k C_a^2}\right]$$

$$k = \exp(16 - 5000/T)$$

$$T_0 = 350$$

$$C_{a0} = 1$$

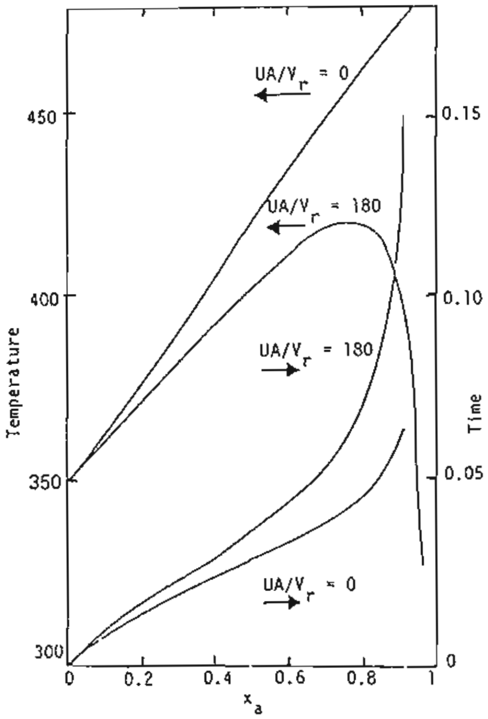


TABLE 2.4. Material and Energy Balances of a CSTR

The sketch identifies the nomenclature
Mean residence time:

$$\bar{t} = V_r/V' \tag{1}$$

Temperature dependence:

$$k = \exp(a' - b'/T) \tag{2}$$

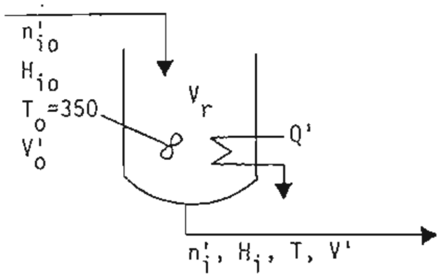
Rate equation:

$$r_a = kC_a^\alpha = kC_{a0}^\alpha(1-x)^\alpha,\ x = (C_{a0} - C_a)/C_{a0} \tag{3}$$

Material balance:

$$C_{a0} = C_a + k\bar{t}C_a \tag{4}$$

$$x = k\bar{t}C_{a0}^{\alpha-1}(1-x)^\alpha \tag{5}$$



Enthalpy balance:

$$\sum n_i'H_i - \sum n_{i0}'H_{i0} = Q' - \Delta H_r(n_{a0}' - n_a') \tag{6}$$

$$H_i = \int_{298}^{T} C_{pi}\,dT \tag{7}$$

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p\,dT \tag{8}$$

For the reaction $aA + bB \rightarrow rR + sS$,

$$\Delta C_p = rC_{pr} + sC_{ps} - aC_{pa} - bC_{pb} \tag{9}$$

When the heat capacities are equal and constant, the heat balance is

$$\bar{C}_p\rho V'(T - T_0) = Q' - \Delta H_{r298}V'(C_{a0} - C_a) \tag{10}$$

Eqs. (2) and (5) combine to

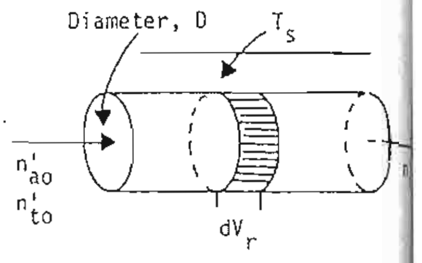
$$T = \frac{5500}{16 - \ln[x/5\bar{t}(1-x)^2]}$$

and Eq. (10) becomes

$$Q' = 2[0.9(T - 350) - 25x],\quad \text{Mcal/hr}$$

The temperature and the rate of heat input Q' are tabulated as functions of the residence time for conversions of 90 and 95%

TABLE 2.5. Material and Energy Balances of a Plug Flow Reactor (PFR)



The balances are made over a differential volume dV_r of the reactor
Rate equation:

$$dV_r = \frac{-dn'_a}{r_a} \tag{1}$$

$$= -\frac{1}{k}\left(\frac{V'}{n'_a}\right)^{\alpha} dn'_a \tag{2}$$

$$= -\exp(-a' + b'/T)\left(\frac{n'_t RT}{Pn'_a}\right)^{\alpha} dn'_a \tag{3}$$

Enthalpy balance:

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p \, dT \tag{4}$$

$$dQ = U(T_s - T)\, dA_p = \frac{4U}{D}(T_s - T)\, dV_r$$

$$= -\frac{4U(T_s - T)}{Dr_a} dn'_a \tag{5}$$

$$dQ + \Delta H_r \, dn'_a = \sum n_i \, dH_i = \sum n_i C_{pi} \, dT \tag{6}$$

$$\frac{dT}{dn'_a} = \frac{\Delta H_r - 4U(T_s - T)/Dr_a}{\sum n_i c_{pi}} = f(T, T_s, n'_a) \tag{7}$$

At constant T_s, Eq. (7) may be integrated numerically to yield the temperature as a function of the number of mols

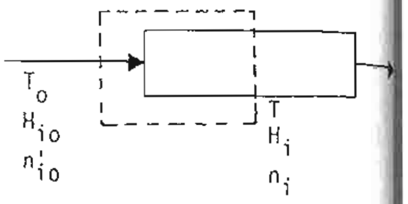
$$T = \phi(n'_a) \tag{8}$$

Then the reactor volume is found by integration

$$V_r = \int_{n'_a}^{n'_{a0}} \frac{1}{\exp[a' - b'/\phi(n'_a)][Pn'_a/n'_t R\phi(n'_a)]^{\alpha}} dn'_a \tag{9}$$

Adiabatic process:

$$dQ = 0 \tag{10}$$



The balance around one end of the reactor is

$$\sum n_{i0} H_{i0} - \sum H_{r0}(n'_{a0} - n'_a) = \sum n_i H_i = \sum n_i \int C_{pi} \, dT \tag{11}$$

With reference temperature at T_0, enthalpies $H_{i0} = 0$

$$\Delta H_{r0} = \Delta H_{r298} + \int_{298}^{T_0} \Delta C_p \, dT \tag{12}$$

Substituting Eq. (12) into Eq. (10)

$$\left[-\Delta H_{r298} + \int_{298}^{T_0} \Delta C_p \, dT\right](n'_{a0} - n'_a) = \sum n_i \int_{T_0}^{T} C_{pi} \, dT \tag{13}$$

Adiabatic process with $\Delta C_p = 0$ and with constant heat capacities

$$T = T_0 - \frac{\Delta H_{r298}(n'_{a0} - n'_a)}{\sum n_i C_{pi}} \tag{14}$$

This expression is substituted instead of Eq. (8) to find the volume with Eq. (9)

TABLE 2.6. Material and Energy Balances of Packed Bed Reactors

Diffusivity and thermal conductivity are taken appreciable only in the radial direction
Material balance equation:

$$\frac{\partial x}{\partial z} - \frac{D}{u}\left(\frac{\partial^2 x}{\partial r^2} + \frac{1}{r}\frac{\partial x}{\partial r}\right) - \frac{\rho}{u_0 C_0} r_c = 0 \qquad (1)$$

Energy balance equation:

$$\frac{\partial T}{\partial z} - \frac{k}{GC_p}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \frac{\Delta H_r \rho}{GC_p} r_c = 0 \qquad (2)$$

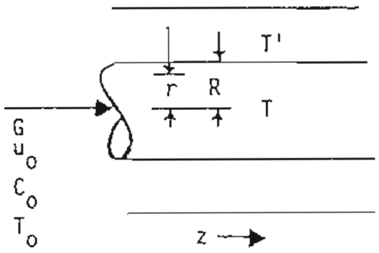
At the inlet:

$$x(0, r) = x_0 \qquad (3)$$

$$T(0, r) = T_0 \qquad (4)$$

At the center:

$$r = 0, \quad \frac{\partial x}{\partial r} = \frac{\partial T}{\partial r} = 0 \qquad (5)$$



At the wall:

$$r = R, \quad \frac{\partial x}{\partial r} = 0 \qquad (6)$$

$$\frac{\partial T}{\partial r} = \frac{U}{k}(T' - T) \qquad (7)$$

When the temperature T' of the heat transfer medium is not constant, another enthalpy balance must be formulated to relate T' with the process temperature T.

A numerical solution of these equations may be obtained in terms of finite difference equivalents, taking m radial increments and n axial ones. With the following equivalents for the derivatives, the solution may be carried out by direct iteration:

$$r = m(\Delta r)$$
$$z = n(\Delta z) \qquad (8)$$

$$\frac{\partial T}{\partial z} = \frac{T_{m,n+1} - T_{m,n}}{\Delta z} \qquad (9)$$

$$\frac{\partial T}{\partial r} = \frac{T_{m+1,n} - T_{m,n}}{\Delta r} \qquad (10)$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{T_{m+1,n} - 2T_{m,n} + T_{m-1,n}}{(\Delta r)^2} \qquad (11)$$

Expressions for the x-derivatives are of the same form:

r_c = rate of reaction, a function of s and T
G = mass flow rate, mass/(time)(superficial cross section)
u = linear velocity
D = diffusivity
k = thermal conductivity

PROBLEMS, CHAPTER 2

P2.01.01. STOICHIOMETRIC BALANCES

The reactions are $3A \Leftrightarrow 2B$ and $B + 2C \Rightarrow D$, two reactions involving four components. Express C and D in terms of A and B and formulate a pair of solvable ODEs.

Consider the reactions to proceed consecutively, and identify intermediate concentrations of those substances that participate in more than one reaction, in this case substance B.

$$\frac{A_0-A}{3} = \frac{B_1-Bo}{2}$$

$$B_1 - B = \frac{C_0-C}{2} = D - D_0$$

Eliminate the intermediate concentration B_1 from these two equations

$$B_1 = B_0+\frac{2}{3}(A_0-A)$$

$$= B+ \frac{C_0-C}{2}$$

$$= B+D-D_0$$

$$C = C_0- \frac{4}{3}(A_0-A)-2(B_0-B) \qquad (1)$$

$$D = D_0 +\frac{2}{3}(A_0-A)+(B_0-B) \qquad (2)$$

The differential equations are

$$\frac{dA}{dt} = -k_1A^3+k_2B^2 \qquad (3)$$

$$\frac{dB}{dt} = k_1A^3-k_2B^2-k_3BC^2$$

$$= k_1A^3-k_2B^2-k_3B[C_0-\frac{4}{3}(A_0-A)-2(B_0-B)]^2 \qquad (4)$$

A and B are found as functions of t by integration. Then C and D are found by algebra.

P2.01.02. THREE REACTIONS. FOUR PARTICIPANTS

The reactions are

$A \Rightarrow B$
$A \Rightarrow C$
$B + 2C \Rightarrow D$

They are assumed to proceed consecutively. Accordingly the relations between the conversions are

$$A_0-A_1 = B_1-B_0 \qquad (1)$$
$$A_1-A_0 = C_1-C_0 \qquad (2)$$
$$B_1-B = 0.5(C_1-C) = D-D_0 \qquad (3)$$

Only D needs to be found algebraically. Eliminate A_1, making

$$A_0-A = B_1-B_0 + C_1-C_0 \qquad (4)$$

From (3),

$$B_1 = B + (D-D_0)$$
$$C_1 = C + (2(D-D_0)$$

Substitute into (4) and solve.

$$D = D_0 + \frac{(A_0-A)+(B_0-B)+(C_0-C)}{3} \tag{5}$$

The differential equations are

$$\frac{dA}{dt} = -(k_1+k_2)A$$

$$\frac{dB}{dt} = k_1A-k_3BC^2$$

$$\frac{dC}{dt} = k_2A-k_3BC^2$$

After integration for A, B and C, D = f(t) is found with (5).

P2.01.03. PAIR OF SECOND ORDER EQUATIONS

The reactions are

$A+B \Rightarrow C+E$

$A+C \Rightarrow D+E$

The relations between the changes in concentration are

$$A_0-A_1 = B_0-B = C_1-C_0 = E_1-E_0 \tag{1}$$

$$A_1-A = C_1-C = D-D_0 = E-E_1 \tag{2}$$

Combine these relations so as to eliminate the concentrations with subscript 1 and to find C, D and E in terms of A and B.

$$A_0-A = 2C_1-C-C_0$$

$$C_1 = \frac{A_0-A+C+C_0}{2} = C_0+B_0-B$$

$$C_0-C = (A_0-A) -2(B_0-B) \tag{3}$$

$$= -(B_0-B)-(D_0-D)$$

$$D_0-D = -(B_0-B)-(A_0-A)+2(B_0-B) = -(A_0-A)+(B_0-B) \tag{4}$$

$$E_0-E = -(A_0-A) \tag{5}$$

Eqs (3), (4) and (5) are the desired stoichiometric relations. The rate equations for A and B are,

$$\frac{dA}{dt} = -k_1AB - k_2AC = -A\{k_1B+k_2[C_0-(A_0-A)+2(B_0-B)]\} \tag{6}$$

$$\frac{dB}{dt} = -k_1AB \tag{7}$$

P2.01.04. THE REACTIONS $2A \Rightarrow B$, $2B \Rightarrow C$

The relations between the changes in concentration are

$$\frac{A_0-A}{2} = B_1-B_0 \tag{1}$$

$$\frac{B_1-B}{2} = C-C_0 \tag{2}$$

Combining,

$$B_1 = B_0+ \frac{A_0-A}{2} = B + 2(C-C_0)$$

$$C-C_0 = \frac{A_0-A}{4} + \frac{B_0-B}{2} \tag{3}$$

The differential equations are

$$\frac{dA}{dt} = -k_1A^2$$

$$\frac{dB}{dt} = k_1A^2-k_2B^2$$

After integration, C is found from (3).

P2.01.05. THREE REACTIONS, FIVE COMPONENTS

The reactions are

$$2A \Rightarrow B+C,\quad A+C \Rightarrow D,\quad A+D \Rightarrow E$$

D and E are to be found in terms of A, B and C. The stoichiometric balances are

$$\frac{A_0-A_1}{2} = B-B_0 = C_1-C_0 \qquad (1)$$

$$A_1-A_2 = C_1-C = D_1-D_0 \qquad (2)$$

$$A_2-A = D_1-D = E-E_0 \qquad (3)$$

Eliminating A_1 and A_2,

$$A_0-A = 2(B_0-B) - (D_0-D) - 2(E_0-E) \qquad (4)$$

Also,

$$A_0-A = 2(C_1-C_0)+C_1-C+E-E_0$$

$$C_1 = \frac{C+(A_0-A)+(E_0-E)+2C_0}{3}$$

$$= C_0-(B_0-B)$$

Rearranging,

$$C_0-C = (A_0-A)+3(B_0-B)+(E_0-E) \qquad (5)$$

and

$$E_0-E = -(A_0-A)-3(B_0-B)+(C_0-C) \qquad (6)$$

Then,

$$D_0-D = -(A_0-A)-2((B_0-B)-2((E_0-E) \qquad (4)$$

$$= (A_0-A)+4(B_0-B)-2(C_0-C) \qquad (7)$$

The differential equations are

$$-\frac{dA}{dt} = k_1A^2+k_2AC+k_3AD$$

$$= A\{k_1A +k_2C+k_3[(A_0-A)+4(B_0-B)-2(C_0-C)+D_0]\}$$

$$-\frac{dB}{dt} = -\frac{k_1}{2}A^2$$

$$-\frac{dC}{dt} = A(-\frac{k_1}{2} A + k_2C)$$

After these three equations have been integrated, D and E are found from Eqs (6) and (7).

P2.01.06. THE SHIFT REACTION

Carbon monoxide is shifted to the dioxide for ease of removal by the reactions

$$CO+3H_2 \Leftrightarrow CH_4+H_2O,\qquad A+3B \underset{2}{\overset{1}{\Leftrightarrow}} C+D$$

$$CO+H_2O \Leftrightarrow H_2+CO_2,\qquad A+D \underset{4}{\overset{3}{\Leftrightarrow}} B+E$$

Components C, D and E are to be expressed in terms of A and B.

The stoichiometric relations are

$$A_0-A_1 = \frac{B_0-B_1}{3} = C-C_0 = D_1-D_0 \tag{1}$$

$$A_1-A = D_1-D = B-B_1 = E-E_0 \tag{2}$$

Eliminating A_1,

$$(A_0-A) = -(C_0-C) - (E_0-E) \tag{3}$$

Solving for B_1,

$$B_1 = B+3(C_0-C)$$
$$= B+(E_0-E)$$

which becomes,

$$(B_0-B) = -3(C_0-C) + (E_0-E) \tag{4}$$

Combining (3) and (4),

$$(C_0-C) = -\frac{1}{4}(A_0-A) - \frac{1}{4}(B_0-B) \tag{5}$$

Substituting into (3),

$$(E_0-E) = -(A_0-A)-(C_0-C)4$$
$$= -\frac{3}{4}(A_0-A)+\frac{1}{4}(B_0-B) \tag{6}$$

Solving for D_1,

$$D_1 = D_0+C-C_0$$
$$= D+E-E_0$$

from which

$$D_0-D = (C_0-C)-(E_0-E)$$
$$= \frac{1}{2}(A_0-A)-\frac{1}{2}(B_0-B) \tag{7}$$

Items (5), (6) and (7) are the required stoichiometric relations.

The differential equations of the two reversible reactions are

$$\frac{dA}{dt} = -k_1AB^3+k_2CD-k_3AD+k_4BE$$

$$\frac{dB}{dt} = -k_1AB^3+k_2CD+k_3AD-k_4BE$$

Substitute for C, D and E before integrating.

P2.01.07. STOICHIOMETRIC BALANCE IN TERMS OF AMOUNTS CONVERTED BY SUCCESSIVE REACTIONS.

For the reactions, $A+2B \Rightarrow C$ and $A+2C \Rightarrow D+2E$, only A and B are present initially. Find the minimum number of differential equations that will give the composition of the mixture as a function of time.

Let x = amount of A converted by the first reaction

y = amount of A converted by the second reaction

$$\begin{array}{cccc} A & +\ 2B & \Rightarrow\ C & \\ A_0-x & B_0-2x & x & \\ A & +\ 2C & \Rightarrow\ D & +\ 2E \\ A_0-x-y & x-2y & y & 2y \end{array}$$

The final values are

$A = A_0-x-y$
$B = B_0-2x$
$C = x-2y$
$D = y$
$E = 2y$

Elimination of x and y results in

$$C = \frac{3(B_0-B)-4(A_0-A)}{2} \qquad (1)$$

$$D = \frac{2(A_0-A)-(B_0-B)}{2} \qquad (2)$$

$$E = 2D \qquad (3)$$

The differential equations are

$$-\frac{dA}{dt} = k_1AB^2 + k_2AC^2$$

$$= A\{k_1B^2 + \frac{k_2}{4}[3(B_0-B)-4(A_0-A)]^2\}$$

$$-\frac{dB}{dt} = 2k_1AB^2$$

After these have been integrated, the other compositions are found from (1) (2) and (3).

P2.02.01. REACTION, qA ⇒ Products, AT CONSTANT V OR CONSTANT P

At constant volume, the rate equation is

$$-\frac{dC}{dt} = kC^q$$

and the integral is

$$k(t-t_0) = \frac{1}{q-1}(C^{1-q} - C_0^{1-q})$$

$$\frac{C}{C_0} = \frac{1}{[1+(q-1)kC_0^{q-1}(t-t_0)]^{1/(q-1)}} \qquad q \neq 1$$

$$\exp[-k(t-t_0)] \qquad q = 1$$

At constant pressure,

$$qA = \nu_bB + \nu_cC + \dots$$

$$\delta_a = \frac{(\nu_b+\nu_c+\dots)-q}{q}$$

The total mols and the ideal gas volume are

$$n_t = n_{t0} + \delta_a(n_{a0}-n_a)$$

$$V = \frac{RT}{\pi}n_t$$

and the rate equation,

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = k(\frac{n_a}{V})^q$$

$$-\frac{dn_a}{dt} = k(\frac{\pi}{RT})^{q-1}\frac{n_a^q}{[n_{t0}+\delta_a(n_{a0}-n_a)]^{q-1}}$$

The variables are separable,

$$k(t-t_0)(\frac{\pi}{RT})^{q-1} = \int_{n_a}^{n_{a0}} \frac{[n_{t0}+\delta_a(n_{a0}-n_a)]^{q-1}}{n_a^q} dn_a$$

When q = 2 for instance,

$$k(t-t_0)(\pi/RT) = (n_{t0}+\delta_a n_{a0})\left(\frac{1}{n_a} - \frac{1}{n_{a0}}\right) - \delta_a \ln\left(\frac{n_{a0}}{n_a}\right)$$

P2.02.02. FIRST ORDER REVERSIBLE, $A \Leftrightarrow B$

The reaction, $A \overset{1}{\underset{2}{\Leftrightarrow}} B$, has the equilibrium constant

$$K_e = k_1/k_2 = B_e/A_e = (A_0+B_0-A_e)/A_e$$

The rate equation is

$$-\frac{dA}{dt} = k_1A-k_2B = (k_1+k_2)A - k_2(A_0+B_0)$$

$$= k_1[(k_1+1/K_e)A - (A_0+B_0)/K_e]$$

The integral is

$$(k_1+k_2)(t-t_0) = \ln \frac{(k_1+k_2)A-k_2(A_0+B_0)}{k_1A_0-k_2B_0}$$

When $B_0 = 0$, $K_e = (A_0-A_e)/A_e$, $k_2 = k_1A_e/(A_0-A_e)$

$$-\frac{dA}{dt} = \frac{k_1A_0}{A_0-A_e}(A-A_e)$$

and the integral is

$$\frac{k_1A_0}{A_0-A_e}(t-t_0) = \ln \frac{A_0-A_e}{A-A_e}$$

P2.02.03 SECOND ORDER REVERSIBLE. $A+B \Leftrightarrow C+D$

The reaction is $A+B \overset{1}{\underset{2}{\Leftrightarrow}} C+D$ and the stoichiometric balances are

$$A_0-A = B_0-B = C-C_0 = D-D_0 \tag{1}$$

The equilibrium constant is

$$K_e = k_2/k_1 = \frac{C_eD_e}{A_eB_e} = \frac{(A_0+C_0-A_e)(A_0+D_0-A_e)}{A_e(B_0-A_0+A_e)} \tag{2}$$

The rate equation is

$$-\frac{dA}{dt} = k_1AB - k_2CD$$

$$= k_1A(B_0-A_0+A) - k_2(A_0+C_0-A)(A_0+D_0-A)$$

$$= \frac{k_1}{K_e}[K_eA(B_0-A_o+A)-(A_0+C_0-A)(A_0+D_0-A)]$$

$$= \frac{k_1}{K_e}(K_e-1)A^2+[K_e(B_0-A_0)+2A_0+C_0+D_0]A -(A_0+C_0)(A_0+D_0) \tag{3}$$

$$= (k_1-k_2)A^2+[k_1(B_0-A_0)+2A_0+C_0+D_0]A-k_2(A_0+C_0)(A_0+D_0) \tag{4}$$

Special case with $A_0 = B_0$ and $C_0 = D_0 = 0$.

$$-\frac{dA}{dt} = (k_1+k_2)A^2+2k_2A_0A-k_2A_0^2 \tag{5}$$

In terms of $x = A_0-A = B_0-B = C-C_0 = D-D_0$ (6)

$$\frac{dx}{dt} = k_1(A_0-x)(B_0-x)-k_2(C_0+x)(D_0+x) \tag{7}$$

$$= \frac{k_1}{K_e}[(K_e(A_0-x)(B_0-x) - (C_0+x)(D_0+x)] \quad (8)$$

$$= \frac{k_1}{K_e}\{(K_e-1)x^2 -[C_0+D_0+K_e(A_0+B_0)]x +K_eA_0B_0-C_0D_0\} \quad (9)$$

$$= \frac{k_1}{K_e}(\alpha x^2 -\beta x +\gamma) \quad (10)$$

The coefficients α, β and γ are defined by comparison of Eqs (9) and 10. The discriminants are

$$q = \sqrt{\beta^2 -4\alpha\gamma} \quad (11)$$

$$q' = \sqrt{4\alpha\gamma -\beta^2} \quad (12)$$

There are three cases: When $q^2>0$, the integrals of several cases are in the tabulation. When $q^2 0$,

$$\frac{k_1}{K_e}t = \frac{2}{q'}[\arctan(\frac{2\alpha x+\beta}{q'}) - \arctan(\beta/q')] \quad (13)$$

and when $q = 0$,

$$\frac{k_1}{K_e}t = -2(\frac{1}{2\alpha x-\beta} + \frac{1}{\beta}) \quad 14)$$

The graph shows the effect of K_e on fractional conversion x when the rate equation is

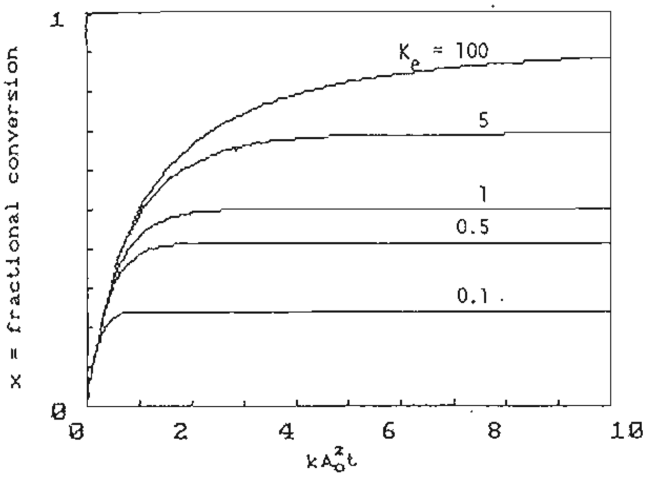
$$\frac{dx}{dt} =kA_0^2[(1-x)^2 -x^2/K_e] \quad (15)$$

REVERSIBLE SECOND-ORDER REACTIONS

$$\frac{k(t-t_0)}{KV} = \frac{1}{q}\ln\frac{(2\alpha x-\beta-q)(2\alpha x_0-\beta+q)}{(2\alpha x-\beta+q)(2\alpha x_0-\beta-q)}$$

$$q = \sqrt{\beta^2 - 4\alpha\gamma}$$

Reaction	$\frac{dx}{dt}$	α	β	γ
$A \rightleftharpoons C + D$	$\frac{k}{KV}[KV(n_{a0}-x)-(n_{c0}+x)(n_{d0}+x)]$	-1	$KV + n_{c0} + n_{d0}$	$KVn_{a0} - n_{c0}n_{d0}$
$2A \rightleftharpoons C$	$\frac{k}{KV}\left[K(n_{a0}-x)^2 - V\left(n_{c0}+\frac{x}{2}\right)\right]$	K	$2Kn_{a0} + \frac{V}{2}$	$Kn_{a0}^2 - Vn_{c0}$
$2A \rightleftharpoons C + D$	$\frac{k}{KV}\left[K(n_{a0}-x)^2 - \left(n_{c0}+\frac{x}{2}\right)\left(n_{d0}+\frac{x}{2}\right)\right]$	$K - \frac{1}{4}$	$2Kn_{a0} + \frac{n_{c0}+n_{d0}}{2}$	$Kn_{a0}^2 - n_{c0}n_{d0}$
$A + B \rightleftharpoons C$	$\frac{k}{KV}[K(n_{a0}-x)(n_{b0}-x) - V(n_{c0}+x)]$	K	$K(n_{a0}+n_{b0}) + V$	$Kn_{a0}n_{b0} - Vn_{c0}$
$A + B \rightleftharpoons C + D$	$\frac{k}{KV}[K(n_{a0}-x)(n_{b0}-x) - (n_{c0}+x)(n_{d0}+x)]$	$K - 1$	$K(n_{a0}+n_{b0}) + n_{c0} + n_{d0}$	$Kn_{a0}n_{b0} - n_{c0}n_{d0}$



P2.02.04. $A + B \overset{1}{\underset{2}{\Leftrightarrow}} C + D$, IN TERMS OF EQUILIBRIUM CONVERSION

Solutions of three of the cases in the Table of problem P2.02.03 are rewritten in terms of the conversion, $x_e = A_0 - A_e$. Substitute for K_e in terms of x_e.

(i) $A + B \Leftrightarrow C + D$, with $C_0 = D_0 = 0$

$$\frac{dx}{dt} = k_1[(A_0-x)^2 - \frac{(A_0-x_e)^2}{x_e^2}x^2]$$

$$= \frac{k_1A_0}{x_e^2}[(2x_e-A_0)x^2 - 2x_e^2x + A_0x_e^2]$$

$$q^2 = \beta^2-4\alpha\gamma = 4x_e^2(x_e-A_0)^2$$

$$k_1t = \frac{x_e}{2A_0(A_0-x_e)}\ln\frac{A_0x_e+x(A_0-2x_e)}{A_0(x_e-x)} \qquad (1)$$

(ii) $A \Leftrightarrow B + C$, with $B_0 = C_0 = 0$

$$\frac{dx}{dt} = k_1[A_0-x - \frac{A_0-x_e}{x_e^2}x^2]$$

$$= \frac{k_1}{x_e^2}[(x_e-A_0)x^2 - x_e^2x + A_0x_e^2]$$

$$q^2 = \beta^2-4\alpha\gamma = x_e^2(x_e-2A_0)^2$$

$$k_1t = \frac{x_e}{2(A_0-x_e)}\ln\frac{A_0x_e+x(A_0-x_e)}{A_0(x_e-x)} \qquad (2)$$

(iii) $A + B \Leftrightarrow C$, with $C_0 = 0$

$$\frac{dx}{dt} = k_1[(A_0-x)^2 - \frac{(A_0-x_e)^2}{x_e}x]$$

$$= \frac{k_1}{x_e}(x_e-x)(A_0^2-xx_e)$$

Application of the standard integral gives the desired result.

$$\int\frac{dx}{(ax+b)(px+q)} = \frac{1}{bp-aq}\ \ln\frac{px+q}{ax+b},\quad (bp-aq\neq 0)$$

$$k_1t = \frac{x_e}{A_0^2 - x_e^2}\ \ln\frac{x_e(A_0^2 - x_ex)}{A_0^2(x_e-x)} \tag{3}$$

P2.02.05. aA + bB ⇒ cC + dD, at Constant Pressure

The change in the total mols per mol decrease of A is

$$\delta_a = \frac{c+d-a-b}{a}$$

The total mols present and the ideal gas volume are

$$n_t = n_{t0}+ \delta_a(n_{a0}-n_a) = n_{t0}+\delta_ax_a$$

$$V = n_t\ \frac{RT}{\pi} = (n_{t0}+\delta_ax_a)\frac{RT}{\pi}$$

The stoichiometric relations are

$$\frac{1}{a}\ x_a = \frac{1}{a}(n_{a0}-n_a) = \frac{1}{b}(n_{b0}-n_b) = -\frac{1}{c}(n_{c0}-n_c) = -\frac{1}{d}(n_{d0}-n_d)$$

The rate equation is

$$\frac{dx_a}{dt} = \frac{k}{V^{a+b-1}}(n_{a0}-x_a)^a(n_{b0}-\frac{b}{a}x_a)^b$$

$$= k(\frac{\pi}{RT})^{a+b-1}\ \frac{(n_{a0}-x_a)^a(n_{b0}-bx_a/a)^b}{(n_{t0}+\delta_ax_a)^{a+b-1}}$$

Standard integrals cover the cases with a = 1 and b = 1 or 2.

$$\int\frac{dx}{(a+fx)(c+gx)} = \frac{1}{ag-cf}\log\left|\frac{c+gx}{a+fx}\right|,\quad [ag\neq cf].$$

If $ag = cf$, see 90.2.

$$\int\frac{x\,dx}{(a+x)(c+x)} = \frac{1}{(a-c)}\{a\log|a+x| - c\log|c+x|\}.$$

$$\int\frac{dx}{(a+x)(c+x)^2} = \frac{1}{(c-a)(c+x)} + \frac{1}{(c-a)^2}\log\left|\frac{a+x}{c+x}\right|.$$

$$\int\frac{x\,dx}{(a+x)(c+x)^2} = \frac{c}{(a-c)(c+x)} - \frac{a}{(a-c)^2}\log\left|\frac{a+x}{c+x}\right|.$$

$$\int\frac{x^2dx}{(a+x)(c+x)^2} = \frac{c^2}{(c-a)(c+x)} + \frac{a^2}{(c-a)^2}\log|a+x| + \frac{c^2-2ac}{(c-a)^2}\log|c+x|.$$

P2.02.06. THIRD ORDER, A+B+C ⇒ Products

Four cases of irreversible thiord order reactions are considered.

(i) When the reaction is A+B+C ⇒ Products

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

The integral is evaluated after application of the partial fraction rule,

$$\frac{1}{(x+a)(x+b)(x+c)} \equiv \frac{A}{x+a} + \frac{B}{x+b} + \frac{C}{x+c},$$

$$\text{where } A = \frac{1}{(b-a)(c-a)}, \quad B = \frac{1}{(a-b)(c-b)}, \quad C = \frac{1}{(a-c)(b-c)}.$$

The integral is

$$kt = A\ \ln\frac{a-x_0}{a-x} + B\ \ln\frac{b-x_0}{b-x} + C\ \ln\frac{c-x_0}{c-x} \qquad (1)$$

(ii) When a = b and $dx/dt = k(a-x)^2(c-x)$, the integral is quoted in problem P2.02.05,

$$kt = \frac{1}{(c-a)^2}[(c-a)(\frac{1}{a-x} - \frac{1}{a-x_0}) + \ln\frac{(a-x)(c-x_0)}{(c-x)(a-x_0)} \qquad (2)$$

(iii) When the reaction is 2A+B ⇒ Products and

$$dx/dt = k(a-2x)^2(b-x)$$

the integral is given in problem P2.02.05,

$$kt = \frac{1}{(2b-a)^2}[(2b-a)(\frac{1}{a-2x} - \frac{1}{a-2x_0}) + \ln\frac{(a-2x)(b-x_0)}{(b-x)(a-2x_0)}$$

(iv) When the reaction is 3A ⇒ Products and

$$dx/dt = k(a-x)^3$$

the integral is

$$kt = \frac{1}{2}\ [\frac{1}{(a-x)^2} - \frac{1}{(a-x_0)^2}]$$

P2.02.07. CONSECUTIVE REACTIONS, A ⇒ B, B ⇒ C

The pair of differential equations are solved either directly or with Laplace transform, with a table of inverses.

(a) A pair of consecutive reactions,

Reactions:

$$A \xrightarrow{k_1} B, \quad B \xrightarrow{k_2} C$$

Rate equations:

$$\frac{dn_a}{dt} = -k_1 n_a$$

$$\frac{dn_b}{dt} = k_1 n_a - k_2 n_b$$

Material balance:

$$n_{a0} + n_{b0} + n_{c0} = n_a + n_b + n_c$$

The solution of the first rate equation is direct:

$$n_a = n_{a0}e^{-k_1t}$$

Substitution into the other rate equation results in a linear differential equation of the first order:

$$\frac{dn_b}{dt} + k_2n_b = k_1n_{a0}e^{-k_1t}$$

of which the solution is

$$n_b = n_{b0}e^{-k_2t} + \frac{k_1n_{a0}}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t})$$

Also,

$$\begin{aligned} n_c &= n_{a0} + n_{b0} + n_{c0} - n_a - n_b \\ &= n_{a0} + n_{b0} + n_{c0} - n_{a0}e^{-k_1t} - n_{b0}e^{-k_2t} \\ &\quad - \frac{k_1n_{a0}}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t}) \end{aligned}$$

(b) Solution of part (a) by Laplace transformation.

$$s\bar{n}_a - n_{a0} = -k_1\bar{n}_a$$

$$s\bar{n}_b - n_{b0} = k_1\bar{n}_a - k_2\bar{n}_b$$

$$\bar{n}_a = \frac{n_{a0}}{k_1 + s}$$

$$\bar{n}_b = \frac{n_{b0} + k_1\bar{n}_a}{k_2 + s} = \frac{n_{b0}}{k_2 + s} + \frac{k_1n_{a0}}{(k_1 + s)(k_2 + s)}$$

P2.02.08. CONSECUTIVE REACTIONS. A ⇒ B ⇒ C ⇒ D. LAPLACE TRANSFORM

The consecutive first order reactions have the rate equations

$$\frac{dA}{dt} = -k_1A \tag{1}$$

$$\frac{dB}{dt} = k_1A-k_2B \tag{2}$$

$$\frac{dC}{dt} = k_2B-k_3C \tag{3}$$

Component D can be found by material balance after the three differenti equations have been integrated.

$$D = A_0+B_0+C_0+D_0-A-B-C \tag{4}$$

The Laplace transforms are

$$s\bar{A} - A_0 = -k_1\bar{A} \quad \text{or} \quad (s+k_1)\bar{A} = A_0 \tag{5}$$

$$s\bar{B} - B_0 = k_1\bar{A} - k_2\bar{B} \quad \text{or} \quad k_1\bar{A} - (s+k_2)\bar{B} = B_0 \tag{6}$$

$$s\bar{C} - C_0 = k_2\bar{B} - k_3\bar{C} \quad \text{or} \quad k_2\bar{B} - (s+k_3)\bar{C} = C_0 \tag{7}$$

The determinant of the coefficients is

$$\Delta = \begin{bmatrix} (s+k_1) & 0 & 0 \\ k_1 & -(s+k_2) & 0 \\ 0 & k_2 & -(s+k_3) \end{bmatrix} = (s+k_1)(s+k_2)(s+k_3) \tag{8}$$

Accordingly the individual transforms are

$$\bar{A} = \frac{1}{\Delta}\begin{bmatrix} A_0 & 0 & 0 \\ B_0 & -(s+k_2) & 0 \\ C_0 & k_2 & -(s+k_3) \end{bmatrix} = \frac{A_0}{s+k_1} \tag{9}$$

$$\bar{B} = \frac{1}{\Delta}\begin{bmatrix} (s+k_1) & A_0 & 0 \\ k_1 & B_0 & 0 \\ 0 & C_0 & -(s+k_3) \end{bmatrix} = -\frac{B_0}{s+k_2} + \frac{k_1A_0}{(s+k_1)(s+k_2)} \tag{10}$$

$$\bar{C} = \frac{1}{\Delta}\begin{bmatrix} (s+k_1) & 0 & A_0 \\ k_1 & (-(s+k_2) & B_0 \\ 0 & k_2 & C_0 \end{bmatrix}$$

$$= \frac{k_1k_2A_0}{(s+k_1)(s+k_2)(s+k_3)} - \frac{k_2B_0}{(s+k_2)(s+k_3)} - \frac{C_0}{s+k_3} \tag{11}$$

Inversion with a table of Laplace transforms gives the results,

$$A = A_0 \exp(-k_1t) \tag{12}$$

$$B = \frac{k_1A_0}{k_2-k_1}[\exp(-k_1t) - \exp(-k_2t)] - B_0 \exp(-k_2t) \tag{13}$$

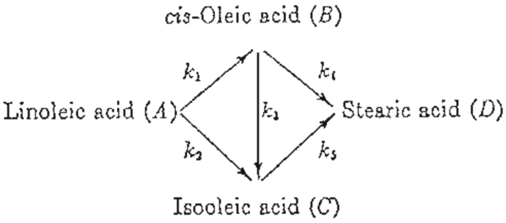
$$C = k_1k_2A_0\left[\frac{\exp(-k_1t)}{(k_2-k_1)(k_3-k_1)} + \frac{\exp(-k_2t)}{(k_1-k_2)(k_3-k_2)} + \frac{\exp(-k_3t)}{(k_1-k_3)(k_2-k_3)}\right]$$

$$- \frac{k_2B_0}{k_3-k_2}[\exp(-k_2t) - \exp(-k_3t)] - C_0 \exp(-k_3t) \tag{14}$$

Finally D is found with Eq (4).

P2.02.09. HYDROGENATION OF COTTONSEED OIL

For the hydrogenation of cottonseed oil, the main reactions are postulated by Eldib & Albright (*Ind Eng Chem* 49 825, 1957) as



On the assumption of all first order reactions, integrate the equations for A, B and C.

$$\frac{dA}{dt} = -(k_1+k_2)A \tag{1}$$

$$\frac{dB}{dt} = k_1A - (k_3+k_4)B \tag{2}$$

$$\frac{dC}{dt} = k_2A + k_3B - k_5C \tag{3}$$

The first equation has separable variables, the other two turn out to be linear.

$$A = A_0\exp[-(k_1+k_2)t] \tag{4}$$

Substitute into Eq (2).

$$\frac{dB}{dt} +(k_3+k_4)B = k_1A_0\exp[-(k_1+k_2)t]$$

$$B \exp[(k_3+k_4)t] = k_1A \int \exp[(k_3+k_4-k_1-k_2)t]dt + I$$

$$B = B_0 \text{ when } t = 0$$

$$B = \frac{k_1A_0}{k_3+k_4-k_1-k_2}\{\exp[-(k_1+k_2)t] - \exp[-(k_3+k_4)t]\}$$

$$+ B_0\exp[-(k_3+k_4)t] \tag{5}$$

Substitute into Eq (3),

$$\frac{dC}{dt} + k_5C = k_2A_0\exp[-(k_1+k_2)t] + \frac{k_1k_3A_0}{k_3+k_4-k_1-k_2}\exp[-(k_1+k_2)t]$$

$$+k_3[B_0- \frac{k_1A_0}{k_3+k_4-k_1-k_2}] \exp[-(k_3k_4)t]$$

$$= \alpha \exp[(-k_1+k_2)t] +\beta \exp[-(k_3+k_4)t] \tag{6}$$

$$\alpha = A_0(k_2 +\frac{k_1k_3}{k_3+k_4-k_1-k_2}) \tag{7}$$

$$\beta = k_3(B_0 - \frac{k_1A_0}{k_3+k_4-k_1-k_2}) \tag{8}$$

The integrating factor of Eq (6) is $\exp(k_5t)$ and the solution is

$$C \exp(k_5t) = \int\{ \alpha \text{ exo}[-(k_1+k_2)t] + \beta\exp\{-(k_3+k_4-k_5)t] \}dt + I$$

$$= \frac{\alpha}{k_1+k_2-k_5}\exp[-(k_1+k_2-k_5)t] -\frac{\beta}{k_3+k_4-k_5}\exp[-(k_3+k_4-k_5)t] + I$$

Evaluate the integration constant I, taking $C = C_0$ when $t = 0$. Then multiply by $\exp(-k_5t)$.

$$C = \frac{\alpha}{k_1+k_2-k_5}\{\exp(-k_5t) -\exp[-(k_1+k_2)t]\}$$

$$+ \frac{\beta}{k_3+k_4-k_5}\{\exp(-k_5t) -\exp[-(k_3+k_4)t]\}$$

For the final results substitute the values of α and β from (7) and (8). Component D can be found by solving the equation

$$\frac{dD}{dt} = k_4B + k_5C$$

after substitution for B and C, or by stoichiometric balance with the results for A, B and C.

P2.02.10. REVERSIBLE AND CONSECUTIVE REACTIONS

For the reversible first order reaction followed by a first reaction

$$A \underset{2}{\overset{1}{\rightleftharpoons}} B \overset{3}{\rightarrow} C$$

The rate equations are

$$\frac{dB}{dt} = -k_1A + k_2B \tag{1}$$

$$\frac{dB}{dt} = k_1A - (k_2+k_3)B \qquad (2)$$

$$C = A_0+B_0+C_0-A-B \qquad (3)$$

Transforming (1) and (2),

$$s\bar{A} - A_0 = -k_1\bar{A} + k_2\bar{B} \quad \text{or} \quad (s+k_1)\bar{A} - k_2\bar{B} = A_0$$

$$s\bar{B} - B_0 = k_1\bar{A} - (k_2+k_3)\bar{B} \quad \text{or} \quad -k_1\bar{A} + (s+k_2+k_3)\bar{B} = B_0$$

The determinant of the coefficients is

$$\Delta = \begin{pmatrix} s+k_1 & -k_2 \\ -k_1 & s+k_2+k_3 \end{pmatrix} = s^2+(k_1+k_2+k_3)s-k_1k_3 = (s+\beta_1)(s+\beta_2)$$

where β_1 and β_2 are the roots of the quadratic. Solving for the transforms,

$$\bar{A} = \frac{1}{\Delta}\begin{pmatrix} A_0 & -k_2 \\ B_0 & s+k_2+k_3 \end{pmatrix} = \frac{A_0s+A_0(k_2+k_3)+k_2B_0}{(s+\beta_1)(s+\beta_2)}$$

$$\bar{B} = \frac{1}{\Delta}\begin{pmatrix} s+k_1 & A_0 \\ -k_1 & B_0 \end{pmatrix} = \frac{B_0s+k_1(B_0-A_0)}{(s+\beta_1)(s+\beta_2)}$$

When $B_0 = 0$ the inverses are,

$$A = \frac{A_0}{\beta_2-\beta_1}[(k_2+k_3-\beta_1)\exp(-\beta_1t) - (k_2+k_3-\beta_2)\exp(-\beta_2t)]$$

$$B = \frac{k_1A_0}{\beta_1-\beta_2}[\exp(-\beta_1t)-\exp(-\beta_2t)]$$

P2.02.11. $A \Leftrightarrow B \Leftrightarrow C$, CONSECUTIVE REVERSIBLE.

These consecutive reversible first order reactions, $A \underset{2}{\overset{1}{\Leftrightarrow}} B \underset{4}{\overset{3}{\Leftrightarrow}} C$, have the rate equations

$$\frac{dA}{dt} = -k_1A + k_2B$$

$$\frac{dB}{dt} = k_1A - (k_2+k_3)B - k_3C$$

$$\frac{dC}{dt} = k_3B - k_4C$$

The transforms are,

$$s\bar{A} - A_0 = -k_1\bar{A} + k_2B \quad \text{or} \quad (s+k_1)\bar{A} - k_2\bar{B} = A_0$$

$$s\bar{B} - B_0 = k_1\bar{A} - k_2\bar{B} - k_3\bar{C} \quad \text{or} \quad -k_1\bar{A} + (s+k_2)\bar{B} + k_3\bar{C} = B_0$$

$$s\bar{C} - C_0 = k_3\bar{B} - k_4\bar{C} \quad \text{or} \quad -k_3\bar{B} + (s+k_4)\bar{C} = C_0$$

The determinant of the coefficients is

$$\Delta = \begin{pmatrix} (s+k_1 & -k_2 & 0 \\ -k_1 & (s+k_2) & k_3 \\ 0 & -k_3 & (s+k_4) \end{pmatrix}$$

$$= (s+k_1)(s+k_2)(s+k_4) - k_1k_2(s+k_4) + k_3^2(s+k_1)$$
$$= (s+\beta_1)(s+\beta_2)(s+\beta_3)$$

where the β_i are roots of the cubic equation. Solving for the individual transforms,

$$\bar{A} = \frac{1}{\Delta}\begin{vmatrix} A_0 & -k_2 & 0 \\ B_0 & (s+k_2) & k_3 \\ C_0 & -k_3 & (s+k_4) \end{vmatrix}$$

$$= \frac{A_0(s+k_2)(s+k_4)-k_2k_3C_0+k_2B_0(s+k_4)+k_3A_0^2(s+k_4)+k_3^2A_0(s+k_4)}{\Delta}$$

$$= \frac{s^2+\alpha_1 s+\alpha_2}{(s+\beta_1)(s+\beta_2)(s+\beta_3)}$$

Formulas for $\bar{B}$ and $\bar{C}$ are similar in form, a ratio of a quadratic and a factored cubic. Formulas for the inverses are given, but since no simplification appears possible, the final answers will not be written down.

$\frac{1}{(s+a)(s+b)(s+c)}$	$\frac{1}{(b-a)(c-a)}\epsilon^{-at}+\frac{1}{(a-b)(c-b)}\epsilon^{-bt}+\frac{1}{(a-c)(b-c)}\epsilon^{-ct}$
$\frac{s}{(s+a)(s+b)(s+c)}$	$\frac{-a}{(b-a)(c-a)}\epsilon^{-at}-\frac{b}{(a-b)(c-b)}\epsilon^{-bt}-\frac{c}{(a-c)(b-c)}\epsilon^{-ct}$
$\frac{s^2}{(s+a)(s+b)(s+c)}$	$\frac{a^2}{(b-a)(c-a)}\epsilon^{-at}+\frac{b^2}{(a-b)(c-b)}\epsilon^{-bt}+\frac{c^2}{(a-c)(b-c)}\epsilon^{-ct}$

P2.02.12. SECOND AND FIRST ORDER CONSECUTIVE

The reactions are, $2A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, with the rate equations,

$$\frac{dA}{dt} = -2k_1A^2$$

$$A = \frac{A_0}{(1+2k_1A_0t)}$$

$$\frac{dB}{dt} + k_2B = k_1A^2$$

$$= \frac{k_1A_0^2}{(1+2k_1A_0t)^2}$$

The integrating factor of this first order linear equation is $\exp(k_2t)$ so the solution is,

$$B\exp(k_2t) = \int \frac{k_1A_0^2\exp(k_2t)}{(1+2k_1A_0t)^2} + I$$

An analytical integration is possible after expansion of the exponential in a power series, namely $\exp(x) = \sum_0^\infty x^n/n!$. The indefinite integral that applies is

$$\begin{aligned}&\int x^m(ax+b)^n\,dx \\ &= \frac{1}{a(m+n+1)}\left[x^m(ax+b)^{n+1}-mb\int x^{m-1}(ax+b)^n\,dx\right] \\ &= \frac{1}{m+n+1}\left[x^{m+1}(ax+b)^n+nb\int x^m(ax+b)^{n-1}dx\right]. \quad \begin{pmatrix}m\ \text{pos.}\\ m+n\\ +1\neq 0\end{pmatrix}\end{aligned}$$

For practical purposes, however, a numerical solution may be easier.

P2.02.13. THE REACTIONS, $A \Rightarrow B$ AND $A+B \Rightarrow C$

The rate equations are

$$\frac{dA}{dt} = -k_1A - k_2AB = -A(k_1+k_2B) \qquad (1)$$

$$\frac{dB}{dt} = k_1A - k_2AB = A(k_1-k_2B) \qquad (2)$$

$$C = C_0 + 0.5(A_0-A) + 0.5(B_0-B) \qquad (3)$$

Eliminate the variable t between (1) and (2).

$$\frac{dB}{dA} = -\frac{k_1-k_2B}{k_1+k_2} = \frac{B-k}{B+k}$$

$$k = k_1/k_2$$

Integrating,

$$A = A_0-B_0+B - 2k\ \ln\frac{B-k}{B+k} \qquad (4)$$

Substituting into (2),

$$\frac{dB}{dt} = (k_1-k_2B)(A_0-B_o+B - 2k\ \ln\frac{B-k}{B+k}) \qquad (5)$$

Although the variables are separable, the integral cannot be found analytically, but

$B = f(t)$, numerically.

Then substitute into Rq (4) to obtain A as a function of t, and finally find C with Eq (3).

Alternately the numerical solution of Eqs (1) and (2) can be found directly by software ODE, without going through Eq (5).

P2.02.14. PAIR OF SECOND ORDER REACTIONS, $A+B \Rightarrow C$ AND $B+C \Rightarrow D$.

The rate equations are,

$$\frac{dA}{dt} = -k_1AB \qquad (1)$$

$$\frac{dB}{dt} = -k_1AB - k_2BC \qquad (2)$$

$$\frac{dC}{dt} = k_1AB - k_2BC \qquad (3)$$

$$D = D_0 + (A_0-A) + (C_0-C) \qquad (4)$$

The variable t is eliminated to give

$$\frac{dB}{dA} = 1 + \frac{k_2C}{k_1A} = 1 + ky \qquad (5)$$

$$\frac{dC}{dA} = -1 + \frac{k_2C}{k_1A} = -1 + ky \qquad (6)$$

where $k = k_2/k_1$ and

$$y = C/A \qquad (7)$$

Equations (5) and (6) are first order homogeneous types. Differentiating (7),

$$dC = Ady + ydA$$

$$\frac{dC}{dA} = y + A\frac{dy}{dA} = -1 + ky \qquad (8)$$

The integral of (8) is

$$\ln(A/A_0) = \int_{C_0/A_0}^{C/A} \frac{dy}{(k-1)y-1} = \frac{1}{k-1}\ln\frac{(k-1)C/A-1}{(k-1)C_0/A_0-1} \qquad (9)$$

which could be rearranged as

$$C/A = f_1(A) \qquad (10)$$

and substituted into (5). Then the variables will be separable with the integral,

$$B = B_0 + \int_{A_0}^{A} [1+f_1(A)]dA = f_2(A) \qquad (11)$$

Substitution into (1) and integration gives

$$-k_1(t-t_0) = \int_{A_0}^{A} \frac{dA}{Af_2(A)} \qquad (12)$$

from which

$$A = f_3(t) \qquad (13)$$

Some further juggling will yield B, C and D also as functions of t, but for most values of $k = k_1/k_2$ none of the required integrations can be done analytically. The alternative solution is numerical integration of the differential equations from the beginning.

P2.02.15. SIMULTANEOUS REACTIONS, A+B ⇒ C+E AND A+C ⇒ D+E

The solution proceeds by first eliminating the variable t from the two rate equations.

The reactions are $A + B \rightarrow C + E$ and $A + C \rightarrow D + E$, with $C_0 = D_0 = 0$. The stoichiometric balances are

$$A_0 - A = C + 2D \qquad (1)$$

$$B_0 - B = C + D \qquad (2)$$

$$A = A_0 - 2(B_0 - B) + C \qquad (3)$$

The rate equations are

$$\frac{dB}{dt} = -k_1AB \qquad (4)$$

$$\frac{dC}{dt} = k_1AB - k_2AC \qquad (5)$$

Dividing out dt and rearranging,

$$\frac{dC}{dB} - \frac{r}{B}C = -1, \qquad r = \frac{k_2}{k_1}$$

The integrating factor for this first-order linear equation is

$$z = \exp\int\left(-\frac{r}{B}\right)dB = B^{-r}$$

and the solution is

$$CB^{-r} = \int(-B^{-r})\,dB + I = -\frac{B^{1-r}}{1-r} + I = \frac{B_0^{1-r} - B^{1-r}}{1-r}$$

Rearranging,

$$C = \frac{B}{r-1}\left[1 - \left(\frac{B}{B_0}\right)^{r-1}\right] \qquad (6)$$

Substitute (6) into (3) and that result into (4), which becomes

$$\frac{dB}{dt} = -k_1AB$$

$$= -k_1B\left\{A_0 - 2(B_0 - B) + \frac{B}{r-1}\left[1 - \left(\frac{B}{B_0}\right)^{r-1}\right]\right\} \qquad (7)$$

The variables are separable, but for most values of r a numerical integration will be called for.

P2.02.16. SIMULTANEOUS REACTIONS A+B ⇒ C AND A+C ⇒ D

The specific rates are $k_1 = 0.3$ and $k_2 = 0.1$. Initial concentrations are $A_0 = 0.9$, $B_0 = 0.3$, $C_0 = D_0 = 0$. The stoichiometric balances are

$C = 3(B_0-B)-(A_0-A) = A-3B$

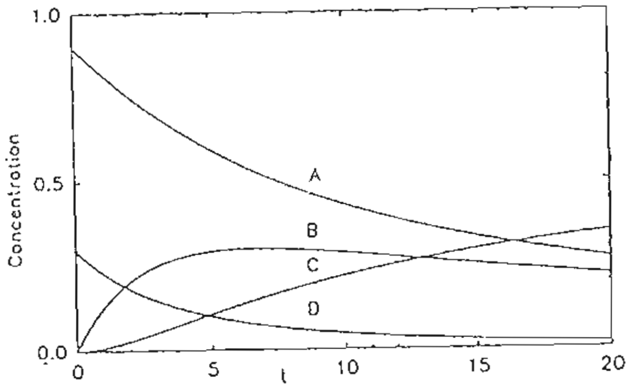
$D = (A_0-A)-(B_0-B) = 0.6+B-A$

The rate equations are

$$-\frac{dA}{dt} = k_1AB + k_2AC = 0.3AB + 0.15A(A-3B)$$

$$-\frac{dB}{dt} = k_1AB = 0.3AB$$

The process of eliminating the variable t from the rate equations, as in problem P2.02.14, does not lead to an analytically solvable problem, but a numerical solution is developed by ODE and is plotted.



P2.02.17. SECOND ORDER SEQUENCES. ANALYTICAL SOLUTIONS

Several cases are solved in terms of higher transcendental functions by Chien (JACS 76 2256, 1948). These are (a) A ⇒ B and 2B ⇒ C; (b) 2A ⇒ B ⇒ C; (c) 2A ⇒ B and 2B ⇒ C. Only case (a) is reported here, with $B_0 = 0$. The rate equations are

$$\frac{dA}{dt} = -k_1A \qquad (1)$$

$$\frac{dB}{dt} = k_1A - k_2B^2 \qquad (2)$$

$$C = C_0 + 0.5(A_0+B_0-A-B) \qquad (3)$$

Substitute the integral of (1) into (2),

$$\frac{dB}{dt} = k_1A_0\exp(-k_1t) - k_2B^2 \qquad (4)$$

This is a Riccati equation. On applying the transformation

$$B = \frac{1}{k_2 u}\frac{du}{dt} \qquad (5)$$

the result is a linear second order equation,

$$\frac{d^2u}{dt^2} - k_1k_2A_0\exp(-k_1t)\, u = 0 \qquad (6)$$

A change of the independent variable according to

$$\tau = \exp(-k_1t) \qquad (7)$$

leads to a Bessel equation,

$$\frac{d}{d\tau}(\tau\frac{du}{d\tau}) - Ku = 0, \quad K = k_1k_2A_0 \qquad (8)$$

whose solution may be written

$$u = a_1J_0(2j\sqrt{K\tau}) + a_2j\, H_0^{(1)}(2j\sqrt{K\tau}) \qquad (9)$$

where a_1 and a_2 are integration constants and J_0 and $H_0^{(1)}$ are Bessel functions of the first and third kinds of zero order, in the notation of Jahnke & Emde (1943 or 1966), and $j = \sqrt{-1}$.

After return from the variable u to the variable B and application of the condition $B_0 = 0$, the solution becomes

$$B = A_o\sqrt{\frac{\tau}{K}}\,\frac{jJ_1(\gamma) - \beta H_1^{(1)}(\gamma)}{J_0(\gamma) + \beta jH_0^{(1)}(\gamma)} \qquad (10)$$

$$\gamma = 2j\sqrt{K\tau}, \qquad \beta = jJ_1(\gamma)/H_1^{(1)} \qquad (11)$$

P2.03.01. DIFFUSION AND n-th ORDER REACTION

The rate of diffusion is proportional to the difference of concentrations between the bulk of the fluid and at the interface. In the steady state, the rates of diffusion and reaction are equal.

$$r = k_1(C-C_s) = k_2C_s^n = k_2(C-r/k_1)^n$$

For integral values of $n \le 4$, theoretically this polynomial always can be solved for r in terms of C, although some questions may arise about the proper choice from among multiple solutions.

When n = 1,

$$r = \frac{k_1k_2}{k_1+k_2}C$$

When n = 2,

$$\frac{r}{k_2} = C^2 - \frac{2r}{k_1} + \frac{r^2}{k_1^2}$$

$$r = \frac{k_1^2}{2}\left[\frac{k_1+2k_2}{k_1k_2} \pm \sqrt{\left(\frac{k_1+2k_2}{k_1k_2}\right)^2 - \frac{4C^2}{k_1^2}}\,\right]$$

A quadratic equation for r also results when the surface rate equation is a simple L-H type, as

$$r = k_1(C-C_s) = k_2C_s/(1+k_3C_s) = \frac{k_2(C-r/k_1)}{1+k_3(C-r/k_1)}$$

P2.03.02. ENZYME KINETICS. MICHAELIS-MENTEN EQUATION

The enzyme E and the reactant or substrate S are assumed to combine to form a complex ES that subsequently dissociates into product P and uncombined enzyme (Michaelis & Menten, *Biochem Zeit* 49 333, 1913).

$$S + E \underset{2}{\overset{1}{\Leftrightarrow}} ES$$

$$ES \overset{3}{\Rightarrow} E + P$$

If equilibrium always exists,

$$\frac{(S)(E)}{(ES)} = \frac{(S)[(E_0-(ES)]}{(ES)} = K_m$$

where (E_0) is the total of the free and combined enzyme and K_m is a dissociation constant. Solving for (ES),

$$(ES) = \frac{(E_0)}{1+K_m/(S)} = \frac{(E_0)(S)}{K_m+S}$$

The rate of formation of the product is

$$r = \frac{dP}{dt} = k_2(ES) = \frac{k_2(E_0)(S)}{K_m+(S)}$$

Several different linearized arrangements of this equation are in use for determination of the constants from rate data. In the simplified notation,

$$r = \frac{dC}{dt} = \frac{k_1C}{1+k_2C},$$

four modes are,

(i) $k_1(t-t_0) = k_2 \ln(C/C_0) + C - C_0$ Integrated equation

(ii) $\frac{1}{r} = \frac{k_2}{k_1}\left(\frac{1}{C}\right) + \frac{1}{k_1}$ Lineweaver-Burk

(iii) $\frac{C}{r} = \frac{1}{\frac{d\ln(C)}{dt}} = \frac{k_2}{k_1} + \left(\frac{1}{k_1}\right)C$ Hanes

(iv) $\frac{r}{C} = \frac{k_1}{k_2} - \left(\frac{1}{k_2}\right)r$ Eadie

P2.03.03. ENZYME KINETICS WITH REVERSIBLE DECOMPOSITION

The postulated mechanism is

$$S + E \underset{2}{\overset{1}{\Leftrightarrow}} ES \underset{4}{\overset{3}{\Leftrightarrow}} E + P$$

where E is the concentration of the enzyme, S is that of the nutrient and P that of the product. The concentration of ES is assumed to attain constancy.

$$\frac{d(ES)}{dt} = k_1(E)(S) - (k_2+k_3)(ES) - k_4(E)(P) \Rightarrow 0$$

The material balance on the enzyme is

$$(E_0) = (E) + (ES)$$

Accordingly,

$$(ES) = \frac{k_1(E_0)(S)+k_4(E_0)(P)}{k_2+k_3+k_1(S)+k_4(P)}$$

The net rate of formation of the product is

$$r = \frac{d(P)}{dt} = k_3(ES) - k_4(E)(P)$$

After substitution for (ES),

$$r = \frac{k_1k_3(E_0)(S)-k_2k_4(E_0)(P)}{k_2+k_3+k_1(S)+k_4(P)}$$

P2.03.04. CELL GROWTH RATE. MONOD EQUATION

The growth rate of cells is taken proportional to the cell concentration, x, and to an empirical form of the dependence on the cencentration , p, of the nutrient. That empirical form was assumed by Monod (1942) to be the same as in the Michaelis-Menten model for enzyme kinetics. This makes the rate of cell growth,

$$\frac{dx}{dt} = \frac{k_1px}{k_2+p} \qquad (1)$$

An additional assumption is that the change in cell concentration is proportional to the change in nutrient concentration, that is,

$$\frac{dx}{dp} = k_3 \qquad (2)$$

Solving this for p and substituting into Eq (1),

$$p = p_0(x-x_0)/k_3 \qquad (3)$$

$$\frac{dx}{dt} = \frac{k_1k_3(k_3p_0-x_0+x}{k_2k_3+k_3p_0-x_0+x} \qquad (4)$$

Integrating,

$$k_1k_3(t-t_0) = \int_{x_0}^{x} [\frac{\beta}{x(\alpha+x)} + \frac{1}{\alpha+x}]dx$$

$$= \frac{\beta}{\alpha} \ln\frac{(\alpha+x_0)x}{x_0(\alpha+x)} + \ln\frac{\alpha+x}{\alpha+x_0} \qquad (5)$$

$\alpha = k_3p_0-x_0$

$\beta = k_2k_3+k_3p_0-x_0$

P2.03.05. REACTION CATALYZED BY SOLIDS. LANGMUIR-HINSHELWOOD MECHANISM.

The pioneers are Langmuir (JACS 40 2361, 1918) and Hinshelwood (*Kinetics of Chemical Change*, 1940).

For a gas phase reaction, A + B ⇒ Products, catalyzed by a solid, the postulated mechanism consists of the following steps:

1. The reactants are first adsorbed on the surface where they subsequently react and the products are desorbed.
2. The rate of adsorption of A is proportional to its partial pressure and to the fraction, ϑ_v, of uncovered surface.
3. The rate of desorption of A is proportional to the fraction, ϑ_a, of the surface covered by A.
4. Adsorptive equilibrium is maintained.
5. The rate of reaction between adsorbed species is proportional to their amounts on the surface.

ϑ_a = fraction of surface covered by A

ϑ_b = fraction of surface covered by B

$$\vartheta_v = \text{fraction of uncovered surface} = 1-\vartheta_a-\vartheta_b$$

The net rates of adsorption are

$$r_a = k_a p_a \vartheta_v - k_{-a}\vartheta_a \Rightarrow 0$$

$$r_b = k_b p_b \vartheta_v - k_{-b}\vartheta_b \Rightarrow 0$$

Substitute for ϑ_v and rearrange to

$$(k_a p_a - k_{-a})\vartheta_a + k_a p_a \vartheta_b = k_a p_a$$

$$k_b p_b \vartheta_a + (k_b p_b - k_{-b})\vartheta_b = k_b p_b$$

The last two equations are solved for the surface coverages as,

$$\vartheta_a = \frac{K_a p_a}{1+K_a p_a+K_b p_b} = K_a p_a \vartheta_v, \quad K_a = k_a/k_{-a}$$

$$\vartheta_b = \frac{K_b p_b}{1+K_a p_a+K_b p_b} = K_b p_b \vartheta_v, \quad K_b = k_b/k_{-b}$$

$$\vartheta_v = \frac{1}{1+K_a p_a+K_b p_b}$$

The rate of surface reaction is

$$r = k\vartheta_a\vartheta_b = kK_aK_bp_ap_b\vartheta_v^2 = \frac{k' p_a p_b}{(1+K_a p_a+K_b p_b)^2}$$

From measured rate data, the constants may be found with the linearized form,

$$y = \sqrt{p_a p_b/r} = (1+K_a p_a+K_b p_b)/\sqrt{k'}$$

P2.03.06. CHAIN POLYMERIZATION

The process of chain growth of a polymer postulates a three step mechanism:

1. An initiator, I, generates a free radical $R^{\cdot}$.
2. The free radical reacts repeatedly with monomer by a process called propagation.
3. The free radical eventually disappears by some reaction called termination.

The stoichiometric equations are:

Initiation,

$$I \overset{k_1}{\Rightarrow} 2R^{\cdot}$$

$$R^{\cdot} + M \overset{k_2}{\Rightarrow} RM^{\cdot}$$

Propagation,

$$RM^{\cdot} + M \overset{k_p}{\Rightarrow} RM_2^{\cdot} \quad \text{or} \quad RM_n^{\cdot} + M \overset{k_p}{\Rightarrow} RM_{n+1}^{\cdot}$$

Termination,

$$RM_n^{\cdot} + RM_m^{\cdot} \overset{k_t}{\Rightarrow} R_2M_{n+m} \quad \text{or} \quad RM_n+RM_m$$

The rates of formation of the free radicals $R^{\cdot}$ and $M^{\cdot}$ reach steady states.

$$\frac{dR^{\cdot}}{dt} = 2k_1(I) - k_2(R^{\cdot})(M) = 0$$

$$\frac{dM^{\cdot}}{dt} = k_2(R^{\cdot})(M) - 2k_t(M^{\cdot})^2 = 0$$

These equations are solved for $R^\cdot$ and $M^\cdot$ and substituted into the propagation equation. The rate of polymerization becomes

$$r_p = -\frac{dM}{dt} = k_p(M^\cdot)(M) = k_p(\frac{k_1}{k_t})^{1/2}(I)^{1/2}(M)$$

Thus the process of chain polymerization is first order with respect to the monomer and half order with respect to the content of initiator.

P2.03.07. RICE-HERZFELD MECHANISM OF THERMAL DECOMPOSITIONS

Thermal decompositions of gaseous organic compounds are found to involve free radicals (Rice & Herzfeld, JACS 56 284, 1934). The process consists of an initiation step that forms free radicals, then propagation steps, and finally termination steps that destroy the free radicals. Three different kinds of termination steps will be examined.

The first step is the decomposition of the molecule into two radicals by dissociation of a carbon-carbon bond:

$$M \overset{k_1}{\Rightarrow} R_1^\cdot + R_1^\cdot, \quad \text{(initiation)} \qquad (1)$$

The radical $R_1^\cdot$, is not involved in the propagation but $R_1^\cdot$ participates in the following chain,

$$R_1^\cdot + M \overset{k_2}{\Rightarrow} R_2^\cdot + R_1H \quad \text{(propagation)} \qquad (2)$$

$$R_2^\cdot \overset{k_3}{\Rightarrow} R_1^\cdot + M' \quad \text{(propagation)} \qquad (3)$$

In reaction (2), $R_1^\cdot$ abstracts a hydrogen from M and forms the radical $R_2^\cdot$. In reaction (3), $R_2^\cdot$ dissociates at a carbon-carbon bond and regenerates the radical $R_1^\cdot$. The sequence continues until one of the following termination steps occurs:

$$R_1^\cdot + R_1^\cdot \overset{k_{4a}}{\Rightarrow} \text{Product} \qquad (4a)$$

$$R_2^\cdot + R_2^\cdot \overset{k_{4b}}{\Rightarrow} \text{Product} \qquad (4b)$$

$$R_1^\cdot + R_2^\cdot \overset{k_{4c}}{\Rightarrow} \text{Product} \qquad (4c)$$

(a) Termination mechanism (4a). Kinetics of 3.2 order.

The free radicals $R_1^\cdot$ and $R_2^\cdot$ are assumed to reach steady states,

$$\frac{d(R_1^\cdot)}{dt} = k_1(M) - k_2(M)(R_1^\cdot) + k_3(R_2^\cdot) - k_{4a}(R_1^\cdot)^2 = 0$$

$$\frac{d(R_2^\cdot)}{dt} = k_2(M)(R_1^\cdot) - k_3(R_2^\cdot) = 0$$

From which

$$R_1^\cdot = \sqrt{k_1/k_{4a}}\,\sqrt{M}$$

The rate of disappearance of M is

$$-\frac{d(M)}{dt} = k_1(M) + k_2(R_1^\cdot)(M) = k_1(M)[1+\frac{k_2}{k_1}(R_1^\cdot)]$$

After substitution for $R_1^\cdot$,

$$-\frac{d(M)}{dt} = k_1(M)[1+\frac{k_2}{\sqrt{k_1k_{4a}}}(M)^{0.5}]$$

The specific rates of the initiation and termination steps are small so unity in the bracket is negligible and the rate becomes

$$-\frac{d(M)}{dt} = k_2\sqrt{k_1/k_{4a}}(M)^{3/2}$$

(b) Termination mechanism (4b). First order reaction.

The steady state hypothesis is applied to the two free radicals.

$$\frac{d(R_1^{\cdot})}{dt} = k_1(M)-k_2(M)(R_1^{\cdot})+k_3(R_2^{\cdot}) = 0$$

$$\frac{d(R_2^{\cdot})}{dt} = k_2(M)(R_1^{\cdot})-k_3(R_2^{\cdot})-k_{4b}(R_2^{\cdot})^2 = 0$$

from which

$$R_2^{\cdot} = \sqrt{k_1/k_{4b}}\ (M)^{0.5}$$

$$R_1^{\cdot} = \frac{k_1}{k_2} + \frac{k_3}{k_2}\sqrt{k/k_{4b}}(M)^{-0.5}$$

The rate of disappearance of M becomes,

$$-\frac{d(M)}{dt} = k_1(M)[1+\frac{k_2}{k_1}(R_1^{\cdot})] = k_1(M)[2+\frac{k_3}{\sqrt{k_1k_{4b}}}(M)^{-0.5}]$$

Neglecting 2 in the bracket,

$$-\frac{d(M)}{dt} = k_3\sqrt{k_1/k_{4b}}\ (M)^{0.5}$$

(c) Termination step (4c). Kinetics of first order.

The steady state equations for the free radicals are

$$\frac{d(R_1^{\cdot})}{dt} = k_1(M)-k_2(R_1^{\cdot})(M)+k_3(R_2^{\cdot})-k_{4c}(R_1^{\cdot})(R_2^{\cdot}) = 0$$

$$\frac{d(R_2^{\cdot})}{dt} = k_2(R_1^{\cdot})(M) - k_3(R_2^{\cdot})-k_{4c}(R_1^{\cdot})(R_2^{\cdot}) = 0$$

By addition,

$$R_2^{\cdot} = \frac{k_1(M)}{2k_{4c}(R_1^{\cdot})}$$

Substitution into the previous equation gives

$$2k_2(R_1^{\cdot})^2 - k_1(R_1^{\cdot}) - k_3k_1/k_{4c} = 0$$

Neglecting the middle term since both k_1 and $R_1^{\cdot}$ are small,

$$(R_1^{\cdot}) = \sqrt{\frac{k_1k_3}{2k_2k_{4c}}}$$

The rate of reaction becomes,

$$-\frac{d(M)}{dt} = k_1(M)[1+\frac{k_2}{k_1}(R_1^{\cdot})] = k_1(M)[1+\sqrt{\frac{k_2k_3}{2k_1k_{4c}}}]$$

which is of the first order..

P2.03.08. REACTION, A+3B ⇒ C+D, BY A THREE STEP PROCESS

Consider the reaction, A+3B ⇒ C+D, for which the postulated mechanism is

$$A+B \underset{k_2}{\overset{k_1}{\Leftrightarrow}} X+D$$

$$X+B \underset{k_4}{\overset{k_3}{\Leftrightarrow}} Y+D$$

$$Y+B \overset{k_5}{\Rightarrow} C+D$$

X and Y are unstable intermediates whose net rates of production are zero. Find the equation for the reaction of A.

$$-\frac{dA}{dt} = k_1AB - k_2XD \qquad (1)$$

$$-\frac{dX}{dt} = -k_1AB + k_2XD + k_3XB - k_4YD = 0$$

$$X = \frac{k_1AB + k_4YD}{k_2D + k_3B} \qquad (2)$$

$$-\frac{dY}{dt} = -k_3XB + k_4YD + k_5YB = 0$$

$$Y = \frac{k_3XB}{k_4D+k_5B} \qquad (3)$$

Combining (2) and (3),

$$(k_2D + k_3B)X = k_1AB + k_4D\left[\frac{k_3XB}{k_4D+k_5B}\right.$$

$$X = \frac{k_1AB}{k_2D+k_3B - \frac{k_4BD}{k_4D+k_5B}} \qquad (4)$$

Substitute into Eq (1) and rearrange into the desired result..

$$-\frac{dA}{dt} = \frac{k_1k_3k_5AB^3}{k_3k_5B^2+k_2k_5BD+k_2k_4D^2} \qquad (5)$$

P2.03.09. ABCD FROM THE COMPONENTS BY A THREE STEP PROCESS

The overall reaction, A+B+C+D ⇒ ABCD, is assumed to proceed by three second order reversible processes,

$$A+B \underset{k_2}{\overset{k_1}{\Leftrightarrow}} AB \qquad (1)$$

$$AB+C \underset{k_4}{\overset{k_3}{\Leftrightarrow}} ABC \qquad (2)$$

$$ABC+D \underset{k_6}{\overset{k_5}{\Leftrightarrow}} ABCD \qquad (3)$$

where AB and ABC represent intermediate products whose net rates of formation are zero. Derive the equation for the rate of formation of ABCD.

For the intermediates,

$$\frac{d(AB)}{dt} = k_1(A)(B) - k_2(AB) - k_3(AB)(C) + k_4(ABC) = 0 \qquad (i)$$

$$\frac{d(ABC)}{dt} = k_3(AB)(C) - k_4(ABC) - k_5(ABC)(D) + k_6(ABCD) = 0 \qquad (ii)$$

The value of (AB) from (i) is substituted into (ii) which is then solved for (ABC) as

$$(ABC) = \frac{k_1k_3(A)(B)(C)+[k_2k_6+k_3k_6(C)](ABCD)}{k_2k_4+k_3k_5(D)+k_3k_5(C)(D)} \qquad (iii)$$

For the net product,

$$\frac{d(ABCD)}{dt} = k_5(ABC)(D) - k_6(ABCD) \qquad (iv)$$

Substitution of (iii) into (iv) gives the desired result,

$$\frac{d(ABCD)}{dt} = \frac{k_1k_3k_5(A)(B)(C)(D) - k_2k_4k_6(ABCD)}{k_2k_4+k_2k_5(D)+k_3k_5(C)(D)} \qquad (v)$$

P2.03.10. REACTION A + 2B ⇒ C + 2D, WITH A TWO STEP SEQUENCE

The reaction, A+2B ⇒ C+2D, proceeds according to the mechanism

$$A + B \underset{k_2}{\overset{k_1}{\Leftrightarrow}} X + D \qquad (1)$$

$$X + B \underset{k_4}{\overset{k_3}{\Leftrightarrow}} C + D \qquad (2)$$

for which

$$\frac{dX}{dt} = k_1AB - k_2XD - k_3XB + k_4CD = 0$$

and

$$X = \frac{k_1AB+k_4CD}{k_2D+k_3B} \qquad (3)$$

Substitution of (3) into

$$-\frac{dA}{dt} = k_1AB - k_2XD \qquad (4)$$

gives the desired result,

$$-\frac{dA}{dt} = \frac{k_1k_3AB^2-k_2k_4CD^2}{k_3B+k_2D} \qquad (5)$$

If reaction (2) is not reversible,

$$-\frac{dA}{dt} = \frac{k_1k_3AB^2}{k_3B+k_2D} \qquad (6)$$

P2.03.11. ACETALDEHYDE THERMAL DECOMPOSITION

For the thermal decomposition of acetaldehyde, a chain reaction propagated by free radicals is postulated:

$CH_3CHO \overset{k_1}{\Rightarrow} CH_3^{\cdot} + CHO^{\cdot}$ Initiation (1)

$CH_3^\cdot + CH_3CHO \overset{k_2}{\Rightarrow} CH_4 + CH_3CO^\cdot$ Propagation (2)

$CH_3CO^\cdot \overset{k_3}{\Rightarrow} CH_3^\cdot + CO$ Propagation (3)

$2CH_3^\cdot \overset{k_4}{\Rightarrow} C_2H_6$ Termination (4)

Apply the steady state hypothesis to the free radicals $CH_3^\cdot$ and $CH_3CO^\cdot$,

$$\frac{dCH_3^\cdot}{dt} = k_1(CH_3CHO) - k_2(CH_3CHO)(CH_3^\cdot)$$

$$+ k_3(CH_3CO^\cdot) - 2k_4(CH_3^\cdot)^2 = 0 \quad (5)$$

$$\frac{d(CH_3CO^\cdot)}{dt} = k_2(CH_3CHO)(CH_3^\cdot) - k_3(CH_3CO^\cdot) = 0 \quad (6)$$

from which

$$k_1(CH_3CHO) = 2k_4(CH_3^\cdot)^2 \quad (7)$$

The rate of reaction of acetaldehyde becomes

$$-\frac{d(CH_3CHO)}{dt} = k_1(CH_3CHO) + k_2(CH_3CHO)(CH_3^\cdot)$$

$$= k_1(CH_3CHO) + \sqrt{\frac{k_2^2k_1}{2k_4}}\,(CH_3CHO)^{3/2} \quad (8)$$

The first term of (8) is the initiation rate and is presumably small comparison with propagation. Accordingly,

$$-\frac{d(CH_3CHO)}{dt} = k(CH_3CHO)^{3/2} \quad (9)$$

Also,

$$\frac{d(CH_4)}{dt} = k_2(CH_3^\cdot)(CH_3CHO) = k_2\sqrt{k_1/2k_4}\,(CH_3CHO)^{3/2} \quad (10)$$

P2.03.12. PYROLYSIS OF ETHYL NITRATE, DATA FROM A CSTR

A chain reaction was proposed for the pyrolysis of ethyl nitrate Houser & Lee (J Phys Chem 71 3422, 1967):

$C_2H_5ONO_2 \overset{k_1}{\Rightarrow} C_2H_5O^\cdot + NO_2$ Initiation (1)

$C_2H_5O^\cdot \overset{k_2}{\Rightarrow} CH_3^\cdot + CH_2O$ Propagation (2)

$CH_3^\cdot + C_2H_5ONO_2 \overset{k_3}{\Rightarrow} CH_3NO_2 + C_2H_5O^\cdot$ Propagation (3)

$2C_2H_5O^\cdot \overset{k_4}{\Rightarrow} CH_3CHO + C_2H_5OH$ Termination (4)

The rate of reaction, mols/(ksec)(m^3), was measured in a CSTR in terms of concentration, mols/m^3, with the results,

C	0.0975	0.07590	0.0713	0.2714	0.2436
r	13.4	12.2	12.1	23.0	20.9

Find a rate equation consistent with the proposed mechanism and check it against the data.

Rewrite the reactions in simplified notation.

$A = C_2H_5ONO_2$

$B = C_2H_5O^\cdot$

$C = CH_3^{\cdot}$

For the free radicals,

$$\frac{dB}{dt} = k_1A-k_2B+k_3AC-k_4B^2 = 0$$

$$\frac{dC}{dt} = k_2B-k_3AC = 0$$

From which

$$B = \sqrt{k_1/k_4}\sqrt{A}$$

$$C = \frac{k_2}{k_3}\sqrt{\frac{k_1}{k_4}}\frac{1}{\sqrt{A}}$$

For the ethyl nitrate,

$$\frac{dA}{dt} = -k_1A - k_3AC = -A(\ k_1+ k_2\sqrt{k_1/k_4}\ \frac{1}{\sqrt{A}}\ )$$

Both k_1 and k_4 are small in comparison with k_4 so the second term dominates. Accordingly,

$$r_a = -\frac{dA}{dt} = k\ A^{0.5}$$

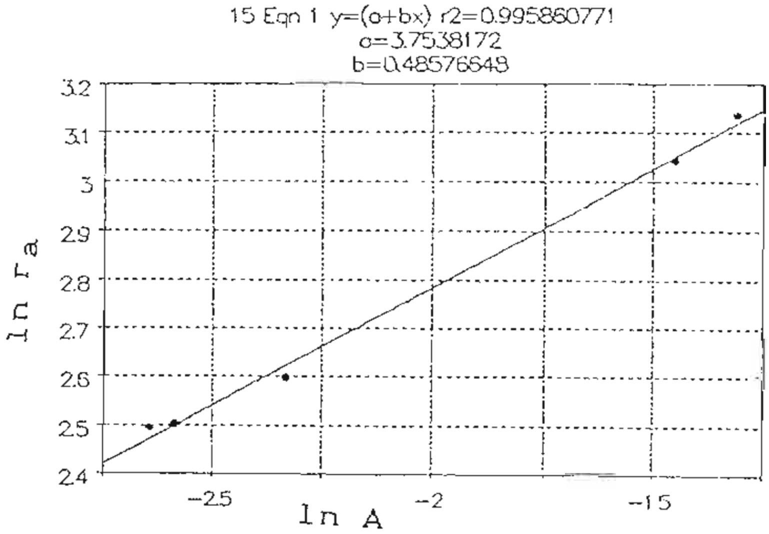
The log-log plot of the data has the equation

$$\ln r_a = 3.754 + 0.4858 \ln A$$

or

$$r_a = 42.69\ A^{0.4858}$$

which confirms the half order closely.



P2.03.13. DECOMPOSITION OF ETHANE

The postulated mechanism for the cracking of ethane involves three free radicals, H, CH_3 and C_2H_5, with the reactions, $C_2H_6 \overset{k_1}{\Rightarrow} 2CH_3$

$$CH_3 + C_2H_6 \overset{k_2}{\Rightarrow} CH_4 + C_2H_5$$

$$C_2H_5 \overset{k_3}{\Rightarrow} C_2H_4 + H$$

$$H + C_2H_6 \overset{k_4}{\Rightarrow} H_2 + C_2H_5$$

$$H + C_2H_5 \overset{k_5}{\Rightarrow} C_2H_6$$

The steady state equations for the free radicals are

$$\frac{d(CH_3)}{dt} = 2k_1(C_2H_6)-k_2(CH_3)(C_2H_6) = 0 \tag{1}$$

$$\frac{d(C_2H_5)}{dt} = k_2(CH_3)(C_2H_6)-k_3(C_2H_5)+k_4(H)(C_2H_6)-k_5(H)(C_2H_5) = 0 \tag{2}$$

$$\frac{d(H)}{dt} = k_3(C_2H_5)-k_4(H)(C_2H_6)-k_5(H)(C_2H_5) = 0 \tag{3}$$

Addition of (1), (2) and (3) followed by rearrangement gives,

$$(H) = \frac{k_1(C_2H_6)}{k_5(C_2H_5)} \tag{4}$$

Insertion of this into (3) gives,

$$k_1k_5(C_2H_5)^2 - k_1k_5(C_2H_6)(C_2H_5) - k_1k_4(C_2H_6)^2 = 0 \tag{5}$$

Since k_1 and k_5 are both small, the middle term can be ignored, so that

$$(C_2H_5) = \sqrt{\frac{k_1k_4}{k_3k_5}}\ (C_2H_6) \tag{6}$$

This makes the rate of production of ethylene,

$$\frac{d(C_2H_4)}{dt} = k_3(C_2H_5) = \sqrt{\frac{k_1k_3k_4}{k_5}}\ (C_2H_6) \tag{7}$$

which is a first order reaction.

P2.03.14. NITROGEN PENTOXIDE DECOMPOSITION

For the decomposition of N_2O_5 this mechanism is postulated,

$N_2O_5 \overset{k_1}{\underset{k_2}{\Leftrightarrow}} NO_2 + NO_3$ Initiation

$NO_2 + NO_3 \overset{k_3}{\Rightarrow} NO + O_2 + NO_2$ Propagation

$NO + NO_3 \overset{k_4}{\Rightarrow} 2NO_2$ Termination

Assume that NO and NO_3 attain steady states.

$$\frac{d(NO)}{dt} = k_3(NO_2)(NO_3) - k_4(NO)(NO_3) = 0$$

$$(NO) = (k_3/k_4)(NO_2) \tag{1}$$

$$\frac{d(NO_3)}{dt} = k_1(N_2O_5)-k_2(NO_2)(NO_3)-k_3(NO_2)(NO_3)-k_4(NO)(NO_3) = 0$$

$$(NO_3) = \frac{k_1(N_2O_5)}{(k_2+2k_3)(NO_2)} \tag{2}$$

For the decomposition of the pentoxide,

$$\frac{d(N_2O_5)}{dt} = k_1(N_2O_5) - k_2(NO_2)(NO_3)$$

$$= (N_2O_5)\ [k_1-\frac{k_1k_2}{k_2+2k_3}] = -\frac{2k_1k_3}{k_2+2k_3}\ (N_2O_5) \tag{3}$$

Also, it turns out that

$$\frac{d(NO_2)}{dt} = \frac{3k_1k_3}{k_2+2k_3}(N_2O_5)$$

P2.03.15. HYDROGEN AND BROMINE REACTION

A proposed mechanism is the following:

$Br_2 \overset{k_a}{\Rightarrow} 2Br$ Initiation

$Br + H_2 \overset{k_b}{\Rightarrow} HBr + H$ Propagation

$H + Br_2 \overset{k_c}{\Rightarrow} HBr + Br$ Propagation

$H + HBr \overset{k_d}{\Rightarrow} H_2 + Br$ Inhibition

$Br + Br \overset{k_e}{\Rightarrow} Br_2$ Termination

The rate of formation of HBr is

$$\frac{d(HBr)}{dt} = k_b((Br)(H_2)+k_c(H)(Br_2)-k_d(H)(HBr) \quad (1)$$

For the free radicals (H) and (Br),

$$\frac{d(H)}{dt} = k_b(Br)(H_2)+k_c(H)(Br_2)-k_d(HBr) = 0 \quad (2)$$

$$\frac{d(Br)}{dt} = 2k_a(Br_2)-k_b(Br)(H_2)$$

$$+k_c(H)(Br_2)+k_d((H)(HBr)-2k_e(Br)^2 = 0 \quad (3)$$

Addition of (2) and (3) gives

$$(Br) = (k_a/k_e)^{0.5}(Br_2)^{0.5} \quad (4)$$

Substitution of (4) into (2) results in

$$(H) = \frac{k_b(k_a/k_e)^{0.5}(H_2)}{k_c(Br_2)+k_d(HBr)} \quad (5)$$

Final substitutions of (4) and (5) into (1) gives Bodenstein's formula

$$\frac{d(HBr)}{dt} = \frac{2k_b(k_a/k_e)^{0.5}(H_2)(Br_2)^{0.5}}{1+[k_d(HBr)/k_c(Br_2)]} \quad (6)$$

$$= \frac{2k_bk_c(k_a/k_e)^{0.5}(H_2)(Br_2)^{1.5}}{k_c(Br_2)+k_d(HBr)} \quad (7)$$

P2.03.16. PHOSGENE FROM CO AND Cl_2

(a) One postulated mechanism consists of these reactions:

$Cl_2 \Leftrightarrow 2Cl$

$Cl + CO \Leftrightarrow COCl$

$COCl + Cl_2 \overset{k_3}{\Rightarrow} COCl_2 + Cl$

The first two reactions are taken to be at equilibrium.

$$\frac{(Cl)^2}{(Cl_2)} = K_1$$

$$\frac{(COCl)}{(CO)(Cl)} = K_2$$

From which the intermediates are

$$(COCl) = K_1^{0.5}K_2(CO)(Cl_2)^{0.5}$$

$$(Cl) = K_1^{0.5}(Cl_2)^{0.5}$$

The rate of formation of phosgene by the third reaction becomes

$$\frac{d(COCl_2)}{dt} = k_3(COCl)(Cl_2) = k_3(K_1^{0.5}K_2(CO)(Cl_2)^{1.5}$$

(b) An alternative mechanism is

$$Cl_2 \Leftrightarrow 2Cl$$
$$Cl + Cl_2 \Leftrightarrow Cl_3$$
$$Cl_3 + CO \Rightarrow COCl_2 + Cl$$

Assuming the first two reactions to be at equilibrium,

$$(Cl)^2/(Cl_2) = K_1$$
$$(Cl_3)/(Cl)(Cl_2) = K_2$$

From which

$$(Cl_3) = K_1^{0.5}K_2(Cl_2)^{1.5}$$

Then

$$\frac{d(COCl_2)}{dt} = k_3(Cl_3)(CO) = k_3K_1^{0.5}K_2(CO)(Cl_2)^{1.5}$$

P2.03.17. PHOTOCHEMICAL OXIDATION OF PHOSGENE.

For the reaction

$$2COCl_2 + O_2 \Rightarrow 2CO_2 + 2Cl_2$$

it was shown (Rollefson & Montgomery, JACS 55 142, 4025, 1933) that a suitable rate equation is

$$\frac{d(CO_2)}{dt} = \frac{kI_0(COCl_2)}{1+k'(Cl_2)/(O_2)} \qquad (1)$$

where I_0 is the intensity of the incident radiation. The experimental rate equation is accounted for by the following mechanism:

$$COCl_2 + h\nu \overset{1}{\Rightarrow} COCl + Cl$$
$$COCl + O_2 \overset{2}{\Rightarrow} CO_2 + ClO$$
$$COCl_2 + ClO \overset{3}{\Rightarrow} CO_2 + Cl_2 + Cl$$
$$COCl + Cl_2 \overset{4}{\Rightarrow} COCl_2 + Cl$$
$$Cl + Cl + M \overset{5}{\Rightarrow} Cl_2 + M$$

It was assumed that the radicals ClO and COCl attain steady state.

$$\frac{d(COCl)}{dt} = k_1I_0(COCl_2) - k_2(COCl)(O_2) - k_4(COCl)(Cl_2) = 0$$

$$(COCl) = \frac{k_1I_0(COCl_2)}{k_2(O_2)+k_4(Cl_2)} \qquad (2)$$

$$\frac{d(ClO)}{dt} = k_2(O_2)(COCl) - k_3(COCl_2)(ClO) = 0$$

$$(ClO) = \frac{k_2(O_2)(COCl)}{k_3(COCl_2)} \qquad (3)$$

The rate of formation of CO_2 is

$$\frac{d(CO_2)}{dt} = k_2(O_2)(COCl)+k_3(COCl_2)(ClO)$$

$$= 2k_2(O_2)(COCl)$$

$$= \frac{2k_1I_0(O_2)(COCl_2)}{k_2(O_2)+k_4(Cl_2)} \tag{4}$$

$$= \frac{2(k_1/k_2)I_0(COCl_2)}{1+(k_4/k_2(Cl_2)/(O_2)} \tag{5}$$

Lines (1) and (5) are of the same form.

P2.03.18. DECOMPOSITION OF OZONE CATALYZED BY CHLORINE

The catalytic decomposition of ozone by chlorine is believed to occur by the following chain reactions,

$Cl_2 + O_3 \xrightarrow{1} ClO + ClO_2$ initiation (1)

$ClO_2 + O_3 \xrightarrow{2} ClO_3 + O_2$ propagation (2)

$ClO_3 + O_3 \xrightarrow{3} ClO_2 + 2\ O_2$ propagation (3)

$ClO_3 + ClO_3 \xrightarrow{4} Cl_2 + 3\ O_2$ termination (4)

The chain carriers ClO_2 and ClO_3 are assumed to attain steady states. The rate of disappearance of ozone is

$$-\frac{d(O_3)}{dt} = k_1(Cl_2)(O_3) - k_2(ClO_2)(O_3) + k_3(ClO_3)(O_2) \tag{5}$$

For the chain carriers,

$$\frac{d(ClO_2)}{dt} = k_1(Cl_2)(O_3)-k_2(ClO_2)(O_3)+k_3(ClO_3)(O_2) = 0 \tag{6}$$

$$\frac{d(ClO_3)}{dt} = k_2(ClO_2)(O_3)-k_3(ClO_3)(O_3)-k_4(ClO_3)^2 = 0 \tag{7}$$

Addition of (6) and (7) followed by rearrangement gives,

$$(ClO_3) = \sqrt{k_1/k_4}\ (Cl_2)^{1/2}(O_3)^{1/2} \qquad ((8)$$

Substitution into (7) then gives

$$(ClO_2) = \frac{k_3}{k_2}\sqrt{\frac{k_1}{k_4}}\ (Cl_2)^{1/2}(O_3) + \frac{k_1}{k_2}(Cl_2) \tag{9}$$

Final substitution of (8) and (9) into (5) gives,

$$-\frac{d(O_3)}{dt} = 2k_3\sqrt{\frac{k_1}{k_4}}\ (Cl_2)^{1/2}(O_3)^{3/2} + 2k_1(Cl_2)(O_3) \tag{10}$$

Since the chains are long compared with the initiation step, the second term of (10) can be dropped and the rate becomes

$$-\frac{d(O_3)}{dt} = k(Cl_2)^{1/2}(O_3)^{3/2} \tag{11}$$

P2.03.19. OZONE DECOMPOSITION

The reaction, $2O_3 \Rightarrow 3\ O_2$, is believed to have the following mechanism,

$O_3 + M \underset{2}{\overset{1}{\rightleftharpoons}} O_2 + O + M$ (1)

$O + O_3 \xrightarrow{3} 2\ O_2$ (2)

where M is any molecule. Find the rate of decomposition of the ozone, with either of the two assumptions of parts (a) and (b).

(a) Assume that (O) attains steady state.

$$\frac{d(O)}{dt} = k_1(O_3)(M)-k_2(O).(O_2)(M) -k_3(O)(O_3) = 0 \qquad (3)$$

$$(O) = \frac{k_1(O_3)(M)}{k_2(O_2)(M) +k_3)(O_3)} \qquad (4)$$

The ozone rate becomes,

$$\frac{d(O_3)}{dt} = -k_1(O_3)(M) +k_2(O_2)(O)(M) -k_3(O)(O_3)$$

$$= -k_1(O_3)(M) + [\frac{k_1(O_3)(M)}{k_2(O_2)(M)+k_3(O_3)}][k_2(O_2)(M)-k_3(O_3)]$$

$$= \frac{-2\ k_1(O_3)^2}{k_2(O_2) + k_3(O_3)/(M)} \qquad (5)$$

(b) Assume that reaction (1) is in equilibrium. Then,

$$(O) = \frac{K_e(O_3)(M)}{(O_2)(M)} = \frac{K_e(O_3)}{(O_2)} \qquad (6)$$

The ozone rate becomes,

$$-\frac{d(O_3)}{dt} = k_3(O_3)(O) = \frac{k_3K_e(O_3)^2}{(O_2)} \qquad (7)$$

When the second part of the denominator of Eq (5) is relatively small, (5) and (7) will be of the same form.

P2.03.20. DECOMPOSITION OF DIETHYL ETHER.

Thermal decomposition of diethyl ether is postulated by Hinshelwood (Kinetics of Chemical Change, 1941) to proceed by the chain mechanism,

$$C_2H_5OC_2H_5 \overset{1}{\Rightarrow} CH_3 + CH_2OC_2H_5$$

$$CH_3 + C_2H_5OC_2H_5 \overset{2}{\Rightarrow} C_2H_6 + CH_2OC_2H_5$$

$$CH_2OC_2H_5 \overset{3}{\Rightarrow} CH_3 + CH_3CHO$$

$$CH_3 + CH_2OC_2H_5 \overset{4}{\Rightarrow} \text{end of chain}$$

$A = C_2H_5OC_2H_5$
$B = CH_3$
$C = CH_2OC_2H_5$

In the steady state the derivatives of the free radicals B and C are zero.

$$\frac{dB}{dt} = k_1A -k_2AB +k_3C -k_4BC = 0 \qquad (1)$$

$$\frac{dC}{dt} = k_1A + k_2AB - k_3C - k_4BC \qquad (2)$$

On combining (1) and (2),

$$B = \sqrt{\frac{k_1k_3}{k_2k_4}} \qquad (4)$$

For the rate of decomposition of A,

$$-\frac{dA}{dt} = k_1A + k_2AB = (k_1 + k_2\sqrt{\frac{k_1k_3}{k_2k_4}})\ A \qquad (5)$$

Since k_1 is small in comparison with k_2 and k_3 and of the same order of magnitude as k_4, the first term in parentheses of (5) can be neglected with the final result,

$$-\frac{d(C_2H_5OC_2H_5)}{dt} = \sqrt{\frac{k_1k_2k_3}{k_4}}\ (C_2H_5OC_2H_5) \qquad (6)$$

P2.03.21. CHLORINATION OF n-HEPTANE

The reaction between chlorine and n-heptane involves the free radicals Cl and C_7H_{15} as follows:

$$Cl_2 \overset{1}{\Rightarrow} 2\ Cl$$

$$Cl + C_7H_{16} \overset{2}{\Rightarrow} C_7H_{15} + HCl$$

$$C_7H_{15} + Cl_2 \overset{3}{\Rightarrow} C_7H_{15}Cl + Cl$$

$$C_7H_{15} \overset{4}{\Rightarrow} \text{end of chain}$$

Find the rate of the reaction,

$$Cl_2 + C_7H_{16} \Rightarrow C_7H_{15}Cl + HCl$$

The free radicals attain steady states.

$$\frac{d(Cl)}{dt} = 2\ k_1(Cl_2)-k_2(C_7H_{16})(Cl) + k_3(C_7H_{15})(Cl_2) = 0 \qquad (1)$$

$$\frac{d(C_7H_{15})}{dt} = k_2(C_7H_{16})(Cl)-k_3(C_7H_{15})(Cl_2)-k_4(C_7H_{15}) = 0 \qquad (2)$$

From (1) and (2),

$$(C_7H_{15}) = \frac{2\ k_1}{k_4}\ (Cl_2) \qquad (3)$$

and the rate of chlorination becomes,

$$-\frac{d(Cl_2)}{dt} = k_1(Cl_2)+k_3(C_7H_{15})(Cl_2) \qquad (4)$$

$$= k_1(Cl_2)[1 + \frac{2k_3}{k_4}\ (Cl_2)] \qquad (5)$$

P2.03.22. DECOMPOSITION OF NITROUS OXIDE.

The decomposition of nitrous oxide is believed to proceed with the intermediate generation of atomic oxygen according to the reactions

$$N_2O \underset{2}{\overset{1}{\Leftrightarrow}} N_2 + O$$

$$N_2O + O \overset{3}{\Rightarrow} N_2 + O_2$$

The atomic oxygen attains a steady state.

$$\frac{d(O)}{dt} = k_1(N_2O) - k_2(N_2)(O) - k_3(N_2O)(O) = 0$$

from which

$$(O) = \frac{k_1(N_2O)}{k_2(N_2)+k_3(N_2O)}$$

For the nitrous oxide,

$$-\frac{d(N_2O)}{dt} = k_1(N_2O) - k_2(N_2)(O) + k_3(N_2O)(O)$$

$$= k_1(N_2O) + \frac{k_1[k_3(N_2O)-k_2(N_2)](N_2O)}{k_2(N_2)+k_3(N_2O)}$$

$$= \frac{2\ k_1k_3(N_2O)^2}{k_2(N_2)+k_3(N_2O)}$$

P2.03.23. PHOSPHOROUS ACID

In the presence of an oxidant (Y), hypophosphorous acid (A) is transformed into phosphorous acid (B). The kinetics of the reaction has these features:

(1) at low concentration of oxidant, $r_b = k(Y)(A)$

(2) at high concentration of oxidant, $r_b = k(H^+)(A)$

To explain this behavior, it is postulated that with hydrogen as catalyst, H_3PO_2 is transformed into an active form, X. This intermediate form then reacts with the oxidant to give H_3PO_3. Show that this scheme explains the observed kinetics. (Levenspiel, 1972).

$$H_3PO_2\ (A) + H^+ \underset{2}{\overset{1}{\rightleftharpoons}} X + H^+$$

$$X + Y \xrightarrow{3} H_3PO_3\ (B)$$

The concentration of the intermediate attains steady state.

$$\frac{d(X)}{dt} = k_1(A)(H^+) - k_2(X)(H^+) - k_3(X)(Y) = 0$$

$$X = \frac{k_1(A)(H^+)}{k_2(H^+)+k_3(Y)} \qquad (1)$$

The rate of formation of phosphorous acid becomes

$$r_b = \frac{d(H_3PO_3)}{dt} = k_3(X)(Y) = \frac{k_1k_3(A)(H^+)(Y)}{k_2(H^+)+k_3(Y)} \qquad (2)$$

At low concentrations of the oxidant Y, the second term of the denominator of (2) becomes negligible and

$r_b = k(Y)(A) = k(\text{oxidant})(\text{hypophosphorous acid})$

At high concentrations of the oxidant, the first term in the denominator becomes negligible and

$r_b = k(H^+)(A) = k\ (\text{hydrogen ion})(\text{hypophosphorous acid})$

both in accordance with observations.

P2.03.24. ACETONE DECOMPOSITION

The following mmechanism has been proposed for the decomposition of acetone by Rice & Herzfeld:

$$CH_3COCH_3 \xrightarrow{1} CH_3' + CHCO'$$

$$CH_3CO' \xrightarrow{2} CH_3' + CO$$

$$CH_3' + CH_3COCH_3 \xrightarrow{3} CH_3COCH_2' + CH_4$$

$$CH_3COCH_2' \overset{4}{\Rightarrow} CH_3' + CH_2CO$$

$$CH_3' + CH_3COCH_2' \overset{5}{\Rightarrow} C_2H_5COCH_3$$

Let $A = CH_3COCH_3$, $B = CH_3'$, $C = CH_3CO'$, $F = CH_3COCH_2'$. Assume that the concentrations of the free radicals B, C and F reach steady state. The rate equations are

$$\frac{dB}{dt} = k_1A + k_2C - k_3AB + k_4F - k_5BF = 0 \qquad (1)$$

$$\frac{dC}{dt} = k_1A - k_2C = 0 \qquad (2)$$

$$\frac{dF}{dt} = k_3AB - k_4F - k_5BF = 0 \qquad (3)$$

Adding these equations,

$$2k_1A - 2k_5BF = 0$$

$$F = \frac{k_1A}{k_5B} \qquad (4)$$

From (3) alone,

$$F = \frac{k_3AB}{(k_4+k_5)B} \qquad (5)$$

From (4) and (5),

$$k_3k_5B^2 - k_1k_5B - k_1k_4 = 0 \qquad (6)$$

Since both k_1 and k_5 are small, neglect the middle term of (6) and solve for

$$B = \sqrt{\frac{k_1k_4}{k_3k_5}} \qquad (7)$$

Substitute into

$$\frac{dA}{dt} = \frac{d(CH_3COCH_3)}{dt} = (k_1+k_3B)A = (k_1+k_3\sqrt{\frac{k_1k_4}{k_3k_5}})\ A$$

$$= (k_1\sqrt{k_5} + \sqrt{k_1k_3k_4/k_5})\ A \Rightarrow \sqrt{k_1k_3k_4/k_5}\ (CH_3COCH_3)$$

on again neglecting a relatively small term. Thus the decomposition of acetone is a first order process.

P2.03.25. THERMAL CRACKING OF PROPANE

The thermal cracking of propane is practiced industrially for the primary purpose of making ethylene and propylene, but other reactions also occur. A scheme worked out by Sundaram & Froment (Chem Eng Sci 32 601, 1977) consists of the nine reactions of the table. Equilibrium constants were deduced from thermodynamic data and the other constants by nonlinear regression from the extensive data on this topic in the literature and laboratory.

	Reaction	Rate Rate equation
1	$C_3H_8 \longrightarrow C_2H_4 + CH_4$	$r_1 = k_1C_{C_3}H_8$
2	$C_3H_8 \rightleftharpoons C_3H_6 + H_2$	$r_2 = k_2\left(C_{C_3H_8} - \frac{C_{C_3H_6}C_{H_2}}{K_{C_3}}\right)$
3	$C_3H_8 + C_2H_4 \longrightarrow C_2H_6 + C_3H_6$	$r_3 = k_3C_{C_3H_8}C_{C_2H_4}$
4	$2C_3H_6 \longrightarrow 3C_2H_4$	$r_4 = k_4C_{C_3H_6}$

5	$2C_3H_6 \longrightarrow 0.5C_6 + 3CH_4$	$r_5 = k_5C_{C_3H_6}$
6	$C_3H_6 \rightleftharpoons C_2H_2 + CH_4$	$r_6 = k_6\left(C_{C_3H_6} - \frac{C_{C_2H_2}C_{CH_4}}{K_{C_6}}\right)$
7	$C_3H_6 + C_2H_6 \longrightarrow C_4H_8 + CH_4$	$r_7 = k_7C_{C_3H_6}C_{C_2H_6}$
8	$C_2H_6 \rightleftharpoons C_2H_4 + H_2$	$r_8 = k_8\left(C_{C_2H_6} - \frac{C_{C_2H_4} \cdot C_{H_2}}{K_{C_8}}\right)$
9	$C_2H_4 + C_2H_2 \longrightarrow C_4H_6$	$r_9 = k_9C_{C_2H_4}C_{C_2H_2}$

P2.03.26. A KINETIC REFORMING MODEL

The purpose of catalytic reforming of gasoline is to improve its octane rating, largely by increasing its aromatic content. The reactions involve a large number of participants. In the development of the Mobil Kinetic Reforming Model (Ramage et al, in Wei (Editor), Advances in Chemical Engineering 13 193-260, 1987), some 300 individual species were identified. These were lumped into a much smaller number of pseudo components identified by carbon number and chemical nature. The lumps vary with the age of the catalyst. The table shows the 13 lumps adopted for the "start of kinetic cycle". The kinetic characteristics of these lumps are proprietary data.

KINPTR START-OF-CYCLE KINETIC LUMPS (INDEX)

Carbon number	Six-carbon-ring naphthenes (N_6)	Five-carbon-ring naphthenes (N_5)	Paraffins (P)	Aromatics (A)
C_{8+}	C_{8+} cyclohexanes (1)	C_{8+} cyclopentanes (2)	C_{8+} paraffins (3)	C_{8+} aromatics (4)
C_7	Methylcyclohexane (5)	Cyclopentanes (6)	Heptanes (7)	Toluene (8)
C_6	Cyclohexane (9)	Methylcyclopentane (10)	Hexanes (11)	Benzene (12)
C_{5-}				C_{5-} hydrocarbons (13)

P2.04.01. ALKYLATION OF ISOPROPYLBENZENE

Isopropylbenzene (A) is alkylated with propylene (P) using HF catalyst. The mono (B), di (C), tri (D) and tetra (E) derivatives are formed. Relative specific rates are given by Rodiguin & Rodiguina (*Consecutive Chemical Reactions*, 1964) for the case of a large excess of propylene which makes the reactions pseudo first order. The relative specific rates used here are $k_1 = 1.0$, $k_2 = 0.5$, $k_3 = 0.3$ and k_4 0.2. The system of linear differential equations can be solved by Laplace transform but the result is quite cumbersome. The nonlinear system with limited propylene is not solvable analytically.

Here, both linear and nonlinear systems are solved numerically with Constantinides ODE software. The nonlinear set is solved with $P_0 = 4A_0 = 400$, just enough to convert $A_0 = 100$ to the tetra derivative.

The differential equations are

$r_a = -k_1AP$

$r_b = (k_1A-k_2B)P$

$r_c = (k_2B-k_3C)P$

$r_d = (k_3C-k_4D)P$

$r_e = k_4DP$

$A_0 = 100$

$B_0 = C_0 = D_0 = E_0 = 0$

$P + 400 - B - 2C - 3D - 4E$

The tables shown how the equations are entered into the program. For the linear case, P is incorporated in the specific rates as constants.

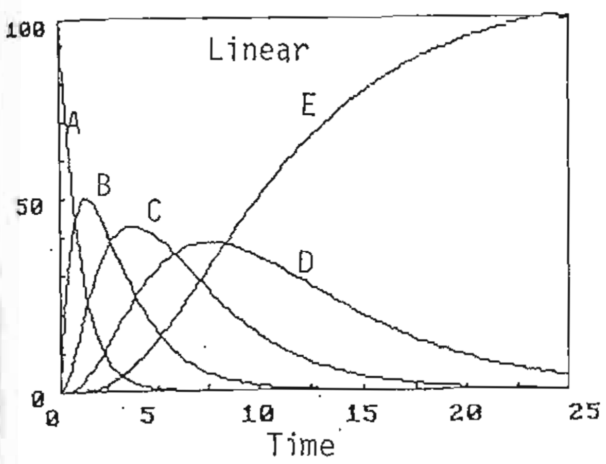
The solutions of both cases are obtained equally readily by the program. The graphs show behaviors to be similar. The true time behaviors are not known because only relative values of the specific rates have been used.

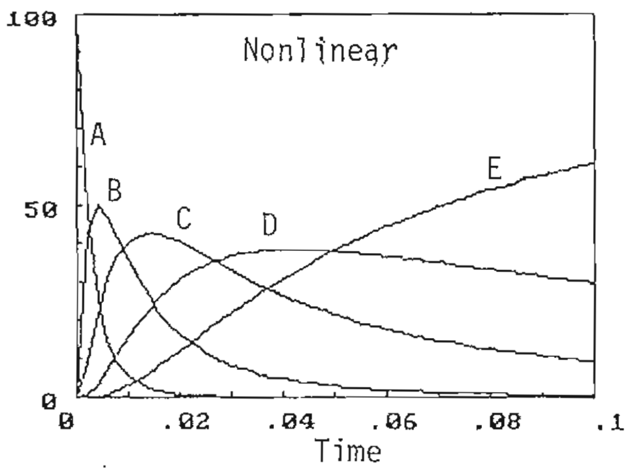
Linear equations,

```
g(1) = -y(1)
g(2) = y(1) - 0.5*y(2)
g(3) = 0.5*y(2)-0.3y*y(3)
g(4) = 0.3*y(3)-0.2*y(4)
g(5) = 0.2*y(4)
```

Nonlinear equations,

```
g(1)=-y(1)*(400-y(2)-2*y(3)-3*y(4)-4*y(5))
g(2)=y(1)-0.5*y(2))*(400-y(2)-2*y(3)-3*y(4)-4*y(5))
g(3)=(0.5*y(2)-0.3*y(3))*(400-y(2)-2*y(3)-3*y(4)-4*y(5))
g(4)=(0.3*y(3)-0.2*y(4))*(400-y(2)-2*y(3)-3*y(4)-4*y(5))
g(5)=0.2*y(4)*(400-y(2)-2*y(3)-3*y(4)-4*y(5))
```





P2.04.02. DIFFUSION AND SOLID CATALYSIS.

A reaction, $A_2 \Rightarrow$ Products, has the rate equation

$$r = 1.25(C-C_s) = \frac{1.5C_s}{(1+0.3\sqrt{C_s}+0.1C_s)^2}$$

where C_s is the interfacial concentration. This is a case of diffusion to the surface followed by reaction with dissociation on the surface. Eliminating C_s,

$$-\frac{dC}{dt} = r = \frac{1.5(C-0.8r)}{[1+0.3\sqrt{C-0.8r}+0.1(C-0.8r)]^2}$$

The available software for numerical integration of first order ODEs is applicable only when dC/dt is available explicitly. Here a "root solver" is used to find the relation between C and r. Then the relation to t is obtained by integration with the trapezoidal rule,

$$t = \int_C^{C_0} \frac{dC}{r}$$

The work is tabulated.

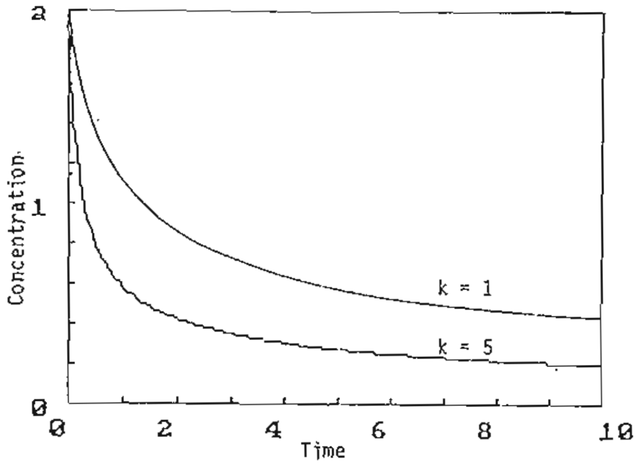
C	1/r	t
2	1.1189	0
1.9	1.1601	0.114
1.8	1.2054	0.232
1.7	1.2566	0.355
1.6	1.3141	0.484
1.5	1.3795	0.619
1.4	1.4541	0.760
1.3	1.5406	0.910
1.2	1.6412	1.069
1.1	1.7603	1.239
1.0	1.9033	1.422
0.9	2.0777	1.621
0.8	2.2952	1.840
0.7	2.5747	2.084
0.6	2.9464	2.360
0.5	3.4650	2.680
0.4	4.2391	3.065
0.3	5.5218	3.553
0.2	8.0710	4.233
0.1	15.70	5.422

P2.04.03. FILLING A BATCH REACTOR.

A vessel is being filled with a reacting solution. The material balance is derived as Eq 2.44 of Section 2.6.1. In the present application it is

$$\frac{dC}{dt} = \frac{2-C}{t} - kC^2$$

Although this ODE is quite innocent looking, it must be solved numerically. The graphs are of solutions with k = 1 and k = 5.



P2.04.04. A HEATED STIRRED REACTOR

Heat and material balances of a batch reactor are derived in Section 2.6.2. In the present instance, the differential heat balance is

Heat of reaction + Heat tranfer = Sensible heat gain

or

$$9000\,dx + UA(T-500)dt = 450\,dT \qquad (1)$$

The rate equation is

$$\frac{dx}{dt} = k\ (1-x)^2 \qquad (2)$$

and the specific rate is

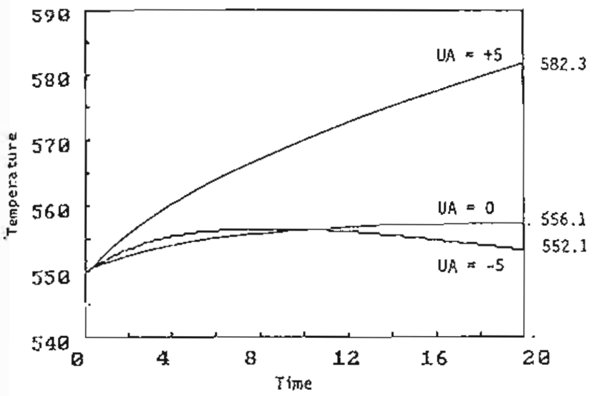
$$k = \exp(18 - 11000/T) \qquad (3)$$

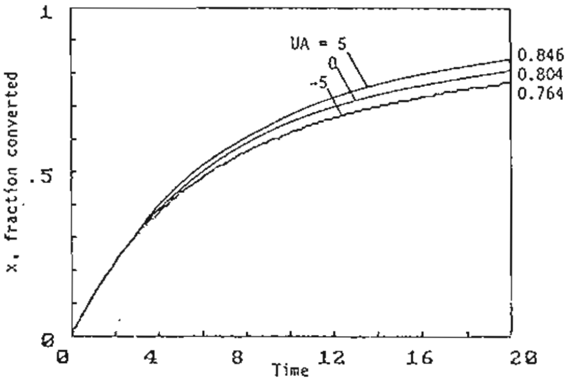
Substitute dx from Eq (2) into Eq (1) and rearrange,

$$\frac{dT}{dt} = \frac{9000\ k\ (1-x)^2 + UA(T-500)}{450} \qquad (4)$$

Substitute for k in terms of T and solve ODEs (2) and (4) simultaneously.

The graphs show solutions with UA = -5, 0 and +5.





P2.04.05. MAXIMUM MIXEDNESS

A reaction of order 1.5 is conducted under such flow conditions that its residence time distribution is like that of a three stage CSTR. Under maximum mixedness conditions the rate equation is

$$\frac{df}{dt_r} = 2\ f^{1.5} - \Lambda(t_r)(1-f)$$

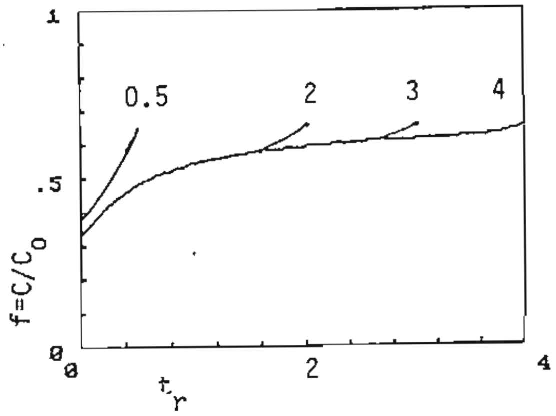
$$\Lambda(t_r) = \frac{13.5t_r^2}{1+3t_r+4.5t_r^2}$$

$$\Lambda(\infty) = 3$$

$$2\ f_\infty^{1.5} - 3(1-f_\infty) = 0$$

$$f_\infty = 0.650$$

The equation is to be integrated. The endpoint of the integration is $f = f_{exit}$ at $t_r = 0$. The starting point is $f_\infty = 0.650$ and any value of t_r above 2 or so. The graph shows the result to be insensitive above this value of t_r. The exit value is $f_{exit} = C_{exit}/C_0 = 0.330$.



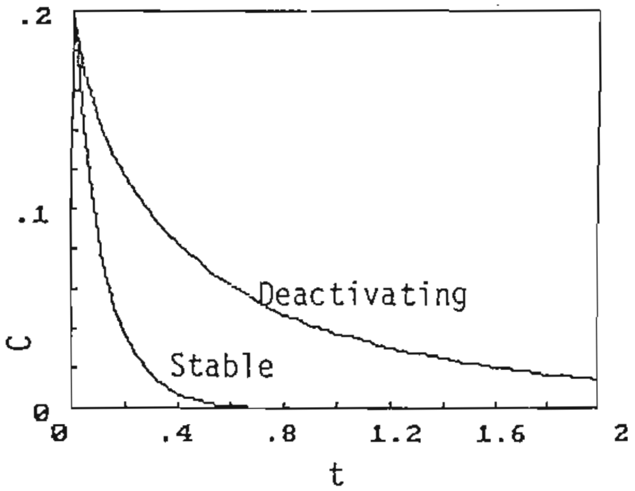
P2.04.06. DEACTIVATING CATALYST.

The activity of a cracking catalyst declines with time on stream. A case of gas oil cracking has the rate equation,

$$\frac{dC}{dt} = \frac{8.5C}{(1+6.5t^{0.4})(1+0.02C)}$$

with inlet concentration $C_0 = 0.2$. Find C as a function of t with (a) deactivating catalyst; (b) with stable catalyst of the initial specific rate.

The variables of the differential equation are separable, but to find C as a function of t requires a numerical quadrature and application of "root solver" many times. A direct solution by ODE program is simpler.



P2.04.07. PROCESS WITH A POROUS CATALYST.

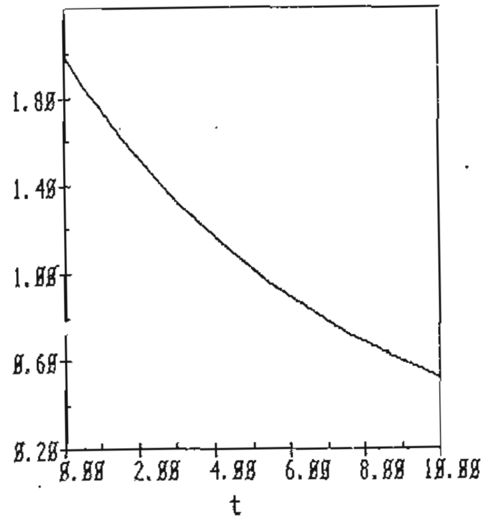
A process with a porous catalyst has the rate equation

$$-\frac{dC}{dt} = 0.7\ \eta\ C^{1.5}$$

The Thiele modulus is $\phi = 12\sqrt{C^{0.5}}$ and the effectiveness is

$$\eta = \frac{1.0357+0.3173\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2}$$

POLYMATH ODE is used for the integration in preference to Constantinides ODE because it allows printout of algebraic as well as differential variables. In the tabulation, x = C, f = ϕ and e = η.



```
     t            x           f           e
0.0          2.0000      16.971      0.1361
1.0000       1.7484      15.867      0.1450
2.0000       1.5291      14.839      0.1545
3.0000       1.3380      13.881      0.1646
4.0000       1.1714      12.988      0.1751
5.0000       1.0262      12.156      0.1863
6.0000       0.8995      11.381      0.1980
7.0000       0.7889      10.659      0.2104
8.0000       0.6925      9.9858      0.2233
9.0000       0.6083      9.3590      0.2368
10.000       0.5347      8.7751      0.2508
```

P2.04.08. REACTION WITH DISPERSION.

The dispersion model of a reaction has the equation

$$\frac{d^2f}{dz^2} = \mathrm{Pe}\left[\frac{df}{dz} + \frac{1.5\,f}{(1+0.3\sqrt{f})^2}\right]$$

$\mathrm{Pe} = 5$

at $z = 1$, $f' = \frac{df}{dz} = 0$

at $z = 0$, $1 = (f - f'/\mathrm{Pe})_0$, f_0 = unknown

In order to use an ODE program, the second order equation is transformed into a pair of first order ones.

$$\frac{df}{dz} = f'$$

$$\frac{df'}{dz} = 5f' + \frac{7.5f}{(1+0.3\sqrt{f})^2}$$

The shooting procedure is applied to solving this boundary value problem:

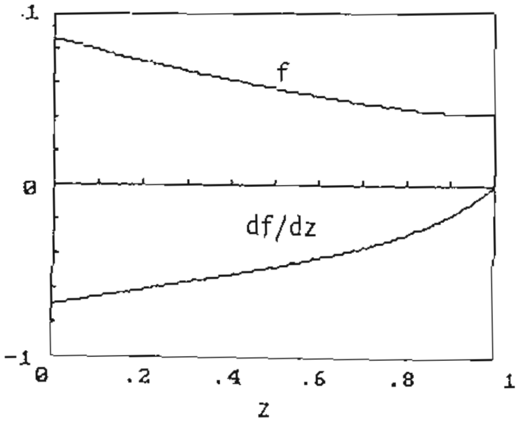
(i) Start at $z = 1$ where $f'_1 = 0$

(ii) Assume a trial value of f_1

(iii) Integrate backwards to $z = 0$, and check if the boundary condition there is satisfied, $(f-f'/5)_0 \overset{?}{=} 1$.

The tabulation shows three trials. The graph is of the final trial.

f_1	f_0	f'_0	$(f-f'/5)_0$	
0.40	0.8268	-0.6741	0.9616	
0.419	0.8615	-0.6971	1.0009	check
0.45	0.9177	-0.7339	1.0645	



P2.04.09.PRIOR ELIMINATION OF t

For the pair of reactions

$$A + B \overset{1}{\Rightarrow} 2C, \quad A+C \overset{2}{\Rightarrow} D$$

these conditions are given:

$k_1 = 0.1,\ k_2 = 0.05$

$A_0 = 0.9,\ B_0 = 0.3,\ C_0 = D_0 = 0$

The concentration profiles are to be found.

The material balances are,

$$C = 3(B_0-B) - (A_0-A) = A-3B \qquad (1)$$

$$D = (A_0-A)-(B_0-B) = 0.6+B-A \qquad (2)$$

The rate equations are,

$$\frac{dA}{dt} = -k_1AB - k_2AC = -k_1AB - k_2A(A-3B) = 0.05A(B-A) \qquad (3)$$

$$\frac{dB}{dt} = -k_1AB = 0.1AB \qquad (4)$$

$$\frac{dC}{dt} = A(0.2B-0.05C) \qquad (5)$$

$$\frac{dD}{dt} = 0.05AC \qquad (6)$$

Method (a). A procedure that requires solving only one differential equation at a time applies when t is first eliminated between Eqs (3) and (4).

$$\frac{dA}{dB} = \frac{k_2A}{k_1B} + \frac{k_1-3k_2}{k_1} = \frac{0.5A}{B} - 0.5 \qquad (7)$$

This is a linear equation whose integrating factor is $1/\sqrt{B}$ and whose solution is

$$A = \sqrt{B}\ [\ \int \frac{-0.5dB}{\sqrt{B}} + I] = B + \sqrt{B}\ (\ \frac{A_0}{\sqrt{B_0}} - \sqrt{B_0}\ ) \qquad (8)$$

Substitute this result into Eq (4).

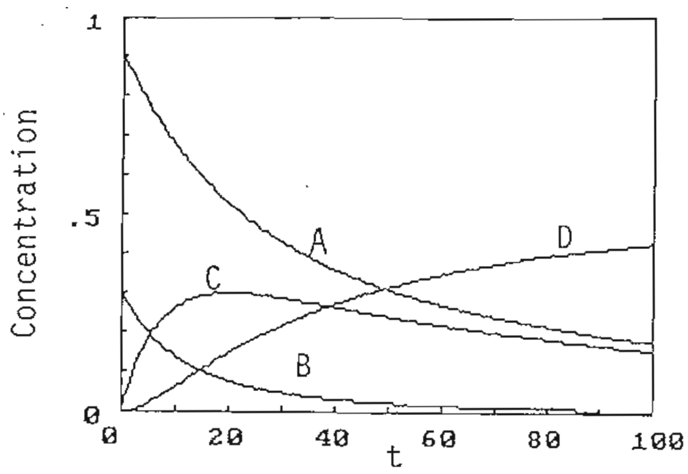
$$\frac{dB}{dt} = 0.1B^{1.5}(\sqrt{B} + \frac{A_0}{\sqrt{B_0}} - \sqrt{B_0}) \qquad (9)$$

The variables are separable, but analytical integration is not possible. A numerical integration will provide the solution

$B = f(t)$

This can be substituted into Eq (3), but analytical integrations of the differential equations stop at this point.

Method (b). Numerical integration of the four equations, (3) to (6) is accomplished with ODE, either Constantinides or POLYMATH. Alternately, the material balances (1) and (2) and only the two differential equations (3) and (4) can be solved together. This procedure is better carried out with POLYMATH ODE.



P2.04.10. THE SEQUENCE A ⇒ B AND 2B ⇒ C

The rate equation are

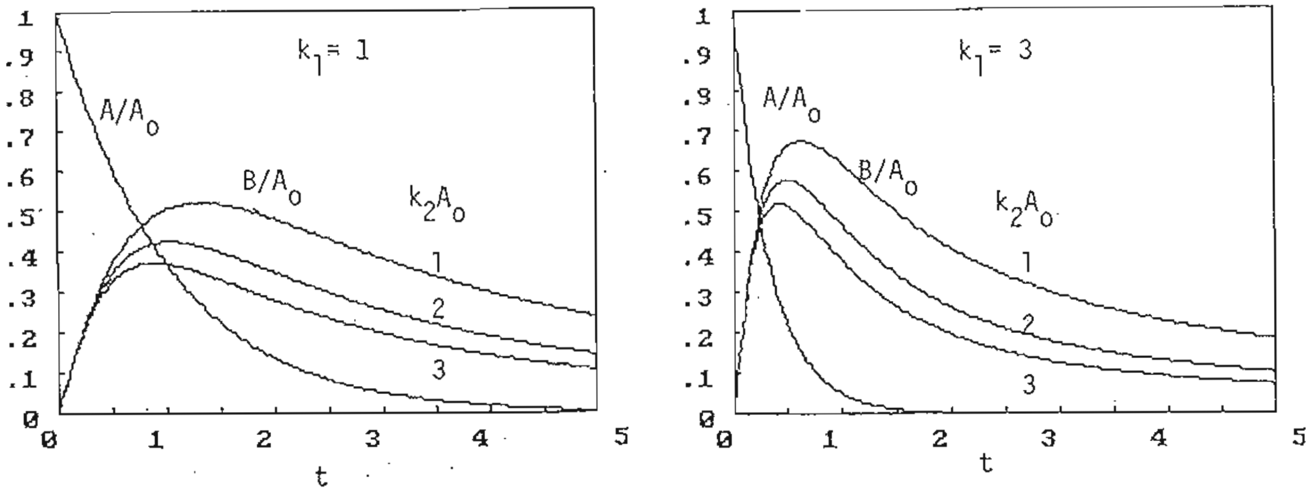
$$\frac{dA}{dt} = -k_1 A,$$

$$\frac{dB}{dt} = k_1 A - k_2 B^2 = k_1 A_0 \exp(-k_1 t) - k_2 B^2$$

These were integrated analytically in problem P2.02.17. Here they are done numerically with program ODE. The second equation is rewritten as

$$\frac{d(B/A_0)}{dt} = k_1 \exp(-k_1 t) - k_2 A_0 (B/A_0)^2$$

The plots are for several combinations of the constants k_1 and k_2A_0. The intermediate participant, B, reaches the peak values that are typical of many sequential reactions.



CHAPTER 3
TREATMENT OF EXPERIMENTAL DATA

THEORY

PROBLEMS

Data of the behavior of chemical reactions are obtained from laboratory units designed for or adapted to the purpose, or from pilot plant or commercial units. The larger units have the advantages of more instrumentation and controls but have less flexibility. Fundamentally what is determined is the time dependence of composition or pressure, or some measurement that can be related to these properties, and of the temperature.

3.1. KINDS OF LABORATORY REACTORS.

Various kinds of laboratory reactors differ in some important respects, some definitely better than others. The criteria include:

1. Equipment cost
2. Ease of operation
3. Ease of data analysis.
4. Accuracy
5. Versatility

6. Temperature uniformity and control
7. Suitability for mixed phases.

In terms of cost and versatility the batch reactor is the unit of choice. One disadvantage is the need for frequent sampling or monitoring of the performance, although instrumentation can be provided at moderate cost nowadays. The residence time can be varied over a wide range and many different reactions can be handled at different times. The quality of mixing and heat transfer may not be easy to relate to those in an eventual commercial unit.

CSTRs and other devices that require flow control are more expensive and troublesome to operate. Particularly in the steady state condition, however, their great merits are isothermicity and the fact that their mathematical representation is algebraic, not involving differential equations, thus making data analysis easier.

Tubular flow units, like the CSTR, usually are operated at steady state. It is not always easy to measure the temperature profile accurately. In some high temperature operations, the coil is immersed in a fluidized sand bed or lead bath so there is fairly good temperature control. Sometimes it is felt desirable to do the laboratory work in a tubular unit if the commercial unit is to be of that type, but rate data from any kind of equipment are adaptable to the design of PFR.

Reactions between phases -- gas-liquid, liquid-liquid or fluid-solid -- is carried out in CSTR-like devices. With granular solids such as catalysts or immobilized enzymes, the preferred laboratory equipment nowadays is a rotating basket or fixed basket through which the fluid is recirculated continuously, with net input and output to the chamber.

Laboratory operation of equipment with a fixed bed of granules is not highly satisfactory because of difficulty of temperature control and measurement in both radial and axial directions. A short packed bed with extensive recycle, however, can achieve substantially isothermal behavior and measurable differential conversion.

Reactions between liquids and gases of low solubility is conducted in stirred vessels. The liquid is charged first and the gas is fed continuously at the rate of solution or reaction, sometimes with internal recirculation in larger units. Miscible liquid reactions may be conducted similarly in order to moderate undesirable temperature play.

3.2. CHEMICAL COMPOSITION

Most analyses of kinetic data have the object of identifying the constants of a rate equation based on the law of mass action and possibly some mass transfer relation.. The law of mass action is expressed in terms of concentrations of the participants, so ultimately the chemical composition must be known as a function of time. In the laboratory the chemical composition is determined by some instrument that is suitably calibrated to provide the needed information. Titration, refractive index, density, chromatography, spectrometry, polarimetry, conductimetry, absorbance, magnetic resonance -- all of these are used at one time or another to measure chemical composition. In some cases, the calibration to chemical composition is linear with the reading.

3.3 POWER LAW RATE EQUATIONS

Three of the more frequently occurring examples of power law rate equations are

$$r_a = -\frac{dC_a}{dt} = kC_a^{\alpha} \qquad (3.1)$$

$$r_a = kC_a^{\alpha}C_b^{\beta} \qquad (3.2)$$

$$r_a = k_1C_a^{\alpha}C_b^{\beta} - k_2C_c^{\gamma}C_d^{\delta} = k_1(C_a^{\alpha}C^{\beta} - C_c^{\gamma}C_d^{\delta}/K_e) \qquad (3.3)$$

By stoichiometric balances all concentrations can be expressed in terms of C_a. For the evaluation of the constants from measurements of data of (C_a, t), the three equations require somewhat different techniques. Some of the methods are summarized on the graphs of Figure 3.1.

3.3.1. THE INTEGRATED FORM OF $r = kC^{\alpha}$

The integral of the rate equation is

$$k = \frac{1}{(\alpha-1)t}\left(\frac{1}{C^{\alpha-1}} - \frac{1}{C_0^{\alpha-1}}\right) \quad , \alpha \neq 1 \qquad (3.4)$$

$$\frac{1}{t}\ln(C_0/C) \quad , \alpha = 1 \qquad (3.5)$$

By one procedure, values of α are chosen until one is found that makes all calculated values of k substantially the same, or that makes a plot of t against $1/C^{\alpha-1}$ or against ln C a linear one (see Figure 3.1).

3.3.2. METHOD USING THE DIFFERENTIAL EQUATION, $-dC/dt = kC^{\alpha}$

The data of (C, t) are fitted by a polynomial or other algebraic equation and differentiated to obtain the derivative. The constants then are found from a linear plot of $\ln r = \ln k + \alpha \ln C$. Figure 3.1 shows this plot also.

3.3.3. HALF TIME DATA

The time by which half the reactant has been converted is called the half time, $t_{1/2}$. The equation is particularly simple:

$$kt_{1/2} = \ln 2 \qquad \alpha = 1$$

$$\frac{2^{\alpha-1}-1}{(\alpha-1)C_0^{\alpha-1}} \qquad \alpha \neq 1 \qquad (3.6)$$

When several sets of $(C_0, t_{1/2})$ are known, values of α are tried until one is found that makes all k values substantially the same. Alternatively, the constants may be found from a linearized plot,

$$\ln t_{1/2} = \ln\frac{2^{\alpha-1}-1}{(\alpha-1)k} + (1-\alpha)\ln C_0 \qquad (3.7)$$

Such a plot appears in Figure 3.1.

3.3.4. CSTR DATA

The steady state material balance of a CSTR with uniform volumetric flow rate is

$$C_{a0} = C_a + \bar{t}\, r_a$$

$$= C_a + k\bar{t}\, C_a^{\alpha}C_b^{\beta} \qquad (3.8)$$

$$r_a = \frac{C_{a0}-C_a}{\bar{t}} = kC_a^{\alpha}C_b^{\beta} \qquad (3.9)$$

or in linearized form,

$$\ln r_a = \ln k + \alpha \ln C_a + \beta \ln C_b \qquad (3.10)$$

The constants can be found by multilinear regression or by solving sets of three suitably spaced data. When only one exponent is involved, a linear plot is made, as in Figure 3.1.

3.3.5. INTEGRATED FORM OF $-dC_a/dt = kC_a^\alpha C_b^\beta$

By stoichiometry the equation is converted, for example, into

$$-\frac{dC_a}{dt} = kC_a^\alpha(C_{b0}-C_{a0}+C_a)^\beta \qquad (3.11)$$

After values of α and β are assumed, this equation can be integrated either analytically or numerically over the time ranges of the data. If the values of the k's are substantially constant, the correct choices of α and β had been made. It is usual in this method to try only integral or half integral values of the exponents, starting with the assumption that the rate equation conforms to the stoichiometry.

3.3.6. THE DIFFERENTIAL FORM OF $-dC_a/dt = kC_a^\alpha C_b^\beta$.

When the rate data come from a CSTR, the analysis was indicated in Section 3.3.4. Other data of (C_a, t) can be fitted by an algebraic equation and differentiated to obtain the derivative. Then the analysis is continued by Equation 3.10.

3.3.7. THE REVERSIBLE RATE EQUATION

The reversible rate equation, Equation 3.3, is easier to handle when the equilibrium constant is known. Then

$$r_a = k_1(C_a^\alpha C_b^\beta - C_c^\gamma C_d^\delta/K_e) \qquad (3.12)$$

Method (a). The burden of finding the five or six constants can be placed on a computer program of nonlinear regression. At the start, that procedure requires estimates of all the parameters. Those may be suggested by the stoichiometry of the reaction and by trial.

Method (b). The equation may be integrated following trial values of the exponents. The correct choices were made when the specific rate k_1 is substantially the same for all times.

Method (c). A portion of the problem can be solved with initial rate data. Thus,

$$r_0 = k_1C_{a0}^\alpha C_{b0}^\beta \qquad (3.13)$$

With subsequent rate the data, the equation to be analyzed becomes

$$y = (r - k_1C_a^\alpha C_b^\beta) = -k_2C_c^\gamma C_d^\delta \qquad (3.14)$$

which is handled as in Section 3.3.5 or 3.3.6. Problem P3.11.13 deals with a reversible reaction in this way.

3.4. RATE EQUATIONS DEPENDING ON MULTIPLE MECHANISMS.

Some examples of processes whose rate equations depend on rates of subsidiary processes appear in Section P2.3. In such cases, specific rates and exponents may appear in all sorts of places. Non linear regression is in principle always applicable, but that procedure sometimes is harassed by convergence problems and does not always appeal to engineers who do not like black boxes. A fairly general technique is to arrange the differential equation or its integral into a form that can be handled by linear plotting or multilinear regression. As a last resort, a number of equations at selected data points equal to the number of constants can be set up and solved simultaneously, although the solution of sets of nonlinear equations also presents problems. Particular equations, of course, may suggest particular solutions.

3.4.1. SOLID CATALYSIS AND ENZYME CATALYSIS

The mechanism of solid catalysis involves processes of diffusion, formation of loose combinations with the solid and reactions of those combinations. Reactions with enzymes also involve intermediate, temporary combinations with the enzymes. The rate equations that may proposed in particular cases depends on what are believed to be controlling mechanisms. Many such eqautions are considered in Chapter 6. Here only one of the simpler forms will be examined for evaluation of the parameters, namely,

$$r_a = -\frac{dp_a}{dt} = \frac{k_1(p_ap_b-p_cp_d/K_e)}{(1+k_ap_a+k_bp_b+k_cp_c+k_dp_d)^2} \qquad (3.15)$$

The data are of the rate and all the corresponding partial pressures. The rate may have been obtained in a CSTR or by differentiation of (p_a, t) data correlated by an algebraic equation. The obvious linearization when the equilibrium constant is known is

$$y = \left(\frac{p_ap_b-p_cp_d/K_e}{r}\right)^{1/2} = (1+k_ap_a+k_bp_b+k_cp_c+k_dp_d)/\sqrt{k_1} \qquad (3.16)$$

The constants are found by multilinear regression or by solving an appropriate number of linear eqautions. The constants of the simpler equation,

$$r = \frac{k_1p^2}{(1+k_2p)^2} \qquad (3.17)$$

are found by linear plotting of

$$p/\sqrt{r} = 1/\sqrt{k_1} + (k_2/\sqrt{k_1})p \qquad (3.18)$$

3.4.2. MULTIPLE REACTIONS

There are two main kinds of multiple reactions:

(a) Those involving short lived intermediates such as free radicals known to exist or invented to account for a particular form of rate equation that is tested against data. Several examples are cited in Section P2.3. Catalysts also are believed to form transient compounds.

(b) Those involving known species engaged in a variety of simultaneous and consecutive processes. Some examples are cited in Section P3.3.

So many kinds of rate equations can arise that the only general solution method is nonlinear regression, although simpler techniques may apply in particular cases. Reliance must be placed on ingenuity. For the case of problem P3.03.08, the equation is

$$-\frac{dA}{dt} = \frac{k_1AB^3}{k_2B^2+k_3BD+k_4D^2} \qquad (3.19)$$

If the exponents are accepted the k's can be found after linearization, but there is no simple approach to verifying the exponents.

3.4.3. MIXTURES OF HYDROCARBONS.

Industrial hydrocarbon reactions are a complex between a variety of feed compositions and a variety of products. Compounds that have been formed go on to form other compounds, and so on. Dozens of reactions may need to be taken account of. Sometimes the approximation of a network of first order and pseudo first order reactions is made, for which the mathematical foundation has been largely laid. As a different example, a model for the cracking of propane is cited in problem P2.03.25 that consists of nine first and second order reactions.

When a very large number of reactants occurs, as in the treatment of petroleum fractions with a virtually continuous spectrum of boiling points, the problem is made more tractable by lumping the composition. The lumps are made up of pseudo components with limited boiling ranges and of partcular chemical types such as aromatics, paraffins, naphthenes, olefins and so on.

In a model for catalytic reforming of gasoline, cited in problem P2.03.26, some 300 chemical species are identified, broken up in one case into 13 lumps characterized by carbon number and hydrocarbon class. The kinetic characteristics of such lumps are proprietary information.

3.5. PRESSURE DATA

A common way of following the progress of a gas phase reaction with a change in the number of mols is to monitor the time variation of the total pressure, π. From this information and the stoichiometry, the partial pressures of the participants can be deduced, and a rate equation developed in those terms. Usually it is adequate to assume ideal gas behavior, but nonideal behavior can be taken into account with extra effort. Problem P3.03.06 is an example of nonideality.

In the simplest case, the rate of the reaction, A $\Rightarrow$ Products, becomes

$$r_a = f(p_a) \text{ or } = k_p p_a^q = k_c C_a^q \qquad (3.20)$$

A key relation is that for the total number of mols which is determined by the stoichiometry of the reaction. This and other relations are

$$n_t = n_{t0} + \delta_a(n_{a0}-n_a)$$
$$p_a = (n_a/n_t)\pi$$
$$V = n_t RT/\pi$$
$$C_a = n_a/V = p_a/RT$$

so the rate equation becomes

$$r_a = k_c C_a^q = k_p p_a^q = k_p(RT)^q C^q$$

which relates the two specific rates as

$$k_c = k_p(RT)^q \qquad (3.21)$$

Usually k_c is the specific rate that is sought because the law of mass action is expressed in concentrations and is the basis of rate equations

3.5.1 RATE EQUATION IN TERMS OF TOTAL PRESSURE

Since some adulteration of raw data occurs when they are transformed mathematically, by differentiation or taking logarithms or reciprocals or otherwise, it is better from a statistical point of view to change the rate equation to read in terms of total pressure, rather than to change the data to partial pressures or concentrations. Such a transformation is worked out for a reaction, aA + bB $\Rightarrow$ cC + dD, with a typical rate equation, $-dC_a/dt = kC_a^\alpha C_b^\beta$.

The familiar series of equations using the ideal gas law is:

$$n_t = n_{t0} + \delta_a(n_{a0}-n_a)$$

$$\frac{\pi}{\pi_0} = \frac{n_t}{n_{t0}} = 1 + \frac{\delta_a(n_{a0}-n_a)}{n_{t0}}$$

$$n_a = n_{a0} + \frac{n_{t0}}{\delta_a \pi_0}(\pi_0 - \pi)$$

$$dn_a = -\frac{n_{t0}}{\delta_a \pi_0}\,d\pi$$

$$C_a = \frac{n_a}{V} = \frac{n_a\,\pi_0}{n_{t0}RT} = \frac{\pi_0}{n_{t0}RT}[n_{a0} + \frac{n_{t0}}{\delta_a \pi_0}(\pi_0 - \pi)]$$

$$dC_a = -\frac{1}{\delta_a RT}d\pi$$

Then the rate equation, $- dC_a dt = kC_a^{\alpha}$, becomes

$$-\frac{1}{\delta_a RT}\frac{d\pi}{dt} = \frac{k}{(RT)^{\alpha}}(\frac{n_{a0}}{n_{t0}}\pi_0 + \frac{\pi_0 - \pi}{\delta_a})^{\alpha} \qquad (3.22)$$

3.6. OTHER PROPERTIES RELATED TO COMPOSITION

Some of the properties that are being used to follow the course of reaction are indicated by the data of the problems in Section P3.4. Such a property should depend strongly and uniquely on the quantity of a key participant. Reports of the experimental work usually need not provide the instrument reading, I, but only the calibrated value of the concentration or amount of the key. When the calibration is linear, such as a polarimeter reading or electrical conductivity, it may be convenient to develop a rate equation of the form

$$r = k_I[I]^q$$

but this is transformable to an equation in terms of k_c.

3.7. TEMPERATURE VARIATION

One of the longest standing equations of chemical kinetics is that of Arrhenius for the effect of temperature on specific rate,

$$k = k_0\exp(-E/RT) = \exp(A-E/RT) \qquad (3.23)$$

or

$$\ln k = A - \frac{E}{R}(\frac{1}{T}) \qquad (3.24)$$

where k_0 is the frequency factor, E is the energy of activation, T is the absolute temperature, and R is the gas constant, say 1.987 cal/(gmol)(K). The constants are readily evaluated from the straight line plot of this equation , as on Figure 3.1.

Deviation from linearity may occur when the net reaction is a composite of subsidiary reactions with differently varying sensitivities to temperature, or when the mechanism of the reaction changes with temperature. One kind of composite process is that of a reaction occurring both homogeneously in the pores and on the surface of a granular catalyst.

Activation energies of chemical processes usually amount to tens of kcal/gmol, but those of physical processes such as mass transfer have only a few hundred cal/gmol. Several of the examples of Section P3.06 have variable activation energies.

A particular modified equation has theoretical justification for some reactions, namely,

$$k = k_0T^n\exp(-E/RT) \qquad (3.25)$$

but normally it is needed only over very wide ranges of temperature.

Data are sometimes taken of the time dependence of temperature as well as composition. Then a reaction equation of the following type is applicable,

$$-\,dC_a/dt = \exp(A-B/T)\,C_a^q \qquad (3.26)$$

After linearization by taking logarithms, the three constants can be found by multilinear regression.

3.8. HOMOGENEOUS CATALYSIS

All catalytic reactions appear to involve the formation of intermediate compounds of the catalyst and the substance undergoing the reaction (the substrate, S), the sequence of reactions being

$$S + Cat \Rightarrow X \Rightarrow Product + Cat$$

Many ions catalyze homogeneous reactions. The hydronium ion, H_3O^+, and the hydroxyl ion, OH^- catalyze hydrolyses such as those of esters, ferrous ion catalyzes the decomposition of hydrogen peroxide, decomposition of nitramide is catalyzed by acetate ion. Many such effects are known.

Some catalytic reactions proceed at a reduced rate in the absence of catalyst. For a reaction, $A \Rightarrow$ Products, the rate equation then will be

$$r = (k_1 + k_2[Cat]^\alpha)[A]^\beta \qquad (3.27)$$

Some reactions will not proceed at all without catalyst, for instance some enzyme reactions. Then the rate equation is

$$r = k[Cat]^\alpha[A]^\beta \qquad (3.28)$$

The exponent α in both cases is often unity.

Enzymes also are homogeneous catalysts, although they are sometimes attached to solid surfaces without degradation. They possess a different form of rate equation, for which the development may be found in problem P2.03.02. Their behavior is especially sensitive to temperature and to substrate concentration.

3.9. CSTR DATA. LIQUID OR GAS PHASE.

Data obtained in continuous stirred tank reactors have the merits of isothermicity and of an algebraic relation between the variables rather than a differential one. At steady state in a CSTR the material balance on a reactant A is

$$V'_0C_{a0} = V'C_a + r_aV_r \qquad (3.29)$$

The rate may have any mathematical form, say,

$$r_a = kC_a^\alpha C_b^\beta = kC_a^\alpha(C_{b0}-C_{a0}+C_a)^\beta \qquad (3.30)$$

In most liquid phase reactions the volumetric flow rates are nearly the same in and out, so

$$C_{a0} = C_a + k\bar{t}C_a^\alpha(C_{b0}-C_{a0}+C_a)^\beta \qquad (3.31)$$

where $\bar{t} = V_r/V'$ is the mean residence time.

The three constants k, α and β are found by multilinear regression with data of (C_a, t) of this arrangement of the material balance,

$$\ln\frac{C_{a0}-C_a}{\bar{t}} = \ln k + \alpha \ln C_a + \beta \ln C_b \qquad (3.32)$$

For gas phase reaction with a change in the number of mols, the material balance is made in terms of molal flows,

$$n_{a0} = n_a + r_aV_r = n_a + kV_r\left(\frac{n_a}{V'}\right)^\alpha\left(\frac{n_b}{V'}\right)^\beta$$

$$V' = n_t\left(\frac{RT}{\pi}\right) = [n_{t0}+\delta_a(n_{a0}-n_a)]\frac{RT}{\pi}$$

Substitute and rearrange into,

$$\frac{n_{a0}-n_a}{V_r} = k\left(\frac{\pi}{RT}\right)^{\alpha+\beta}\left(\frac{n_a}{n_t}\right)^{\alpha}\left(\frac{n_b}{n_t}\right)^{\beta} \quad (3.33)$$

This is analyzed after linearization just as Eq 3.32.

3.10. PLUG FLOW REACTORS. LAMINAR FLOW.

Experimental plug flow reactors may be small diameter tubes or packed beds with a larger ratio of diameter to length. The argument in favor of their employment is that they may simulate commercial units more closely. Rate data from pilot plant or commercial units also may need to be analyzed. A short packed bed may be operated with a high recycle ratio and will thus achieve substantially isothermal behavior and may have appreciable change in conversion between the net input and output streams.

A PFR operates at substantially constant pressure. A typical material balance on a differential volume of reactor is

$$-dn_a = n_{a0}dx = r_a dV_r = k\left(\frac{n_a}{V'}\right)^{\alpha}\left(\frac{n_b}{V'}\right)^{\beta}$$

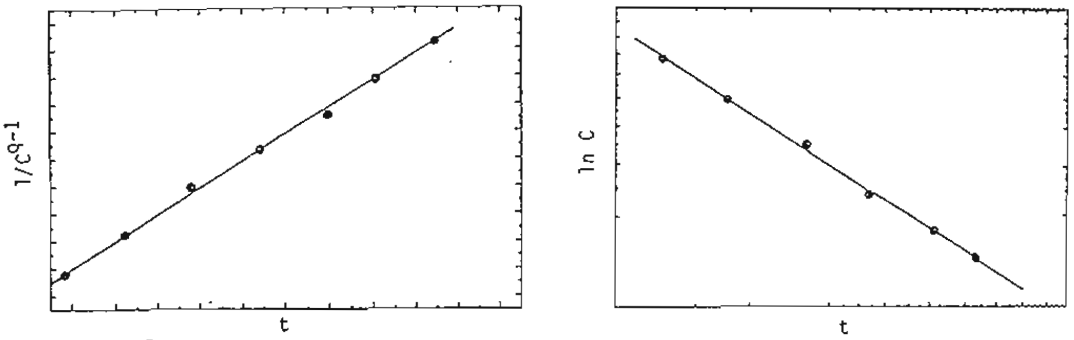
Substitute $V' = n_t RT/\pi$ and rearrange into

$$n_{a0}\frac{dx}{dV_r} = -\frac{dn_a}{dV_r} = k\left(\frac{\pi}{RT}\right)^{\alpha+\beta}\left(\frac{n_a}{n_t}\right)^{\alpha}\left(\frac{n_b}{n_t}\right)^{\beta} \quad (3.33)$$

When values of the derivative can be obtained from the experimental data, the constants are found by multilinear regression as usual, or by plotting when only one exponent is to be found.

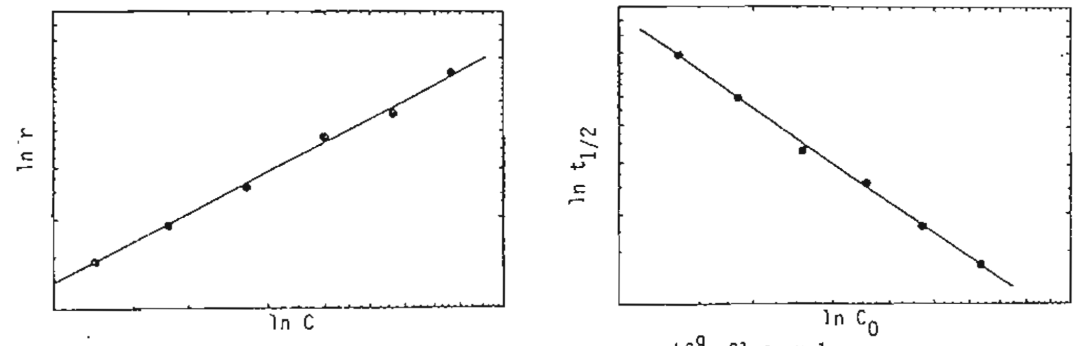
The constants also can be found by trial after integration. Values of α and β are assumed, the integration is completed and values of k are calculated at different values of n_{a0}/V_r. If they are substantially constant the correct assumptions had been made.

A special kind of tubular flow reactor has laminar flow. The specific rate of such a case is found and compared with plug flow in problem P3.09.15.



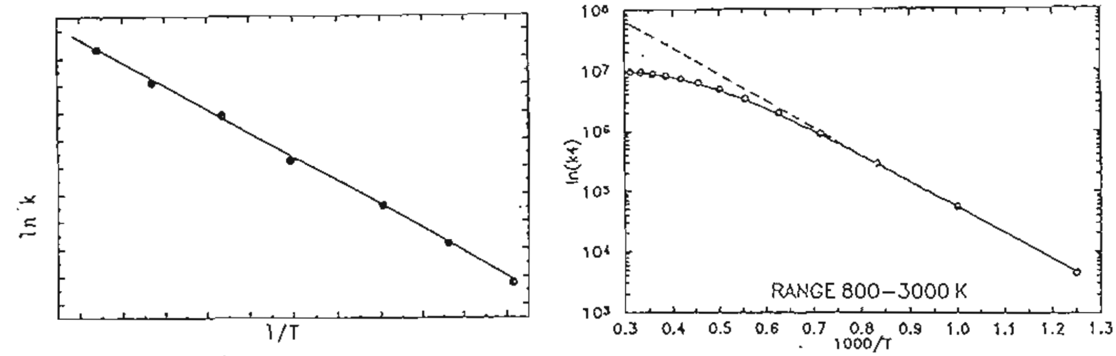
$r = kC^q$, Slope = $k(q-1)$

$r = kC$, Slope = $-k$



$r = kC^q$, Slope = q

$r = kC^q$, Slope = $1-q$



$k = \exp(A-E/RT)$, Slope = $-E/R$

Problem P3.06.18. Variable activation energy.

Figure 3.1. Linear Plots of Rate Equations.

P3.01.01. UNITS OF THE SPECIFIC RATE

The units of the specific rate depend on the order of a power law rate equation and on the units of the rate of reaction which are basically, (mass)/(time)(volume).

(a) A specific rate is $k = 3.0(10^{-5})\ \text{liter}^{1/2}\text{mol}^{-1/2}\text{sec}^{-1}$. In other units,

$$k = 3.0(10^{-5})\ \frac{\text{liter}^{1/2}}{\text{mol}^{1/2}\text{sec}}\ \frac{1000\ \text{cc}^{1/2}}{\text{liter}^{1/2}}\ \frac{60\ \text{sec}}{1\ \text{min}} = 1.8\ \frac{\text{cc}^{1/2}}{\text{mol}^{1/2}\text{min}}$$

$$k = 3.0(10^{-5})\ \frac{\text{liter}^{1/2}}{\text{mol}^{1/2}\text{sec}}\ \frac{1000\ \text{cc}^{1/2}}{\text{liter}^{1/2}}\ \frac{\text{mol}^{1/2}}{6.06(10^{23})\ \text{molecule}^{1/2}}$$

$$= 4.95(10^{-26})\ \frac{\text{cc}^{1/2}}{\text{molecule}^{1/2}\text{sec}}$$

(b) In the rate equation, $r = k_cC_a^2$, the rate is in lbmol/(hr)(ft^3), C_a is in lbmol/ft^3) , k_c = 0.004 and the temperature is 700 K. Changing the units,

$$k_c = 0.004\ \frac{\text{cuft}}{\text{lbmol hr}}\ \frac{28300\ \text{cc}}{\text{cuft}}\ \frac{\text{lbmol}}{453.5\ \text{gmol}}\ \frac{\text{hr}}{60\ \text{min}}$$

$$= 0.00416\ \text{cc/(gmol)(min)}$$

(c) In the rate equation, $r = k_pp_a^2$, the rate is in lbmol/(hr)(cuft), p_a is in atm, and k_c = 0.004 cuft/(hr)(lbmol).
The temperature is 700 K. Then

$$k_p = k_c/(RT)^2$$

$$= 0.004\ \frac{\text{cuft}}{\text{lbmol hr}}\ \frac{0.0283\ \text{m}^3}{\text{cuft}}\ \frac{\text{lbmol}}{453.5\ \text{gmol}}\ \frac{(RT)^2}{[82.05(10^{-6})(700)\ \frac{\text{m}^3\ \text{atm}}{\text{gmol}}]^2}$$

$$= 7.57(10^{-5})\ \frac{\text{gmol}}{\text{hr m}^3\ \text{atm}}$$

(d) A third order reaction in a perfect gas system has a specific rate $k_c = 300(\text{cuft})^2/(\text{h})(\text{lbmol})^2$ at 700 R. Find k_p in the units h, atm, cuft and lbmol.

$$RT = 0.73(700)\ \text{atm cuft/lbmol}$$

$$k_p = k_c/(RT)^3$$

$$= 300\ \frac{(\text{cuft})^2}{\text{hr}\ (\text{lbmol})^2(RT)^3}\ [\frac{RT}{511\ \text{atm(cuft)/lbmol)}}]^3$$

$$= 2.25(10^{-6})\ \frac{\text{lbmol}}{\text{hr cuft atm}^3}$$

(e) A first order reaction in an ideal gaseous system at 800 R has a specific rate, k = 0.14 lbmol/(350 cuft)(atm)(h). Find the value in 1/sec.

$$k = 0.14\ \frac{\text{lbmol}}{(359\ \text{cuft})(\text{atm})(\text{h})}\ \frac{350(1.626)\ \text{cuft atm}}{\text{lbmol}}\ \frac{\text{h}}{3600\ \text{sec}}$$

$$= 63.2(10^{-6})\ /\text{sec}$$

(f) A rate equation is $r = 0.0031\ C^2$ gmol/(min)(22.41 liters) at 700 K, with C in the units gmol/(22.41 liters). Find the specific rate k_p when the pressure is in atm and the rate is lbmol/(cuft)/(min).

The ideal gas volume is 22.41 liters/gmol at 273.2 K and 1 atm.

$$RT = \frac{700}{273.2} = 2.562\ \frac{\text{atm}(22.41\ \text{liter})}{\text{gmol K}}$$

$$k_p = k_c/(RT)^2$$

$$= 0.0031\ \frac{22.4\ \text{liters}}{\text{gmol min}}\ \left[\frac{\text{gmol}}{2.562\ \text{atm}\ (22.4\ \text{liters})}\right]^2$$

$$= 4.72(10^{-4})\ \frac{\text{gmol}}{\text{min atm}^2\ (22.4\ \text{liters})}\ \frac{\text{lbmol}}{453.5\ \text{gmol}}\ \frac{22.4\ \text{liters}}{0.792\ \text{cuft}}$$

$$= 1.316(10^{-6})\ \frac{\text{lbmol}}{\text{atm}^2\ \text{cuft min}}$$

P3.01.02. TRUE CONTACT TIME OF FORMIC ACID REACTION

The gas phase decomposition of formic acid,

$HCOOH \Rightarrow H_2O + CO$

is studied in a plug flow reactor. In one run the space velocity 1.29 (liters feed at STP)/(min)(liter of reactor volume) results in a conversion of 60% when starting with pure formic acid. The reactor operates at 150 C and 1 atm. The reaction rate is first order with k = 2.46/min. What is the actual residence time?

$$n_{a0} = \frac{1.29}{22.4} = 0.0576\ \text{gmol/(liter)(min)}$$

Volumetric feed rate,

$$V'_0 = 1.29(473.2)/273.2) = 1.549\ \text{liters/(liter)(min)}$$

Apparent residence time,

$$t_{\text{apparent}} = 1/1.549 = 0.646\ \text{min} \qquad (1)$$

Material balance on the plug flow reactor,

$$-dn_a = r_a dV_r = k(n_a/V')dV_r$$

from which

$$t = \int_0^{V_r} \frac{dV_r}{V'} = \int_n^{n_{a0}} \frac{dn_a}{kn_a} = \frac{\ln(2.5)}{2.46} = 0.373\ \text{min} \qquad (2)$$

P3.01.03. TRUE CONTACT TIME. POWER LAW AND L-H RATE EQUATIONS

Find the true contact time in terms of the rate equation and the flowing mol rate, n_t, when the rate equation is $r_a = kC_a^q$ or $r_a = k_1\left(\frac{p_a}{1+k_2p_a}\right)^2$

(a) Power law rate equation. n_t is found by stoichiometric balance, and the flowing volumetric rate is

$$V' = \frac{n_t RT}{\pi}$$

Material balance on a plug flow reactor,

$$-dn_a = r_a dV_r = k\left(\frac{n_a}{V'}\right)^q dV_r = k\left(\frac{n_a^q}{V'^{\,q-1}}\right)\frac{dV_r}{V'}$$

The contact time then is

$$\bar{t} = \int_0^{V_r}\frac{dV_r}{V'} = \int_{n_a}^{n_{a0}}\frac{V'^{\,q-1}}{kn_a^q}\,dn_a$$

(2) Take the reaction, 2A ⇒ 3B, for which $n_t = \frac{3n_{a0}-n_a}{2}$ and $q = 2$. The volumetric flow rate is

$$V' = \frac{(3n_{a0}-n_a)RT}{2\pi}$$

and the equation for the contact time is

$$\bar{t} = \frac{RT}{k\pi}\int_{n_a}^{n_{a0}}\frac{3n_{a0}-n_a}{2n_a^2}\,dn_a \qquad (3)$$

(b) With the L-H type rate equation,

$$p_a = \frac{n_a RT}{V'} = \frac{n_a}{n_t}\pi$$

$$V' = \frac{n_t RT}{\pi}$$

$$r_a = k_1\left(\frac{p_a}{1+k_2p_a}\right)^2 = \frac{k_1 n_a^2\pi/n_t}{(1+k_2n_a\pi/n_t)^2}\left(\frac{RT}{V'}\right)$$

Substitute into

$$-dn_a = r_a dV_r$$

and rearrange into

$$\bar{t} = \int\frac{dV_r}{V'} = \frac{1}{k_1\pi RT}\int\frac{1}{n_t}\left(\frac{n_t+k_2\pi n_a}{n_a}\right)^2 dn_a$$

P3.01.04. SPACE VELOCITY IN BENZENE HYDROGENATION

The hydrogenation of benzene to cyclohexane, $C_6H_6 + 3H_2 \Leftrightarrow C_6H_{12}$, is carried out at 500 psig and 400 F in the vapor phase over a nickel catalyst. The space velocity is WHSV = 2.0 lb benzene/(h)(cuft of reactor). A 200% excess of hydrogen is used. Benzene purity is 99% and that of hydrogen is 65 mol%, the balance being methane. Find the total feed rate in the units (a) lbmol/(h)(cuft of reactor); (b) actual cuft/(h)(cuft of reactor).

Benzene, $B = \frac{2}{78}$ lbmol/(h)(cuft of reactor)

$H_2 = 3\ B$

$CH_4 = 3(65/35)B$

inerts = B/99

The total feed is

$$F = \frac{2}{78}(1 + 3 + 3(65/35) + 1/99) = 0.1445 \text{ lbmol/(h)(cuft)}$$

$$\Rightarrow 0.1445(359)(\frac{860}{492})(\frac{14.7}{515}) = 2.60 \frac{\text{actual cfh}}{\text{cuft of reactor}}$$

P3.01.05. SPACE VELOCITY IN TOLUENE SYNTHESIS

The production of toluene from benzene and xylenes was studied by Johanson& Watson (National Petroleum News, 7 Aug 1946) in a standard 1-inch pipe reactor with a silica-alumina catalyst. At the reaction temperature of 932 F (773 K) the reaction mixture was vapor phase, but the feeds were measured as liquids. The feed consisted of an equimolal mixture of reactants. The stated LHSV is (ml feed at 60 F/h)/(ml reactor). The reactor contained 85 g catalyst packed in a volume of 135 ml. The densities of benzene and xylenes at 60 F are 0.879 and 0.870, respectively.

Given the data of the first two columns of the table, find (a) (g catalyst)/(gmol feed/h); (b) (ml feed/h)/(ml reactor); (c) the actual contact time, sec. There is no change in the number of mols of mixture on reaction.

1 gmol C_6H_6 = 78.1/0.879 = 88.85 ml

1 gmol C_8H_{10} = 106.2/0.870 = 122.07 ml

1 gmol mixture = 105.46 ml

Feed rate is

$$n_0' = \frac{V_r(\text{LHSV})}{105.46} = \frac{135(\text{LHSV})}{105.46} = 1.2801(\text{LHSV}), \quad \text{gmol feed/h}$$

$$\frac{W_c}{n_0'} = \frac{85}{1.2801(\text{LHSV})} = \frac{66.40}{\text{LHSV}} \qquad \text{(a)}$$

These values are recorded in column 3 of the Table.

$$\frac{V'}{V_r} = \frac{n_0RT}{PV_r} = \frac{82.05(773)(1.2801)(\text{LHSV})}{(P/14.7)(135)} = \frac{8842(\text{LHSV})}{P} \qquad \text{(b)}$$

These values are in column 4 of the Table.

Assuming the voidage to be 40%, the true residence time is

$$\bar{t} = \frac{V_r\varepsilon}{V'} = \frac{0.4}{V'/V_r} \qquad \text{(c)}$$

These are in the last column of the table.

LHSV	P	W_c/n'	V'/V_r	$\bar{t}$
0.5	20	132.8	221.1	6.51
0.25	20	265.6	110.5	13.03
1	65	66.4	136.0	10.59
2	65	33.2	272.1	5.29
2	115	33.2	153.8	9.36
4	115	16.6	307.6	4.68

P3.02.01. PSEUDO FIRST ORDER

The aqueous reaction, A ⇔ R + S, proceeds with the data of the first two columns of the Table and the initial conditions,

C_{a0} = 0.1823 mol/liter, C_{r0} = 0, $C_{s0} \simeq 55$

Find the rate equation.

From the data, the reaction appears to reach equilibrium. Assuming the rate equation corresponding to the stoichiometry,

$$r_a = -\frac{dC_a}{dt} = k_1(C_a - C_rC_s/K_e)$$

$$= k_1[C_a - (0.1863-C_a)(55.1863-C_a)/K_e] \qquad (1)$$

At equilibrium, $r_a = 0$, $C_{ae} = 0.0494$, $K_e = 152.8$. Integrating,

$$k_1 = \frac{1}{t}\int_0^{C_a} \frac{dC_a}{C_a-(0.1863-C_a)(55.1863-C_a)/152.8} \qquad (2)$$

The integration is performed numerically. The values are tabulated in column 3 and are perhaps nearly enough the same to confirm the assumed rate equation.

If the water content is assumed constant at $C_s = 55$, then $C_{ae} = 0.0494$ and $K_e = 2.771$. The integration is

$$k_1' = \frac{1}{t}\int_0^{C_a} \frac{dC_a}{C_a-(0.1863-C_a)/2.771} \qquad (3)$$

These are tabulated in column 4 and are nearly the same as those of column 3.

t	C_a	10^3k_1	$10^3\ k_1'$
0	0.1863		
35	0.1458	7.47	7.36
65	0.1216	7.23	7.23
100	0.1025	6.96	6.96
160	0.0795	6.96	6.96
∞	0.0494		

P3.02.02. BATCH REACTOR PROCESSES

(a). Liquid A decomposes by first order kinetics, and in a batch reactor 50% of A is converted in 5 minutes. How much longer would it take to reach 75% conversion?

$$k = \frac{1}{t}\ln(C_0/C) = \frac{1}{5}\ln 2 = 0.1386$$

$$\Delta t = \frac{1}{0.1386}\ln\frac{1-0.5}{1-0.75} = 5 \text{ min}$$

(b). Repeat the previous problem if the reaction is second order

$C = C_{a0}(1-x)$

$$kC_{a0} = \frac{1}{t}\left(\frac{1}{1-x_1} - \frac{1}{1-x_0}\right) = \frac{1}{5}(2-1) = 0.2$$

$$t_{0.75} = \frac{1}{0.2}\left(\frac{1}{1-0.75} - 1\right) = 15$$

$$\Delta t = 15 - 5 = 10 \text{ min}$$

(c). A 10 minute run shows that 75% of a liquid reactant is converted by a 0.5 order rate. What would be the conversion in a half hour?

$$\frac{dC}{dt} = kC^{1/2}$$

$$\frac{dx}{dt} = \frac{k}{\sqrt{C_0}}(1-x)^{1/2} = k'(1-x)^{1/2}$$

$$k' = \frac{1}{t}[1-(1-x)^{1/2}] = 0.1(1 - 0.25^{1/2}) = 0.05$$

$t = 20[1- (1-x)^{1/2}]$

When $x = 0$, $t = 20$, and x remains 0 when $t = 30$ min.

(d). In a homogeneous isothermal liquid polymerization, 20% of the monomer disappears in 34 min for initial monomer concentration of 0.04 mol/liter and when it is 0.8 mol/liter. Find the rate equation.

Try the power law equation,

$$-\frac{dC}{dt} = kC^{\alpha} \quad \text{or} \quad \frac{dx}{dt} = kC_0^{\alpha-1}(1-x)^{\alpha}$$

Since the fractional conversion is independent of C_0 the reaction is first order.

$$k = \frac{1}{t}\ln\frac{1}{1-x} = \frac{1}{34}\ln 1.25 = 0.0656$$

(e). After 8 minutes in a batch reactor with $C_{a0} = 1$ mol/liter, conversion is 80%, and after 18 minutes it is 90%. Find the rate equation.

Try the equation, $\frac{dx}{dt} = kC_0^{\alpha-1}(1-x)^{\alpha}$, whose integral is

$$kC_0^{\alpha-1}t = \frac{1}{\alpha-1}\left[\frac{1}{(1-x)^{\alpha-1}} - 1\right]$$

Substitute the data,

$$\frac{18}{8} = 2.25 = \frac{(1/0.1)^{\alpha-1} - 1}{(1/0.2)^{\alpha-1} - 1}$$

Therefore, $\alpha = 2$, second order.

(f). The decomposition rate of pure ethane is 7.7%/sec, but with 85.26% inerts present the decomposition rate falls to 2.9%/sec. Find the rate equation.

The given data are of initial rates, $(\frac{dx}{dt})_0 = kC_0^{\alpha-1}(1-x)_0^{\alpha} \Rightarrow kC_0^{\alpha-1}$

$$\frac{r_{pure}}{r_{impure}} = \frac{0.077}{0.029} = \left(\frac{C_{pure}}{C_{impure}}\right)^{\alpha-1} = \left(\frac{1}{0.1474}\right)^{\alpha-1}$$

whence $\alpha = 1.51$

(g). The first order reversible liquid reaction, $A \Leftrightarrow R$, takes place in a batch reactor with $C_{a0} = 0.5$ mol/liter, $C_{r0} = 0$. After 8 minutes, conversion of A is 33.3% while equilibrium conversion is 66.7%. Find the rate equation.

$$-\frac{dC_a}{dt} = k_1[C_a - (C_{a0}-C_a)/K_e]$$

$$K_e = \frac{1-0.333}{0.333} = 2$$

$$-\frac{dC_a}{dt} = k(1.5C_a - 0.25)$$

$$kt = \frac{1}{1.5} \ln \frac{1.5(0.5)-0.25}{1.5C_a-0.25}$$

When t = 8, $C_a/C_{a0} = 0.667$, $C_a = 0.333$

$$k = \frac{1}{1.5(8)} \ln \frac{0.5}{0.25} = 0.0578$$

Thus the rate equation is

$$-\frac{dC_a}{dt} = 0.0578\ [C_a-(0.5-C_a)/2]$$

P3.02.03. CHANGES OF VOLUME.

These two reactions are first order, inconsistent with the stoichiometry. Find the specific rates.

(a). The stoichiometric equation is A ⇒ 1.6 R. The pressure is 1.2 atm, the temperature is 25 C. When starting with pure A, the volume of the mixture increases 50% in 4 minutes.

$$n_t = n_a+n_r = 1.6n_{a0}- 0.6n_a$$

$$\frac{V}{V_0} = \frac{n_t}{n_{a0}} = \frac{1.6n_{a0}-0.6n_a}{n_{a0}} = 1.5 \text{ when } t = 4$$

$$n_a/n_{a0} = 1/6$$

$$k = \frac{1}{t} \ln (n_{a0}/n_a) = 0.25 \ln 6 = 0.448$$

(b). For the first order reaction with stoichiometric eqaution, 2A ⇒ R, the volume decreases by 20% in 3 minutes when starting with 80% A.

$$n_{t0} = 1,\ n_{inert}= 0.2,\ n_{a0} = 0.8$$
$$n_t = n_a + n_i + 0.5(n_{a0}-n_a) = 0.6 + 0.5n_a$$

$$\frac{V}{V_0} = \frac{n_t}{n_{t0}} = 0.6 + 0.5n_a = 0.8 \quad \text{when } t = 3$$

$$n_a = (0.8-0.6)/0.5 = 0.4$$

$$k = \frac{1}{t} \ln \frac{n_{a0}}{n_a} = \frac{1}{3} \ln \frac{0.8}{0.4} = 0.231$$

P3.02.04. THE RATE IS KNOWN NUMERICALLY

A gas phase reaction, 2A ⇒ B, occurs at 50 atm and 700 R. Originally 5 lbmols of A were present. When one-half of the A has disappeared, the rate of disappearance of A is 0.34 lbmol/(h)(cuft). Find the specific rate.

$$n_t = n_a + 0.5(n_{a0}-n_a) = 0.5(n_{a0}+n_a)$$
$$= 0.5(5+2.5) = 3.75 \quad \text{at 50\% conversion}$$

$$V = \frac{n_tRT}{\pi} = \frac{3.75(0.73)(700)}{50} = 38.33 \text{ cuft}$$

$$k = \frac{r_a}{(n_a/V)^2} = 0.34(\frac{38.33}{2.5})^2 = 79.9 \text{ cuft/(h)(lbmol)}$$

P3.02.05. CATALYTIC PRODUCTION OF A LACTONE

The acid catalyzed conversion of gamma-hydroxy-butyric acid into its lactone was studied in 0.2 N HCl solution at 25 C. The initial concentration of the acid was 18.23 in arbitrary units. The lactone concentration was observed in the same units at different times, in minutes. The data are in the first two columns of the table.

$$CH_3CHOHCH_2COOH \overset{1}{\underset{2}{\Leftrightarrow}} O(CH_2)_3CO + H_2O, \quad A \Leftrightarrow B + C$$

Find the specific rates of the forward and reverse processes.

Water is present is great excess so its concentration does not change appreciably as the reaction proceeds, and the magnitude is incorporated in the reverse constant.

$$-\frac{dC_b}{dt} = k_1C_a - k_2C_b = k_1(C_a - C_b/K_e) = k_1(C_{a0}-C_b-C_b/K_e)$$

From the data,

$$K_e = \frac{13.28}{18.23-13.28} = 2.683$$

and the rate equation becomes

$$-\frac{dC_b}{dt} = k_1(18.23-1.373C_b)$$

The specific rate is given by

$$k_1 = \frac{1}{t}\int_{C_b}^{0} \frac{dC_b}{18.23-1.373C_b} = \frac{1}{1.373t} \ln \frac{1}{1-0.0753C_b}$$

The values are in column 3 of the table, and are nearly constant. The reverse coefficient is $k_2 = k_1/K_e = k_1/2.683$.

t	C_b	k_1
0	0	
21	2.41	6.95
36	3.73	6.67
50	4.96	6.81
65	6.10	6.89
80	7.08	6.94
100	8.11	6.87
∞	13.28	

P3.02.06. <u>DATA AT CONSTANT V AND AT CONSTANT P</u>

A first order gas phase reaction, A ⇒ 3R, is first studied at constant pressure of 2 atm starting with pure A. After 15 minutes the volume increases by 75%. When the same reaction is carried out at constant volume and the initial pressure is 2 atm, how much time is needed for the pressure to reach 3 atm?

The rate equation is

$$-\frac{dn_a}{dt} = kn_a$$

$$kt = \ln (n_{a0}/n_a)$$

At constant P,

$$\frac{V}{V_0} = \frac{n_t}{n_{a0}} = \frac{3n_{a0}-2n_a}{n_{a0}} = 3 - 2n_a/n_{a0}$$

$$= 1.75 \quad \text{when } t = 15.$$

Then

$$n_a/n_{a0} = 0.625$$

$$k = \frac{1}{15}\ln(1/0.625) = 0.0313$$

At constant V,

$$\frac{\pi}{\pi_0} = \frac{n_t}{n_{a0}} = 3 - 2(n_a/n_{a0})$$

$$= 3/2$$

$$n_a/n_{a0} = 0.75$$

$$t = \frac{1}{0.0313}\ln(1/0.75) = 19.2 \text{ min, when } \pi = 3.$$

P3.02.07. EQUILIBRIUM AND INITIAL RATE DATA

A reaction has the rate equation

$$r = -\frac{dC}{dt} = k_1[C^2 - \frac{(2.2-C)^2}{K_e}]$$

Initial concentration is $C_0 = 1.5$, initial rate is $r_0 = 1.076$, and equilibrium concentration is $C_e = 0.6798$. Find the constants.

$$K_e = (\frac{2.2 - C_e}{C_e})^2 = (\frac{2.2-0.6798}{0.6798})^2 = 5.000$$

$$k_1 = \frac{r_0}{C_0^2 - 0.2(2.2-C_0)^2} = \frac{1.076}{2.25 - 0.2(0.7)^2} = 0.500$$

P3.02.08. DATA OF RATE VERSUS CONCENTRATION

For the reaction, A ⇒ Products, measurements of the rate as a function of the concentration were made with a CSTR.

C_a	1.5	1.3	1.1	0.9	0.7	0.5	0.3
r_a	28.0	20.0	12.8	7.7	4.1	1.8	0.5

Find the order of the reaction and the specific rate.

Assume a power law rate,

$$r_a = kC_a^q$$

and in linearized form

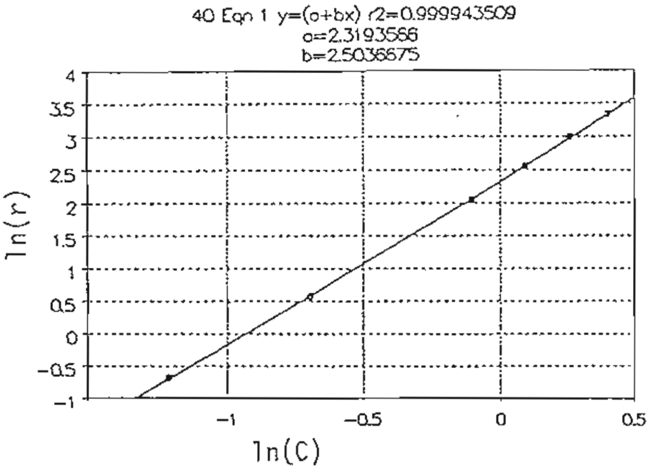
$$\ln(r_a) = \ln(k) + q\ln(C_a)$$

$$= 2.319 + 2.504\ln(C_a)$$

which makes the rate equation

$$r_a = 10.166\, C_a^{2.504}$$

The plot is a good linear fit of the data.



P3.02.09. DATA OF CONVERSION AND EQUILIBRIUM. SIMPSONS RULE.

The liquid phase reaction, $2A \Leftrightarrow B$, has equilibrium constant $K_e = 5$ and initial concentrations $C_{a0} = 0.6$, $C_{b0} = 0.05$. In 30 minutes, 50% conversion of A is realized. What is the specific rate of the forward reaction?

$$C_b = C_{b0} + 0.5(C_{a0}-C_a) = 0.05 + 0.5(0.6 - C_a) = 0.35 - 0.5C_a$$

$$-\frac{dC_a}{dt} = k[C_a^2 - 0.2(0.35 - 0.5C_a)]$$

$$k = \frac{1}{t}\int_{C_a}^{C_{a0}} \frac{dC_a}{C_a^2 + 0.1C_a - 0.07} = \frac{1}{30}\int_{0.3}^{0.6} I\, dC_a$$

The integrand is evaluated at three points and the integration is accomplished with Simpsons rule.

$$k = \frac{1}{30}\left(\frac{0.15}{3}\right)[2.857 + 4(5.634) + 20.000] = 0.076$$

For comparison, integration with the trapezoidal rule with 100 intervals gives $k = 0.0716$.

P3.02.10. TIME-CONVERSION DATA

A second order reaction, $A + B \Rightarrow$ Products, is found to be 25% complete in 50 minutes when both starting concentrations are 0.2 mol/liter. Find the specific rate and the half life of the reaction.

$$-\frac{dC_a}{dt} = kC_a^2$$

$$k = \frac{1}{tC_{a0}}\left(\frac{C_{a0}}{C_a} - 1\right) = \frac{1}{50(0.2)}\left(\frac{1}{0.75} - 1\right) = 0.0333\ \frac{\text{liters}}{\text{mol min}}$$

$$t_{1/2} = \frac{1}{kC_{a0}}\left(\frac{C_{a0}}{C_a} - 1\right) = \frac{1}{0.0333(50)}(2 - 1) = 150 \text{ min.}$$

P3.02.11. CHLORINATION OF TOLUENE

Data of the reaction of toluene (A) and chlorine (B) in glacial acetic acid were taken by Brown & Stock (JACS 79 5175, 1957) with time in seconds and molar concentrations . Find a suitable rate equation.

Assume first that the mechanism corresponds to the stoichiometry, thus second order.

$$-\frac{dA}{dt} = kAB = kA(A-0.1595)$$

$$k = \frac{1}{t}\int_0^{0.1908} \frac{dA}{A(A-0.1595)}$$

The integration is done numerically and values are given in column 4 of the table. The average value is

$$k = 5.248(10^{-4}) \text{ liters/(mol)(sec)}$$

t	C_a	C_b	10^4k
0	0.1908	0.0313	
2790	0.1833	0.0238	5.255
7690	0.1745	0.0150	5,269
9690	0.1719	0.0123	5.316
14000	0.1682	0.0086	5.169
19100	0.1650	0.0055	5.232

P3.02.12. ETHYL ETHANOATE AND NaOH

A quantity of ethyl ethanoate (A) is reacted with an excess of sodium hydroxide (B) at 25 C. 100 cc of the reaction mixture required 68.2 cc of Of 0.05 mol/liter HCl for neutralization at the beginning of the reaction. After 30 minutes, 100 cc of the mixture similarly required 49.7 cc of the acid, and when the reaction was complete, 100 cc of the mixture required 15.6 cc of the acid. The reaction is not reversible. Find the specific rate.

$A + B \Rightarrow \text{Products}$

$$\text{Excess NaOH} = B_0 - A_0 = \frac{15.6(0.05)}{100} = 0.0078 \text{ mol/liter}$$

$$\text{Initial NaOH, } B_0 = \frac{68.2(0.05)}{100} = 0.0341$$

$$A_0 = 0.0341 - 0.0078 = 0.0263$$

When t = 30,

$$x = A_0 - A = B_0 - B = \frac{(68.2-49.7)(0.05)}{100} = 0.00925$$

$$\frac{dx}{dt} = k(0.0263-x)(0.0341-x)$$

$$k = \frac{1}{30}\int_0^{0.00925} \frac{dx}{(0.0263-x)(0.0341-x)} = 0.500 \frac{\text{liters}}{\text{mol min}}$$

P3.02.13. ALKALINE HYDROLYSIS OF AN ESTER

In a study of the alkaline hydrolysis of ethyl 2-methylpropenoate in 84.7% ethanol, Thomas & Watson (JACS 77 3962, 1956) obtained the data of the first two columns of the table, t in sec, NaOH titre/cc. The initial concentrations of both ester (A) and alkali (B) were 0.058 mol/liter. 10 cc of the reaction mixture were removed from the vessel at the time stated, pipetted into 10 cc of 0.0668 mol/liter HCl and the excess titrated with 0.0511 mol/liter NaOH. Find the mean value of the second order specific rate.

EMP2 (A) + NaOH (B) ⇒ Products

y = titre, cc, column 2 of table

NaOH balance,

$$B = 0.0668 - 0.0511\left(\frac{y}{1000}\right)\left(\frac{1}{0.1}\right) = 0.0668 - 0.000511y, \text{ mol/liter}$$

The values are tabulated in column 3.

$$-\frac{dB}{dt} = kAB = kB^2$$

$$k = \frac{1}{t}\left(\frac{1}{B} - \frac{1}{0.0508}\right)$$

The values are tabulated in column 4. The mean value is

k = 0.198 liter/(mol)(min)

t	NaOH, cc	B	k
10	4.03	0.0462	0.196
25	5.11	0.0407	0.195
40	5.98	0.0362	0.198
60	6.86	0.0317	0.198
80	7.57	0.0281	0.199
110	8.36	0.0241	0.198

P3.02.14. CIS-TRANS ISOMERIZATION

The cis-trans isomerization of 1,2-dimethylcyclopropane at 453 C is a reversible first order reaction. The percentage of cis is shown as a function of t in sec in the table. Find the constants of the rate equation.

$$\text{cis (A)} \overset{1}{\underset{2}{\Leftrightarrow}} \text{trans (B)}$$

$$f = A/A_0 = \frac{\text{column 2}}{100}$$

$$B = A_0+B_0-A = A_0-A = A_0(1-f)$$

$$-\frac{dA}{dt} = -A_0\frac{df}{dt} = k_1A_0[f-(1-f)/K_e)$$

$$k_1 = \frac{K_e}{t}\int_f^1 \frac{df}{(K_e+1)f-1} = \frac{K_e}{t(K_e+1)} \ln \frac{K_e}{(K_e+1)f-1} \qquad (1)$$

$$K_e = B_e/A_e = 70/30 = 2.333$$

The values calculated from Eq (1) are tabulated. The mean values are

$$k_1 = 0.002402 \text{ /sec}, \ k_2 = k_1/K_e = 0.001029\text{/sec}$$

t	cis %	10^3k
0	100	
45	89.2	2.607
90	81.1	2.448
225	62.3	2.406
270	58.2	2.357
360	50.7	2.369
495	43.5	2.327
585	39.9	2.340
675	37.2	2.359
∞	30.0	

P3.02.15. HYDROLYIS OF ETHYL ACETATE

Data of the hydrolysis of ethyl acetate in the presence of a constant amount of HCl have been obtained by Knoblauch (Z physik Chem 22 268, 1897).

$$\text{EA (A)} + H_2O \text{ (B)} \overset{1}{\underset{2}{\Leftrightarrow}} \text{Ethanol (C) + Acetic Acid (D)}$$

Initially the mixture was 1.00 molar in EA, 12.215 molar in water and ethanol, and free of acetic acide. The data are of time, min, against acetic acid, mol/liter. Find the constants of the rate equation.

The equilibrium constant is

$$K_e = \frac{(12.215+0.2644)(0.2644)}{(1-0.2644)(12.215-0.2644)} = 0.3753$$

The rate equation is

$$\frac{dD}{dt} = k_1(AB-CD/K_e) = k_1[(1-D)(12.215-D)-\frac{(12.215+D)D}{0.3753}]$$

The integral is solved for the specific rate,

$$k_1 = \int_0^D \frac{dD}{(1-D)(12.215-D)-2.665(12.215+D)D}$$

Integration is done numerically and the values are in column 3. The approximate constancy of k_1 confirms the assumed rate equation.

t, min	D	$10^5 k_1$
0	0	
78	0.0777	9.646
94	0.0930	9.966
138	0.1285	10.410
169	0.1414	9.774
348	0.2093	9.711
415	0.2246	9.828
464	0.2326	9.830
∞	0.2644	

P3.02.16. A SULFONE AND HYDRAZINE

The reaction of phenyl α-disulfone with hydrazine,

$PhSO_2SO_2Ph$ (A) + N_2H_4 (B) ⇒ $PhSO_2NHNH_2$ + $PhSO_2H$

was studied by Kice & Legan (JACS 95 3912, 1073). In runs with initial concentrations of sulfone of $3(10^{-5})$ mol/liter, the reaction is pseudo first order. The values of k_{app}, 1/sec, vary with $[N_2H_4]$ mol/liter, as tabulated. Find the rate equation.

Try the rate equation,

$$-\frac{dC_a}{dt} = kC_aC_b^{\alpha} = k_{app}C_a$$

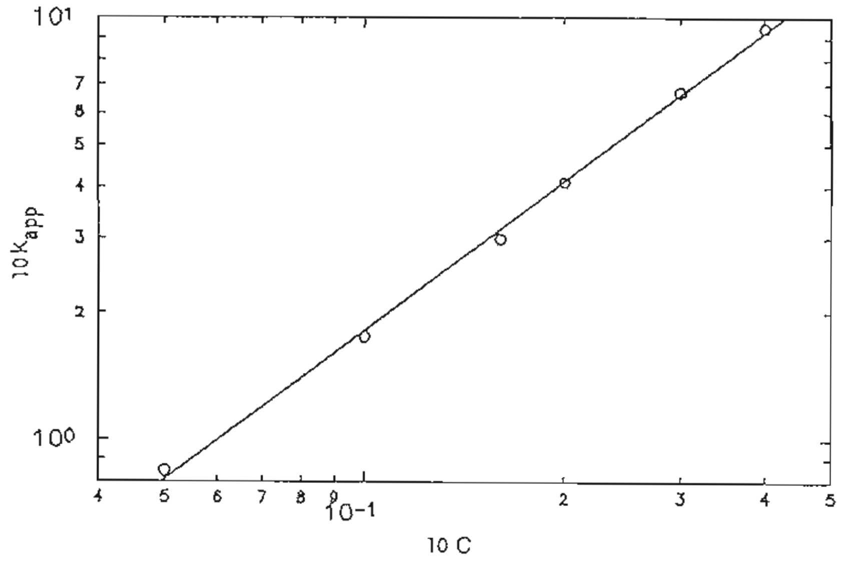
$$k_{app} = kC_b^{\alpha}$$
$$\ln k_{app} = \ln k + \alpha \ln C_b$$

The linearity of the plot confirms the assumed rate equation. The correlation is

$$k_{app} = 43.1\ C_b^{1.19}$$

Data:

$100\ [N_2H_4]$	0.5	1	1.6	2.0	3.0	4.0
k_{app}	0.085	0.176	0.30	0.41	0.67	0.95



P3.02.17. BUTADIENE DIMERIZATION AT 350 C

Butadiene is dimerized at 350 C in the gas phase according to second order kinetics. Data were taken at constant volume, time in minutes and total pressure in Torr, starting with pure butadiene.

$$2A \Rightarrow B$$

$$n_t = 0.5(n_{a0}+n_a)$$

$$\pi = n_t \frac{RT}{V} = (n_{a0}+n_a)\frac{RT}{2V}$$

$$\pi_0 = n_{a0}\frac{RT}{V}$$

$$\frac{n_a}{V} = \frac{2\pi - \pi_0}{RT} = \frac{2\pi - 500}{RT}$$

$$RT = 62.3(350+273.2) = 38834 \text{ liter Torr/mol}$$

The rate equation in mol and pressure units is

$$-\frac{1}{V}\frac{dn_a}{dt} = k(n_a/V)^2$$

$$-\frac{2}{RT}\frac{d\pi}{dt} = \frac{k}{(RT)^2}(2\pi - 500)^2$$

Integrating,

$$k = \frac{2RT}{t}\int_{\pi}^{500}\frac{d\pi}{(2\pi-500)^2} = \frac{38834}{t}\left(\frac{1}{2\pi-500} - \frac{1}{500}\right)$$

The four values are tabulated. Their average is

$$k = 1.95 \text{ liter/(mol)min)}$$

t	Π	k
0	500	
6	467	1.97
12	442	1.96
26	401	1.96
38	378	1.95
60	350	1.94

P3.02.18. DIMERIZATION OF BUTADIENE AT 326 C

Data for the dimerization of gaseous butadiene to vinyl cyclohexene were obtained at 326 C in a constant volume apparatus by Vaughan (JACS 54 3863, 1932), with time in minutes and total pressure π in Torr. Find the constants of the rate equation.

(a) Assume a rate equation in terms of the partial pressure,

$$-\frac{dp}{dt} = kp^2$$

The result of integration is

$$t-t_0 = \frac{1}{k}\left(\frac{1}{p} - \frac{1}{p_0}\right) \quad (1)$$

The partial pressure of butadiene is related to the total pressure by

$$p = 2\pi - \pi_0 = 2\pi - 634.1$$

The plot of Eq (1) has the equation

$$1000/p = 1.5801 + 0.023097$$

and confirms the assumed rate equation, making

$$-\frac{dp}{dt} = 2.3097\ p^2$$

Also,

$$-\frac{d\pi}{dt} = \frac{2.3097}{2}(2\pi-\pi_0)^2$$

(b) Another method is make a curve fit of the data and then find dp/dt by differentiation. If the plot of ln (dp/dt) against p is linear, the constants of the rate equation will be known. POLYMATH is used to fit (p,t) data with a cubic spline from which the derivatives are obtained also by POLYMATH. The cubic spline plot and the (rate, p) plots are shown. The derivative is in column 5 of the table. The linear plot has the equation

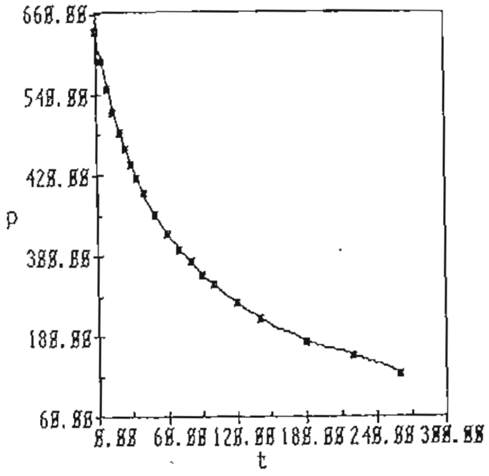
$$-\frac{dp}{dt} = \exp(a+b\ \ln p) = \exp(-10.194 + 1.919\ p)$$

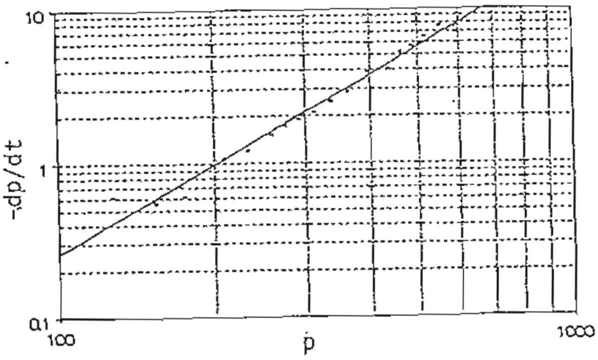
$$= 3.74(10^{-5})\ p^{1.919}$$

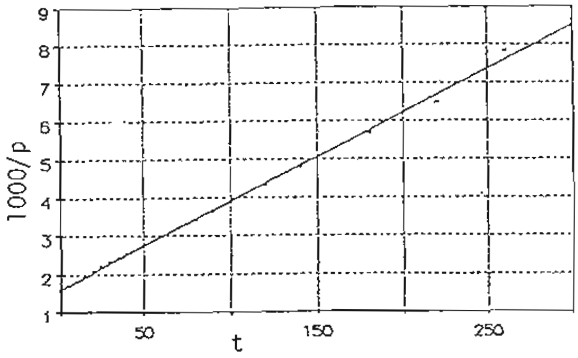
This formula and the one derived in part (a) give about the same results.

DATA

t	π	p	1000/p	-dp/dt
0	634.1	634.1	1.577	
5	611.0	590.0	1.695	7.632
10	591.9	551.8	1.812	7.656
15	573.7	515.4	1.940	6.506
20	559.1	486.2	2.057	5.678
25	545.7	459.4	2.177	5.224
30	533.6	435.2	2.297	4.028
35	523.9	415.8	2.405	3.958
40	513.7	395.4	2.529	3.902
50	497.4	362.8	2.756	2.874
60	483.9	335.8	2.978	2.486
70	427.5	313.0	3.195	2.128
80	462.4	292.8	3.415	1.902
90	453.4	274.8	3.639	1.726
100	445.2	258.4	3.870	1.514
120	432.2	232.4	4.302	1.206
140	420.5	209.0	4.785	1.076
180	404.1	176.2	5.675	0.612
220	393.3	154.6	6.458	0.554
260	380.9	127.7	7.830	0.606







P3.02.19. SULFURIC ACID AND DIETHYLSULFATE

Data for the reaction

$$H_2SO_4\ (A) + (C_2H_5)_2SO_4\ (B) \underset{2}{\overset{1}{\rightleftarrows}} 2\ C_2H_5SO_4H\ (R)$$

were obtained by Hellin & Jungers (Bull Soc Chim 386, 1957). Initial concentrations were $A_0 = B_0 = 5.5$ and $R_0 = 0$. The rate equation is to be found.

Try the stoichiometric form,

$$-\frac{dR}{dt} = 2[k_1(5.5-0.5R)^2 - k_2R^2] \qquad (1)$$

$$= 2k_1[(5.5-0.5R)^2 - R^2/K_e] \qquad (2)$$

From the tabulated data,

$$K_e = \frac{5.8^2}{(5.5-2.9)^2} = 4.976 \qquad (3)$$

Integrating Eq (2),

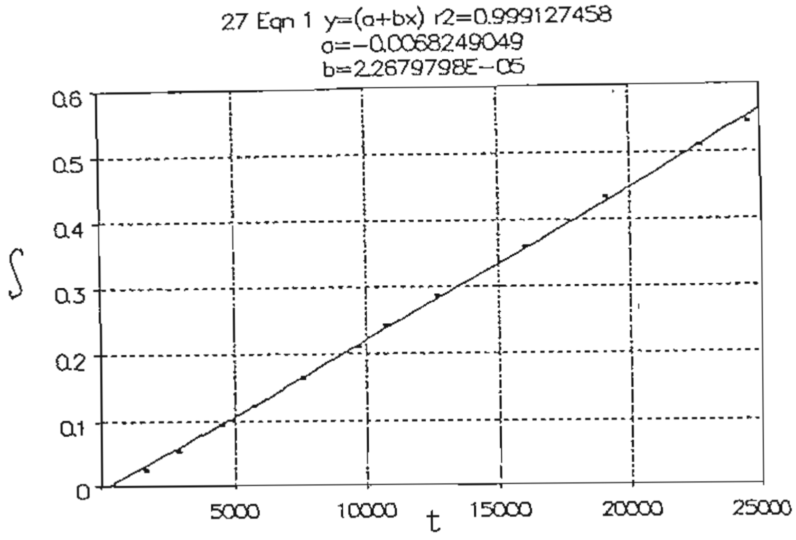
$$2k_1t = \int_0^R \frac{dR}{(5.5-0.5R)^2-R^2/4.976} \qquad (4)$$

The integral is found numerically and is tabulated in column 3. The straight line plot of $(\int_0^R, t)$ has a slope $2k_1 = 2.268(10^{-5})$ from which

$$k_1 = 1.134(10^{-5})$$

The assumed rate equation, Eq (2), is confirmed.

t	R	$\int$
0	0	
1680	0.69	0.0244
2880	1.38	0.0543
4500	2.24	0.0947
5760	2.75	0.1250
7620	3.31	0.1651
9720	3.81	0.2095
10800	4.11	0.2421
12720	4.45	0.2870
16020	4.86	0.3596
19080	5.15	0.4338
22740	5.35	0.5080
24600	5.42	0.5422
∞	5.80	



P3.02.20. HYDROGEN PEROXIDE

The catalyzed decomposition of H_2O_2 in aqueous solution is followed by removing equal volume samples at various times and titrating them with $KMnO_4$ to determine the undecomposed H_2O_2. The results are tabulated. Confirm that the reaction is first order and find the cc of $KMnO_4$ required for the titration of the sample removed at t = 0.

For a first order reaction

$$k_1 = \frac{1}{t-t_0}\int_C^{37.1}\frac{dC}{C} = \frac{1}{t-5}\ln(37.1/C)$$

The values are tabulated in column 3, and are nearly enough constant to confirm first order, the average being k = 0.0438/min.

When t = 0, C = 37.1 exp(5k) = 37.1 exp(0.219) = 46.2.

t	cc $KMnO_4$	k
5	37.1	
10	29.8	0.0438
20	19.6	0.0425
30	12.3	0.0442
50	5.0	0.0445

P3.02.21. ACID HYDROLYSIS OF METHYL ACETATE

The rate of hydrolysis of methyl acetate is reversible and proceeds according to the equation

$$\frac{dx}{dt} = k_1[\text{Acid}](a-x - x^2/K_e)$$

where [Acid] is concentration of the acid, a-x that of the ester and x that of each of the products at time t. In aqueous acetone at 80.2C methyl acetate initially 0.05 M was 90% hydrolyzed at equilibrium. The data of the table were obtained by Newling & Hinshelwood (J Chem Soc 1357, 1936) for hydrolysis in the presence of 0.05 M HCl. t is in sec, and y is % hydrolyzed.

The mols converted per liter is

$x = 0.05(0.01)y = 0.0005y$

The equilibrium constant is

$$K_e = \frac{[0.0005(90)]^2}{0.05-0.0005(90)} = 0.405$$

The rate equation becomes

$$0.0005\frac{dy}{dt} = 0.05k_1[0.05-0.0005y - (0.0005y)^2/0.405]$$

Integrating,

$$k_1 = \frac{100}{t}\int_0^y \frac{dy}{0.05-0.0005y-(0.0005y)^2/0.405}$$

The integration is done numerically, trapezoidal rule, 200 intervals. The almost constant results of column 4 confirm the rate equation and have an average value

$k = 36.26$

t	y	$\int_0^y$	k_1
0	0		
1350	21.2	477.6	35.38
2070	30.7	737.6	35.63
3060	43.4	1154.1	37.72
5340	59.5	1875.4	35.12
7740	73.45	2899.5	37.46
∞	90		

P3.02.22. SAPONIFICATION OF METHYL ACETATE

The rate of saponification of methyl acetate at 25C was studied by making up a solution 0.01 molar in both base and ester and titating the mixture at various times with standard acid. The data are tabulated. Show that the reaction is second order and find the specific rate.

C = concentration of MA

$$-\frac{dC}{dt} = kC^2$$

$$k = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{0.01}\right)$$

The values are tabulated and appear to be nearly constant, thus confirming the second order mechanism.

t	C	k
0	0.01	
3	0.0074	11.71
5	0.00634	11.55
7	0.0055	11.69
10	0.00464	11.55
15	0.00363	11.70
21	0.00288	11.77
25	0.00254	11.75

P3.02.23. SODIUM THIOSULFATE AND METHYL IODIDE

The table gives kinetic data (Slator, J Chem Soc 85 1286, 1904) for the reaction between $Na_2S_2O_3$ (A) and CH_3I (B) at 25 C. The concentrations are in arbitrary units, the time in minutes.
Show that the reaction is second order.

$$-\frac{dB}{dt} = kAB = k(17.1+B)$$

$$k = \frac{1}{t}\int_B^{18.25} \frac{dB}{B(17.1+B)} = \frac{1}{17.1t}\ln\frac{18.25(17.1+B)}{35.35B}$$

The values are tabulated and appear to be nearly constant, confirming the second order mechanism. Average value is $k = 1.98(10^{-3})$.

t	$Na_2S_2O_3$	CH_3I	10^3k
0	35.35	18.25	
4.75	30.5	13.4	1.99
10	27.0	9.9	2.00
20	23.2	6.1	1.97
35	20.3	3.2	1.98
55	18.6	1.5	1.98
∞	17.1		

P3.02.04. HYDROXYVALERIC ACID

The conversion of hydroxyvaleric acid into valerolactone at 25°C in 0.025 N HCl was followed by titration with standard base. Given the tabulated data, find the order and specific rate of the reaction.

Assume that complete conversion occurs as $t \Rightarrow \infty$.

$$x = \text{fraction of lactone formed} = \frac{19.04-V}{19.04-10.71} = \frac{19.04-V}{8.33}$$

If the reaction is first order,

$$k = \frac{1}{t}\ln\frac{1}{1-x} = \frac{1}{t}\ln\frac{8.33}{V-10.71}$$

The calculated values are in column 3 of the table. They are nearly enough constant to confirm a first order mechanism.

t, min	Base, cc	10^3k
0	19.04	
48	17.60	3.954
124	15.80	3.972
289	13.37	3.950
∞	10.71	

P3.02.25. DIFFERENT SOLVENTS

Data for the acid hydrolysis of methyl acetate (A) at 25°C

$CH_3CO_2CH_3 + H_2O \Rightarrow CH_3COOH + CH_3OH$

have been obtained as t in minutes and conversion x in mols/liter. Find the orders and specific rates of the reactions in the two solvents.

(a) For aqueous solution with initial 0.1 mols/liter for HCl, 52.19 for H_2O and 0.7013 for A the data are in Table (a).

(b) For aqueous acetone with initial 0.1 mols/liter for H_2SO_4, 0.933 for H_2O, and 2.511 for A the data are in Table (b).

Assume that the rates are proportional to the concentrations of the acid catalysts, and that the stoichiometry represents the mechanism, thus second order.

x = conversion of A, mols/liter

$$\frac{dx}{dt} = k(\mathrm{Acid})(A)(H_2O)$$

Part (a).

$$\frac{dx}{dt} = k_a(0.1)(0.7013-x)(52.19-x)$$

$$k_{a1} = \frac{1}{0.1t}\int_0^x \frac{dx}{(0.7013-x)(52.19-x)} \quad (1)$$

If the slight change in water concentration is neglected,

$$k_{a2} = \frac{1}{0.1(52.19)}\int_0^x \frac{dx}{0.7013-x} \quad (2)$$

Part (b).

$$k_b = \frac{1}{0.1t}\int_0^x \frac{dx}{(2.511-x)(0.933-x)} \quad (3)$$

All three integrals are evaluated numerically and tabulated. The pseudo first order k_{a2} is as nearly constant as the second order value, k_{a1}.

(a) Aqueous solution

t	x	10^4k_{a1}	10^4k_{a2}
0	0		
200	0.08455	1.235	1.231
280	0.1171	1.254	1.250
445	0.1727	1.222	1.217
620	0.2311	1.241	1.235
1515	0.4299	1.209	1.201
1705	0.4588	1.202	1.193

(b) Acetone solution

t	x	10^4k_b
0	0	
60	0.1379	109.0
120	0.2611	115.3
180	0.3589	116.7
240	0.4177	108.7

P3.02.26. ETHYL NITROBENZOATE

The results of the alkaline hydrolysis of ethyl nitrobenzoate at various times are in the table. Check first and second order mechanisms.

$$-\frac{dA}{dt} = kA^q$$

For first order

$$\ln(A/A_0) = kt \qquad (1)$$

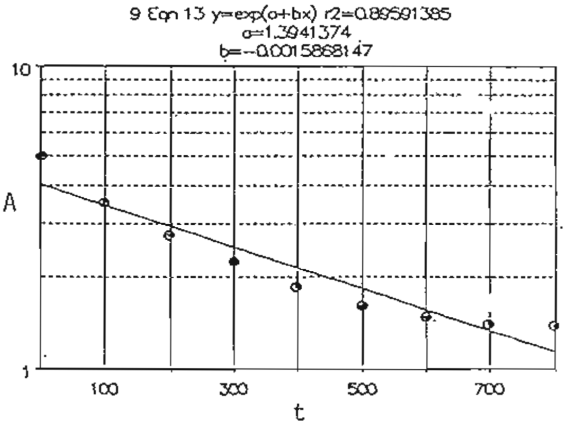
For second order,

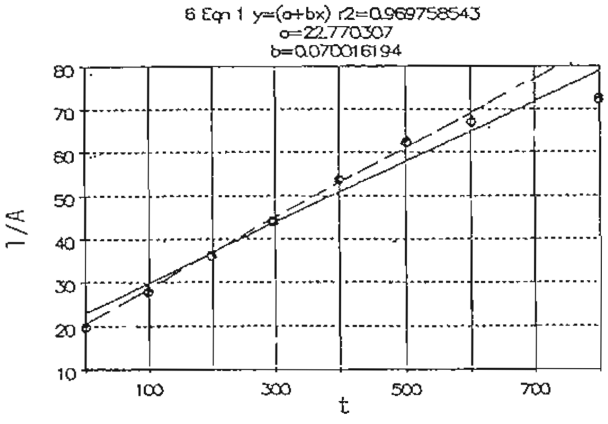
$$\frac{1}{A} = \frac{1}{A_0} + kt \qquad (2)$$

The plot of the data as ln A against t is not straight, so the reaction is not first order.

The plot of Eq (2) is more nearly straight with k = 0.070 liter/(mol)(s). If the last point is ignored, the fit is better with k = 0.083 liter/(mol)(s).

100 t	0	1	2	3	4	5	6	7	8
100 A	5.00	3.55	2.75	2.25	1.85	1.60	1.48	1.40	1.38





P3.02.27. NITROUS OXIDE

Data for the thermal decomposition of nitrous oxide on gold at 900°C and an initial pressure of 200 Torr are tabulated. Check the order of the reaction.

$$2\ N_2O \Rightarrow 2\ N_2 + O_2$$

x = fraction decomposed

For first order,

$$k_1 = \frac{1}{t} \ln \frac{1}{1-x} \qquad (1)$$

For second order,

$$\frac{n_0}{V} \frac{dx}{dt} = k[\frac{n_0(1-x)}{V}]^2$$

$$k_2 = \frac{kn_0}{V} = \frac{1}{t}(\frac{1}{1-x} - 1) \qquad (2)$$

The calculations are summarized in the table. A first order process is indicated.

t	x	k_1	k_2
30	0.32	0.0128	0.0157
53	0.50	0.0131	0.0199
100	0.73	0.0131	0.0370

P3.02.28. FORMALDEHYDE AND SODIUM PARAPHENOLSULFONATE

Rate data for the condensation of formaldehyde (F) with sodium paraphenolsulfonate (M) were taken by Stults et al (CEP Symp Series 4 38, 1952) at 100°C and pH = 8.35. Equal quantities of the reactants were present initially. Check first and second order mechanisms with the tabulated data. Integrated rate equations are

$$k_1 = \frac{1}{t} \ln \frac{0.131}{F}$$

$$k_2 = \frac{1}{t}(\frac{1}{F} - \frac{1}{0.131})$$

The results of the calculations are tabulated. Neither first nor second order appears to be a good fit.

t	F	10^3k_1	10^2k_2
0	0.131		
10	0.125	4.69	3.66
20	0.121	3.97	3.15
30	0.117	3.77	3.04
40	0.111	4.14	3.44
60	0.104	3.85	3.30

P3.02.29. REVERSIBLE FIRST ORDER

One solution contains A_0 = 1.6 mol/cuft and the other B_0 = 1.0 mol/cuft. The reaction is $A \Leftrightarrow B$. Equal amounts of solutions are mixed quickly and measurements of A versus time are made. Find the specific rates.

Equilibrium evidently is attained when the concentration is $A_e = 0.52$.

$B_e = A_0+B_0-A_e = 0.8+0.5-0.52 = 0.78$

$K_e = 0.78/0.52 = 1.5$

The rate equation is

$$-\frac{dA}{dt} = k_1A-k_2B = k_1A - k_2(A_0+B_0-A) = k_1[A- (A_0+B_0-A)/K_e]$$

$$= k_1[A- (1.3-A)/1.5] = k_1(1.667A-0.867)$$

$$k_1 = \frac{1}{t} \int_0^{0.8} \frac{dA}{1.667A - 0.867} = \frac{1}{1.667t} \ln \frac{0.4667}{1.667A-0.867}$$

The calculated k_1 are tabulated and appear to be fairly constant. The average values are

$k_1 = 0.747$
$k_2 = k_1/K_e = 0.498$

t	A	k_1
0	0.800	
0.5	0.670	0.749
1	0.600	0.752
1.5	0.563	0.749
2	0.543	0.750
3	0.527	0.738
4	0.522	0.741
5	0.520	
10	0.520	

P3.02.30. RATE DATA OF A REVERSIBLE REACTION

The tabulated data of rate versus concentration refer to a reaction that is believed of the second order in the forward direction and first order in reverse. Initial concentrations of the two reactants were 1.2 mol/cuft each and there was no product to start with. (a) Find the specific rates; (b) How long does it take to convert 60% of the reactants?

$$A + B \Leftrightarrow C$$

$$K_e = \frac{C_e}{A_e B_e} = \frac{1.2-0.4}{(0.4)(0.4)} = 5$$

The rate equation is

$$r_a = -\frac{dA}{dt} = k_1(A^2 - C/K_e) = k_1(A^2 - \frac{1.2-A}{5})$$

$$= k_1(A^2 + 0.2A - 0.24) = k_1 z$$

The plot of -dA/dt against $z = A^2+0.2A-0.24$ is straight, with

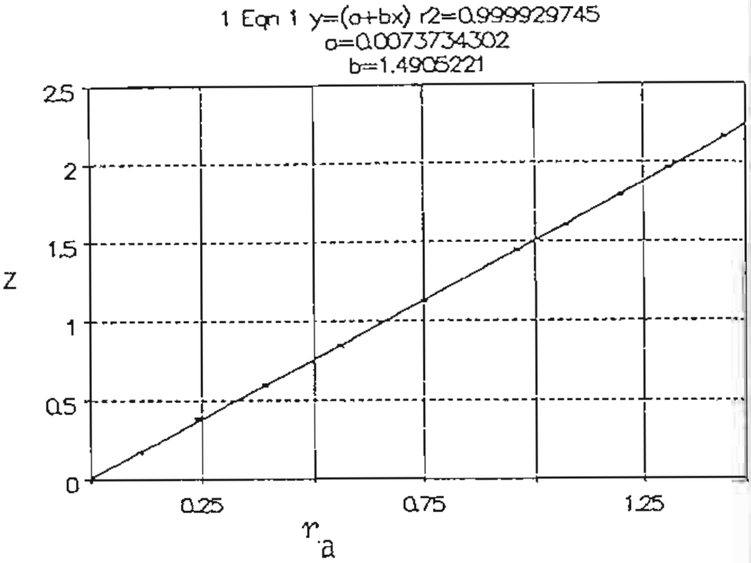
$k_1 = 1.4905$ (a)

When $A = 0.4A_0 = 0.48$,

$$t = \frac{1}{1.4905}\int_{0.48}^{1.2} \frac{dA}{A^2+0.2A-0.24} = 1.202 \text{ min} \qquad \text{(b)}$$

Analytical integration is possible, but the given result was obtained by numerical integration.

1.2-A	-dA/dt
0	2.16
0.05	1.96
0.10	1.79
0.15	1.60
0.20	1.44
0.30	1.12
0.40	0.84
0.50	0.59
0.60	0.38
0.70	0.17
0.80	0.00



P3.02.31. VINYL CHLORIDE AND HYDROGEN BROMIDE

Gaseous vinyl chloride (A) reacts with hydrogen bromide (B) at 372°C to make vinyl bromide (C) and hydrogen chloride. $A_0 = 12.6(10^{-4})$ mol/liter, $B_0 = 13.2(10^{-4})$. Products are initially absent. t is in minutes. Find the specific rate.

Try a second order mechanism.

$$-\frac{dA}{dt} = \frac{dC}{dt} = kAB = kA(A+B_0-A_0) = kA[A+0.6(10^{-4})]$$

$$kt = \int_A^{A_0} \frac{dA}{A(A+0.6)} = \frac{1}{0.6(10^{-4})} \ln \frac{12.6[A+0.6(10^{-4})]}{13.2A}$$

$$= \frac{1}{0.6(10^{-4})} \ln \frac{12.6(13.2-C)}{13.2(12.6-C)}$$

The values of k are recorded in the last column and appear to be nearly constant.

t	10^4C	k
0	0.00	
5	0.12	1.456
10	0.27	1.658
15	0.40	1.654
20	0.54	1.694
25	0.65	1.646
30	0.78	1.664
35	0.90	1.662
40	1.01	1.647

P3.03.32. SODIUM ETHOXIDE AND ETHYL DIMETHYL SULFONIUM IODIDE

The reaction, $NaOC_2H_5$ (A) + $C_2H_5(CH_3)_2SI$ (B) ⇒ Products, was conducted in ethanol at 64°C by Hughes et al (J Chem Soc 2072, 1948). Data are of the times in minutes and the concentrations in mols/liter. Find the specific rate.

Try the rate equation,

$$-\frac{dA}{dt} = kA(B_0-A_0+A)$$

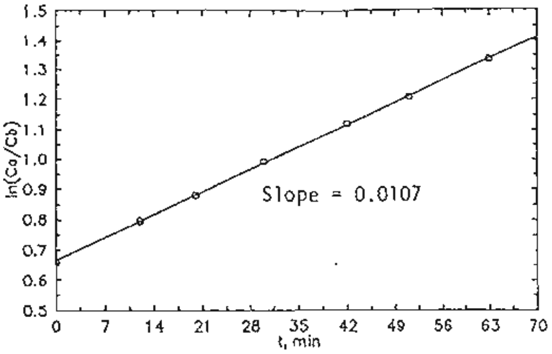
whose integral is

$$kt = \int_A^{A_0} \frac{dA}{A(B_0-A_0+A)} = \frac{1}{A_0-B_0} \ln \frac{B_0A}{A_0B}$$

The plot of ln(A/B) against t is straight, with slope = 0.0107.

$$k = \frac{0.0107}{A_0-B_0} = \frac{0.0107(100)}{9.625-4.92} = 0.227 \text{ mol/(liter)(min)}$$

t	100A	100B
0	9.625	4.920
12	8.578	3.876
20	8.046	3.342
30	7.485	2.783
42	6.985	2.283
51	6.709	2.005
63	6.386	1.682



P3.02.33. GLYCOL FROM ETHYLENE OXIDE.

Data for the formation of glycol (C) from ethylene oxide (A) and water (B) with sulfuric acid catalyst at 55°C are cited by Fogler (110, 1992).

$(CH_2)_2O + H_2O \Rightarrow (CH_2OH)$

The starting solution contained 1.0 mol/liter of ethylene oxide, 55 mol/liter of water and 0.9 wt% of acid. Neglect any changes in water concentration and find the pseudo first order specific rate.

The rate equation is

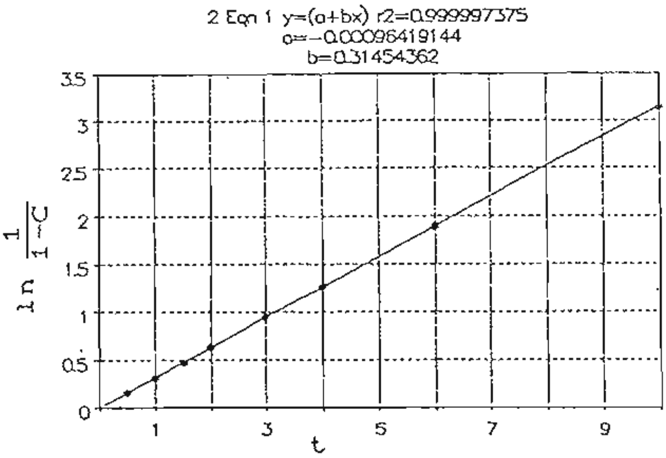
$$\frac{dC}{dt} = k[\mathrm{Acid}][\mathrm{Water}]A = k'A = k'(A_0 - C) = k'(1 - C)$$

$$k't = \ln \frac{1}{1-C} \qquad (1)$$

The plot of this equation is straight with slope

$k' = 0.315/\mathrm{min}$

t	Glycol, mol/liter
0	0
0.5	0.145
1	0.270
1.5	0.376
2	0.467
3	0.610
4	0.715
6	0.848
10	0.957



P3.02.34. B-HYDROXY CROTONIC ACID ISOMERIZATION

The fraction, x, of β-hydroxy crotonic acid that isomerizes into acetoacetic ester was measured at 25°C at various times. The data indicate reversibility. Find the rate equation.

Try first order.

$$K_e = \frac{x_e}{1-x_e} = \frac{0.922}{0.078} = 11.82$$

$$\frac{dx}{dt} = k_1(1-x - x/K_e) = k_1(1-x-x/11.82) = k_1(1-1.0846x)$$

$$k_1 = \frac{1}{t}\int_{0.634}^{x} \frac{dx}{1-1.0846x} = \frac{1}{1.0846t} \ln \frac{0.4506}{1-1.0846x}$$

The values of k_1 are listed in the third column and are not constant.

Try second order.

$$\frac{dx}{dt} = k_2(1-x)^2$$

$$k_2 = \frac{1}{t}\left(\frac{1}{1-x} - \frac{1}{1-0.634}\right)$$

These values are more nearly constant, so the reaction is approximately second order.

t, h	x	10^3k_1	10^2k_2
0	0.634		
71.8	0.723	9.45	1.22
145.5	0.785	7.03	1.32
215.8	0.826	6.26	1.40
264.3	0.848	6.02	1.46
333.3	0.870	5.75	1.49
383.5	0.879	5.45	1.44
478.3	0.894	5.20	1.40
506.0	0.900	5.35	1.44
∞	0.922		

P3.02.35. CONDENSATION POLYMERIZATION

A linear polymer is formed by the condensation polymerization of diethylene glycol and adipic acid,

$$O(CH_2)_2O(CH_2)_2OH + HO_2C(CH_2)_4CO$$
$$\Rightarrow \quad O(CH_2)_2O(CH_2)_2O_2(CH_2)_4CO \quad + H_2O$$

The reaction between equivalent amounts of acid and alcohol was studied at 166°C by Flory (JACS 61 3334, 1939) who followed the reaction by titration of weighed samples against standard alkali to determine the number of free carboxyl groups. Data of (t, f) are tabulated, where t is in minutes and f is the fraction of carboxyl groups esterified. The order of the reaction is to be investigated.

When the reaction is second order,

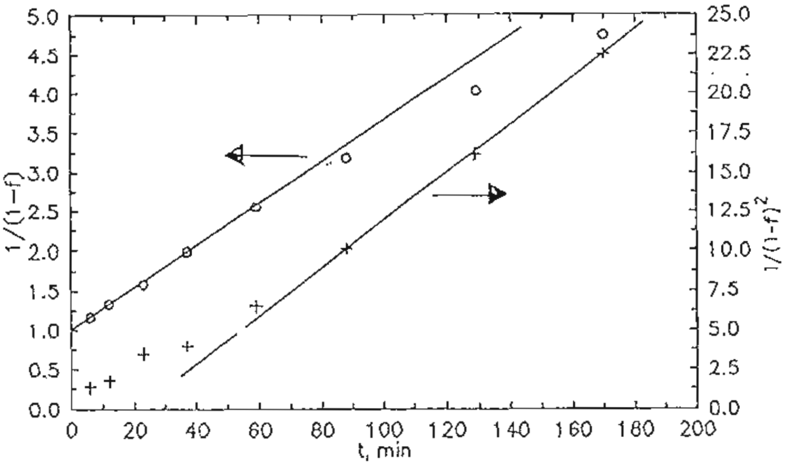
$$k_2t = \frac{1}{1-f} - 1$$

and when third order,

$$k_3t = \frac{1}{(1-f)^2} - 1$$

The two straight line plots suggest second order at lower conversions and shorter times, and third order for the higher points.

t	f	1/(1-f)	$1/(1-f)^2$
0	0		
6	0.138	1.16	1.346
12	0.247	1.33	1.764
23	0.368	1.58	3.504
37	0.498	1.99	3.968
59	0.608	2.55	6.508
88	0.686	3.18	10.14
129	0.751	4.02	16.13
170	0.789	4.74	22.46



P3.02.36. ETHYLENE DIBROMIDE AND POTASSIUM IODIDE

Data are reported (Dillon, JACS 70 952, 1932) on the kinetics of the reaction between ethylene dibromide (A) and potassium iodide (B) at 59.7°C. Initial concentrations were A_0 = 0.02864 mol/liter and B_0 = 0.1531. The stoichiometry of the reaction is

$$C_2H_4Br_2 + 3\ KI \Rightarrow C_2H_4 + 2\ KBr + KI_3$$

The rate equation is to be investigated.

Try the rate equation

$$-\frac{dA}{dt} = kAB = kA(B_0-3A_0+3A) = kA(0.06718 + 3A)$$

In terms of the fractional conversion of A,

$$A = A_0(1-x) = 0.02864(1-x)$$

$$\frac{dx}{dt} = k(1-x)(0.1531-0.08592x)$$

$$k = \frac{1}{t-495}\int_{0.2863}^{x}\frac{dx}{(1-x)(0.1531-0.08592x)}$$

The integral is evaluated numerically, the results are tabulated and appear to be nearly constant, with

k = 0.0052 liter/(mol)(min)

t	x	10^3k
495	0.2863	
675	0.3630	5.05
795	0.4099	5.16
930	0.4572	5.21
1035	0.4890	5.20
1215	0.5396	5.23
1395	0.5795	5.14

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$$A = A_0(1-x) = 0.02864(1-x)$$

$$\frac{dx}{dt} = k(1-x)(0.1531-0.08592x)$$

$$k = \frac{1}{t-495}\int_{0.2863}^{x}\frac{dx}{(1-x)(0.1531-0.08592x)}$$

The integral is evaluated numerically, the results are tabulated and appear to be nearly constant, with

k = 0.0052 liter/(mol)(min)

P3.02.37. TRIMETHYLAMINE AND n-PROPYL BROMIDE

The tabulated data for reaction between trimethylamine (A) and n-propyl bromide were obtained with initial concentrations of 0.1 mol/liter each. The rate equation is to to be found.

x = fractional conversion of A

$A = A_0(1-x)$

Try second order.

$$-\frac{dA}{dt} = A_0\frac{dx}{dt} = k[A_0(1-x)]^2$$

$$k = \frac{1}{A_0(t-13)}\int_{0.112}^{x}\frac{dx}{(1-x)^2} = \frac{10}{t-13}\left(\frac{1}{1-x} - \frac{1}{1-0.112}\right)$$

The values are tabulated, with an average

$k = 1.02$ liter/(mol)(min)

t	x	k
13	0.112	
34	0.257	1.05
59	0.367	0.99
120	0.552	1.03

P3.02.38. REACTION ORDER 1.5

Show that the tabulated observations conform to kinetics of order 1.5.

$$-\frac{dA}{dt} = kA^{\alpha}$$

$$k = \frac{1}{(\alpha-1)t}\left(\frac{1}{A^{\alpha-1}} - \frac{1}{16^{\alpha-1}}\right)$$

The values with $\alpha = 1.5$ are tabulated and are nearly enough constant to confirm the assumed α. The average value is

$k = 5.02\ (\text{liter/g})^{1/2}/\text{min}$

t min	A g/l	k
0	16.0	
10	13.2	5.05
20	11.1	5.02
35	8.8	4.98
50	7.1	5.01

P3.02.39. ACETONE AND HCN. NUMERICAL INTEGRATION.

The reaction between acetone (A) and HCN (B) was studied in aqueous solution (Svirbely & Roth, JACS 75 3109, 1953). The tabulated data were obtained with initial concentrations of 0.1164 normal for acetone and 0.0758 for HCN. The equilibrium constant is $K_e = 13.87$ liter/gmol.

$CH_3COCH_3 + HCN \Leftrightarrow (CH_3)_2C(CN)(OH)$

Try a rate equation conforming to the stoichiometry.

$A = A_0 - B_0 + B = 0.0406 + B$

$C = C_0 - B = 0.0758 - B$

$$-\frac{dB}{dt} = k(AB - C/K_e) = k[B(0.0406+B) - (0.0758-B)/13.87]$$

$$k = \frac{1}{t-4.37}\int_{B}^{0.0758}\frac{dB}{B(0.0406+B)-(0.0758-B)/13.87}$$

The integration is done numerically. The values are tabulated and appear to be only roughly constant. Perhaps more work should be done.

t	B	10^3 k
4.37	0.0758	
73.2	0.0710	6.85
172.5	0.0655	7.57
265.4	0.0610	7.93
346.7	0.0584	7.62
434.4	0.0557	7.56

P3.02.40. FORMIC ACID DECOMPOSITION

Formic acid decomposes in 98% sulfuric acid to give carbon monoxide and water. The tabulated results refer to the decomposition at 25°C, time in sec and cc of CO evolved.

Try a first order rate equation. V = cc of CO evolved.

$$\frac{dV}{dt} = k(V_\infty - V) = k(41.5 - V)$$

$$k = \frac{1}{t} \ln \frac{41.5}{41.5-V}$$

The k's are nearly constant, with a mean value

$$k = 6.60(10^{-3})/\text{sec}$$

t	V	10^3k
0	0	
25	6.3	6.59
50	11.6	6.56
75	16.3	6.65
100	20.2	6.67
150	26.1	6.61
200	30.4	6.59
250	33.5	6.59
∞	41.5	

P3.02.41. HYDROLYSIS OF ETHYL M-NITROBENZOATE

The tabulated results (Newling & Hinshelwood, J Chem Soc 1357, 1936) refer to the hydrolysis of ethyl m-nitrobenzoate by hydroxyl ions in aqueous solution at 15.2°C. Initial concentrations were both 0.05 mol/liter. t is in sec, x = % change. Check the order of the reaction.

$$C = 0.05(1-\frac{x}{100}) = 0\ 0005(100-x)$$

For first order,

$$\frac{dx}{dt} = k_1(100-x)$$

$$k_1 = \frac{1}{t-120} \int_{32.95}^{x} \frac{dx}{100-x} = \frac{1}{t-120} \ln \frac{67.05}{100-x} \quad (1)$$

For second order,

$$\frac{dx}{dt} = 0.0005k_2(100-x)^2$$

$$k_2 = \frac{1}{0.0005(t-120)}(\frac{1}{100-x} - \frac{1}{67.05}) \quad (2)$$

The tabulations of k_1 and k_2 show that the reaction is more nearly second order. Average value is

$$k_2 = 8.00(10^{-4}) \text{ liter/(mol)(s)}$$

t	x, %	$100k_1$	10^4k_2
120	32.95		
180	41.75	0.39	7.51
240	48.80	0.33	7.70
330	58.05	0.27	8.50
530	69.00	0.18	8.46
600	70.35	0.16	7.84

P3.02.42. HYDROGEN IODIDE FORMATION

The given data apply to the reaction

$$H_2 + I_2 \Leftrightarrow 2\ HI$$

at 698.6°K (Taylor & Crist JACS 63 1384, 1931. a, b and c are initial concentrations of H_2, I_2 and HI in mols/cc; x is the change in concentration of HI in the same units. The equilibrium constant is $K_e = 1/1.0182$.

Assume the rate equation

$$\frac{dx}{dt} = k[(a-x)(b-x)-0.0182(c+x)^2]$$

$$k = \frac{1}{t}\int_0^x \frac{dx}{(a-x)(b-x) - 0.0182(c+x)^2}$$

The four sets of corresponding values of (t,a,b,c) and the upper limit of integration, x, are substituted. Numerical integrations give the tabulated values which are all nearly the same, confirming the assumed rate equation.

t, sec	10^5x	10^5a	10^5b	10^5c	10^4k
4500	1.2753	1.0915	1.0086	0	7.011
6600	1.4057	1.1035	0.9710	0	7.141
7200	-0.19732	0	0	1.6812	6.611
10800	-0.15574	0	0	1.2178	6.866

P3.02.43. ETHYL ACETATE SAPONIFICATION. BACK TITRATION.

The reaction between ethyl acetate (A) and aqueous sodium hyroxide (B) (present in slight excess) was followed by withdrawing 10 cc samples of the reaction mixture, pipetting into an excess of 0.01 N HCl and back titrating the excess acid with alkali. The tabulated results are of the volume, V, of 0.01 N acid necessary to neutralize the NaOH in 10 cc of reaction mixture at the time, sec, shown. The rate equation is to be found.

There is an excess of NaOH corresponding to the 8.6 cc of HCl at t_∞.

$A + B \Rightarrow$ Products

$B_0 = 16.45(100)(0.01) = 16.45$ mol/liter

$A = V - 8.6$ mol/liter

$B = 8.6 + A = V$

Try the rate equation

$$-\frac{dA}{dt} = \frac{dV}{dt} = kAB = k((V-8.6)V$$

$$k = \frac{1}{t}\int_V^{16.45} \frac{dV}{V(V-8.6)} = \frac{1}{8.6t}\ln\frac{7.85V}{16.45(V-8.6)}$$

The values are tabulated. The average is

$k = 1.098(10^{-4})$ liter/(mol)(sec).

t	V, cc HCl	10^4k
0	16.45	
250	13.80	1.099
500	12.25	1.095
750	11.25	1.095
1000	10.55	1.103
∞	8.6	

P3.02.44. n-PROPYL BROMIDE AND SODIUM THIOSULFATEC

In a study of the reaction between n-propyl bromide (A) and sodium thiosulfate (B),

$$C_3H_7Br + S_2O_3^{=} \Rightarrow C_3H_7S_2O_3^{-} + Br^{-}$$

the reaction was followed by withdrawing samples from time to time, adding ice water to stop the reaction, and titrating the residual thiosulfate with standard iodine solution (Crowell & Hammett, JACS 70 3444, 1948). Their data at 37.5°C are converted here to mol/liter of $S_2O_3^{=}$ as a function of t in minutes. The initial concentration of the other component was 0.0395 mol/liter. Check a second order rate equation.

$$-\frac{dB}{dt} = kAB = k(B-0.0966+0.0395)B = kB(B-0.0571)$$

$$k = \frac{1}{t}\int_B^{0.0966} \frac{dB}{B(B-0.0571)} = \frac{1}{0.0571t} \ln \frac{0.0395B}{B-0.0571}$$

The values are tabulated, and are constant enough to confirm the assumed second order mechanism

t	$S_2O_3^{=}$	100k
0	0.0966	
18.5	0.0904	9.88
33.5	0.0863	9.90
53.2	0.0819	9.89
84.2	0.0766	9.86
123.0	0.0720	9.70
187.	0.0668	9.69
1314	0.0571	

P3.02.45. BENZALDEHYDE AND PHOSPHOROUS TRICHLORIDE

Benzaldehyde (A) reacts with phosphorous trichloride (B) in benzene solution to form an addition compound (C),

$$C_6H_5CHO + PCl_3 \Leftrightarrow C_6H_5CHOPCl_3$$

In an experiment at 25°C, starting with pure compound C at 0.02250 mols/liter, the concentration of benzaldehyde was found to be 0.01025 mol/liter after 53.8 hr. The equilibrium constant is 0.424. The reaction is believed second order in the forward direction and first order in reverse. Find the specific rate.

x = change in concentration of C

$C = C_0 - x = 0.0225 - x$

$A = B = x$

$$\frac{dC}{dt} = -\frac{dx}{dt} = k(AB - C/K_e) = k(x^2 - \frac{0.0225-x}{0.424})$$

$$k = \frac{1}{53.8}\int_{0.01025}^{0} \frac{dx}{x^2-(0.0225-x)/0.424}$$

$$= 4.80(10^{-3}) \text{ liter/(mol)(h)}$$

Numerical integration was used.

P3.02.46. HYDROCARBON CRACKING.

A high molecular weight hydrocarbon gas (A) is thermally cracked in a continuous stirred vessel. The stoichiometry is approximated by A ⇒ 5R.

Initial concentration was C_{a0} = 100 millimol/liter . Different extents of cracking were obtained by changing the feed rate, n_{a0} millimols/h. Outlet concentration is C_a. The results are in the first two columns of the table. A rate equation is to be found.

The CSTR material balance is

$$n_{a0} = n_a + kV_rC_a^\alpha$$

or

$$1 = \beta + \frac{kV_r}{n_{a0}} C_a^\alpha \qquad (1)$$

$$\beta = n_a/n_{a0} \qquad (2)$$

The total flowing mols is

$$n_t = n_a + 5(n_{a0}-n_a) = 5n_{a0}-4n_a$$

Volumetric feed rate is

$$V'_0 = n_{a0}/C_{a0}$$

and the volumetric rate in the reactor is

$$V' = V'_0(n_t/n_{a0}) = \frac{5n_{a0}-4n_a}{C_{a0}}$$

$$C_a = n_a/V' = \frac{n_a}{5n_{a0}-4n_a} C_{a0} = \frac{\beta}{5-4\beta} C_{a0} = \frac{100\beta}{5-4\beta}$$

$$\beta = n_a/n_{a0} = \frac{5}{4+100/C_a} \qquad (3)$$

Rearrange Eq (1),

$$k = \frac{n_{a0}}{V_r} \frac{(1-\beta)}{C_a^\alpha} = 10 \frac{n_{a0}(1-\beta)}{C_a^\alpha} \qquad (4)$$

The procedure is: (i) Assume a value of α, say 1; (ii) Take a value of C_a from the table and evaluate β from (3); (iii) Find k from (4).

For α = 1, the various values of k are tabulated in the last column. They are sufficiently constant to confirm that α does really equal 1.

n_{a0}	C_a	$\beta=n_a/n_{a0}$	$k_{\alpha=1}$
300	16	0.4878	96.0
1000	30	0.6818	106.1
3000	50	0.8333	100.0
5000	60	0.8824	98.0.

P3.02.47. A NON-INTEGRAL ORDER

The constants of the rate equation

$$r = -\frac{dC}{dt} = kC^q$$

are to be found with the experimental data of the first two columns of the table. Those data are fitted by the equation

$$C = \frac{1}{3.0494+0.1597t+0.00189t^2}$$

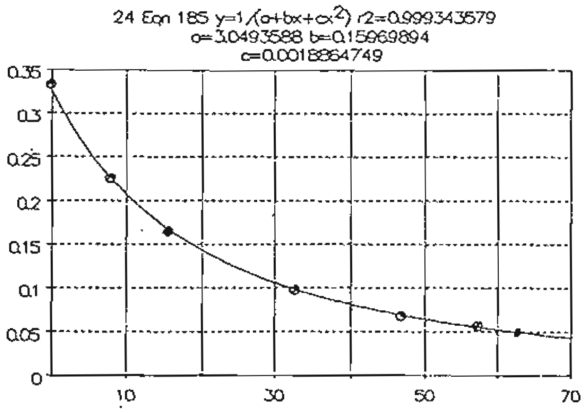
The rates are found by differentiation and are tabulated. The straight line plot of r = -dC/dt against t has the equation

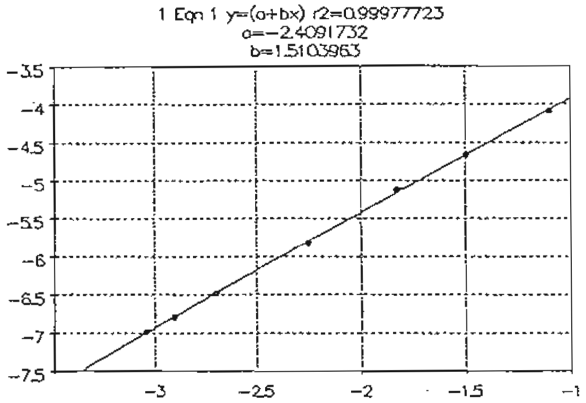
$$\ln r = -2.409 + 1.510 \ln C$$

or

$$-\frac{dC}{dt} = 0.090\ C^{1.51}$$

t	C	10^3r
0	0.0482	0.931
8	0.0553	1.114
15.6	0.0678	1.544
30	0.1053	2.972
47	0.1632	6.000
57	0.2255	9.465
63	0.3335	16.88





P3.02.48. DATA OF 2 A ⇒ B ⇒ C

The series reaction system

$$2A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$$

has been studied in a constant volume batch reactor with the results in the table. Time is in hrs and concentrations in mols/liter. Assuming that the orders conform to the stoichiometries, find the values of the specific rates.

The rate equations are

$$\frac{dA}{dt} = -k_1A^2$$

$$\frac{dB}{dt} = k_1A^2 - k_2B$$

$$\frac{dC}{dt} = k_2B$$

$$k_1 = \frac{1}{t}\left(\frac{1}{A} - \frac{1}{A_0}\right) = \frac{1}{t}\left(\frac{1}{A} - 1\right) \qquad (1)$$

The values are tabulated, with a mean value $k_1 = 10.09$.
The (C, t) data are correlated by

$$C = 3.678(10^{-5}) + 0.6002t + 5.719t^2 - 13.871t^3 \qquad (2)$$

from which the derivative is

$$\frac{dC}{dt} = 0.6002 + 11.438t - 41.613t^2 \qquad (3)$$

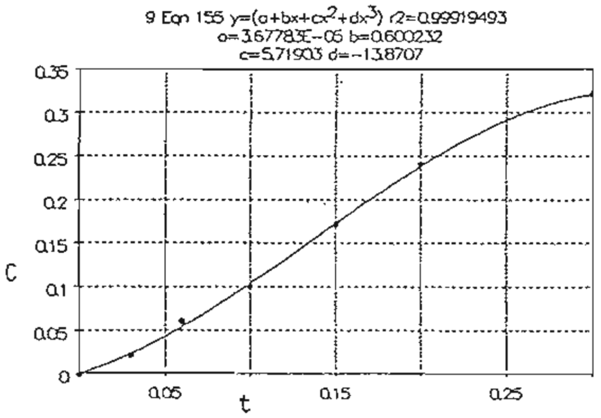
The specific rate is found from

$$k_2 = \frac{1}{B}\frac{dC}{dt}$$

and tabulated. The mean value (after omitting the last point) is

$$k_2 = 10.38 \tag{4}$$

t	A	B	C	$\frac{dC}{dt}$	k_1	k_2
0	1.0	0	0			
0.03	0.76	0.098	0.02	0.906	10.53	9.25
0.06	0.63	0.122	0.06	1.14	9.79	9.32
0.10	0.51	0.140	0.10	1.33	9.61	9.50
0.15	0.39	0.120	0.17	1.38	10.43	11.53
0.2	0.33	0.100	0.24	1.23	10.15	12.31
0.3	0.25	0.050	0.32	0.286	10.00	5.72



P3.02.49. HEXAMETHYLENE TETRAMINE

Hexamethylene tetramine was made at 0°C from aqueous ammonia and formaldehyde (Meissner, Ind Eng Chem 46 724, 1954). The volume of the reactor was 1 liter. Find the order of the reaction with respect to NH_3.

Wt% NH_3 present	0.8	0.6	0.41	0.20	0.016
Conversion, mols NH_3/min	0.025	0.020	0.010	0.002	0.00002

Take the rate equation

$$r = k(NH_3)^q$$

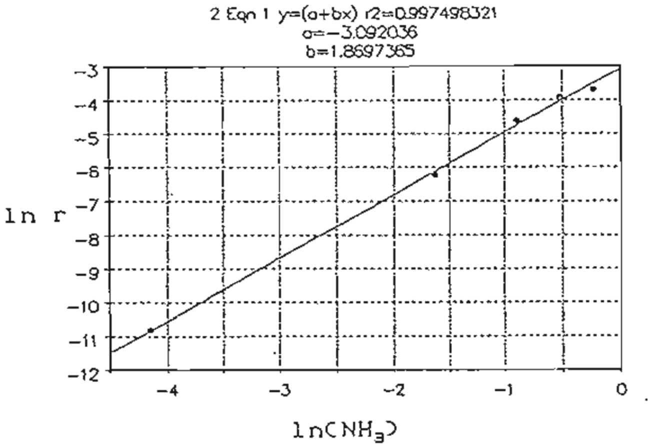
$$\ln r = \ln k + q \ln(NH_3)$$

A good straight line plot is obtained with equation

$$\ln r = -3.092 + 1.8697 \ln(NH_3)$$

or

$$r = 0.0454\ (NH_3)^{1.8697}$$



P3.02.50. RADON DECOMPOSITION

Observations of the decomposition of radon gave the results

t, hrs	0	70	100	140	165	200	250	360
V, cc	0.102	0.062	0.044	0.033	0.025	0.019	0.016	0.007

Try a first order rate equation which has the integral

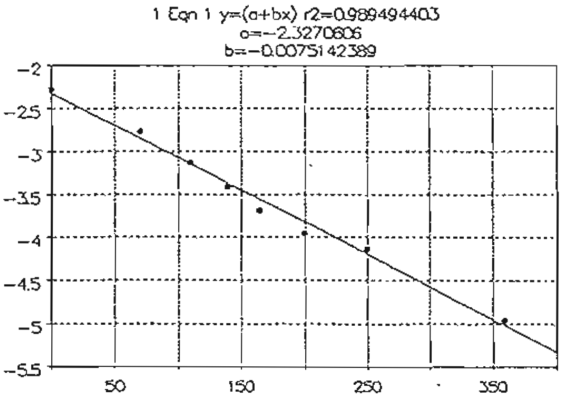
$$k_1 t = \ln(V_0/V) = \ln V_0 - \ln V$$

The logarithmic plot is a good fit to a straight line with equation

$$-\ln V = 2.327 + 0.00751\ t$$

which makes

$$k_1 = 0.0075/\text{hr}$$



P3.02.51. HYDROLYSIS IN NON-AQUEOUS SOLUTION. THIRD ORDER

The hydrolysis of ethyl acetate (B) with an alkaline hydroxide (A) non-aqueous solutions is believed to have the third order rate equation

$$-\frac{dB}{dt} = kA^2B$$

In terms of the fraction, x, of ester converted

$$B = B_o(1-x)$$

$$A = A_0-B_0+B = A_0-B_0x$$

$$dB = -B_0dx$$

and the rate equation becomes

$$\frac{dx}{dt} = k(A_0-B_0x)^2(1-x)$$

from which

$$k = \frac{1}{t}\int_0^x \frac{dx}{(A_0-B_0x)^2(1-x)} \qquad (1)$$

The integration can be done analytically, but here it will be done numerically. Experiments were done in an ethanol solution for several ratios by Koivisto (Acta Chem Scand 8 1223, 1954). Those data and calculated k's are tabulated. All 12 of the k's are quite close.

$A_0 = 0.2$
$B_0 = 0.2$

$10^{-3}t$	x	k
3.6	0.133	1.147
6.6	0.213	1.164
23.4	0.437	1.151
46.2	0.566	1.166

$A_0 = 0.2$
$B_0 = 0.4$

$10^{-3}t$	x	k
2.69	0.096	1.165
7.8	0.197	1.182
16.8	0.284	1.199
32.4	0.347	1.159

$A_0 = 0.4$
$B_0 = 0.2$

$10^{-3}t$	x	k
1.57	0.234	1.208
3.18	0.389	1.224
4.8	0.495	1.221
12	0.743	1.247

P3.02.52. TRIPHENYL METHYL CHLORIDE AND METHANOL

The reverse reaction of triphenyl methyl chloride (A) and methanol (B)

$$(C_6H_5)_3CCl + CH_3OH \Leftrightarrow (C_6H_5)_3COCH_3 + HCl$$

was prevented by precipitating the HCl with pyridine. The data of the table are provided by Swain (JACS 70 1119, 1948). The reaction proceeded in dry benzene in the presence of pyridine. Initial conditions were $A_0 = 0.106$ molar, $B_0 = 0.054$ molar. time is in minmutes Verify that the reaction is first order with respect to the chloride and second order with respect to methanol.

x = TPMC reacted, mol/liter

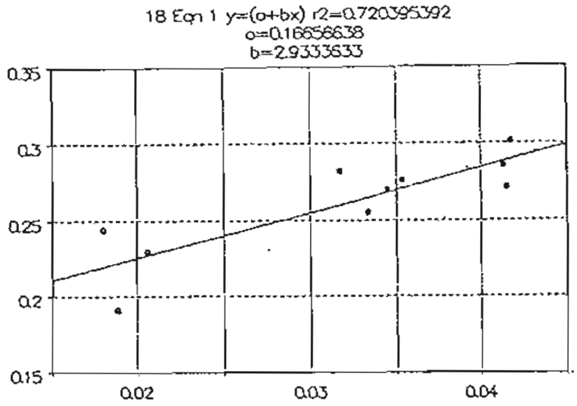
$$-\frac{dC_a}{dt} = \frac{dx}{dt} = kC_aC_b^2 = k(0.106-x)(0.054-x)^2$$

from which

$$k = \frac{1}{t-168}\int_{0.0091}^{x} \frac{dx}{(0.106-x)(0.054-x)^2}$$

The integration is done numerically. The results are tabulated and plotted. They are only roughly constant with the mean value k = 0.26.

t	x	k
168	0.0091	
174	0.0110	1.71
418	0.0181	0.243
426	0.0189	0.190
444	0.0207	0.228
1150	0.0318	0.281
1440	0.0334	0.255
1510	0.0345	0.270
1660	0.0354	0.275
2890	0.0418	0.301
2900	0.0414	0.285
3120	0.0416	0.270
193000	0.0514	



P3.02.53. FERRIC AND STANNOUS CHLORIDES. THIRD ORDER.

For the reaction

$$2\ FeCl_3 + SnCl_2 \Rightarrow 2\ FeCl_2 + SnCl_4$$

at 25°C the initial concentration of $FeCl_3$ (A) was 0.0625 and that of $SnCl_2$ (B) was 0.03125 mol/literThe data are t in minutes and x = mols/liter of $FeCl_3$ reacted. Find a rate equation.

Try the third order rate equation,

$$\frac{dx}{dt} = kA^2B = k(0.0625-x)^2(0.03125-\frac{x}{2}) = 0.5k(0.0625--x)^3$$

$$k = \frac{2}{t}\int_0^x \frac{dx}{(0.0625-x)^3} = \frac{1}{t}\left[\frac{1}{(0.0625-x)^2} - \frac{1}{(0.0625)^3}\right]$$

The values are tabulated and appear to be fairly constant, thus confirming the assumed third order mechanism.

t	x	k
1	0.01434	175.15
3	0.0266	173.88
7	0.03612	168.71
11	0.04102	173.76
40	0.05058	169.55

P3.02.54. PARA NITROBENZOYL CHLORIDE AND n-BUTANOL

Some data for the reaction between para nitrobenzoyl chloride (A) and n-butanol (B) were obtained at two starting concentrations with stoichiometric proportions (Ashdown, JACS 52 268, 1930). The reaction is

$A + 2B \Rightarrow \text{Products}$

Assume the rate equation follows the stoichiometry.

x = fraction of A converted.

$$-A_0\frac{dx}{dt} = kA_0^3(1-x)^3$$

$$ktA_0^2 = 0.5\left[\frac{1}{(1-x)^2} - 1\right] = \frac{x(2-x)}{2(1-x)^2}$$

The substantially linear plots of t against the right hand side confirm the assumed rate equation.

When $A_0 = 0.5$, $k = 0.090$

$A_0 = 1.0$, $k = 0.083$

	x, A_0=0.5	x, A_0=1.0
1	0.0266	0.0717
2	0.0452	0.1366
3	0.0727	0.1877
4	0.0854	0.2302
5	0.1035	0.2614
6	0.1146	0.2895
7	0.1366	0.3212
8	0.1506	0.3439
9	0.1632	0.3663
10	0.1736	0.3862
11	0.1840	0.4071
12	0.1963	

P3.02.55. SILVER ACETATE AND SILVER FORMATE

In aqueous solution at 100°C silver acetate reacts slowly with sodium formate

$$2\ AgC_2H_3O_2 + NaCHO_2 \Rightarrow 2\ Ag + CO_2 + HC_2H_3O_2 + NaC_2H_3O_2$$

The starting mixture has A_0 =0.1 mol/liter and B_0 = 0.05. The data are of t in minutes and change of concentration of the silver compound. Check second and third order equations.

$$\frac{dx}{dt} = k_2(0.1-x)(0.05-x/2)$$

$$\frac{dx}{dt} = k_3(0.1-x)^2(0.05-x/2)$$

$$k_2 = \frac{1}{t}\int_0^x \frac{dx}{(0.1-x)(0.05-x/2)}$$

$$k_3 = \frac{1}{t}\int_0^x \frac{dx}{(0.1-x)^2(0.05-x/2)}$$

The integrals are found numerically. They are tabulated and support the third order mechanism.

t	x	k_2	k_3
0	0		
2	0.0330	2.46	61.4
6	0.0562	1.89	59.4
14	0.0677	1.50	61.4

P3.02.56. IRON AND TIN CHLORIDES

The reaction, $2\ FeCl_3 + SnCl_2 \Rightarrow$ Products, was studied with stoichiometric proportions of reactants. The data are time in minutes and tin chloride (B) mol/liter. Check the third order rate equation corresponding to the stoichiometry.

With stoichiometric proportions, A = 2B.

$$-\frac{dB}{dt} = k_3A^2B = 4k_3B^3$$

The integration gives,

$$k_3 = \frac{1}{8t}\left(\frac{1}{B^2} - \frac{1}{(0.07)^2}\right)$$

The values are tabulated and confirm the third order reaction.

t	B	k_3
0	0.0700	
2	0.0423	22.17
5	0.0304	21.95
10	0.0225	22.14
25	0.0147	22.12

P3.02.57. HYDROGEN AND BROMINE. LINEAR REGRESSION

Data for the reaction between hydrogen (A) and bromine (B) with equal concentrations are tabulated. Time is in minutes and concentrations in mols/liter. A complex mechanism has been established (see problem P2.03.15) but here a power law equation will be fitted,

$$r = -\frac{dA}{dt} = kA^aB^b = kA^{a+b}$$

or

$$\ln r = \ln(k) + (a+b)\ln(A)$$

The concentration data are curve fitted by the equation shown with the graph. The derivative is obtained by differentiation and is tabulated in column 3. Linear regression by POLYMATH gives the relation

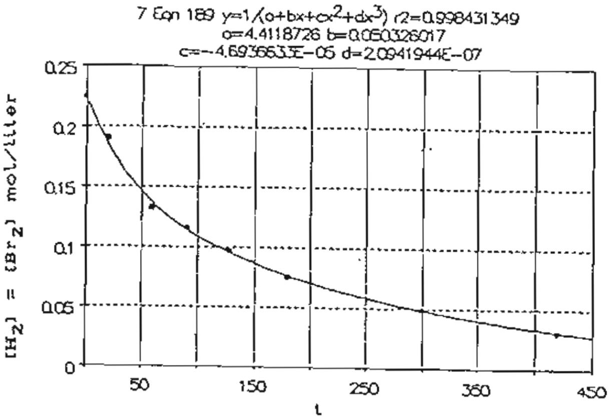
$$\ln r = -3.8712 + 1.5612 \ln [H_2]$$

or

$$-\frac{d[H_2]}{dt} = 0.02083\ [H_2]^{1.5612}$$

The exponents a and b could be found independently by POLYMATH multilinear regression if data were available with unequal starting concentrations of the reactants.

t	$[H_2]$	10^3r
0	0.225	2.586
20	0.1898	1.669
60	0.1323	0.879
90	0.1158	0.619
120	0.0667	0.439
180	0.0752	0.310
300	0.0478	0.1795
420	0.0305	0.1132



P3.02.58. IODINATION. FOURTH ORDER

In a study of the iodination of meta xylene by ICl at 20 C the reaction was followed by the analysis of unreacted ICl (cited by Pannetier, 1967). Two different solvent mixtures were used. (a) 60 vol% m-xylene and 40 vol% $C_6H_5NO_2$; (b) with solvent 50 vol% CH_3NO_2, 40% $ClCH_2$-CH_3Cl, 10% $(CH_3CO)_2CO$ and initial concentrations [ICl] = [m-xylene] = 0.1078 mol/liter. For case (a), determine the order with respect to ICl, and for case (b) find the order with respect to both reactants.

Case (a). The large excess of m-xylene allows neglect of its variation in concentration and only variation in [ICl] need be taken into account. Try

$$-\frac{d[\mathrm{ICl}]}{dt} = k_q[\mathrm{ICl}]^q$$

$$k_q = \frac{1}{t(q-1)}\left(\frac{1}{[\mathrm{ICl}]^{q-1}} - \frac{1}{0.175^{q-1}}\right)$$

The values are recorded in the first table, and show that q = 3 is satisfactory. This is confirmed by the plot of ln r against ln C which has a slope of 2.86. The curve fit of (C,t) was differentiated to find r.

$$r = -0.00159 + 25.432(10^{-7})t^2 - 0.12665\exp(-t)$$

Case (b). Try the rate equation,

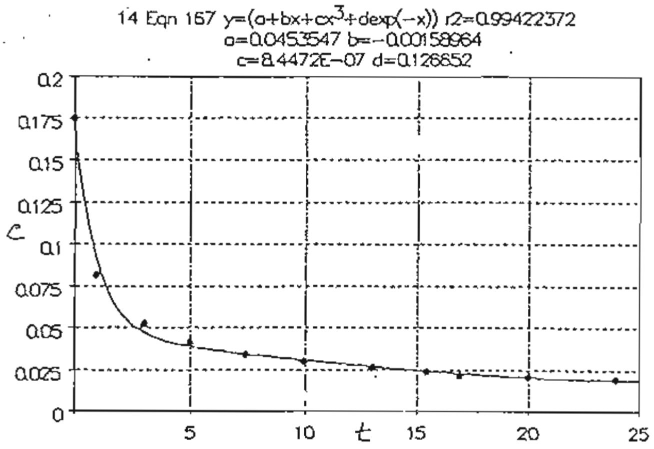
$$-\frac{dB}{dt} = k_4AB^3 = k_4B^4$$

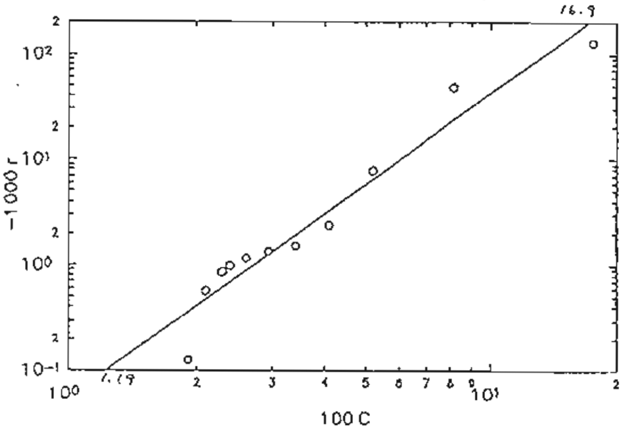
$$k_4 = \frac{1}{3t}\left(\frac{1}{B^3} - \frac{1}{0.1078^3}\right)$$

The results are recorded in the second table and confirm the fourth order.

t, min	[ICl]	k_1	k_2	k_3
0	0.1750			
1	0.0815	0.764	6.56	58.9
3	0.0519	0.405	4.52	56.4
5	0.0409	0.291	3.75	56.5
7.5	0.0341			
10	0.0294	0.178	2.83	56.2
13	0.0261	0.146	2.51	55.
15.5	0.0239	0.128	2.33	55.4
17	0.0229	0.120	2.23	55.1
20	0.0210	0.106	2.10	55.9
24	0.0191	0.092	1.94	56.4

t	[ICl]	k_4
0.5	0.0805	745.8
2	0.0574	748.3
3.5	0.0485	758.9
5	0.0438	740.4
7.5	0.0384	749.7
10	0.0349	757.9
14	0.0312	765.4
17	0.0295	748.7
21	0.0275	751.2
27	0.0253	753.3
38	0.0226	754.0





P3.02.59. IODINE AND AN ORGANOMETALLIC. FOURTH ORDER

For the reaction of iodine with an organo tin compound,

$Sn(nC_4H_9)_4 + I_2 \Rightarrow ISn(nC_4H_9)_3 + IC_4H_9$

in benzene at 20 C and wth 0.1 mol/liter of the tin compound the results were obtained by following the disappearance of the iodine. Verify that the reaction is first order with respect to the tin compound and third order with respect to iodine.

$$-\frac{dB}{dt} = kAB^3 = k(B-0.1)B^3$$

The integral is found in tables,

$$k = \frac{1}{t}\int_B^{0.2} \frac{dB}{(B-0.1)B^3}$$

$$= \frac{1000}{t}[-1.56815 - 0.5(\frac{B-0.1}{B})^2 + 2(\frac{B-0.1}{B}) + \ln\frac{B}{B-0.1}\ ]$$

Integration also is done with the trapezoidal rule, 100 intervals, and the results are obtained.

t, min	$[I_2]$	k
0	0.200	
10	0.1830	2.675
20	0.1715	2.683
40	0.1585	2.466
60	0.1480	2.565
90	0.1385	2.549
125	0.1305	2.605
180	0.1230	2.584
270	0.1150	2.672

P3.02.60. TERT-BUTYL BROMIDE

Kinetic data at 25 C for the conversion of tert-butyl bromide to tert-butyl alcohol in a solvent of 90% acetone and 10% water are tabulated. Time is in hours, concentration in gmol/liter. Find the rate equation.

A curve fit is applied to the (C,t) data,

$$C = 0.1045 - 0.004866t + 6.9982(10^{-5})t^2$$

from which the derivative is

$$\frac{dC}{dt} = -0.004866 + 13.996(10^{-5})t$$

The second plot has the equation

$$\ln r = -4.524 + 0.3487 \ln C$$

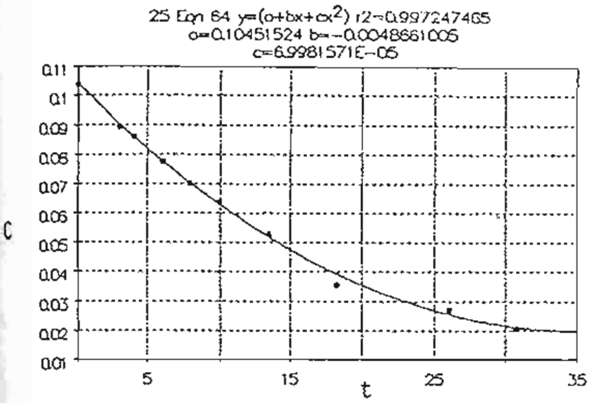
or

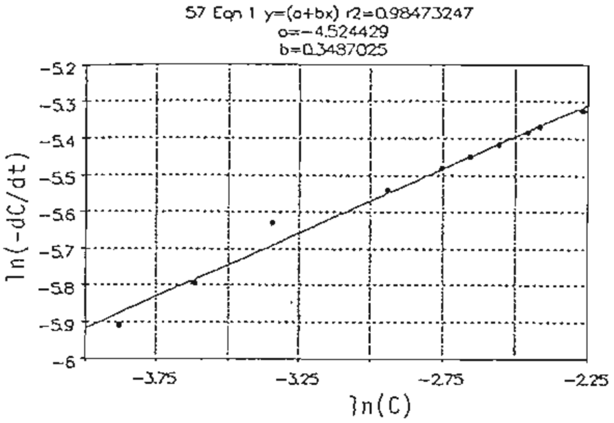
$$r = -\frac{dC}{dt} = 0.0108C^{0.3487}$$

First and second order specific rates also are figured and tabulated. The k_1 prove to be almost constant.

$$k_1 = \frac{1}{t}\ln(0.1039/C), \quad k_2 = \frac{1}{t}(1/C - 1/0.1039)$$

t	C	k_1	k_2
0	0.1039		
3.15	0.0896	0.0470	0.4876
4.1	0.0859	0.0464	0.4919
6.2	0.0776	0.0471	0.5261
8.2	0.0701	0.0480	0.5659
10.0	0.0639	0.0486	0.6025
13.5	0.0529	0.0500	0.6873
18.3	0.0353	0.0590	1.0221
26.0	0.0270	0.0518	1.0543
30.8	0.0207	0.0524	1.2560





P3.02.61. ACETONE AND HCN

The reaction

$CH_3COCH_3 + HCN \Leftrightarrow (CH_3)_2CO.CN.OH, \quad A + B \Leftrightarrow C$

was studied in aqueous solution (Svirbely & Roth, JACS 75 3109, 1953). In one run with initial concentrations of 0.0758 normal for HCN and 0.1164 normal for acetone, the tabulated data were obtained. The equilibrium constant was K_e = 13.87. Find the specific rate.

If the reaction is in accord with the stoichiometry,

$$-\frac{dA}{dt} = \frac{dC}{dt} = k(AB-C/K_e) = k[(0.1164-C)(0.0758-C)-C/13.87]$$

The integral is

$$k = \frac{1}{t}\int_0^c \frac{dC}{f(C)} = \frac{5.36}{t}\ \ln\frac{2C-0.4508}{11.59C-0.4508}$$

The values of k are tabulated. Neglecting the first point, the mean value is k = 0.00807.

t, min	C	10^3k
4.37	0.0748	26.6
73.2	0.0710	8.08
172.5	0.0655	8.11
265.4	0.0610	8.30
346.7	0.0584	7.93
434.4	0.0557	7.82

P3.0.62. SODIUM METHOXIDE.

Data have been reported for the reaction at 64 C between sodium ethoxide (A) and ethyl dimethyl sulfonium iodide (B) using ethanol as a solvent.

$$NaOC_2H_5 + C_2H_5(CH_3)_2SI \Rightarrow NaI + C_2H_5OC_2H_5 + S(CH_3)_2$$

Find a rate equation.

$$B = A+B_0-A_0 = A + 11.53-22.55 = A - 11.02$$

Second order,

$$-\frac{dA}{dt} = k_2A(A-11.02)$$

$$k_2 = \frac{1}{t}\ \ln\frac{11.53A}{22.55(A-11.02)}$$

First order,

$$k_1 = \frac{1}{t}\ \ln\frac{22.55}{A}$$

The values are tabulated. Second order seems to be more nearly correct,.with average k_2 = 0.0134.

t, min	A	B	k_1	k_2
0	22.55	11.53		
12	20.10	9.08	0.0096	0.0150
20	18.85	7.83	0.0090	0.0137
30	17.54	6.52	0.0084	0.0133
42	16.37	5.35	0.0076	0.0130
51	15.72	4.10	0.0071	0.0127
63	14.96	3.94	0.0065	0.0127
100	11.02	0		

P3.03.01. AT CONSTANT V OR CONSTANT P

(a) An isothermal ideal gas phase reaction, 2A ⇒ 2B + 3c, started with 2 lbmols of pure A at 5 atm and 600°R. . It proceeds at constant volume. At a certain time the total pressure is changing at the rate of 0.5 atm/sec. What is the rate of formation of C, lbmol/(cuft)(h)?

$$n_t = n_{a0} + 1.5(n_{a0}-n_a) = 5 - 1.5n_a$$

$$\pi = \frac{n_t}{n_{t0}}\pi_0 = \frac{(5-1.5n_a)}{2}5 = 12.5 - 3.75n_a$$

$$\frac{dn_a}{dt} = -\frac{1}{3.75}\frac{d\pi}{dt} = -\frac{0.5}{3.75} = -\frac{1}{7.5}\ \text{lbmol/sec}$$

$$V = \frac{n_{a0}RT}{\pi_0} = \frac{2(0.73)(600)}{5} = 175.2\ \text{cuft}$$

$$r_c = -1.5r_a = -1.5(\frac{1}{V})\frac{dn_a}{dt} = \frac{1.5(3600)}{175.2(7.5)} = 4.11\ \frac{\text{lbmol}}{\text{(cuft)(hr)}}$$

(b) The preceding reaction occurs at constant pressure and temperature with a specific rate k = 0.5/h. When the volume becomes 350.4 cuft, what is the value of dV/dt, cuft/h?

$$V = \frac{(5-1.5n_a)(0.73)(600)}{5} = 87.6(5-1.5n_a) = 350.4$$

$$n_a = 0.6667\ \text{lbmol}$$

$$\frac{dn_a}{dt} = -kn_a = -0.5(0.667) = -0.333\ \text{lbmol/h}$$

$$\frac{dV}{dt} = -1.5(87.6)\frac{dn_a}{dt} = 43.8\ \text{cuft/h}$$

P3.03.02. RATES OF CHANGE AT CONSTANT V OR CONSTANT P

Consider the ideal gas reaction, 2A ⇒ B + 2C, occuring at 800°R, starting with 5 lbmols of pure A at 10 atm. The rate equation is

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = 700\ C_a^2\ \text{lbmols/(h)(cuft)}$$

Evaluate the various rates of change of the table at the time that the rate of reaction is r_a = 0.1 lbmols/(h)(cuft) when the reaction proceeds at (a) constant volume; (b) constant pressure.

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = 700\ C_a^2 = 0.1$$

$$C_a = \sqrt{0.1/700} = 0.01195$$

$$V_0 = \frac{n_{a0}RT}{\pi_0} = \frac{5(0.729)(800)}{10} = 291.6$$

$$C_{a0} = \frac{n_{a0}}{V_0} = \frac{5}{291.6} = 0.01715$$

$$n_t = 0.5(3n_{a0}-n_a)$$

$$V = \frac{(3n_{a0}-n_a)RT}{2\pi_0} = 29.16(15-n_a)$$

$$\pi = \frac{n_t}{n_{t0}}\,\pi_0 = 3n_{a0}-n_a$$

At constant volume, $n_a = V_0C_a = 291.6(0.01195) = 3.4853$

$$\frac{dn_a}{dt} = V_0\frac{dC_a}{dt} = -291.6(0.1) = -29.16$$

$$N_a = \frac{n_a}{n_t} = \frac{2n_a}{3n_{a0}-n_a}$$

$$\frac{dN_a}{dt} = \frac{6}{n_{a0}(3-n_a/n_{a0})^2}\,(\frac{dn_a}{dt}) = \frac{6}{5(3-3.4853/5)^2}\,(-29.16)$$

$$= -6.598$$

$$p_a = \frac{n_aRT}{V_0}$$

$$\frac{dp_a}{dt} = \frac{RT}{V_0}(\frac{dn_a}{dt}) = \frac{0.729(800)}{291.6}(-29.16) = -58.32$$

$$\pi = \frac{n_t}{n_{t0}}\,\pi_0 = \frac{3n_{a0}-2n_a}{2n_{a0}}\,\pi_0 = 5(3-n_a/n_{a0})$$

$$\frac{d\pi}{dt} = -\frac{5}{n_{a0}}\,\frac{dn_a}{dt} = 29.16$$

At constant pressure, $n_a = VC_a = 29.16(15-n_a)(0.01195) = 3.8768$

$$\frac{dn_a}{dt} = -Vr_a = -324.4(0.1) = -32.44$$

$$C_a = \frac{n_a}{V} = \frac{n_a}{29.16(15-n_a)}$$

$$\frac{dC_a}{dt} = \frac{1}{29.16}[\frac{15}{(15-n_a)^2}]\,\frac{dn_a}{dt} = \frac{1}{29.16}[\frac{15}{(15-3.8768)^2}](-32.44)$$

$$= 0.1349$$

$$\frac{dN_a}{dt} = \frac{6n_{a0}}{(3n_{a0}-n_a)^2}\,\frac{dn_a}{dt} = \frac{30}{(15-3.8768)^2}\,(-32.44) = -7.8658$$

$$p_a = N_a\pi_o = \frac{2\pi_0n_a}{3n_{a0}-n_a}$$

$$\frac{dp_a}{dt} = \frac{6\pi_0}{(3n_{a0}-n_a)^2}\,\frac{dn_a}{dt} = \frac{(6)(10(5)}{(15-3.8768)^2}\,(-32.44) = -78.66$$

$$V = \frac{(3n_{a0}-n_a)RT}{2\pi_0}$$

$$\frac{dV}{dt} = \frac{RT}{2\pi_0}(-\frac{dn_a}{dt}) = \frac{0.729(800)}{20}(32.44) = 945.95$$

$$\frac{dx_a}{dt} = \frac{d}{dt}(\frac{n_{a0}-n_a}{n_{a0}}) = -\frac{1}{n_{a0}}\frac{dn_a}{dt} = -\frac{1}{5}(-32.44) = 6.488$$

SUMMARY

Rate	@ const V	@ const P
$dn_a dt$	-29.16	-32.44
dN_a/dt	-6.598	-7.7.866
dp_a/dt	-58.32	-78.66
$d\pi/dt$	29.16	0
dV/dt	0	946.0
dx_a/dt	5.832	6.488

P3.03.03. ZERO ORDER

A zero order gas reaction, A ⇒ rR, proceeds in a constant volume bomb with 20% inerts, and the pressure rises from 1.0 to 1.3 atm in 2 min. When the same reaction proceeds at constant pressure of 3 atm and with 40% inerts, what is the fractional change of volume in 4 minutes?

At constant volume,

$n_{t0} = 1$, $n_{a0} = 0.8$, $n_i = 0.2$, $\pi_0 = 1$, $p_{a0} = 0.8$

$n_t = n_a+n_i+r(n_{a0}-n_a) = 0.2+0.8r+(1-r)n_a$

$$-\frac{dC_a}{dt} = k = -\frac{1}{RT}\frac{dp_a}{dt}$$

$p_{a0}-p_a = kRTt$

When t = 2,

$$\frac{\pi}{\pi_0} = 1.3 = \frac{n_t}{n_{t0}} = 0.2+0.8r+(1-r)n_a$$

$$n_a = \frac{0.8r-1.1}{r-1}$$

$$\frac{p_a}{p_{a0}} = \frac{n_a}{n_{a0}} = \frac{0.8r-1.1}{0.8(r-1)} \qquad (1)$$

$$p_{a0}-p_a = kRTt = 2kRT = p_{a0}(1-\frac{p_a}{p_{a0}}) = \frac{0.3}{r-1}$$

$$kRT = \frac{0.15}{r-1} \qquad (2)$$

At constant pressure,

$\pi_0 = 3$, $n_{a0} = 0.6$

$n_t = n_a+n_i+r(n_{a0}-n_a) = 0.4+0.6r+(r-1)n_a$

$$dn_a = \frac{1}{1-r}dn_t$$

The rate equation is

$$-\frac{1}{V}\frac{dna}{dt} = -\frac{\pi}{n_tRT}\frac{dn_a}{dt} = -\frac{\pi}{RT(1-r)}\frac{dn_t}{dt} = k = \frac{0.15}{(r-1)RT}$$

Integrating,

$$\frac{0.15t}{\pi} = \int_{n_{t0}}^{n_t}\frac{dn_t}{n_t} = \ln\frac{n_t}{n_{t0}}$$

$$\frac{V}{V_0} = \frac{n_t}{n_{t0}} = \exp\frac{0.15t}{\pi} = \exp\frac{0.15(4)}{3} = 1.2214 \qquad (3)$$

P3.03.04. FIRST ORDER

The first order gaseous decomposition, A ⇒ 2.5 B, is carried out at 2 atm with 20% inerts present, and the volume increases by 60% in 20 minutes. In a constant volume reactor, find the time required for the pressure to reach 8 atm if the initial pressure is 5 atm, 2 atm of which consist of inerts.

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = k\frac{n_a}{V}$$

At constant pressure,

$$\frac{V}{V_0} = \frac{n_t}{n_{t0}} = 1.6$$

$$\pi_0 = 2,\ n_{t0} = 1,\ n_{a0} = 0.8,\ n_i = 0.2$$

$$n_t = n_a+n_i+2.5(n_{a0}-n_a) = 2.2-1.5n_a$$

$$n_a = \frac{1}{1.5}(2.2-n_t)$$

$$dn_a = -0.667\ dn_t = kn_a$$

$$\frac{dn_t}{dt} = k(2.2-n_t)$$

$$k = \frac{1}{t}\int_{n_{t0}}^{n_t}\frac{dn_t}{2.2-n_t} = \frac{1}{20}\ln\frac{2.2-1}{2.2-1.6} = 0.0347 \qquad (1)$$

At constant volume,

$$\frac{\pi}{\pi_0} = \frac{n_t}{n_{t0}} = 1.6$$

$$\pi_0 = 5,\ n_{t0} = 1,\ n_{a0} = 0.6,\ n_i = 0.4$$

$$n_t = n_a+n_i+2.5(n_{a0}-n_a) = 1.9-1.5n_a$$

$$n_a = \frac{1.9-n_t}{1.5}$$

$$dn_a = -\frac{1}{1.5}dn_t$$

$$= kn_a = k(\frac{1.9-n_t}{1.5})$$

$$t = \frac{1}{k}\ln\frac{1.9-n_{t0}}{1.9-n_t} = \frac{1}{0.0347}\ln\frac{1.9-1}{1.9-1.6} = 31.7\ \text{min}$$

P3.03.05. SECOND ORDER

The gas reaction, 2A ⇒ B + 2C, is second order with respect to A. When pure A is introduced at 1 atm into a constant volume reactor, the pressure rises 40% in 3 minutes. For a constant pressure batch reactor, find (a) the time required for the same conversion, and (b) the fractional increase in volume at that time.

$$-\frac{1}{V}\frac{dn_a}{dt} = k\left(\frac{n_a}{V}\right)^2$$

$$n_t = n_a + 1.5(n_{a0}-n_a) = 1.5n_{a0}-0.5n_a$$

At constant volume,

$$\pi_0 = 1,\ n_{a0} = 1,\ V = \frac{n_{a0}RT}{\pi_0} = RT$$

$$-\frac{dn_a}{dt} = \frac{k}{RT}n_a^2$$

When t = 3,

$$\pi/\pi_0 = n_t/n_{a0} = 1.5-0.5n_a = 1.4$$

$$n_a = 0.2$$

$$\frac{k}{RT} = \frac{1}{t}\left(\frac{1}{n_a} - \frac{1}{n_{a0}}\right) = \frac{1}{3}\left(\frac{1}{0.2} - 1\right) = 4/3 \qquad (1)$$

At constant pressure,

$$\pi = \pi_0 = 1$$

$$\frac{V}{V_0} = \frac{n_t}{n_{a0}} = 1.5-0.5n_a = 1.5-(0.5)(0.2) = 1.4 \qquad (2)$$

$$V = \frac{n_tRT}{\pi} = n_tRT$$

$$-\frac{dn_a}{dt} = \frac{k}{V}n_a^2 = \frac{k}{RT}\frac{n_a^2}{1.5-0.5n_a} = 1.333\frac{n_a^2}{1.5-0.5n_a}$$

$$t = 0.75\int_{0.2}^{1}\frac{1.5-0.5n_a}{n_a^2}dn_a = 3.90 \text{ minutes} \qquad (3)$$

P3.03.06. NON-IDEAL GAS

The reaction

$C_3H_6 + CH_4 \Rightarrow C_4H_{10}$, $A + B \Rightarrow C$

is assumed to occur at 510°K amd 175 atm, starting with 1 gmol each of the reactants and finishing with 0.5 gmol of product. The required value of kt will be found.

$$n_{a0} = n_{b0} = 1$$

$$n_a = n_{a0}-n_c = 1-n_c$$

$$n_b = n_a$$

$$n_t = 2-n_c$$

$$N_a = N_b = n_a/n_t = \frac{1-n_c}{2-n_c} \qquad (1)$$

$$N_c = \frac{n_c}{2-n_c} \qquad (2)$$

$$V_t = n_tV$$

V = molal volume, liters/mol

The rate equation is

$$r_c = \frac{1}{V_t}\frac{dn_c}{dt} = k(\frac{n_a n_b}{V_t^2})$$

$$\frac{dn_c}{dt} = \frac{k(1-n_c)^2}{n_t V} = \frac{k(1-n_c)^2}{(2-n_c)V}$$

$$kt = \int_0^{0.5} \frac{(2-n_c)V}{(1-n_c)^2}\, dn_c \qquad (3)$$

V and consequently kt will be found three ways.

(a) Ideal gas

$V = 0.082T/\pi = 0.082(510)/75 = 0.5578$

$kt = 0.5578(1.697) = 0.9464$ (4)

(b) Reduced equation of state (Walas, Phase Equilibria in Chemical Engineering, 1985).

	C_3H_6	CH_4	C_4H_{10}
T_c	365	190.6	425
P_c	45.6	45.4	37.5

With Kay's Rules, at the start,

$T_c = 0.5365+190.6) = 277.8$

$P_c = 0.5(45.6+45.4) = 45.5$

$T_r = 1.83,\ P_r = 1.65,\ z = 0.920$

At the end,

$T_c = (365+190.6+425)/3 = 326.9$

$P_c = (45.6+45.4+37.5)/3 = 42.8$

$T_r = 1.56,\ P_r = 1.75,\ z = 0.910$

Take an average, $z = 0.915$

$kt = 0.915(0.9464) = 0.8660$ (5)

(c) With van der Waals equation (Walas, 1985).

$(P+\alpha/V^2)(V-\beta) = 0.082(510) = 41.82$

The constants are (CRC Handbook of Chemistry and Physics, 60th edition, D-194),

	$C_3H_6(A)$	$CH_4(B)$	$C_4H_{10}(C)$
α	8.379	2.253	14.47
β	0.08272	0.04278	0.1226

For the mixture,

$\alpha = (\Sigma N_i\sqrt{\alpha_i})^2$

$\beta = \Sigma N_i \beta_i$

The mol fractions are given by Eqs (1) and (2). Find V for each value of n_c by solving the vdW equation numerically. Substitute into Eq (3) and integrate numerically. The values are tabulated. In this case,

$kt = 0.8531$ (6)

n_c	α	β	V	$\frac{(2-n_c)V}{(1-n_c)^2}$
0	4.830	0.0628	0.5095	1.0190
0.05	5.013	0.0656	0.5087	1.0992
0.1	5.209	0.0685	0.5078	1.1911
0.15	5.420	0.0717	0.5068	1.2977
0.2	5.647	0.0749	0.5058	1.4225
0.25	5.892	0.0784	0.5046	1.5698
0.3	6.157	0.0821	0.50321	1.7459
0.35	6.444	0.0861	0.5018	1.9595
0.4	6.757	0.0902	0.5002	2.2231
0.45	7.098	0.0946	0.4985	2.5540
0.5	7.470	0.0994	0.4965	2.9792

P3.03.07. DIFFERENTIATION OF TOTAL PRESSURE DATA

A gas reaction, A ⇒ 2B, is conducted at constant volume and 100°C, starting at 1.30 atm with 76.94% A and the balance inert.. The data are of time in minutes and total pressure in atm. Find the rate equation.

Try the rate equation,

$$-\frac{dC_a}{dt} = kC_a^q$$

$$n_{t0} = 1,\ n_{a0} = 0.7694$$

$$n_t = n_{t0}+n_{a0}-n_a = 1.7694 - n_a$$

$$\pi = \frac{n_t}{n_{t0}}\pi_o = (1.7694-n_a)(1.3) = 2.30 - 1.3n_a$$

$$n_a = \frac{2.3-\pi}{1.3}$$

$$C_a = \frac{n_a}{V} = \frac{n_a}{n_{t0}}\frac{\pi_0}{RT} = \frac{2.3-\pi}{RT}$$

The rate equation becomes

$$\frac{d\pi}{dt} = k\left(\frac{1}{RT}\right)^{q-1}(2.3-\pi)^q$$

or

$$\ln\ (d\pi/dt) = k' + q\ \ln(2.3-\pi) \qquad (1)$$

The $(\pi,\ t)$ data are fitted by the equation,

$$\pi = 1.305+0.433t-0.106t^2+0.0131t^3-0.00061t^4 \qquad (2)$$

from which the derivative is

$$\frac{d\pi}{dt} = 0.433-0.212t+0.0393t^2-0.00244t^3 \qquad (3)$$

The plot of Eq (1) has the equation

$$\ln\ (d\pi/dt) = -0.837 + 1.36\ \ln(2.3-\pi)$$

or

$$\frac{d\pi}{dt} = 0.433(2.3-\pi)^{1.36} \qquad (4)$$

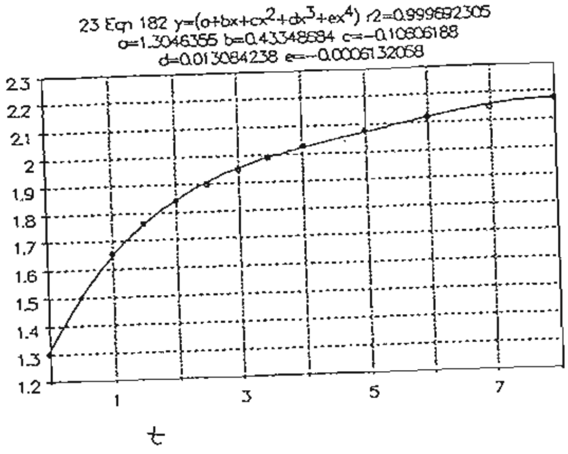
or

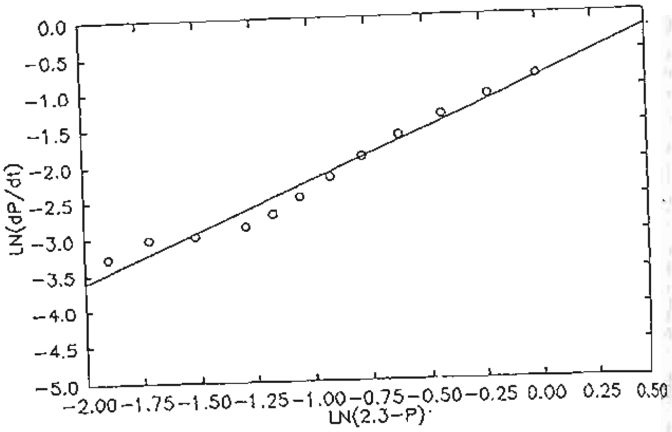
$$-\frac{dC_a}{dt} = 0.433(RT)^{-0.36}C_a^{1.36}$$

$$= 0.433[0.082(373.2)]^{-0.36}C_a^{1.36}$$

$$= 0.1264\ C_a^{1.36}\ \text{mols/(liter)(min)} \qquad (5)$$

t	π		t	π
0.5	1.5		3.5	1.99
1	1.65		4	2.025
1.5	1.76		5	2.08
2	1.84		6	2.12
2.5	1.90		7	2.15
3	1.95		8	2.175





P3.03.08. INITIAL RATE DATA

Two series of initial rate data for the reaction between A and B were taken, one with constant p_{a0} and the other with constant p_{b0}. The pressures are in Torr and r_0 is in Torr/sec.
Find the constants of the rate equation

$$r_0 = k_p p_{a0}^a p_{b0}^b \qquad (1)$$

or

$$\ln r_0 = a \ln(p_{a0}) + \ln(10^b k_p) \qquad (2)$$

$$\ln r_0 = b \ln(p_{b0}) + \ln(10^a k_p) \qquad (3)$$

The plots show that the exponents are a = 0.5 and b = 1.5.

$$k_p = r_0/p_{a0}^{0.5} p_{b0}^{1.5} = 0.01\ \text{Torr}^{-1}\text{sec}^{-1} \qquad (4)$$

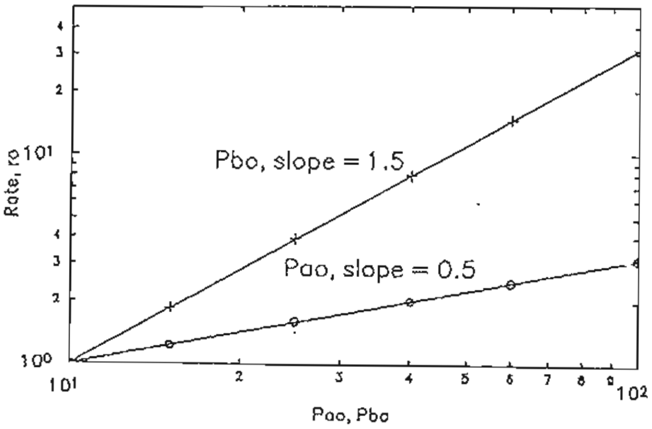
Introducing concentration units,

$p = CRT$

$$RT\frac{dCa}{dt} = k_p(RT)^2 C_a^{0.5} C_b^{1.5}$$

$$k_c = k_p RT = 0.01(62.36)T = 0.6236T\ \text{liter/(gmol)(sec)} \qquad (5)$$

p_{ao}	p_{bo}	r_o
10	10	1.00
15	10	1.22
25	10	1.59
40	10	2.00
60	10	2.45
100	10	3.16
10	10	1.00
10	15	1.84
10	25	3.95
10	40	8.00
10	60	14.7
10	100	31.6



P3.03.09. TOTAL PRESSURE - TIME DATA

The composition of the gas phase reaction, 2A ⇒ B, was monitored by measuring the total presure as a function of time. Find the order of the reaction. At what time will the reaction be 99.99% complete?

$$n_t = n_a + 0.5(n_{a0} - n_a) = 0.5(n_{a0} + n_a)$$

$$\pi = 0.5(n_{a0} + n_a)\ \frac{RT}{V}$$

$$n_a = \frac{2V}{RT}\pi - n_{a0} = (2\pi - \pi_0)\ \frac{V}{RT}$$

Try a second order rate equation.

$$-\frac{1}{V}\frac{dn_a}{dt} = 2k\left(\frac{n_a}{V}\right)^2$$

$$-2\frac{d\pi}{dt} = \frac{2k}{RT}\ (2\pi - \pi_0)^2$$

$$\frac{k}{RT} = \frac{1}{2t}\left(\frac{1}{2\pi - \pi_0} - \frac{1}{\pi_0}\right) \qquad (1)$$

The values are tabulated and have an average value,

$$k/RT = 8.018(10^{-6}) \quad (\text{Torr})^{-1}(\text{sec})^{-1} \qquad (2)$$

When $n_a/n_{a0} = 0.0001$,

$$\pi = \frac{n_{a0} + n_a}{2n_{a0}}\ \pi_0 = \frac{1.0001}{2}\ (400) = 200.02$$

$$t = \frac{1}{2k/RT}\left(\frac{1}{2\pi - \pi_0} - \frac{1}{\pi_0}\right) = 1.56(10^6) \text{ sec} \qquad (3)$$

t, s	π, Torr	$10^6 k/RT$
0	400	
100	322	7.992
200	288	7.955
300	268	8.088
400	256	8.036

P3.03.10. ETHYLAMINE

Gaseous ethylamine decomposes according to the reaction,

$C_2H_5NH_2 \Rightarrow C_2H_4 + NH_3$

At 500°C and an initial pressure of 55 Torr, data were obtained for the pressure increase, Torr, as a function of time in minutes. Find the order of the reaction.

$$n_{a0} = \frac{\pi_0 V}{RT}$$

$$\pi = \pi_0+\Delta\pi = (2n_{a0}-n_a)\frac{RT}{V} = 2\pi_0 - \frac{n_a RT}{V}$$

$$n_a = (2\pi_0-\pi_0-\Delta\pi)\frac{V}{RT} = (\pi_0-\Delta\pi)\frac{V}{RT}$$

$$dn_a = -\frac{V}{RT}d(\Delta\pi)$$

The rate equation is

$$-\frac{1}{V}\frac{dn_a}{dt} = k\left(\frac{n_a}{V}\right)^q$$

$$\frac{1}{RT}\frac{d(\Delta\pi)}{dt} = k\left(\frac{1}{RT}\right)^q(\pi_0-\Delta\pi)^q$$

$$k(RT)^{1-q} = \frac{1}{t}\int_0^{\Delta\pi}\frac{d(\Delta\pi)}{(\pi_0-\Delta\pi)^q} \qquad (1)$$

Integration is done numerically. The tabulation shows values for q = 0.5, 1.0 and 2.0. First order is the best fit.

		$k(RT)^{1-q}$		
t	$\Delta\pi$	q=0.5	q=1	q=2, x1000
0	0			
1	5	0.690	0.0953	0.00181
2	9	0.634	0.0893	0.00178
4	17	0.626	0.0924	0.00203
8	29	0.579	0.0937	0.00254
10	34	0.567	0.0963	0.00294
20	47	0.459	0.0964	0.00534
30	52	0.379	0.0970	0.0105
40	53.5	0.310	0.0901	0.0163

P3.03.11. ACETALDEHYDE DECOMPOSITION. RATE DATA

Acetaldehyde decomposes according to $CH_3CHO \Rightarrow CH_4 + CO$. Rates of deocmposition, Torr/min, corresponding to various % decompositions are tabulated. The process started with pure acetaldehyde and took place at constant volume. Determine the order of the reaction.

$$-\frac{1}{V}\frac{dn}{dt} = k\left(\frac{n}{V}\right)^q$$

p = partial pressure of acetaldehyde

$$= p_0\left(\frac{n}{n_0}\right)$$

$$x = 1 - n/n_0 = 1 - p/p_0$$

$$n = \frac{n_0}{p_0} p$$

In pressure units the rate equation becomes

$$-\frac{n_0}{p_0 V}\frac{dp}{dt} = \frac{k}{V^{q-1}}(\frac{n_0 p}{p_0})^q = \frac{k}{V^{q-1}} n_0^q (1-x)^q$$

$$-\frac{dp}{dt} = kp_0(\frac{n_0}{V})^{q-1}(1-x)^q \qquad (1)$$

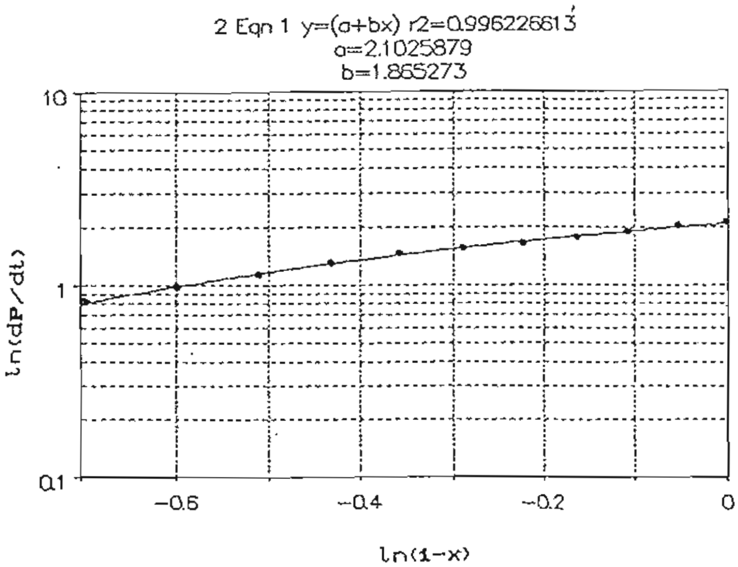
This equation plotted in linearized form is

$$\ln (dp/dt) = 2.103 + 1.865 \ln (1-x) \qquad (2)$$

The slope is the order of the reaction, order = 1.865.

DATA

0	5	10	15	20	25	30	35	40	45	50
8.53	7.49	6.74	5.90	5.14	4.69	4.31	3.75	3.11	2.67	2.29



P3.03.12. ACETALDEHYDE DECOMPOSITION. TOTAL PRESSURE DATA.

The decomposition of acetaldehyde was studied at 518°C with an initial pressure π_0 = 363 Torr (Hinshelwood & Hutchinson, Proc Roy Soc 111A 380, 1926). The data are of time in sec and change in total pressure, $\Delta\pi$ Torr. Verify that the reaction is second order.

$$-\frac{dn_a}{dt} = \frac{kn_a^2}{V} \qquad (1)$$

The relation between pressure and number of mols is

$$\frac{\pi}{\pi_0} = \frac{n_t}{n_{a0}} = \frac{2n_{a0}-n_a}{n_{a0}} = 2 - \frac{n_a}{n_{a0}}$$

$$dn_a = -n_{a0}d(\pi/\pi_0)$$

The rate equation becomes

$$\frac{d(\pi/\pi_0)}{dt} = k(\frac{\pi}{RT})[\frac{(2-\pi/\pi_0)^2}{\pi/\pi_0} = \frac{k\pi_0}{RT}(2-\frac{\pi}{\pi_0})^2$$

The integral is

$$\frac{k}{RT} = \frac{1}{\pi_0 t}\left(\frac{\pi-\pi_0}{2\pi_0-\pi}\right) = \frac{1}{\pi_0 t}\,\frac{\Delta\pi}{\pi_0+\Delta\pi} \qquad (2)$$

The values from Eq (2) are tabulated and confirm a second order mechanism with a mean value of $k/RT = 6.69(10^{-6})$ $\text{Torr}^{-1}\text{sec}^{-1}$

t	$\Delta\pi$	$10^6 k/RT$
42	34	6.79
73	54	6.59
105	74	6.71
190	114	6.64
242	134	6.66
310	154	6.55
384	174	6.61
480	194	6.50
665	224	6.68
840	244	6.72
1070	264	6.86
1440	284	6.88

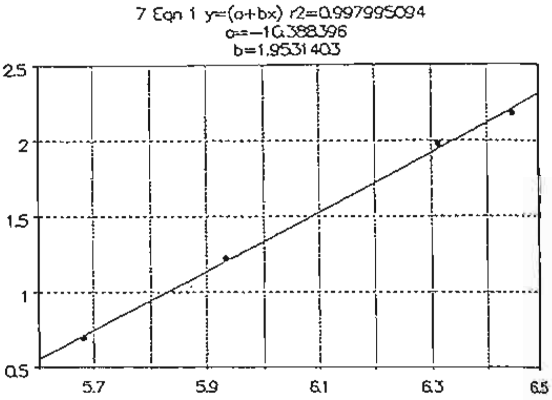
P3.03.13. DIMERIZATION OF BUTADIENE.

Rate data of the dimerization of butadiene at 333°K are tabulated, in minutes and Torrs. Find the constants of the rate equation, $-dC/dt = kC^q$. The gas constant is R = 62.31 liter Torr/(mol)(°K).

$$C_a = p_a/RT$$

$$-\,dC_a = -\frac{1}{RT}\,dp_a = k\left(\frac{p_a}{RT}\right)^q$$

$$-\frac{dp_a}{dt} = \frac{k}{(RT)^{q-1}}\,p_a^q$$



In linearized form, from the plot,

$$\ln\left(-\frac{dp_a}{dt}\right) = \ln\,[k/(RT)^{q-1}] + q\,\ln p_a$$

$$= -10.388 + 1.953\,\ln p_a$$

or

$$-\frac{dp_a}{dt} = 3.08(10^{-5})\;p^{1.953}$$

$$k = 3.08(10^{-5})[62.31(333)]^{0.953} = 0.4005\ \text{liter/(mol)(min)}$$

t	p	-dp/dt
0	632	8.8
10	552	7.2
45	378	3.4
80	294	2.0

P3.03.14. DIMERIZATION OF BUTADIENE

The tabulated data were obtained for the dimerization of butadiene, starting with pure butadiene, in minutes and Torrs. Find the specific rate k_p and the order of the reaction.

$$p_a = \frac{n_a}{n_t}\pi = \frac{2\pi n_a}{n_{a0}+n_a} = \frac{2\pi}{1+n_{a0}/n_a} = \frac{2\pi}{1+\pi_0/p_a} = 2\pi-\pi_0$$

Assume the rate equation,

$$-\frac{dp_a}{dt} = k_p p_a^q \qquad (1)$$

$$-\frac{d\pi}{dt} = (k_p/2)(2\pi-\pi_0) \qquad (2)$$

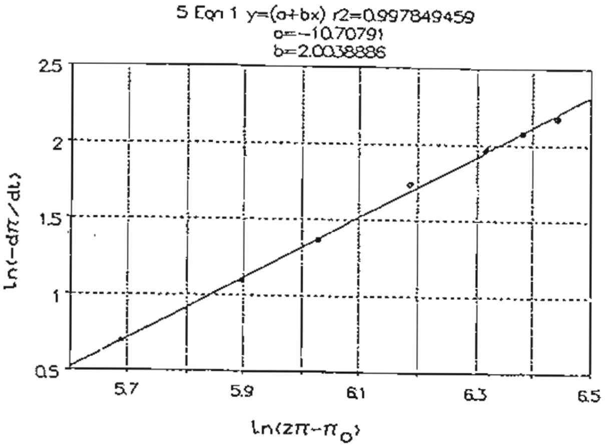
The plot of the linearized form has the equation

$$\ln(-d\pi/dt) = \ln(k_p/2) + q\ln(2\pi-\pi_0)$$
$$= -10.708 + 2.004\ln(p_a)$$

or

$$-\frac{dp_a}{dt} = 4.16(10^{-5})\ p_a^{2.004}$$

t	π	$-d\pi/dt$	$2\pi-\pi_0$
0	630	8.8	630
5	611	8.0	592
10	592	7.2	554
20	559	5.7	488
35	523	3.9	416
50	497	3.0	364
80	463	2.0	296



P3.03.15. METHOXYMETHANE DECOMPOSITION.

The thermal decomposition of gaseous methoxymethane follows the equation

$$(CH_3)_2O \Rightarrow CH_4 + H_2 + CO$$

Data were obtained at two temperatures and two starting pressures. In the table, π_0 = initial pressure of ether in Torr, $\Delta\pi$ is the increase in pressure after t sec. The reaction is believed to be first order. Find the specific rate as a function of temperature.

$$n_t = n_a+3(n_{a0}-n_a) = 3n_{a0}-2n_a$$

$$\frac{\pi}{\pi_0} = \frac{n_t}{n_{a0}} = 3 - \frac{2n_a}{n_{a0}}$$

$$\frac{n_a}{n_{a0}} = 0.5(2 - \frac{\Delta\pi}{\pi_0})$$

$$d(n_a/n_{a0}) = -0.5\ d(\Delta\pi/\pi_0)$$

For first order reaction,

$$-\frac{d(n_a/n_{a0})}{dt} = 0.5\frac{d(\Delta\pi/\pi_0)}{dt} = k(\frac{n_a}{n_{a0}}) = 0.5k(2 - \frac{\Delta\pi}{\pi_0})$$

Integrating,

$$k = \frac{1}{t}\ln\frac{2}{2-\Delta\pi/\pi_0}$$

The values are tabulated for the two cases. The two averages are

$$k = 4.51(10^{-4})/\text{sec at } 504°\text{C with } \pi_0 = 312 \text{ Torr}$$

$$45.92(10^{-4})/\text{sec at } 552°\text{C with } \pi_0 = 420 \text{ Torr}$$

Apply the Arrhenius equation,

$$4.51(10^{-4}) = \exp(A-B/777.2)$$

$$45.92(10^{-4}) = \exp(A-B/825.2)$$

Solving for the constants,

$$k = \exp[32.19-31006/(T+273.2)]$$

$T=504,\ \pi_0=312$

t	$\Delta\pi$	10^4k
320	96	5.22
771	176	4.30
1195	250	4.28
2030	368	4.39
3155	467	4.37
∞	619	

$T=552,\ \pi_0=420$

t	$\Delta\pi$	10^4k
114	323	42.57
219	534	46.11
299	634	47.01
543	778	48.00
∞	838	

P3.03.16. PARALDEHYDE DECOMPOSITION.

The decomposition of gaseous paraldehyde into gaseous acetaldehyde , which may be represented by the equation, A ⇒ 3B, has been followed at 260°C by observing the change in total pressure with time. t in hrs, π in Torr. Find the order of the reaction.

$$n_t = 3n_{a0}-2n_a$$

$$\frac{\pi}{\pi_0} = \frac{n_t}{n_{a0}} = 3 - 2\frac{n_a}{n_{a0}}$$

$$-dn_a = 0.5\left(\frac{n_{a0}}{\pi_0}\right)d\pi$$

Take the rate equation to be

$$-\frac{1}{V}\frac{dn_a}{dt} = k\left(\frac{n_a}{V}\right)^q$$

or

$$\frac{n_{a0}}{2V}\frac{d(\pi/\pi_0)}{dt} = k\left(\frac{n_{a0}}{V}\right)^q\left(\frac{3-\pi/\pi_0}{2}\right)^q$$

When first order,

$$\frac{d(\pi/\pi_0)}{dt} = k(3-\pi/\pi_0)$$

Integrating,

$$k = \frac{1}{t}\int_1^{\pi/\pi_0}\frac{d(\pi/\pi_0)}{3-\pi/\pi_0} = \frac{1}{t}\ln\frac{2}{3-\pi/\pi_0}$$

The values are tabulated and are fairly constant, thus confirming first order.

t	π	k
0	100	
1	173	0.454
2	218	0.446
3	248	0.449
4	266	0.443
∞	300	

P3.03.17. CYCLOPROPANE ISOMERIZATION

Cyclopropane isomerizes into propene when heated to 500°C in the gas phase. The amount converted at various times with various initial pressures has been followed by gas chromatography. In the table, t is in sec and pressures are in Torr. Find the rate equation.

The first order equation,

$$-\frac{dp}{dt} = kp$$

integrates to

$$k = \frac{1}{t}\ln\frac{p_0}{p}$$

The six values are tabulated and confirm the first order mechanism.

p_0	t	p	10^4k
200	100	186	7.26
200	200	173	7.25
400	100	373	6.99
400	200	347	7.11
600	100	559	7.08
600	200	520	7.16

P3.03.18. ETHYLENE OXIDE.

The tabulated data have been obtained for the vapor phase decomposition of ethylene oxide (A) into methane and carbon monoxide at 414.5°C (Heppert & Mack, JACS 51 2706, 1929). Show that the rate equation is first order.

$$n_t = 2n_{a0}-n_a$$

$$\pi = (2n_{a0}-n_a)(\frac{RT}{V})$$

$$n_a = 2n_{a0} - \frac{\pi V}{RT} = (2\pi_0-\pi)(\frac{V}{RT})$$

The rate equation,

$$-\frac{dn_a}{dt} = kn_a$$

becomes

$$\frac{d\pi}{dt} = k(2\pi_0-\pi)$$

and the integral is

$$k = \frac{1}{t}\ln\frac{\pi_0}{2\pi_0-\pi}$$

These values are tabulated and are roughly constant, thus confirming the first order mechanism.

t, min	π, Torr	10^2k
0	116.53	
5	122.56	1.06
7	125.72	1.17
9	128.74	1.23
12	133.23	1.29
18	141.37	1.33

P3.03.19. AZOMETHANE DECOMPOSITION.

The partial pressure of azomethane (A) was followed as a function of time at 600°K. The results are tabulated. Confirm that the decomposition, $CH_3N_2CH_3 \Rightarrow CH_3CH_3 + N_2$, is first order.

$$p_a = n_aRT/V$$

If first order,

$$-\frac{dn_a}{dt} = kn_a$$

or

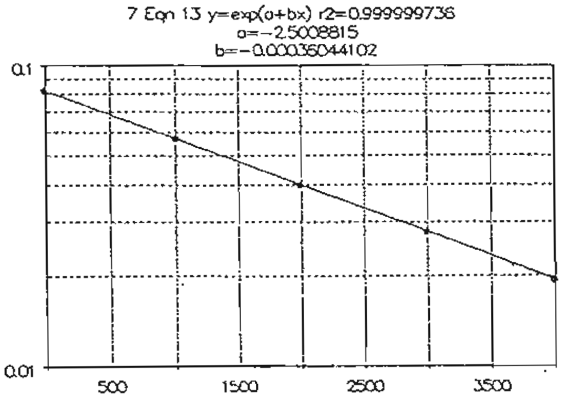
$$-\frac{dp_a}{dt} = kp_a$$

The integral is rearranged and plotted as

$$\ln p_a = \ln p_{a0} - kt$$

$$= -2.5009 - 0.00036t,$$ from the plot. Therefore,

$$k = 0.000360 \text{ /sec}$$



Data:

t, sec	0	1000	2000	3000	4000
$100p_a$, Torr	8.2	5.72	3.99	2.78	1.94

P3.03.20. DIMETHYLETHER

At 504°C dimethylether (A) undergoes the decomposition, $(CH_3)_2O \Rightarrow CH_4+H_2+CO$. The total pressure as a function of time is tabulated (Hinshelwood & Askey, Proc Roy Soc A115 215, 1927).

Find the specific rate.

$$n_t = 3n_{a0}-2n_a$$

$$\pi/\pi_0 = n_t/n_{a0} = 3 - 2n_a/n_{a0}$$

$$n_a/n_{a0} = 0.5(3-\pi/\pi_0)$$

The first order rate equation is

$$-\frac{d(n_a/n_{a0})}{dt} = k(n_a/n_{a0})$$

$$0.5\frac{d(\pi/\pi_0)}{dt} = 0.5k(3-\pi/\pi_0)$$

The integral is

$$k = \frac{1}{t}\ln\frac{2}{3-\pi/\pi_0},\quad \pi_0 = 312$$

The four values are tabulated and are nearly constant, confirming first order mechanism.

t	π	10^4k
0	312	
390	408	4.283
777	562	4.265
1195	779	4.284
3155	931	4.374
∞		

P3.03.21. PHOSGENE

For the gas phase synthesis of phosgene, $CO + Cl_2 \Rightarrow COCl_2$, $A + B \Rightarrow C$, the tabulated data were obtained at 25°C with starting pressure of 4.0 torr for CO. and two different pressures for Cl_2. t is in minutes and the partial pressures are in torr. Find the rate equation. Check the rate equation.

Try the equation

$$\frac{1}{V}\frac{dn_c}{dt} = k\left(\frac{n_a}{V}\right)^a\left(\frac{n_b}{V}\right)^b = k\left(\frac{n_{a0}-n_c}{V}\right)^a\left(\frac{n_{b0}-n_c}{V}\right)^b$$

or

$$\frac{1}{RT}\frac{dp_c}{dt} = \frac{k}{(RT)^{a+b}}(p_{a0}-p_c)^a(p_{b0}-p_c)^b$$

The value of the coefficient is

$$\frac{k}{(RT)^{a+b-1}} = \frac{1}{t}\int_0^{p_c}\frac{dp_c}{(4-p_c)^a(400-p_c)^b}\text{, for points 1, 2 and 3}$$

$$\frac{1}{t}\int_0^{p_c}\frac{dp_c}{(4-p_c)^a(1600-p_c)^b}\text{, for points 5 and 6.}$$

The integrals are evaluated numerically for various combinations of the exponents a and b.

DATA

#	t	p_{a0}	p_{b0}	p_c
1	34.5	4	400	2.0
2	69.0	4	400	3.0
3	138	4	400	3.75
4	∞	4	400	4.0
5	34.5	4	1600	3.0
6	69.0	4	1600	3.75
7	∞	4	1600	4.0

$k/(RT)^{a+b-1}$

#	a=1,b=1	a=0.5,b=1	a=1,b=0.5
1	5.04E-5	8.50E-5	1.006E-3
2	5.04	7.28	1.007
3	5.06	5.47	1.009
5	2.51	3.63	1.005
6	2.52	2.72	1.006

Clearly the correct rate equation is

$$-\frac{dp_{COCl_2}}{dt} = 1.007(10^{-3})p_{CO}p_{Cl_2}^{0.5}$$

P3.03.22. NITRIC OXIDE, MULTILINEAR REGRESSION

For the gas phase reaction

$2\ NO + 2H_2 \Rightarrow N_2 + 2\ H_2O$, $2\ A + 2\ B \Rightarrow$ Products

initial rates were measured at 826°C at several combinations of initial pressures. Find the order with respect to A and B.

Try the initial rate equation

$$r_0 = kp_{a0}^a p_{b0}^b$$

in the linearized form

$$\ln r_0 = \ln k + a \ln p_{a0} \quad b \ln p_{b0}$$

POLYMATH multilinear regression program gives

$$\ln r_0 = -17.461 + 2.1461 \ln p_{a0} + 0.8811 \ln p_{b0}$$

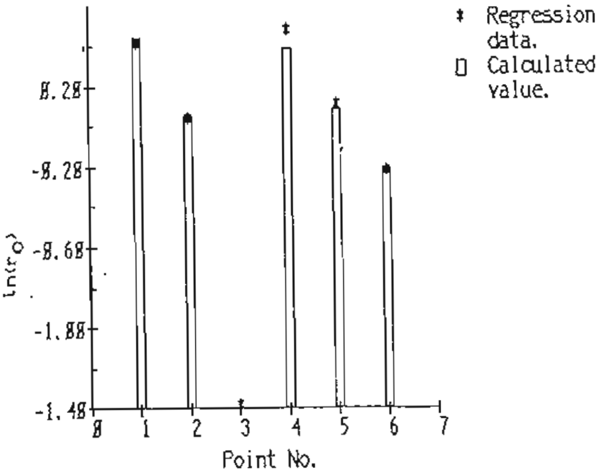
or

$$r_0 = 2.6(10^{-8})p_{a0}^{2.1461}p_{b0}^{0.8811}$$

The graph indicates good correlation of the data except of point 4.

The exponent on p_{NO} also could be found from the first three data points, and the exponent on p_{H_2} from the last three points, without need of the multilinear regression program.

$P_{(NO)0}$	$P_{(H_2)0}$	r_0
359	400	1.50
300	400	1.03
152	400	0.25
400	289	1.60
400	205	1.10
400	147	0.79



P3.03.23. EFFECT OF PRESSURE ON UNIMOLECULAR REACTIONS. CYCLOPROPANE ISOMERIZATION.

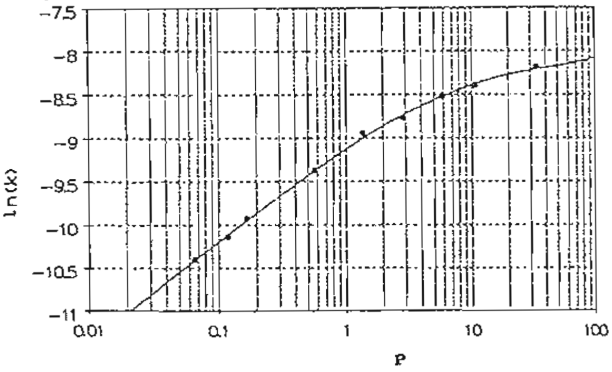
The theory of unimolecular reactions is that the specific rate , k, depends on the pressure as

$$\left(\frac{d \ln k}{dP}\right)_T = -\frac{\Delta V^*}{RT}$$

where ΔV* is the volume change on going to an activated state. The tabulated data obtained for the isomerization of cyclopropane at 491°C (Pritchard et al, Proc Roy Soc A217 563, 1953) are checked in accordance with this theory.

The plots show that the relation between ln k and P is not simple. In the range of the six lowest pressures, there is a fair linear relation, and another perhaps in the range of the three highest pressures; but the two values of slope are much different.

P	10^4k, 1/s	P	10^4k, 1/s
84.1	2.98	1.37	1.30
34.0	2.82	0.569	0.857
11.	2.23	0.170	0.486
6.07	2.00	0.120	0.392
2.89	1.54	0.067	0.303

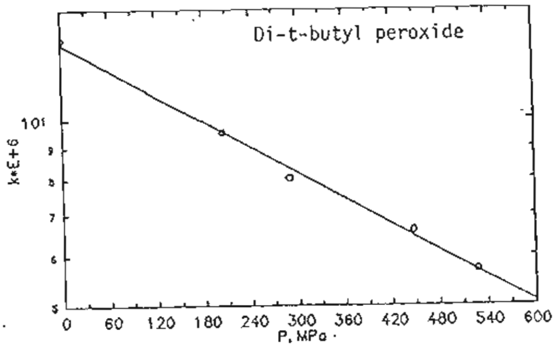


P3.03.24. EFFECT OF PRESSURE ON REACTIONS IN SOLUTION

(a) The pressure dependence of the specific rate of the thermal decomposition of Di-t-butyl peroxide in toluene at 120°C was measured with the results of table (Walling & Metzger, JACS 81 5365, 1959). From the plot it appears that the activation volume ΔV^* is constant. The equation of the plot is

$$\ln(10^6k) = \ln(k_0) - \frac{\Delta V^*}{RT} P = 13.4 - 0.0146P$$

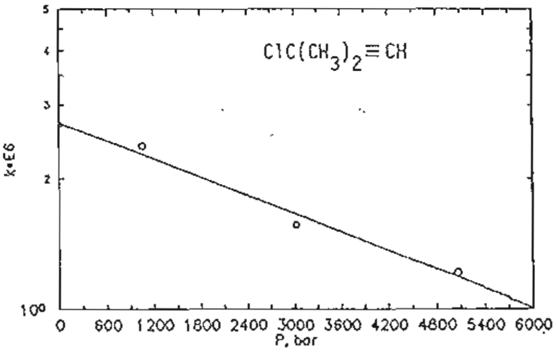
P, MPa	10^6k, 1/s
0.1	13.4
204	9.5
290	8.0
448	6.6
527	5.7



(b). For the base hydrolysis of $ClC(CH_3)_2 \equiv CH$ pressure data (Le Noble et al, JACS 92 5681, 1970) are tabulated and plotted. The plot is fairly linear, with equation

$$\ln (10^6k) = 2.68 - 0.00028P$$

P, bar	10^6k, $mol^{-1}sec^{-1}$
1	2.68
1055	2.38
3023	1.55
5062	1.20



P3.03.25. EFFECT OF P ON k OF BROMPHENOL BLUE FADING

The fading of bromphenol blue in the liquid phase is a second order reaction. The specific rate in liters/(mol)(sec) has been measured at 25 C as a function of pressure (Chem & Laidler, Can J Chem 37 599, 1959):

P, atm	1	272	544	816	1088
10^4k	9.3	11.13	13.1	15.3	17.9

The variation of k with P is represented by the van't Hoff equation,

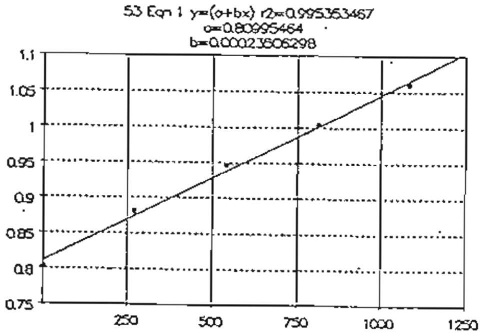
$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^*}{RT}$$

The plot of the data shows

$$\ln k = 0.81 + 0.000235 P$$

from which

$$\frac{\partial \ln k}{\partial P} = 0.000235/atm$$



and ,

$$\Delta V^* = 0.000235(0.082)(298.2)$$
$$= 1.927(10^{-5}) \text{ liter/gmol}$$

P03.04.01. DILATOMETRY. DIACETONE ALCOHOL CLEAVAGE.

The cleavage of diacetone alcohol by alkali catalyst to form acetone was followed by a dilatometer (Akerlof, JACS 49 2955, 1927). Diacetone alcohol was 5% by volume, KOH in water was 2N and the temperature was 25°C. Find the rate equation.

DEA ⇒ 2(Acetone), A ⇒ 2 B

R = cathetometer reading

x = fractional conversion of DEA

$$= \frac{R-8}{43.3-8} \qquad (1)$$

$$C_a = 0.05(1-x)$$

$$-\frac{dC_a}{dt} = k' C_{KOH} C_a^q = k[0.05(1-x)]^q$$

Try first order.

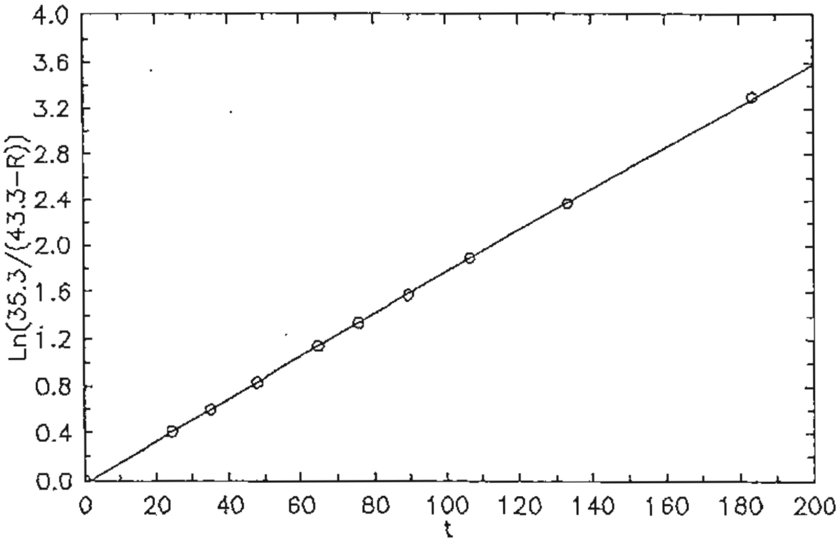
$$\frac{dx}{dt} = k(1-x)$$

$$\frac{dR}{dt} = k(43.3-R)$$

$$kt = \int_0^R \frac{dR}{43.3-R} = \ln \frac{35.3}{43.3-R} \qquad (2)$$

The linear plot confirms first order, with slope k = 3.6/sec.

t	R
0	8.0
24.4	20.0
35.0	24.0
48.0	28.0
64.8	32.0
75.8	34.0
89.4	36.0
106.6	38.0
133.4	40.0
183.6	42.0
∞	43.3



P3.04.02. DILATOMETRY. POLYSTYRENE

Polymerization of styrene was follwed by measuring the change in volume with time. The height, h, of the meniscus in a capillary 0.2 cm dia was noted.

The density of styrene is 0.906, that of polystyrene is 1.061 g/cc. Initial charge was 20 cc of styrene and initial level was 25 cm.

x = wt fraction of polystyrene

m = mass of styrene = 20(0.906) = 18.12 g

$\rho = 0.906(1-x) + 1.061x = 0.906 + 0.155x$, g/cc

$$\Delta V = (0.2)^2(\pi/4)(h-25) = 0.03142(h-25), \text{ cc} \qquad (1)$$

$$\Delta V = 20 - 18.12/(0.9060.155x) \qquad (2)$$

The last two equations relate the fractional conversion and the meniscus height. For first or second order mechanisms,

$$\frac{dx}{dt} = k_q(1-x)^q$$

$$k_1 = \frac{1}{t} \ln \frac{1}{1-x} \qquad (3)$$

$$k_2 = \frac{1}{t} \left(\frac{1}{1-x} - 1\right) \qquad (4)$$

x is found for each measurement of h and tabulated. The tabulated values of k_1 are more nearly constant and confirm the first order mechanism.

t	h	x	10^3k_1	10^3k_2
5	25	0		
6	24.5	0.0046		7.70
8	24	0.0092	3.1	11.6
10	23.25	0.0161	3.2	16.4
20	19.5	0.0509	3.5	26.8
32	15.25	0.0909	3.5	31.3
45	10.5	0.1362	3.7	33.6
57	6.0	0.1798	3.8	38.5

P3.04.03. DILATOMETRY. THREE PARTICIPANTS.

A reaction, $A + B \Leftrightarrow 2\,C$, is monitored by measuring the change in volume with time. The specific volumes are $V_a = 50$, $V_b = 80$ and $V_c = 75$ cc/mol. The reaction starts with 1 mol each of A and B. The equilibrium constant is $K_e = 48$. Given the tabulated data, find the rate equation.

x = fractional conversion

$\Delta V = 50(1-x)+80(1-x)+150x-130 = 20x$

Try the stoichiometric rate equation.

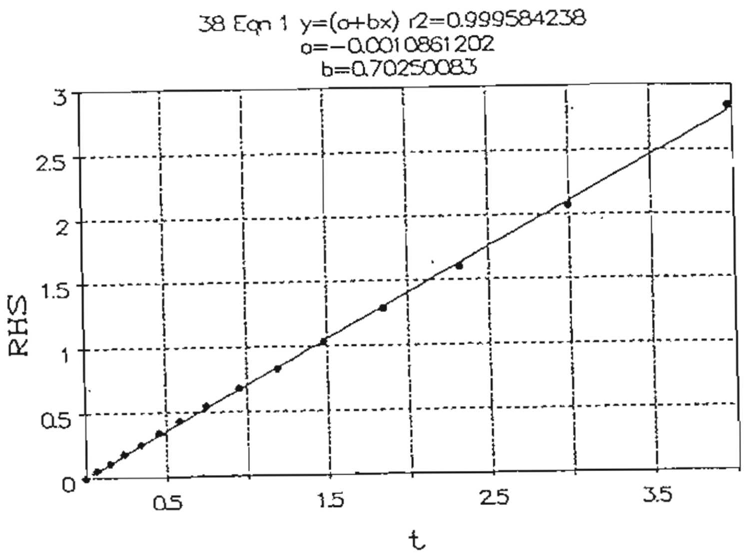
$$\frac{dx}{dt} = k[(1-x)^2-4x^2/K_e] = k\left(\frac{11}{12}x^2 -2x +1\right) \qquad (1)$$

The integral from 0 to x is

$$kt = 1.732 \ln \frac{(1.833x-2.5774)(1.4226)}{(1.833x-1.4226)(2.5744)} \qquad (2)$$

Substitute $x = 0.05\,\Delta V$. The plot of t against the right hand side is a straight line with slope $k = 0.7025$, confirming the assumed rate equation.

t	ΔV
0	0
0.08	1
0.16	2
0.25	3
0.35	4
0.47	5
0.60	6
0.76	7
0.96	8
1.19	9
1.48	10
1.84	11
2.33	12
3.00	13
3.98	14



P3.04.04. DILATOMETRY. ACETAL REACTION WITH WATER

The rate of the reaction

$$CH_3CH(OC_2H_5)_2 + H_2O \overset{H^+}{\Rightarrow} CH_3CHO + 2\ C_2H_5OH$$

is directly proportional to the acetal concentration in the presence of an excess of water and a constant amount of acid catalyst. The products of the reaction occupy a larger volume than the reactants. For a first order reaction,

$$kt = \ln \frac{1}{1-x} = \ln \frac{V_\infty - V_0}{V_\infty - V_t} \qquad (1)$$

where V_∞, V_0 and V_t refer to the volumes at the end, at the beginning and at time t of the reaction. The data of the table have been obtained at two temperatures (Leimu & Vuorinen, Ann Acad Sci Fennicae, Ser A, II, Chem, No 19, pp 1-12, 1946). The times are in minutes and the scale readings in mm. From the slopes of the linear plots,

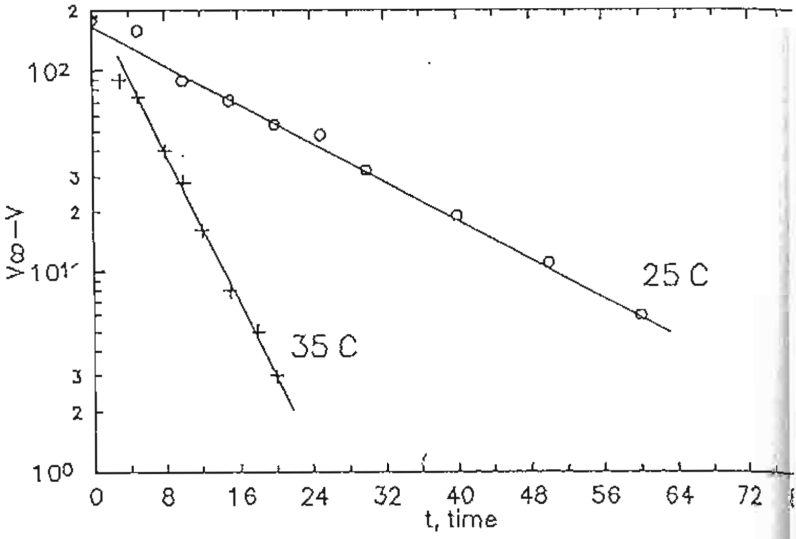
k = 0.055/min at 25°C
0.214/min at 35°C

25°C

t	V
0	0
5	19
10	89
15	107
20	124
25	130
30	146
40	159
50	167
60	172
70	178
80	178

35°C

t	V
0	0
3	97
5	113
8	147
10	159
12	171
15	179
1	182
202	184
22	187
25	187



P3.04.05. DILATOMETRY. ISOPRENE POLYMERIZATION.

Polymerizatioon of isoprene was followed dilatometrically. Some of the data are tabulated, with t in minutes and C in mols/liter (Margerison, in Bamford & Tipper, Comprehensive Chemical Kinetics, vol 1, 410, 1965). Check first and second orders.

For first order, $k(t-t_0) = \ln(C_0/C)$. The semilogarithmic plot has the equation

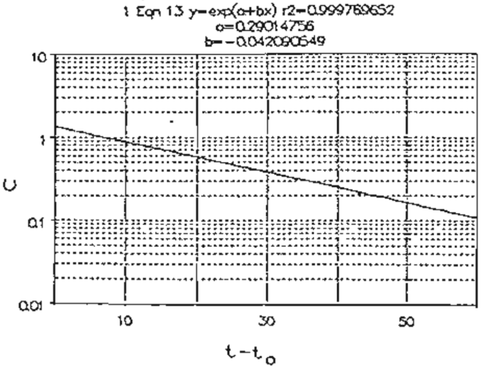
$$\ln C = 0.2901 - 0.0421(t-t_0)$$

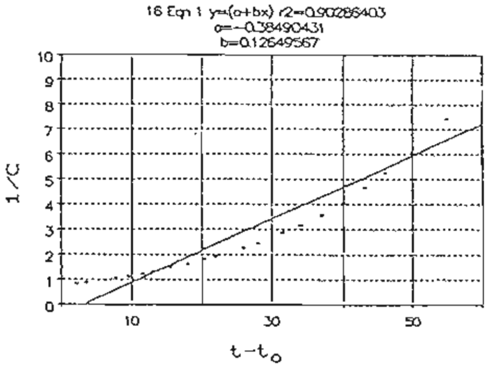
which confirms the first order mechanism.

For second order, $k(t-t_0) = \frac{1}{C} - \frac{1}{C_0}$

but this equation does not plot linearly,

t	C	t	C
2.25	1.2320	28	0.4113
3.5	1.1630	31.5	0.3506
6.25	1.0270	34	0.3166
9.5	0.9729	37	0.2811
11.5	0.8973	40	0.2481
13	0.8258	43	0.2150
15.5	0.7743	46	0.1908
18	0.6864	50	0.1654
20.5	0.6253	55	0.1347
22	0.5631	60	0.1078
26	0.5279		





P3.04.06. ELECTRICAL CONDUCTIVITY. NITROETHANE IODINATION.

The rate of iodination of nitroethane in the presence of pyridine according to the equation

$$C_2H_5NO_2 + C_6H_5N \Rightarrow C_2H_4NO_2 + C_5H_5NH^+ + I^-$$

was followed by measuring the electrical conductivity (Frost & Pearson, 1961) at 25°C in water-alcohol solvent. Initial concentrations were 0.1 M each for nitroethane and pyridine and 0.0045 M for iodine. The time was in minutes and the resistance in ohms. Find the rate equation.

A = nitroethane

The conductivity is proportional to the concentration of the iodide ion.

$$C_{I^-} = \frac{1/R - 1/2503}{1/1470 - 1/2503}(0.0045) = \frac{16.028}{R} - 0.0064$$

Try the second order rate equation,

$$-\frac{dC_a}{dt} = kC_aC_{I_2} = k(0.1 - C_{I^-})(0.0045 - C_{I^-})$$

$$= k(0.1064 - \frac{16.028}{R})(0.1009 - \frac{16.028}{R})$$

Since

$$dC_a = d(\ 0.1064 - \frac{16.028}{R}) = \frac{16.028}{R^2}\,dR$$

$$k = \frac{1}{t}\int_R^{2503} \frac{16.028}{R^2(0.1064-16.028/R)(0.1009-16.028/R)}\,dR$$

The integration is done numerically. The constancy of the calculated values of k confirm the assumed second order.

t	R	10^2k
0	2503	
5	2295	1.236
10	2125	1.220
15	1980	1.214
20	1850	1.224
25	1738	1.229
30	1639	1.234
∞	1470	

P3.04.07. ELECTRICAL CONDUCTIVITY. SO_3 AND HCN

SO_3 and HCN react to form the ions $HCNH^+$ and SO_3CN^-. The reaction between 589 mg SO_3 and 30 cc HCN was followed by measuring the electrical conductivity (Batalin, 335, 1960). The time is in minutes, and the conductance K is $ohm^{-1}cm^{-1}$. Find the rate equation.

The concentrations of the reactants are proportional to (11.08-K). Accordingly the first order rate equation

$$-\frac{dC}{dt} = kC$$

becomes

$$\frac{dK}{dt} = k(11.08-K)$$

From the integral,

$$k = \frac{1}{t-2} \ln \frac{11.08-4.85}{11.08-K}$$

The calculated values in the table are nearly enough constant to confirm a first order mechanism.

t	10^4K	k
2	4.85	
5	7.76	0.210
9	9.63	0.208
12	10.2	0.196
25	11.08	
30	11.08	

P3.04.08. OPTICAL DENSITY .CINNAMAL CHLORIDE ALCOHOLYSIS

The alcoholysis of cinnamal chloride was followed by measuring the optical density of the reaction mixture. (Andrews, JACS <u>69</u> 3062, 1947). The temperature was 22.6°C and the starting concentration was $2.11(10^{-5})$ mol/liter.

Since the product of the reaction is known not to absorb at the 2600 Angstroms that were used in this test, the concentration is proportional to the optical density.

$$C_a = \frac{\rho - 0.01}{0.406 - 0.01} 2.511(10^{-5})$$

For first order reaction,

$$k = \frac{1}{t}\ln\frac{C_{a0}}{C_a} = \frac{1}{t}\ln\frac{0.406-0.010}{\rho-0.010}$$

The values of k are tabulated and are nearly enough constant to confirm the first order mechanism.

t	ρ	10^3k
0	0.406	
10	0.382	6.25
74	0.255	6.49
178	0.143	6.13
1200	0.010	

P3.04.09. OPTICAL DENSITY. HYDROGEN IODIDE DECOMPOSITION

The decomposition of hydrogen iodide is a reversible second order reaction in both directions:

$2\ HI \Leftrightarrow H_2 + I_2,\quad 2A \Leftrightarrow B + C$

A two liter flask was filled with pure HI at 1.24 atm and 683°K, and the decomposition was followed by measuring the absorption of light by the iodine produced. Immediately after the last reading the flask was chilled and an analysis for iodine showed 1.17 g. Evaluate the constants of the second order rate equation.

The optical density, ρ, is proportional to the concentration of the iodine. Assume that equilibrium has been attained by t = 940 when ρ = 6.21.

$$C_e = \frac{1.17}{253.82(2)}\ 2.3048(10^{-3})\ \text{mol}\ I_2/\text{liter} \tag{1}$$

At any density,

$$C = 2.3048(10^{-3})(\frac{\rho}{6.21}) = 3.711(10^{-4})\rho = \beta\rho \tag{2}$$

$$A_0 = \frac{2}{22.4}(\frac{273}{683})(\frac{1.24}{1}) = 0.04425\ \text{mol HI/liter} \tag{3}$$

The equilibrium constant is

$$K_e = (\frac{C_e}{A_0-2C_e})^2 = (\frac{0.0023048}{0.04425-0.00461})^2 = 0.00338 \tag{4}$$

At t = 42,

$$C_{42} = 3.711(10^{-4})(0.81) = 3.006(10^{-4}) \tag{5}$$

The rate equation is

$$\frac{dC}{dt} = k(A^2 - C^2/K_e) = k[(A_0-2C)^2 - C^2/K_e]$$

Integrating,

$$k(t-42) = \int_{C_{42}}^{C} \frac{dC}{(4-1/K_e)C^2-4A_0C+A_0^2}$$

After the necessary substitutions,

$$k(t-42) = \int_{0.81}^{\rho} \frac{d\rho}{-0.1083\rho^2-0.1770\rho+5.276}$$

The values of k are in the last column of the table. The later points may not be reliable because of possible errors in reading the small changes in density that are taking place.

t	ρ	10^3k
42	0.81	
118	2.13	3.65
230	3.66	3.62
397	5.04	3.62
680	6.00	3.89
770	6.12	4.27
940	6.21	5.20

P3.04.10. ABSORBANCE. BROMINATION OF ACETONE.

The progress of a reaction between acetone (A) and bromine (B) was following by measuring the absorbance that is due to the bromine. Initial concentrations were $A_0 = 0.645$ and $B_0 = 0.0193$.

The running concentrations are

$$B = \frac{0.683-R}{0.683-0.201}(0.0193) = 0.04(0.683-R)$$

$$A = A_0 - B_0 + B = 0.645-0.0193+0.04(0.683-R) = 0.653-0.04R$$

Try the rate equation

$$-\frac{dB}{dt} = kA^aB^b$$

$$-0.04\frac{dR}{dt} = k(0.653-0.04R)^a[0.04(0.683-0.04R)]^b$$

$$k = \frac{25}{t}\int_{0.201}^{R}\frac{dR}{(0.653-0.04R)^a[0.04(0.653-R)]^b}$$

Integration is done numerically. Several choices of exponents a and b are tried. The best is a = 1 with b = 0.

t	R	k a=1.b=1	k a=1,b=0
0	0.201		
10	0.257	0.0192	0.217
20	0.313	0.0206	0.218
60	0.558	0.0354	0.233
80	0.665	0.0652	0.228
100	0.683		
150	0.683		

P3.04.11. ABSORBANCE OF Np^{3+}

The course of the reaction, $Np^{3+} + Fe^{3+} \Rightarrow Np^{4+} + Fe^{2+}$, is followed by measuring the absorbance (J Phys Chem 71 3768, 1967).

Simplify the notation to $A + B \Rightarrow C + D$. Initial concentrations were $A_0 = 1.58(10^{-4})$ and $B_0 = 2.24(10^{-4})$ mols/liter.

Assume that the absorbance increases as the concentration decreases.

$$C_a = \frac{0.351-R}{0.351-0.100}\,1.58(10^{-4}) = 6.35(10^{-4})(0.351-R)$$

$$C_b = (2.24-1.58)(10^{-4}) + C_a = 6.35(10^{-4})(0.4549-R)$$

$$dC_a = -6.35(10^{-4})dR$$

Assume the rate equation,

$$-\frac{dC_a}{dt} = kC_aC_b$$

or

$$\frac{dR}{dt} = 6.35(10^{-4})k(0.351-R)(0.4549-R)$$

$$k = \frac{1575}{t}\int_{0.1}^{R}\frac{dR}{(0.351-R)(0.4549-R)}$$

The integration is done numerically and tabulated. The mean value is k = 1600 liter/(mol)(sec).

t	R	$10^{-3}k$
0	0.100	
2.5	0.228	1.616
3	0.242	1.633
4	0.261	1.595
5	0.277	1.609
7	0.300	1.655
10	0.316	1.565
15	0.332	1.537
20	0.341	1.584
∞	0.351	

P3.04.12. ABSORBANCE. INFINITY READING UNKNOWN.

The progress of a second order reaction was followed by readings of absorbance at successive 10 second intervals. The reading at $t \Rightarrow \infty$ was not taken. Readings: 0.920, 0.643, 0.526, 0.462, 0.421, 0.393, 0.372, 0.353, 0.344, 0.334, 0.326, 0.319, 0.313, 0.308. The initial concentration was C_0 = 0.0046 mol/liter.

A linear relation is taken to exist between the concentration and the absorbance,

$$C/C_0 = (R-R_\infty)/(R_0-R_\infty) = (R-R_\infty)/(0.920-R_\infty)$$

which makes the rate equation

$$-\frac{d(R-R_\infty)}{dt} = \frac{kC_0}{R_0-R_\infty}(R-R_\infty)^2$$

and the integral

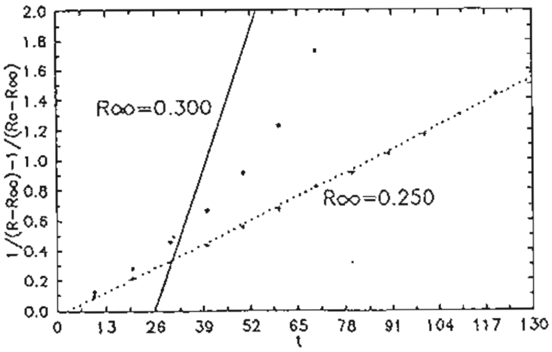
$$\frac{kC_0}{0.920-R_\infty}t = \frac{1}{R-R_\infty} - \frac{1}{0.920-R_\infty} \qquad (1)$$

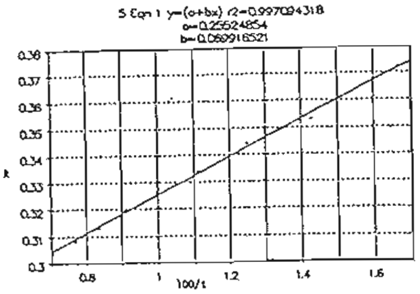
The procedure is to guess a value of R_∞ until one is found that results in a straight line on a plot of t against the right hand side of Eq (1). The plots show that R_∞ = 0.300 is not correct, but that R_∞ = 0.250 is close. The indicated ordinate of the plot should be multiplied by 10. That makes its slope

$$0.120 = \frac{kC_0}{R_0-R_\infty} = \frac{0.0046k}{0.920-0.250}$$

$$k = 17.55 \text{ liter/(mol)(sec)}$$

Another way of estimating R_∞ is to plot R against 1/t and extrapolate to 1/t = 0. The second plot shows this extrapolation to be R_∞ = 0.255, in fair agreement with the other estimate.





P3.04.13. SPECTROGRAPHIC DATA

The composition of a liquid phase reaction, 2 A ⇒ B, was followed as a function of time by a spectrographic method with the tabulated results. The initial concentration was $A_0 = 1.0$ mol/liter. Check first and second orders.

The rate equation is

$$-\frac{1}{2}\frac{dA}{dt} = \frac{dB}{dt} = k_qA^q = k_q(A_0-2B)^q = k_q(1-2B)^q$$

$$k_1 = \frac{1}{2t}\ln\frac{1}{1-2B}$$

$$k_2 = \frac{1}{1-t}\left(\frac{1}{1-2_B} - 1\right)$$

The values for first and second order are tabulated and confirm second order.

t,min	B	10^3k_1	10^3k_2
0	0		
10	0.089	9.80	10.83
20	0.153	9.13	11.02
30	0.200	8.51	11.11
40	0.230	7.70	10.65

P3.04.14. INSTRUMENT READINGS

Data for what is expected to be a second order reaction are reported as instrument readings, α, as a function of time, columns 1 and 2 of the table. The instrument has been calibrated in terms of the concentration of the reactant by the equation

$$\alpha = \sqrt{100 + 2400\ C} \qquad (1)$$

(a) Transform the rate equation in terms of α as the dependent variable, and find the specific rate with its aid; (b) Calculate the value of C at each reading and find the specific rate with the resulting data. The initial concentration is $C_0 = 1$.

$$-\frac{dC}{dt} = kC^2$$

$$k = k_c = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_0}\right) \qquad (2)$$

From the calibration,

$$C = \frac{\alpha^2-100}{2400}$$

$$dC = \frac{2\alpha}{2400}\,d\alpha$$

$$-\frac{2\alpha}{2400}\frac{d\alpha}{dt} = k\left(\frac{\alpha^2-100}{2400}\right)^2$$

$$k = k_\alpha = \frac{4800}{t} \int_\alpha^{50} \frac{\alpha}{(\alpha^2-100)^2} d\alpha \tag{3}$$

The integration is done numerically. Values of k by the two methods are listed in columns 4 and 5 of the table, and yield virtually identical results.

t	α	C	k_α	k_c
0	50.0	1.000		
1	45.7	.829	.207	.2063
2	42.5	.711		
3	40.2	.632		
4	38.0	.560		
5	36.1	.501	.199	.1992
6	34.4	.451		
7	33.3	.420		
8	31.8	.380		
9	31.1	.361		
10	30.0	.333	.200	.2003
15	26.5	.251		
20	24.1	.200	.200	.2000
25	22.4	.167		
30	21.1	.144	.198	.1981
40	19.1	.110		
50	18.4	.0994	.181	.1812

P3.04.15. OPTICAL ROTATION OF GLUCOSE

Data are tabulated for the optical rotation, α, of the mutarotation of glucose at 20 C and 30 C,

α-glucose ⇔ β-glucose, A ⇔ B

The rate equation is expected to be

$$\frac{dB}{dt} = k_1A - k_2B = = k_1(A_0-B - B/K_e)$$

The integral is

$$(k_1+k_2)t = \ln \frac{B_e}{B_e-B} \tag{1}$$

where B_e is the equilibrium concentration. The optical rotation is proportional to the concentration.

B_e is proportional to $\alpha_0-\alpha_e$

B is proportional to $\alpha-\alpha_e$

so Eq (1) becomes

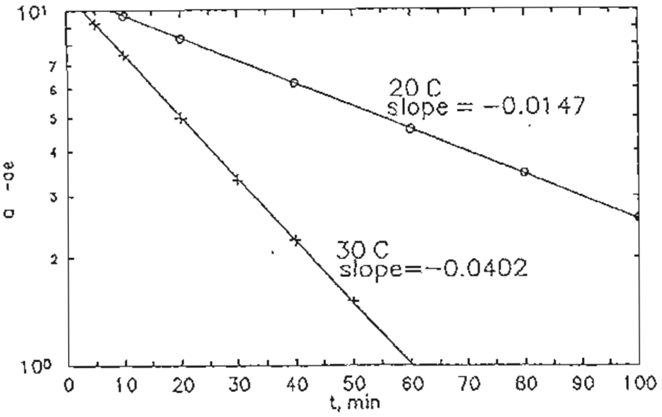
$$(k_1+k_2)t = \ln(\alpha_0-\alpha_e) - \ln(\alpha-\alpha_e) \tag{2}$$

The plots of Eq (2) for the two temperatures are straight, making

k_1+k_2 = 0.0147 at 20 C

0.0402 at 30 C

	20 C		30 C	
t	α	$\alpha-\alpha_e$	α	$\alpha-\alpha_e$
5			19.8	9.2
10	20.26	9.66	18.1	7.5
20	18.92	8.32	15.6	5.0
30			13.93	3.33
40	16.82	6.22	12.84	2.24
50			12.11	1.51
60	15.22	4.62		
80	14.06	3.46		
100	13.18	2.58		
∞	10.6		10.6	



P3.04.16. POLARIMETRY. SUCROSE INVERSION

For the inversion of sucrose in the presence of HCl the tabulated polarimeter readings, α, were obtained at the times shown. Find the specific rate.

The relation between concentration and the readings is

$$\frac{C}{C_0} = \frac{\alpha+4}{13+4}$$

If the reaction is first order,

$$-\frac{d(C/C_0)}{dt} = k(C/C_0)$$

or

$$-\frac{d\alpha}{dt} = k(\alpha+4)$$

$$k = \frac{1}{t}\int_{\alpha}^{13} \frac{d\alpha}{\alpha+4} = \frac{1}{t}\ln\frac{17}{\alpha+4}$$

The values are tabulated in column 3 and are nearly enough constant to confirm the first order mechanism.

t, min	α	100k
0	13.00	
20	9.95	0.989
44	6.95	1.00
90	2.7	1.03
140	0	1.03
175	-1.3	1.05
285	-3.15	1.05
∞	-4.00	

P3.04.17. POLARIMETRY. BROMONITROCAMPHOR

When a sample of pseudo-π-bromonitrocamphor is dissolved in chloroform a spontaneous change in specific rotation, α, occurs and an equilibrium is established in which the pseudo and normal forms exist. The tabulated data refer to the mutarotation at 14 C (Lowry, J Chem Soc, p 211, 1899). Find the sum of the forward and specific rates, k_1+k_2.

The relation between concentration and rotation is

$$\frac{C-C_e}{C_0-C_e} = \frac{\alpha-31.3}{169-31.3} = \frac{\alpha-31.3}{137.7} = \beta \qquad (1)$$

$$dC = (C_0-C_e)d\beta$$

The rate equation is

$$-\frac{dC}{dt} = k_1C-k_2(C_0-C) = (k_1+k_2)C - k_2C_0$$

At equilibrium,

$$-k_2C_0 = (k_1+k_2)C_e$$

so that

$$-\frac{dC}{dt} = (k_1+k_2)(C-C_e)$$

or

$$-\frac{d\beta}{dt} = (k_1+k_2)\beta$$

and

$$k_1+k_2 = \frac{1}{t-3}\int_\beta^1 \frac{d\beta}{\beta} = \frac{1}{t-3}\ln\frac{137.7}{\alpha-31.3}$$

These values are tabulated and have a mean value,

$$k_1+k_2 = 0.0461/\text{hr}$$

t,h	α	k_1+k_2
3	169.0	
7	146.0	0.0457
10	130.3	0.0476
20	94.0	0.0463
30	71.0	0.0461
40	57.0	0.0454
60	41.4	0.0458
∞	31.3	

P3.04.18. POLARIMETRY. REVERSIBLE REACTION

The rate of decomposition of an optically active compound was followed by a polarimeter when the tabulated results were obtained. The equilibrium constant is 3.89. Find the specific rate.

At equilibrium of $A \Leftrightarrow B$,

$$K_e = \frac{C_{a0}-C_{ae}}{C_{ae}} = 3.89$$

$$f_e = C_{ae}/C_{a0} = 0.2045 \qquad (1)$$

The polarimeter reading, α, varies linearly with concentration.

$$\frac{C_{a0}-C_a}{C_{a0}-C_{ae}} = \frac{1-f}{1-f_e} = \frac{115.6-\alpha}{115.6-23.5}$$

$$f = C_a/C_{a0} = 0.0015 + 0.008637\alpha \qquad (2)$$

The assumed rate equation is

$$-\frac{dC_a}{dt} = k_1(C_a-C_b/K_e) = k_1(C_a - \frac{C_{a0}-C_a}{K_e})$$

$$= k_1[(1+1/3.89)C_a - C_{a0}/3.89]$$

In terms of $f = C_a/C_{a0}$,

$$-\frac{df}{dt} = k_1(1.257f-0.257)$$

$$k_1 = \frac{1}{1.257t}\int_f^1 \frac{df}{1.257f-0.257} = \frac{1}{1.257t}\ln\frac{1}{1.257f-0.257} \qquad (3)$$

Substitute for f in terms of α from Eq (2). The values of k are tabulated and are fairly constant with a mean value

$$k = 7.04(10^{-4}) \ / \ \text{min}$$

t	α	10^4k
0	115.6	
180	102.0	7.06
360	90.5	7.03
540	80.6	7.04
900	65.1	7.03
∞	23.5	

P3.04.19. POLAROGRAPHY. BISULFITE-KETONE ADDITION REACTION

The kinetics and mechanism of the ketone-bisulfite addition were studied by the use of the polarographic technique (Rao & Salunke, Reaction Kinetics and Catalysis Letters 26 273, 1984). The specific rate was found to depend on pH. For an equimolar solution of bisulfite and acetone in a deaerated solution of potassium hydrogen phthalate buffer containing potassium iodide as the supporting electrolyte, the tabulated data were obtained. C is $10^3[HSO_3^-]$ mol/liter, t is in minutes. Check a second order rate equation.

For second order,

$$k = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_0}\right) = \frac{1}{t}\left(\frac{1}{C} - \frac{1000}{8}\right)$$

The values of k are recorded in the third column and confirm the second order mechanism.

t	C	k
0	8.00	
30	7.54	0.254
45	7.35	0.246
60	7.10	0.264
75	6.89	0.269
90	6.70	0.269
105	6.54	0.266
120	6.39	0.262
150	6.14	0.252
180	5.92	0.244
210	5.62	0.252
240	5.37	0.255

P3.04.20. NUCLEAR MAGNETIC RESONANCE MEASUREMENTS

The reaction of 2-trimethsilyl-2 chloroprane with antimony pentafluoride was studied by use of NMR (Hairston & O'Brien, J Organometallic Chem 29 79, 1971). The tabulated data were obtained at 40 C. The initial concentration of A $[(CH_3)_3SiC(CH_3)_2Cl]$ was 0.1841 mol/liter and that of B $[SbF_5]$ was 0.1846 mol/liter. Time is in minutes.

Try the rate equation

$$-\frac{dC_a}{dt} = kC_aC_b = kC_a(C_{b0}-C_{a0}+C_a) = kC_a(0.0005+C_a)$$

The integral is

$$k = \frac{1}{t-8}\int_{C_a}^{0.1501} \frac{dC_a}{C_a(0.0005+C_a)}$$

$$= \frac{1}{0.0005(t-8)} \ln \frac{0.1501(0.0005+C_a)}{0.1506C_a}$$

The values are tabulated and have an average value,

$k = 0.16$ liter/(mol)(min)

t	C_a	k
8	0.1501	
10	0.1429	0.1672
21	0.1120	0.1736
44	0.0812	0.1563
76	0.0579	0.1551
114	0.0433	0.1539
151	0.0344	0.1553
153	0.0341	0.1549

P3.04.21. RADIOACTIVE IODINE

A sample of iodine-128 was produced in a Szilard-Chalmers reaction by irradiating a sample of ethyl iodide in a neutron source. The radio-iodine was extracted with sodium thiosulfate solution and then counted in a Geiger counter at various time intervals. Use the tabulated data of t in minutes against C counts/min to find the rate equation and the half time.

The concentration is proportional to the counts/min. Try a first order rate equation for which

$$k = \frac{1}{t-t_0} \ln \frac{C_0}{C} = \frac{1}{t-17} \ln \frac{6985}{C}$$

These values are tabulated and have an average,

$k = 0.0280$/min

The half time of a first order reaction is

$t_{1/2} = \ln(2)/k = \ln(2)/0.028 = 24.8$ min

t	C	k
17	6985	
29	5111	0.0260
50	2735	0.0284
60	2117	0.0278
76	1256	0.0291
105	584	0.0282
123	351	0.0282

P3.05.01. HALF TIME OF POWER LAW RATE EQUATIONS

Half time relations are useful for finding specific rates from data because of the simplicity of the their formulas. To find the order, it is necessary to have half time data with several starting concentrations.

The rate equation

$$-\frac{dC}{dt} = kC^q$$

has the integral

$$kt = \int_C^{C_0} C^{-q}dC = \frac{1}{q-1}\left(\frac{1}{C^{q-1}} - \frac{1}{C_0^{q-1}}\right), \quad q \neq 1$$

When $C/C_0 = 1/2$,

$$kt_{1/2} = \frac{2^{q-1}-1}{(q-1)C_0^{q-1}}, \quad q / 1 \qquad (1)$$

$$\ln(2), \quad q = 1$$

For any fractional conversion, $\alpha = C/C_0$,

$$kt_\alpha = \frac{1}{(q-1)C_0^{q-1}}\left(\frac{1}{\alpha^{q-1}} - 1\right), \quad q / 1$$

$$\ln(1/\alpha), \quad q = 1$$

To find the order, put Eq (1) in linear form,

$$\ln t_{1/2} = k_1 + (1-q) \ln C_0 \qquad (2)$$

$$k_1 = \exp\left[\frac{2^{q-1}-1}{k(q-1)}\right]$$

If the plot is linear, its slope will be 1-q and the order will be q = 1-Slope.

P5.05.02. ACETALDEHYDE. 1/2 AND 3/4 TIME.

For the decomposition of acetaldehyde at 518 C, $CH_3CHO \Rightarrow CH_4 + CO$, data of half and three-quarter times were obtained for several initial pressures P_0, torr, as tabulated. Find the order of the reaction.

Try the rate equation

$$-\frac{dP}{dt} = kP^q$$

whose integral is

$$kt_\alpha = \frac{1}{(q-1)P_0^{q-1}}\left(\frac{1}{\alpha^{q-1}} - 1\right) \qquad (1)$$

Using the $\alpha = 1/2$ data,

$$kt_{1/2} = \frac{2^{q-1}-1}{q-1}\left(\frac{1}{P_0}\right)^{q-1} \qquad (2)$$

$$\ln t_{1/2} = A - (q-1) \ln P_0$$

$$= 11.004 - 0.6602 \ln P_0$$

$$q = 1.6602 \qquad (3)$$

Using the $\alpha = 3/4$ data,

$$kt_{3/4} = \frac{(4/3)^{q-1}-1}{q-1}\left(\frac{1}{P_0}\right)^{q-1} \qquad (4)$$

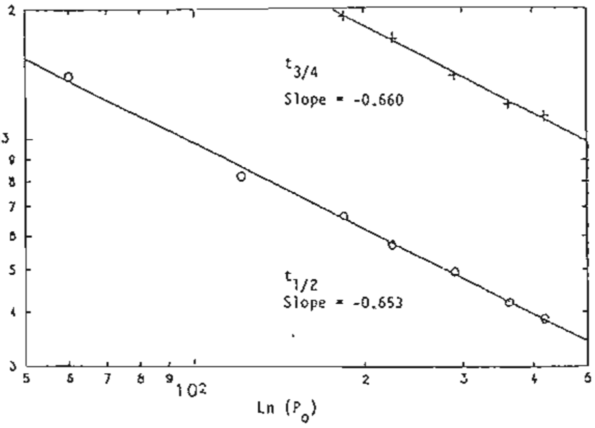
$$\ln t_{3/4} = 9.894 - 0.654 \ln P_0$$

$$q = 1.654 \qquad (5)$$

The two sets of data are in agreement with respect to the order of the reaction.

The value of k can be found at each value of P_0 by substituting the found values of q into Eq 2 or 4. They should all be about the same.

P_0	$t_{1/2}$	$t_{3/4}$
420	385	1135
363	420	1210
290	492	1400
225	572	1710
184	665	1920
121	820	
60	1400	



P3.05.03. SPECIFIC RATE AND ORDER

Find the order and specific rate of a reaction for which these two half time data are known:

C_0	1.5	3.0
$t_{1/2}$	2.0	0.5

From problem P3.05.01 the formula is

$$k = \frac{2^{q-1}-1}{(q-1)t_{1/2}C^{q-1}{}_0}$$

$$(C/C')^{q-1} = t_{1/2}/t'_{1/2}$$

$$(3/1.5)^{q-1} = 2.0/0.5$$

$$q = 3$$

$$k = \frac{2^2-1}{2(2.0)(1.5)^2} = 1/3$$

P3.05.04. TETRAHYDROFURAN

From the tabulated half time and temperature data for the thermal decomposition of tetrahydrofuran (JACS 68 506, 1946) find the order of the reaction and the Arrhenius parameters.

P_0, torr	$t_{1/2}$, min	T, °C
214	14.5	569
204	67	530
280	17.3	560
130	39	550
206	47	539

For the rate equation,

$$-\frac{dP}{dt} = kP^n = k_0 \exp(B/T)\ P^n$$

the half time is

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k_0} \exp(B/T)\ P_0^{1-n}$$

or

$$\ln t_{1/2} = k_1 + B\ (1/T) + (1-n) \ln P_0$$
$$= -25.468 + 26221/T - 0.5582 \ln P_0$$

The numerical values are found from the data with POLYMATH multilinear regression. Hence,

$$1-n = -\ 0.5582$$

$n = 1.5582$, order of the reaction

$B = 26221$, Arrhenius parameter

$$\ln \frac{2^{0.5582}-1}{0.5582k_0} = -25.468$$

$$k_0 = 9.73(10^{10}) = \exp(25.3)$$

Accordingly the rate equation is

$$-\frac{dP}{dt} = \exp\left(25.3 - \frac{26221}{T}\right) P^{1.5582}$$

```
Regression  Data                              Page 1 of 1
  Point  x1              x2            y
    1    569             214           14.5
    2    530             204           67
    3    560             280           17.3
    4    550             130           39
    5    539             206           47

The functions: y'=ln(y)
               x1'=1/(x1+273.2)
               x2'=ln(x2)


Transformed  Data                         Page 1 of 1
  Point  x1'             x2'           y'
    1     1.187×10^-3    5.3660        2.6742
    2     1.245×10^-3    5.3181        4.2047
    3     1.200×10^-3    5.6348        2.8507
    4     1.215×10^-3    4.8675        3.6636
    5     1.231×10^-3    5.3279        3.8502


The correlation is:
   y'=-25.468+ 26221×x1'-0.5582×x2'


Variance=      7.586 ×10^-5
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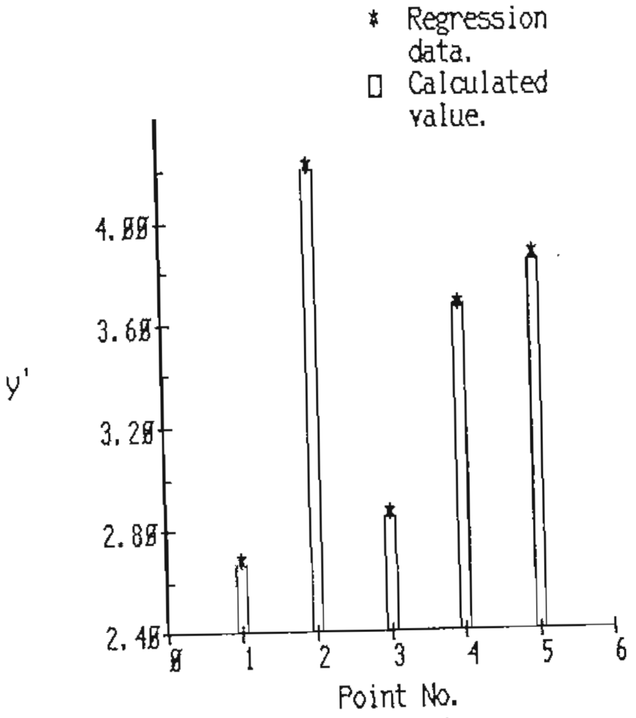


P3.05.05. NITROUS OXIDE DECOMPOSITION

Find the rate equation for the thermal decomposition of nitrous oxide in the gas phase at 1030 K from the tabulated data of half times and initial pressures.

$$2\,N_2O \Rightarrow 2N_2 + O_2$$

$$-\frac{dn}{dt} = \frac{k}{V^{q-1}}\, n^q$$

$$V = \frac{n_0RT}{P_0}$$

$$t_{1/2} = \frac{2^{q-1}-1}{(q-1)k}\left(\frac{RT}{P_0}\right)^{q-1}$$

Plot $t_{1/2}$ against P_0 on loglog.

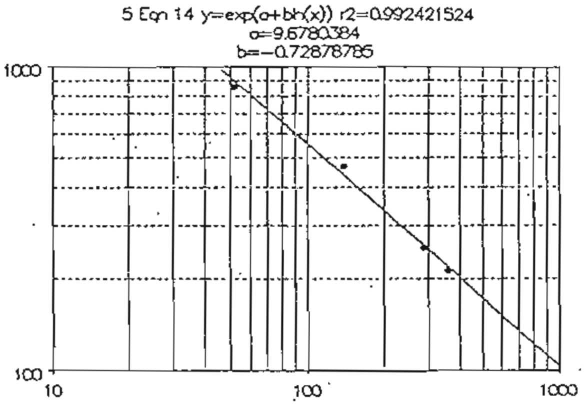
$$\ln t_{1/2} = k_1 + (1-q)\ln P_0$$

$$= 9.678 - 0.7288 \ln P_0$$

$q = 1.7288$, order of the reaction

A point on the regressed line is $t_{1/2} = 200$, $P_0 = 335.8$.

$$k = \frac{2^{0.7288}-1}{0.7288(200)}\left[\frac{62.3(1030)}{335.8}\right]^{0.7288} = 0.2069$$



P_0, torr	52.5	139	290	360
$t_{1/2}$, sec	860	470	255	212

P3.05.06. THIRD ORDER DECOMPOSITION

Data for the reaction, $NO_2 + H_2 \Rightarrow$ Products, at 826 C with equal amounts of reactants are tabulated. The initial pressures are torr, the times are in sec. The process actually is complicated by the equilibrium , $2\ NO_2 \Leftrightarrow N_2O_4$, but here a simple power law will be assumed for the main reaction.

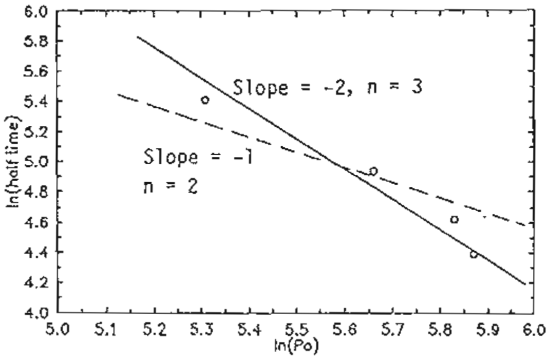
$$t_{1/2} = \frac{2^{n-1}-1}{k(n-1)P_0^{n-1}}$$

The linearized equation is

$$\ln t_{1/2} = k_1 - (n-1)\ln P_0$$

The plots show that the exponent 3 is more nearly valid than the exponent 2.

P_0, torr	354	340.5	288	202
$t_{1/2}$,sec	81	102	140	224



P3.05.07. HALF TIME DATA

Data of initial pressure or concentration and half times are given in the several parts of this problem. From problem P3.05.01, such data are related to the specific rate and reaction order by

$$kt_{1/2} = \frac{2^{q-1}-1}{(q-1)n_0^{q-1}} \quad \text{or} \quad \frac{2^{q-1}-1}{(q-1)P_0^{q-1}} \qquad q \neq 1 \qquad (1)$$

$$\ln 2, \quad q = 1 \qquad (2)$$

In linearized form,

$$\ln t_{1/2} = K - (q-1)\ln n_0 \qquad (3)$$

In each case the data are in the first two rows, and the calculated k for the correct value of q is in the third row. The value of q is established by trial.

(a) $NH_4CO \Rightarrow (NH_4)_2CO$, q = 2

n_0	0.05	0.01	0.20
$t_{1/2}$	370.03	19.15	9.45
k_2	0.54	0.52	0.53

(b) $PH_3 \Rightarrow$ Products, q = 1

P_0	139	52.5
$t_{1/2}$	84	83
k_1	0.0083	0.0084

Since the half time is substantially constant, the reaction order must be one.

(c) For the decomposition of ammonia in contact with tungsten at 1100 C,

P_0, torr	265	130	58
$t_{1/2}$, min	7.6	3.7	1.7
k_1	17.4	17.6	17.1

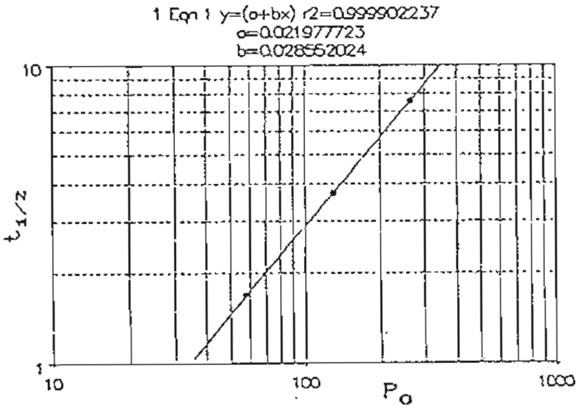
From the loglog plot, q = 1.0285, which is substantially unity.

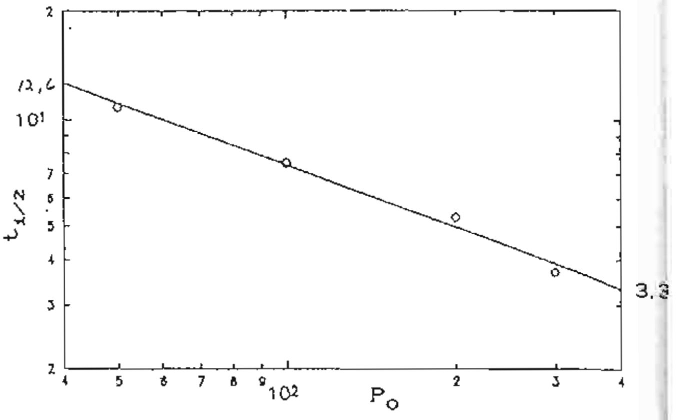
(d) β-hydrogen ⇔ α-hydrogen at 923 K

P_0	50	100	200	300
$t_{1/2}$	10.8	7.5	5.3	3.7
10^3k	6.24	6.01	5.70	6.45

The plot of ln $t_{1/2}$ against ln P_0 is fairly linear with slope 1-q = - 0.58 which makes q = 1.58. The values of k are calculated from

$$k = \frac{2^{0.58}-1}{0.58\, P_0^{0.58} t_{1/2}}$$





P3.05.08. NITRIC OXIDE AND HYDROGEN

Given the half time and initial total pressure data with equimolar amounts of the reactants, find the overall order of the reaction,

$$2\ NO + 2H_2 \Rightarrow N_2 + 2\ H_2O$$

The initial partial pressure is $p_{NO} = \pi_0/2$,

$$kt_{1/2} = \frac{2^{q-1}-1}{(q-1)(\pi_0/2)^{q-1}} = K\pi_0^{1-q}$$

From the straight line plot, although there is some scatter,

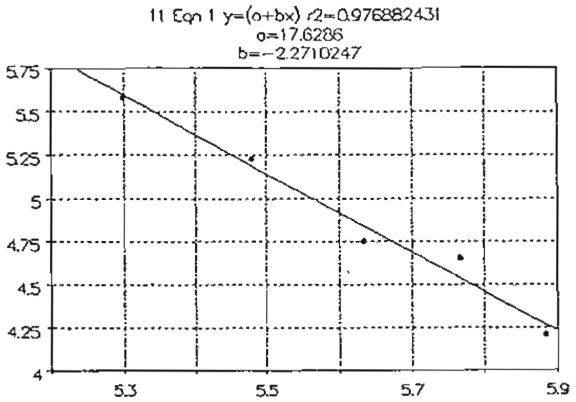
$$\ln t_{1/2} = 17.63 - 2.271 \ln \pi_0$$

whence

$$q = 3.271$$

k can be found from the coefficient 17.63 with this value of q.

π_0, torr	200	240	280	320	360
$t_{1/2}$, sec	265	186	115	104	67



P3.05.09. RATE EQUATION FROM HALF TIME DATA

Half time and initial partial pressure data are available for the gaseous reaction, A + B ⇒ 2 C. Show that the rate equation is $r = kp_ap_b^2$.

Utilize the stoichiometric balance to write the equation

$$-\frac{dp_b}{dt} = kp_ap_b^2 = k(p_{a0} - p_{b0} + p_b)p_b^2$$

Integrating for the half time,

$$k = \frac{1}{t_{1/2}} \int_{p_{b0}}^{p_{b0}/2} \frac{dp_b}{(p_{a0} - p_{b0} + p_b)p_b^2}$$

For the first point,

$$k = \frac{1}{80} \int_{10}^{5} \frac{dp_b}{(490+p_b)p_b^2} = 2.52(10^{-6})$$

Similarly for the other points. The four values are tabulated. They are nearly the same , thus confirming the postulated rate equation.

p_{a0}	p_{b0}	$t_{1/2}$	10^6k
500	10	80	2.52
125	15	213	2.60
250	10	160	2.53
250	20	80	2.56

P3.05.10. HALF TIME. REACTION WITH VARIABLE DENSITY

The volume of a liquid phase depends on the composition with $V = 12+0.5\sqrt{n}$. The rate equation is $r = 0.72(n/V)^2$ mol/(liter)(min) and the initial content of the reactor is $n_0 = 5$ mol. Find the half time of the reaction.

$$-\frac{dn}{dt} = \frac{k}{V}n^2 = \frac{0.72n^2}{12+0.5n^{1/2}}$$

Integrating numerically for convenience,

$$t_{1/2} = \int_{2.5}^{5} \frac{12+0.5n^{1/2}}{0.72n^2} dn = 3.58 \text{ min}$$

P3.05.11. SEVERAL DEFINITIONS OF HALF TIME

For the reaction, 2A + B ⇒ Products, find expressions for the kinds of half times defined in (a), (b) and (c).

x = mols of B converted

$$\frac{dx}{dt} = k(A_a-2x)^2(B_0-x)$$

$$kt = \frac{1}{(2B_0-A_0)^2}\left[\frac{2x(2B_0-A_0)}{A_0(A_0-2x)} + \ln\frac{B_0(A_0-2x)}{A_0(B_0-x)}\right]$$

(a) When $x = A_0/2$,
$t_{1/2} \Rightarrow \infty$

(b) When $x = B_0/2$,

$$kt_{1/2} = \frac{1}{(2B_0-A_0)^2}\left[\frac{B_0(2B_0-A_0)}{A_0(A_0-B_0)} + \ln\frac{2(A_0-B_0)}{A_0}\right]$$

(c) When $\frac{A_0-A}{2} = \frac{B_0-B}{1} = \varepsilon = 1/2$

$x = 1/2$

$$kt_{1/2} = \frac{1}{(2B_0-A_0)^2}\left[\frac{2B_0-A_0}{A_0(A_0-1)} + \ln\frac{B_0(A_0-1)}{A_0(B_0-0.5)}\right]$$

P3.05.12. ACETALDEHYDE. VARIABLE AND INITIAL RATE DATA

Acetaldehyde (A) decomposes according to the reaction, $CH_3CHO \Rightarrow CH_4 + CO$. Two sets of experiments were performed by Letort (Bull Soc Chim France 9 1, 1942) and the tabulated calculations were derived from them. (a) With a pressure of 183 torr, the data are of composition n_a/n_{a0} and the corresponding rates; (b) At several initial pressures the initial rates are given. Find the order of the reaction from the two sets of data.

(a) The rate equation is

$$r = k(n_a/n_{a0})^q$$
$$\ln r = \ln k + q \ln(n_a/n_{a0})$$

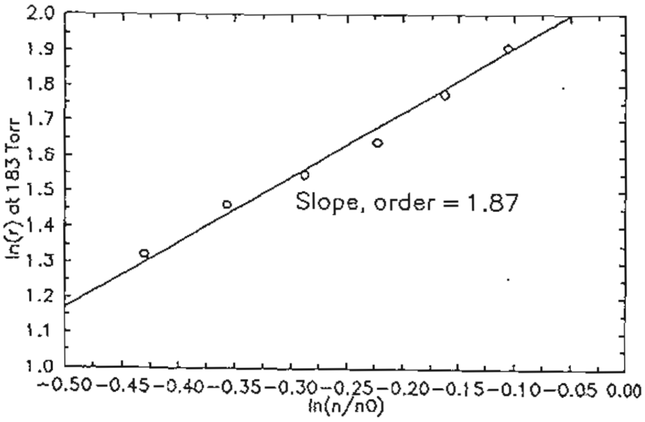
From the first plot, the order is $q = 1.87$.

(b) The initial rate equation is

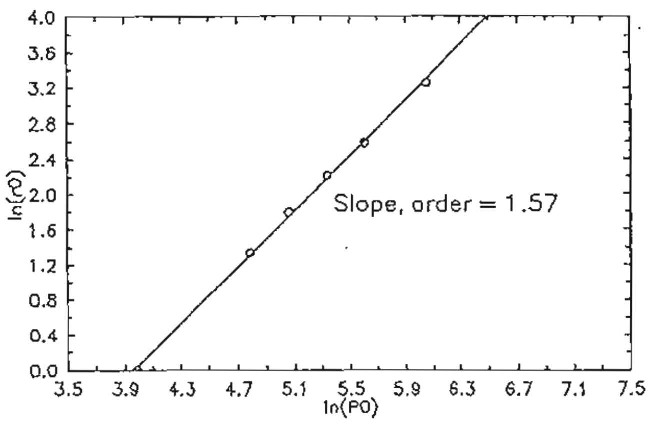
$$r_0 = kP_0^q$$
$$\ln r_0 = \ln k + q \ln P_0$$

From the second plot the order is $q = 1.57$. The difference is attributed to inhibition by the CO that is formed.

n_a/n_{a0}	r
1	
0.95	7.49
0.90	6.74
0.85	5.90
0.8	5.14
0.75	4.69
0.7	4.31
0.65	3.75
0.6	3.11



P_0	r_0
53.5	1.00
120.0	3.76
157.5	5.96
208.0	9.02
272.0	13.2
425.5	26.0



P3.05.13. DIBORANE AND ACETONE.

Initial rate data are reported for the reaction between diborane (A) and acetone (B),

$B_2H_6 + 4Me_2CO \Rightarrow 2(Me_2CHO)_2BH$

Partial pressures are in torr and initial rates in torr/sec. Find the constants of the rate equation, $r = kP_a^mP_b^n$.

For points 1 to 5,

$r_0 = k(20)^nP_a^m$

$\ln r_0 = m \ln P_a + C_1$

For points 6 to 10,

$r_0 = k(10)^mP_b^n$

$\ln r_0 = n \ln P_b + C_2$

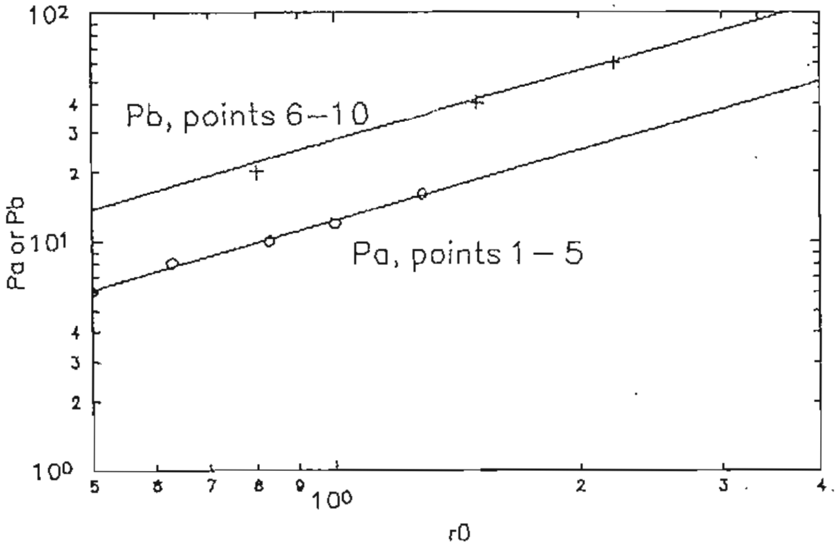
Both plots are straight lines with unit slopes, m = n = 1. The specific rate then is found from

$k = r_0/P_aP_b$

These are tabulated in the last column and are roughly constant. The final rate equation becomes

$r = 3.85P_aP_b$

Run	P_{a0}	P_{b0}	10^3r_0	10^3k
1	6	20	0.5	4.17
2	8	20	0.63	3.94
3	10	20	0.83	4.15
4	12	20	1.00	4.17
5	16	20	1.28	4.00
6	10	10	0.33	3.33
7	10	20	0.80	4.00
8	10	40	1.50	3.75
9	10	60	2.21	3.68
10	10	100	3.33	3.33



P3.05.14. RADIOACTIVE DECOMPOSITION

Radioactive decompositions are first order reactions. The specific rate in this discipline is called the decay constant,

$$k = -\frac{1}{n}\frac{dn}{dt} = \frac{\ln 2}{t_{1/2}}$$

(a) Half time of radium.

The number of radium atoms that break up per second per gram is $3.7(10^{10})$. Given that the molecular weight is 226 and the Avogadro number is $6.023(10^{23})$ atoms/mol, find the half time.

$$k = 3.7(10^{10})\ \frac{\text{atoms}}{\text{gm sec}}\ \frac{226\text{ gm}}{\text{mol}}\ \frac{\text{mol}}{6.023(10^{23})\text{ atoms}}\ \frac{31.6(10^{6})\text{ sec}}{\text{yr}}$$

$$= 4.383(10^{-4})\ /\text{yr}$$

$t_{1/2} = \ln(2)/k = 1581$ yr

(b) Radium from thorium

Radium is related to thorium^{230} by the radioactive sequence

$$T \overset{1}{\Rightarrow} R \overset{2}{\Rightarrow} \text{Products}$$

The half life of the thorium is 8000 yr, that of radium is 1622 yr. A sample of thorium is initially free of radium. What will be the ratio, R/T_0, after 1622 yrs have elapsed?

$$k_1 = 0.693/8000 = 86.6(10^{-6})\ /\text{yr}$$

$$k_2 = 0.693/1622 = 427.3(10^{-6})\ /\text{yr}$$

$$-\frac{dT}{dt} = k_1 T$$

$$T = T_0 \exp(-k_1 t)$$

$$\frac{dR}{dt} = k_1 T_0 \exp(-k_1 t) - k_2 R$$

This is a linear equation with integrating factor $\exp(k_2 t)$ and solution

$$R\exp(k_2 t) = k_1 T_0 \int \exp[(k_2-k_1)t]\,dt + I$$

or

$$\frac{R}{T_0} = \frac{k_1}{k_2-k_1}[\exp(-k_1 t) - \exp(-k_2 t)]$$

$$= \frac{86.6}{427.3-86.6}\{\exp[86.6(1622)(10^{-6})]-\exp[427.3(1622)(10^{-6})]\} = 0.094$$

P3.05.15. DISSOLUTION OF DOLOMITE BY HCl

Dolomite is dissolved by hydrochloric acid. Data at initial conditions give the concentration of acid, gmol/liter, and its rate of reaction, gmol/liter-sqcm-sec, when exposed to 30 sqcm of solid in one liter of solution (Lund et al, Chem Eng Sci 28 691,1973). Find the constants of a power law rate equation.

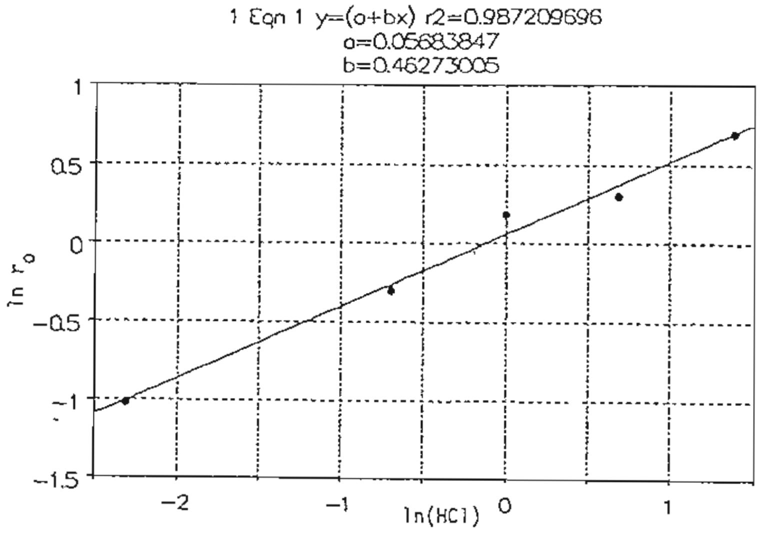
$[HCl]_0$	0.1	0.5	1	2	4
$-10^7 r_0$	0.36	0.74	1.2	1.36	2.0

The rate equation $r_0 = k[HCl]^q$ is plotted in linearized form,

$$\ln(-10^7 r_0) = \ln k + q \ln [HCl]_0$$
$$= 0.0568 + 0.483 \ln [HCl]_0$$

which makes the rate equation

$-10^7 r_0 = 1.058\ [HCl]_0$



P3.06.01. SPECIFIC RATE AS A FUNCTION OF TEMPERATURE

Interdependence of specific rate and temperature is most commonly represented by the Arrhenius equation,

$k = k_0 \exp(-E/RT) = k_0 \exp[-E/R(T_c+273.2)$

where k_0 is the frequency factor, E is the energy of activation and T is absolute temperature. In linearized form, ln k against 1/T, it is,

$\ln k = A - B/T$

Find the constants of the Arrhenius equation for the following cases.

(a) The reaction of ethanol and acetic acid catalyzed by an ion exchange resin was studied by Saletan & Whits (Chem Eng Prog 4 59, 1952).

k, liter/(mol)(h)	0.5	1.1	2.2	4.0	6.0
°C	30	40	50	60	70

(b) The experimental data for the polymerization of styrene dissolved in benzene and with use of butyllithium initiator are reported by Worsford & Bywater (Can J Chem 38 1891, 1960).

$10^6 k$, 1/sec	0.155	0.265	0.387	0.563	0.929
°C	10	15	20	25	30.3

(c) Data for the decomposition of nitrogen pentoxide at different temperatures are cited by Moelwyn-Hughes (Physical Chemistry, 1135, 1962).

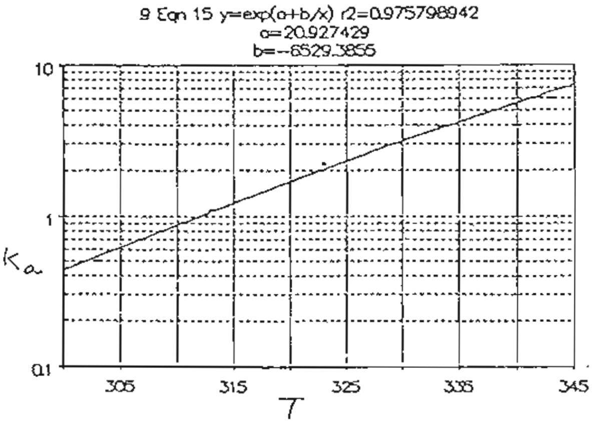
$10^5 k$, 1/sec	1.04	3.38	24.7	75.9	487
°C	15	25	40	50	65

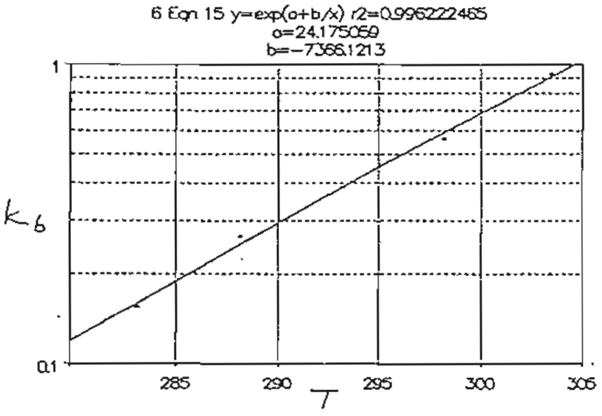
From the linear plots of the three cases, the Arrhenius relations are,

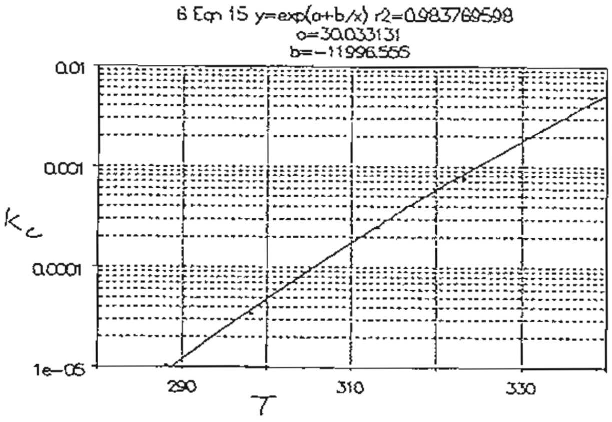
$k_a = \exp(20.927-6529.4/T)$

$k_b = \exp(24.175-7366.1/T)$

$k_c = \exp(30.033-11996.6/T)$







P3.06.02. ACETALDEHYDE DECOMPOSITION

The rate of the second order decomposition of acetaldehyde was measured over a temperature range. Find the activation energy and the frequency factor. The units of k are liter $\text{mol}^{-1}\ \text{s}^{-1}$.

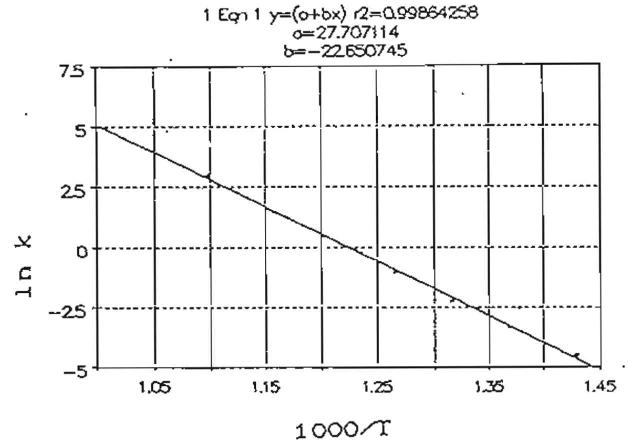
°K	700	730	760	790	810	840	910	1000
k,	0.011	0.035	0.105	0.343	0.789	2.17	20.0	145.0

The data are well fitted by the equation

$$\ln k = \exp(27.707 - 22650.7/T)$$

$$= 1.078(10^{12})\ \exp(-45007/RT)$$

Frequency factor is $1.078(10^{12})$, of the same dimensions as k, and the energy of activation is 45007 cal/gmol.



P3.06.03. ETHYL BROMIDE PYROLYSIS

The pyrolysis of ethyl bromide was found to be of the first order with specific rates

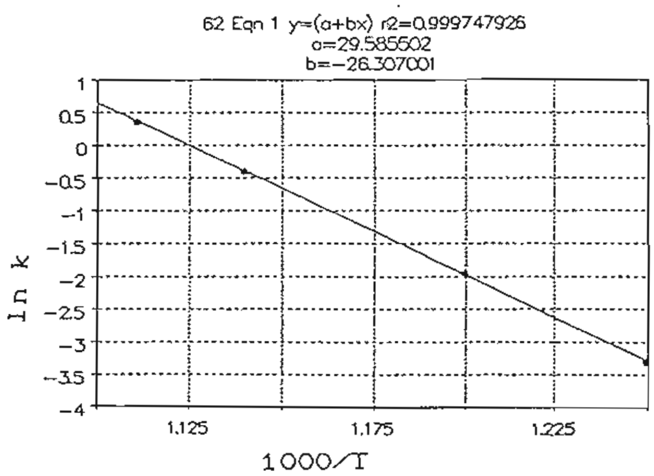
k, 1/s	0.0361	0.141	0.662	1.410
T, °K	800	833	877	900

The plot of these data has the equation

$$\ln k = 29.585 - 26307/T$$

or

$$k = 7.06(10^{12})\ \exp(26307/T)$$



P3.06.04. EFFECT OF A 10 DEGREE TEMPERATURE RISE

For the reaction

$$Co(NH_3)_6^{3+} + Cr(H_2O)_6^{2+} + Cl^- \Rightarrow Co(NH_3)_6^{2+} + Cr(H_2O)_5Cl^{2+}$$

the specific rates at 25 and 37 C are 0.74 and 1.70 $liter^2 mol^{-2} min^{-1}$. Find (a) the activation energy, (b) the temperature at which the specific rate is 10 times that at 25 C.

$$\ln(0.74) = A + \frac{B}{298.2}$$

$$\ln(1.70) + A + \frac{B}{310.2}$$

$$A = 21.20$$
$$B = -6411.4$$

Energy of activation , $E = 1.987\ (6411.4) = 12739$ cal/gmol.

When $k_T = 10\ k_{25} = 7.4$,

$$T = \frac{6411.4}{21.2-\ln(7.4)} = 333.95^oK,\ 60.75°C$$

P3.06.05. TWO ACTIVATION ENERGIES

Observations of the specific rate as a function of temperature were made with the tabulated results. Find the energy of activation as a function of temperature.

The plot of ln k against 1/T has two straight line regions.

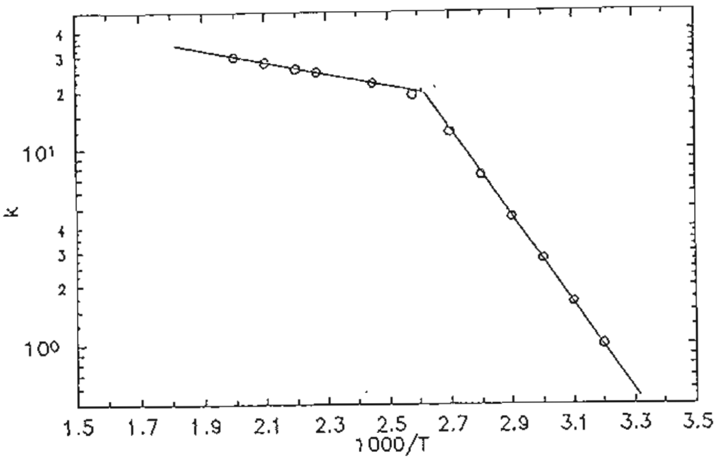
Above 1000/T = 2.6, reading off the plot,

$$-\frac{E}{R} = \frac{1 - 20}{(3.2-2.6)/1000}$$

$$E = 1.987(19)(1000)/0.6 = 62922 \text{ cal/gmol}$$

Below 1000/T = 2.6,

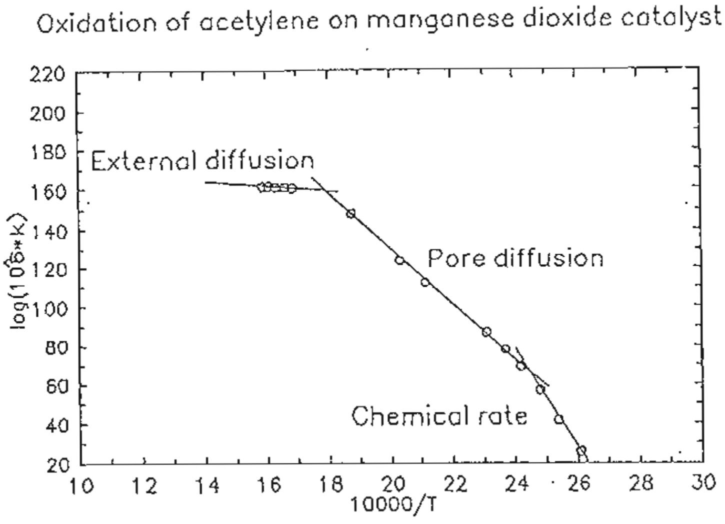
$$E = \frac{1.987(20-30)}{(2.6-2.0)/1000} = 33117 \text{ cal/gmol}$$



P3.06.06. THREE CONTROLLING MECHANISMS

Data of the oxidation of acetylene on MnO_2 catalyst are cited by Batalin (357, 1960). The plot of ln k against reciprocal temperature reveals three zones with distinct controlling mechanisms, namely external diffusion controlling with low activation energy, pore diffusion controlling with intermediate activation energy, and chemical reaction controlling with high activation energy.

$10^4/T$	$\log_{10}(10^6 k)$
26.1	25.53
25.40	41.50
24.80	56.82
24.20	69.02
23.70	77.52
23.10	86.33
21.13	112.39
20.30	123.80
18.75	147.71
16.85	160.31
16.60	160.75
16.30	160.96
16.05	161.28
15.86	161.38


Oxidation of acetylene on manganese dioxide catalyst

P3.06.07. HYDROGEN SULFIDE FORMATION

The initial rate of formation of H_2S from hydrogen and sulfur was measured with the results tabulated. In all experiments the closed reaction vessel contained the same initial weights of sulfur and hydrogen. The rate is g H_2S/(liter)(s). Find the activation energy.

The rate equation is

$$r_0 = \exp(A-\frac{E}{RT})\ f(C_0)$$

or

$$\ln r_0 = A - \frac{E}{RT} + \text{Constant}$$

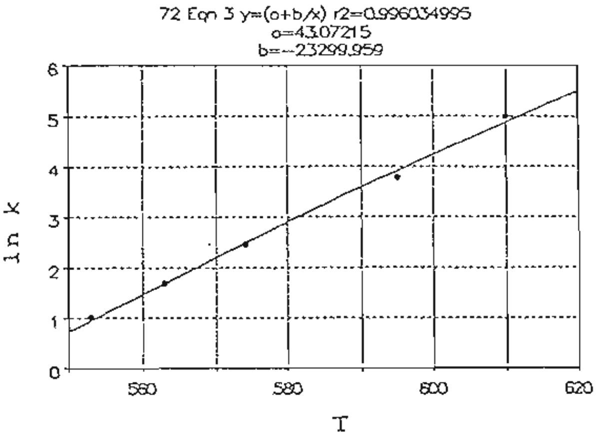
The plot of the data has the equation

$$\ln r_0 = 43.07 - \frac{23300}{T+273.2}$$

from which the energy of activation is

$E = 23300\ R_g = 46297$ cal/gmol

T°C	280	290	301	322	337
$10^7 r_0$	2.77	5.49	11.47	44.23	150.2



P3.06.08. DECOMPOSITION OF NITROGEN DIOXIDE

The decomposition of nitrogen dioxide, $2NO_2 \Rightarrow 2NO + O_2$, has a second order rate equation. Data at different temperatures are tabulated. Find the Arrhenius parameters.

The plot of ln k against reciprocal temperature has the equation

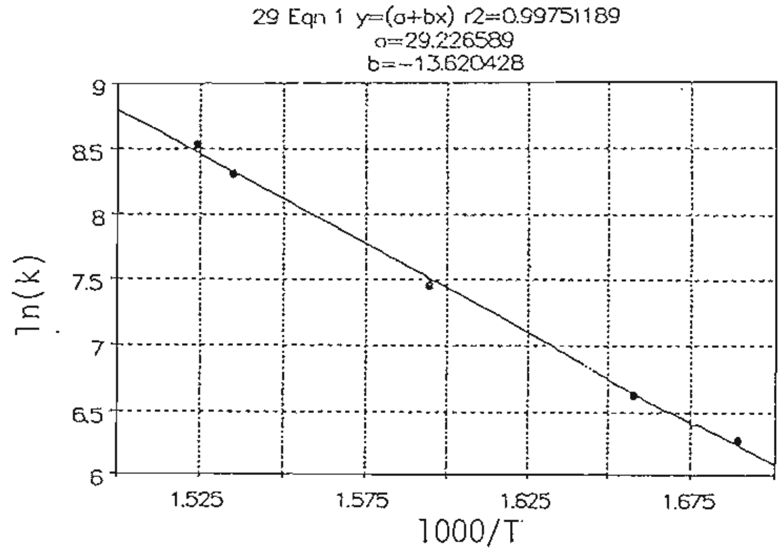
$\ln k = 29.22 - 13620/T$

or

$k = 4.90(10^{12}) \exp(-27063/T)$

with activation energy in cal/gmol and the temperature in °K.

T, °K	592	603	627	651.5	656
k, cc/(gmol)(s)	522	755	1700	4020	5030



P3.06.09. OIL PYROLYSIS

Tests were performed on pyrolysis of an oil in a heated tubular reactor. The reaction is pseudo first order with an activation energy of 56630 cal/gmol, so the specific rate is represented by

$$k = k_{700} \exp\left[28500\left(\frac{1}{700} - \frac{1}{T}\right)\right] \quad (1)$$

where the temperature is °R. The temperature profile is

$$T = 980 - 380 \exp(-0.6z) \quad (2)$$

where z is the fractional distance along the tube. The density of the oil is

$$\rho = 1.27 - 0.0006T,\ \text{g/cc} \quad (3)$$

The volume of the reactor is 340 cc. At a feed rate of $n_0 = 42$ g/min, conversion was 20%. Find the specific rate k_{700} at 700 R.

The flow reactor equation is

$$-dn = n_0 dx = kC\,dV_r = k\left(\frac{n}{V'}\right) dV_r = \frac{kn_0(1-x)}{n_0/\rho}\,dV_r = k\rho(1-x)V_r dz$$

Rearranging and integrating,

$$\int_0^{0.2} \frac{dx}{1-x} = \ln 1.25 = 0.2231$$

$$= \frac{k_{700}V_r}{n_0}\int_0^1 \rho \exp\left[28500\left(\frac{1}{700} - \frac{1}{T}\right)\right] dz \qquad (4)$$

Substitute for T and ρ from Eqs (2) and (3) and complete the integral. Numerical integration gives $\int = 5.1892$. Accordingly,

$$k_{700} = \frac{0.2231\ n_0}{5.1892\ V_r} = \frac{0.2231(42)}{5.1892(340)} = 0.0053/\text{min}$$

P3.06.10. RATE EQUATION WITH THREE CONSTANTS

A rate equation has the form

$$r = C^q \exp(A-B/T)$$

Given the data of the first three columns of the table, find the three constants.

(a) In linearized form,

$$\ln r = q \ln C + A - B/T$$

Substituting the data,

$$\ln 2.6 = q \ln 1.5 + A - B/300$$

and similarly for the other points. By Gaussian elimination, the solution of the three linear equations results in the rate equation

$$r_a = C^{1.08} \exp(10.837-3096/T) \qquad (1)$$

(b) A direct solution of three simultaneous nonlinear equations is accomplished by software SEQS.

$$2.6 = 1.5^q \exp(A - B/300)$$

$$2.87867 = 1.2^q \exp(A-B/310)$$

$$3.36504 = 0.8^q \exp(A-B/330)$$

The solution of these three equations results in

$$r_b = C^{1.546} \exp(13.978-4097/T) \qquad (2)$$

Although the constants of the two solutions differ, calclulated values of the rate check closely the original values, as shown in the table.

C	T	r	r_a	r_b
1.5	300	2.60000	2.5980	2.601
1.2	310	2.84867	2.8486	2.8497
0.8	330	3.36504	3.3676	3.3657

P3.06.11 NON-ISOTHERMAL DATA

During a catalyst test, observations were made of the reaction temperature and the mol fraction, M, of product in the effluent. Show that the variables are related by the equation

$M = a\ T^b \exp(c/T)$

Take logarithms and apply POLYMATH multilinear regression. The result is

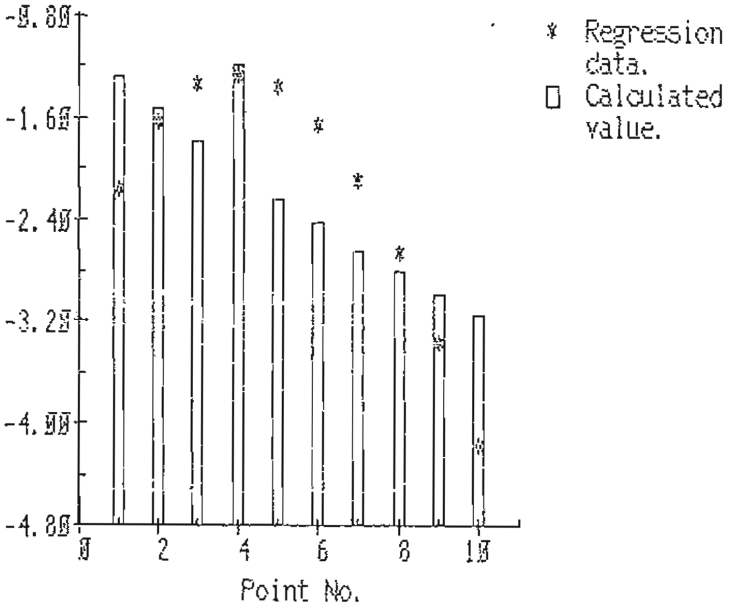
$$\ln M = \ln a + b \ln T + c/T$$
$$= 22.732 - 4.0738 \ln T + 1200.1/T$$

or

$$M = T^{-4.0738} \exp(22.732 + 1200.1/T)$$

The graph indicates that the fit is rather poor.

T, °K	M
598	0.111
623	0.189
648	0.253
673	0.276
698	0.245
723	0.186
748	0.120
773	0.068
798	0.034
823	0.015



P30612. RATE EQUATION FROM NON ISOTHERMAL DATA

Temperatures and concentrations were measured as functions of time, as tabulated. Initial concentration was $C_0 = 1.0$. Check the rate equation

$$r = -\frac{dC}{dt} = C^q \exp(a+b/T) \qquad (1)$$

for first and second orders.

The values of C/C_0 are correlated by the empirical equation,

$$C/C_0 = \exp(0.003418 - 0.4413t + 0.0133t^2) \qquad (2)$$

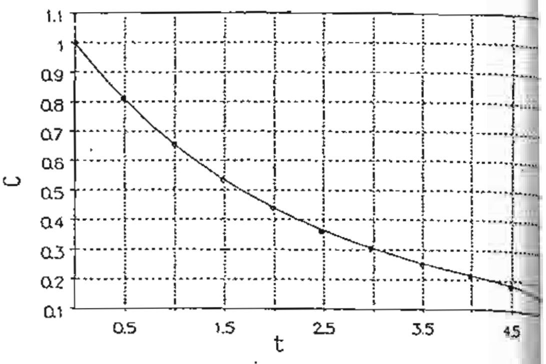
which is differentiated to yield $r = -dC/dt$. Those values are tabulated in column 5 of the table. Put Eq (1) in linear form,

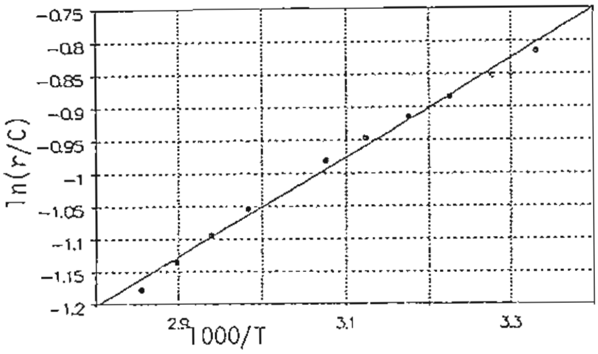
$$\ln(r/C^q) = a + b/T$$

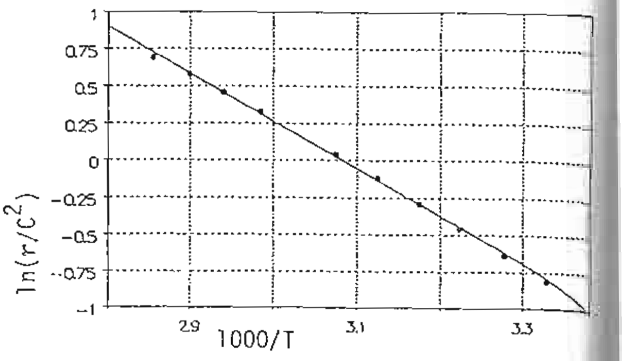
The plot with $q = 2$ represents the data more accurately than the one with $q = 1$. So the better rate equation is

$$r = C^2 \exp(9.834 - 3191/T)$$

t	T	1000/T	C	-r	-r/C	$-r/C^2$
0.0	300	3.333	1.0000	0.4428	0.4428	0.4428
0.5	305	3.279	.08090	0.3456	0.4272	0.5280
1.0	310	3.226	0.6558	0.2712	0.4136	0.6307
1.5	315	3.175	0.5342	0.2141	0.4007	0.7502
2.0	320	3.125	0.4378	0.1699	0.3881	0.8865
2.5	325	3.077	0.3614	0.1356	0.3752	1.0382
3.0	330	3.030	0.3005	0.1088	0.3621	1.2049
3.5	335	2.985	0.2517	0.0878	0.3487	1.3852
4.0	340	2.941	0.2124	0.0712	0.3350	1.5772
4.5	345	2.899	0.1804	0.0580	0.3214	1.7818
5.0	350	2.857	0.1542	0.0475	0.3080	1.9972







P3.06.13. NONISOTHERMAL DATA

Data of temperature and concentration at various times are tabulated. Find a rate equation that combines a power law and the Arrhenius equation,

$$r = C^q \exp(a-b/T)$$

The concentration data are fitted by the empirical equation

$$C = 1.0000 - 0.03700t + 0.000591t^2 - 3.533(10^{-6})t^3$$

from which

$$-r = \frac{dC}{dt} = -0.03700 + 0.001773t - 10.599(10^{-6})t^2$$

POLYMATH multilinear regression handles the rate equation in linearized form,

$$\ln r = a - b/T + q \ln(C/C_0)$$

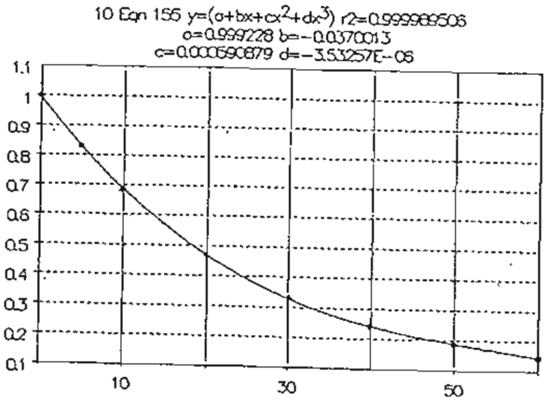
The result may be written

$$r = (C/C_0)^{1.3884} \exp(1.0475 - \frac{1508.4}{T})$$

The graph shows good agreement between original and regressed values of r.

An alternative, less reliable solution could be found by taking three widely spaced points and solving the linear equations by Gaussian elimination.

t	T	C/C_0	-r
0	350	1	0.03700
5	356	0.828	0.03135
10	360	0.684	0.02624
20	368	0.467	0.01760
30	374	0.327	0.01108
40	378	0.239	0.00678
50	380	0.183	0.00440
60	381.5	0.144	0.00424

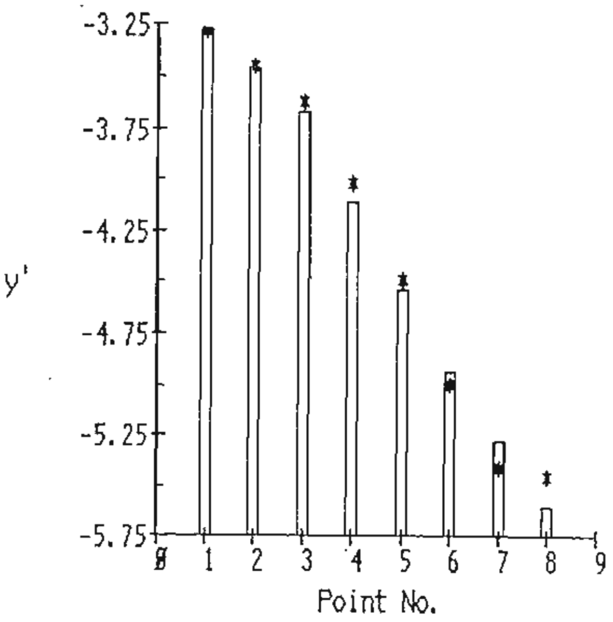


```
Regression Data                                   Page 1 of 1
  Point  x1               x2               y
    1    350              1                .037
    2    356              .828             .0314
    3    360              .684             .0263
    4    368              .467             .0176
    5    374              .327             .01108
    6    378              .239             .00668
    7    380              .183             .0044
    8    381.5            .144             .00424
```

```
Transformed Data                                  Page 1 of 1
  Point  x1'              x2'              y'
    1    2.857×10^-3      0.0              -3.2968
    2    2.809×10^-3      -0.1887          -3.4610
    3    2.778×10^-3      -0.3798          -3.6382
    4    2.717×10^-3      -0.7614          -4.0399
    5    2.674×10^-3      -1.1178          -4.5026
    6    2.646×10^-3      -1.4313          -5.0086
    7    2.632×10^-3      -1.6983          -5.4262
    8    2.621×10^-3      -1.9379          -5.4632
```

The functions: y'=ln(y)
x1'=1/x1
x2'=ln(x2)

The correlation is:
y'= 1.0475-1508.4×x1'+ 1.3884×x2'



P3.06.14. ACTIVATION ENERGY AND HALF LIFE

The half life of a first order reaction was measured at several temperatures. What is the activation energy?

T, °C	20	30	50	60
$t_{1/2}$, min	426	102	10.1	2.76

$$k = \frac{\ln 2}{t_{1/2}}$$

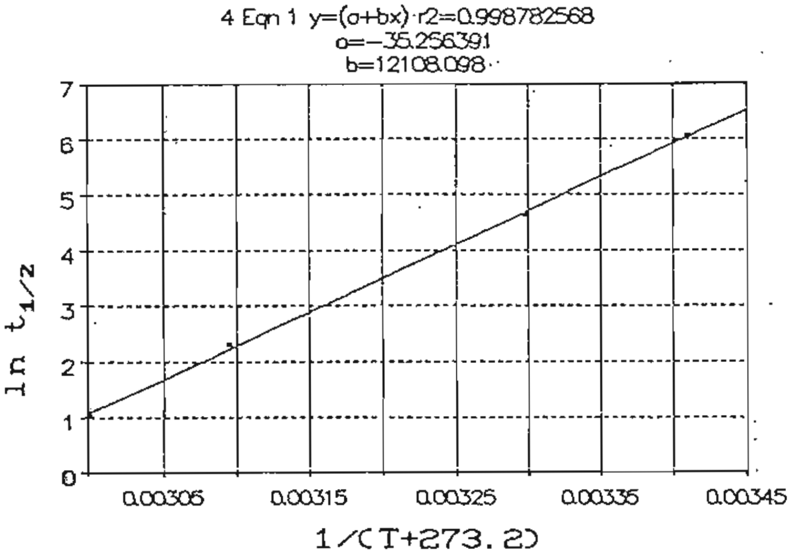
$$\ln \frac{0.693}{t_{1/2}} = A - \frac{E}{RT}$$

The plot of $\ln t_{1/2}$ agains $1/T$ is straight, with slope

$$E/R = 12108$$

making the activation energy

$$E = 12108(1.987) = 24058 \text{ cal/gmol}$$



P3.06.15. VARIABLE PRE-EXPONENTIAL FACTOR

The gas phase reaction between nitric oxide and oxygen is third order. Data of temperature °K and specific rate in cc $\text{mol}^{-1}\text{s}^{-1}$ are

T	80	143	288	300	413	564
$10^{-9}k$	41.8	20.23	10.1	7.1	4.0	2.8

The behavior is interpreted in terms of a variable pre-exponential coefficient, making

$$k = AT^m \exp(-E/RT)$$

Find the constants a, m and E.

Use POLYMATH multilinear regression with the equation in the form,

$$\ln k = \ln A + m \ln T - \frac{E}{R}\left(\frac{1}{T}\right)$$

This equation is simplified by taking k = 7.1 when T = 300, thus eliminating the term in A,

$$\ln (k/7.1) = m \ln(T/300) - \frac{E}{R}\left(\frac{1}{T} - \frac{1}{300}\right)$$

$$= -1.6132 \ln(T/300) - 39.51\left(\frac{1}{T} - \frac{1}{300}\right)$$

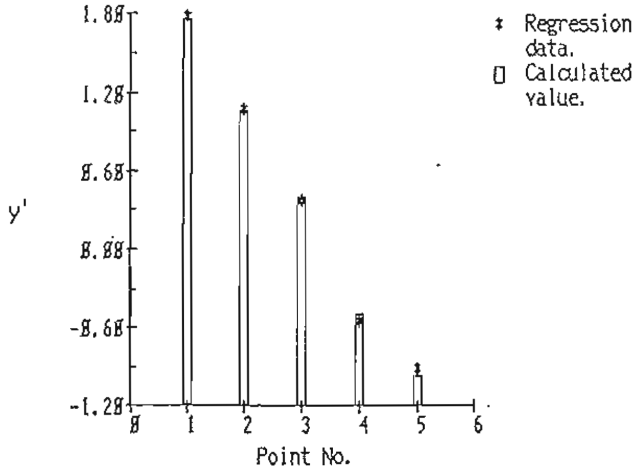
or

$$\ln k = 11.29 - 1.6132 \ln T - 39.51/T$$

or

$$k = 8.00(10^4)\ T^{-1.6132} \exp(-39.51/T)$$

The POLYMATH graph indicates a good fit of the data.



P3.06.16. A NON-ARRHENIUS RELATION

For the decomposition of hydrogen iodide in the range 550-750 K, Bodenstein represented the temperature dependence of the specific rate by

$$k = -\frac{11966}{T} + 15.865 \ln T - 94.5 \qquad (1)$$

This also can be written

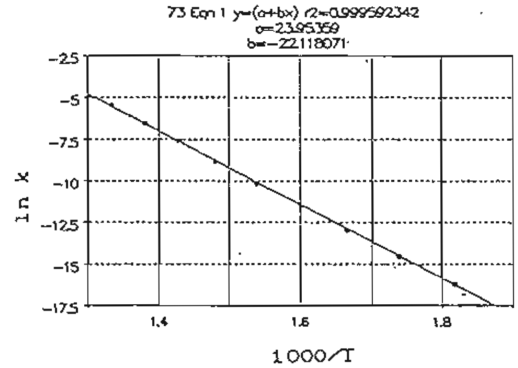
$$k = 0.91(10^{-41})\, T^{15.865} \exp(-\frac{11966}{T}) \qquad (2)$$

When values of k are calculated from Eq (1), they can be related by the Arrhenius equation as

$$k = \exp(23.95\text{-}22118/T) = 2.52(10^{10}) \exp(-22118/T)$$

The graph is of this relationship.

Quite widely different equations with several constants apparently can represent the same data if the constants are found by different methods.



P3.06.17. ENERGY OF ACTIVATION

The energy of activation, E, occurs in the Arrhenius equation which occurs in several forms:

$$k = k_0 \exp(-E/RT) = \exp(A-E/RT)$$

$$\ln k = \ln k_0 - \frac{E}{R}(\frac{1}{T})$$

When the temperature is °K and R = 1.987, the units of E are cal/gmol; when R = 8.320, E is in joules/gmol, etc.

The energies of activation will be found from the following data.

(a) For the hydrolysis of ethyl m-nitrobenzoate by hydroxyl ions in aqueous solution (Newling & Hinshelwood, J Chem Soc p 1357, 1936), the units of k are liter $\text{mol}^{-1}\text{s}^{-1}$.

°C	0.1	15.2	24.9	39.9
100k,	2.31	8.00	17.15	48.8

(b) The first order specific rate for the pyrolysis of trimethyl bismuth (Price & Trotman-Dickenson, Trans Faraday Soc 54 1630, 1958):

°C	370	375	380	385	390	395	400
k, 1/s	0.113	0.145	0.190	0.250	0.325	0.410	0.525

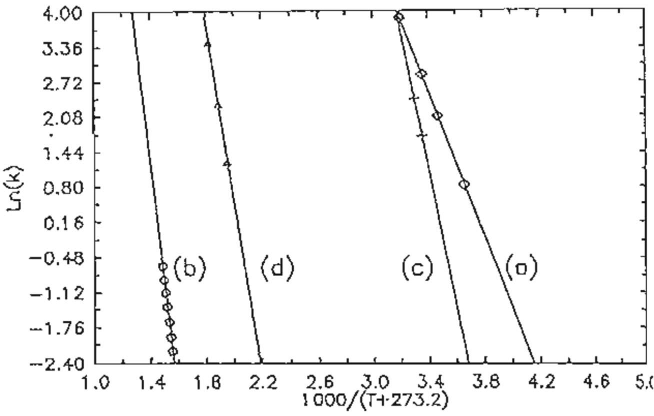
(c) The racemization specific rates of D-tris (1,10-phenanthroline) nickel iodide in 0.08% aqueous solution have been found to be $5.583(10^{-6})$ sec^{-1} and $1.117(10^{-5})$ sec^{-1} at 25 C and 30 C respectively (Davies & Dwyer, Trans Faraday Soc 48 244, 1952).

(d) For the racemization of d-$C_2H_5.CH(CH_3).I$, specific rates were found by Ogg & Polanyi (Trans Faraday Soc 31 482, 1935).

°C	238.0	255.5	276.0
k, 1/s	0.0353	0.101	0.314

Plots are made of ln k against 1/T. The multiples of k that are used are shown in the table summarizing the results.

Case	k multiple	A	-B	E, cal/gmol
a	10^2	24.83	6559	13032
b	1	32.29	22170	44052
c	10^6	43.77	12541	24919
d	10^2	32.85	16145	32080



P3.06.18. A COMPLEX REACTION

In the mechanism

$$A + B \underset{2}{\overset{1}{\Leftrightarrow}} C, \quad C \overset{3}{\Rightarrow} B + D$$

substance C is very reactive and reaches steady state with

$$\frac{dC}{dt} = k_1AB - k_2C - k_3C = 0$$

$$C = \frac{k_1}{k_2+k_3} AB$$

Therefore,

$$-\frac{dA}{dt} = k_1AB - k_2C = k_1(1 - \frac{k_2}{k_2+k_3})AB = \frac{k_1k_3}{k_2+k_3} AB = k_4AB$$

These numerical values are given:

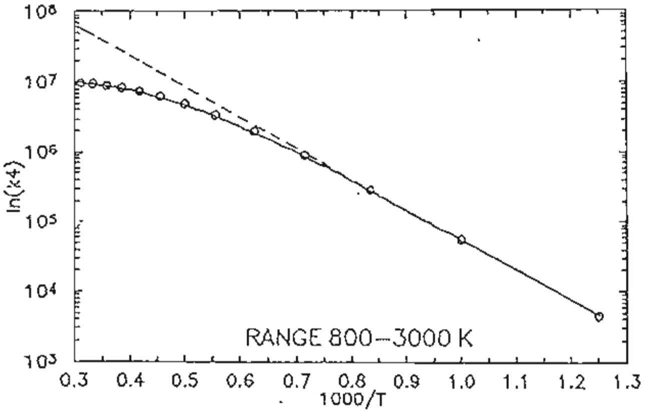
$$k_1 = 10^{11}\exp(-10000/T) \quad \text{cc/mol sec}$$

$$k_2 = 10^{15}\exp(-40000/T) \quad 1/\text{sec}$$

$$k_3 = 10^{13}\exp(-30000/T) \quad 1/\text{sec}$$

$$k_4 = \frac{10^{11}\exp(-10000/T)\,\exp(-30000/T)}{10^{2}\exp(-40000/T) + \exp(-30000/T)}$$

The Arrhenius plot of this composite reaction is not straight over the range 800-3000 K. E/R varies from about 10000 to nearly zero at the left where the plot is nearly horizontal.



P3.06.19. ACETONE DECOMPOSITION BY A CHAIN REACTION

In problem P2.03.24 it is shown that the decomposition of acetone is the result of a chain of five reactions with a net rate equation

$$-\frac{dC}{dt} = \sqrt{k_1k_3k_4/k_5}\; C$$

The activation energies of the individual reactions are, in kcal/gmol: E_1 = 84, E_2 = 10, E_3 = 15, E_4 = 48, and E_5 = 8. What is the overall activation energy?

With the Arrhenius equation,

$$\ln k = 0.5[(A_1+A_3+A_4-A_5) - \frac{1}{RT}(E_1+E_3+E_4-E_5)]$$

Accordingly the overall activation energy is

$$E = 0.5(84+15+48-8) = 69.5 \text{ kcal/gmol}$$

P3.06.20. TETRAHYDROFURAN DECOMPOSITION

Determine the rate equation for the decomposition of tetrahydrofuran with the aid of the tabulated data of initial pressure, half life and temperature.

Try the rate equation

$$-\frac{dp}{dt} = kp^q = \exp(A-B/T)\ p^q$$

From problem P3.05.01 the half life relation is

$$t_{1/2} = \frac{2^{q-1}-1}{k(q-1)}\left(\frac{1}{P_0}\right)^{q-1} = \frac{\beta}{kP_0^{q-1}}$$

Treat the linearized form by POLYMATH multilinear regression,

$$\ln t_{1/2} = \ln \beta - A + \frac{B}{T} -(q-1)\ln P_0$$

$$= -25.625 + \frac{26329}{T} -0.5545 \ln P_0$$

$q = 1.5545$

$B = 26329$

$$\ln \beta - A = \ln \frac{2^{q-1}-1}{q-1} - A = -25.625$$

$A = 0.29+25.625 = 25.915$

and the final form of the rate equation is

$$-\frac{dp}{dt} = \exp(25.915-\frac{26329}{T})\ p^{1.5545}$$

P_0, torr	$t_{1/2}$, min	°C
214	14.5	569
204	67	530
280	17.3	560
130	39	550
206	47	539

P3.06.21. VARIATION OF ACTIVATION ENERGY

Experiment shows that the primary reaction in the homogeneous decomposition of nitrous oxide proceeds with stoichiometry

$N_2O \Rightarrow N_2 + 0.5\ O_2$

and rate equation

$$-r = \frac{k_1[N_2O]^2}{1+k_2[N_2O]}$$

where

$k_1 = \exp(44.65-81800/RT)$

$k_2 = \exp(20.01-28400/RT)$

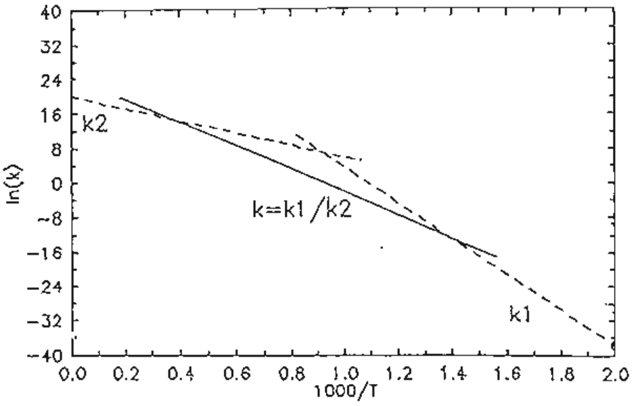
$k_1/k_2 = \exp(24.64-53400/T)$

Plot these values of specific rates and interpret the variation of activation energy over the temperature range 500 to 1000 K.

Some numerical values are

°K	k_1	k_2
500		$2.27(10^{-4})$
600	$6.1(10^{-11})$	0.0258
700		0.786
800	$1.54(10^{-5})$	9.58
900		68.8
1000	42.4	333

At low temperatures, $k_2[N_2O] << 1$ and $E \Rightarrow 81800$. At high temperatures, $k_2[N_2O] >> 1$ and $E \Rightarrow E_1 - E_2 = 53400$.



P3.06.22. HYDROXYLAMINE

In a study of the autoxidation of hydroxylamine (Hughes et al, J Chem Soc A 3485, 1971) the specific rate was found to have the following temperature dependence,

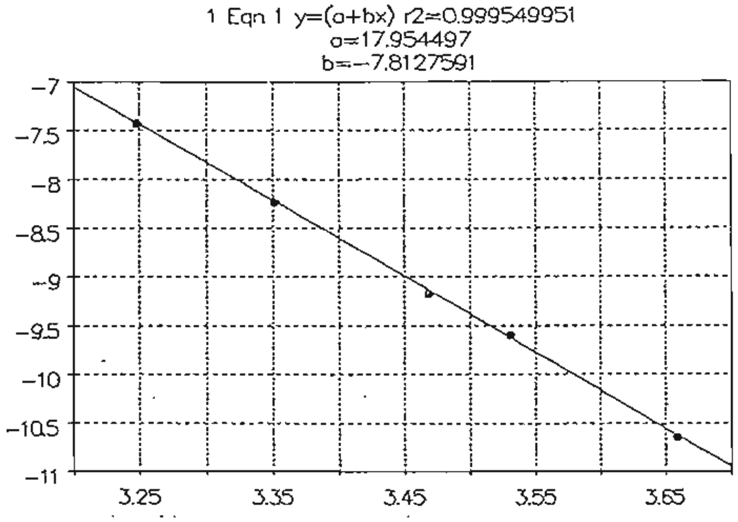
°C	0	10	15	25	34.5
10^4k, 1/s	0.237	0.680	1.02	2.64	5.90

The linearized plot has the equation

$$\ln k = 17.95 - \frac{7813}{T+273.2}$$

so the activation energy is

$$E = 7813\,R_g = 15.524 \text{ kcal/gmol, } 64.8 \text{ kJ/gmol}$$



P3.07.01. DIAZOACETIC ESTER

The specific rate of the hydrolysis of diazoacetic ester

$N_2CHCOOC_2H_5 + H_2O \Rightarrow HOCH_2COOC_2H_5 + N_2$

varies with the hydrogen ion concentration as follows:

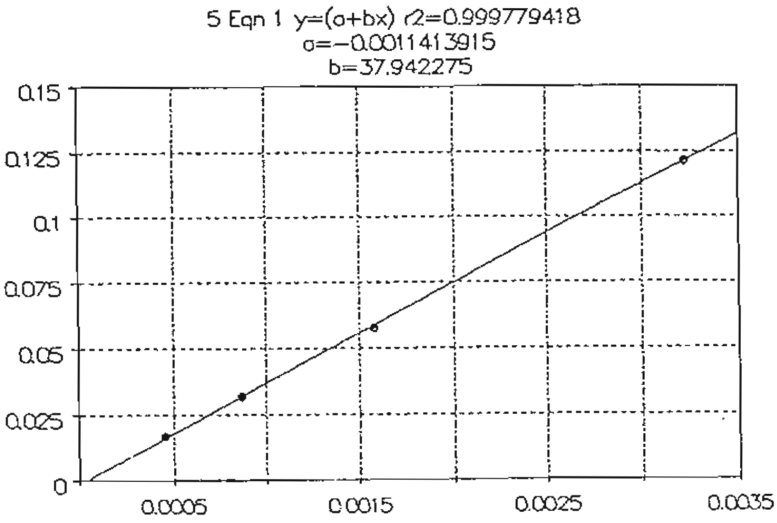
$10^3[H_3O^+]$ mols/liter	0.46	0.87	1.58	3.23
k, liter/mol sec	0.0168	0.0320	0.0578	0.1218

Find the order with respect to the catalyst.

The plot of k against the hydrogen ion concentration is linear, with virtually zero intercept. Thus, first order with

$$k = 37.9[H_3O^+]^{1.00}$$

The overall k depends also on the concentrations of the reactants, but information about their effects is not available in this problem.



P3.07.02. NITRAMIDE DECOMPOSITION

The decomposition of nitramide in aqueous solution

$H_2NNO_2 \Rightarrow NO_2 + H_2O$

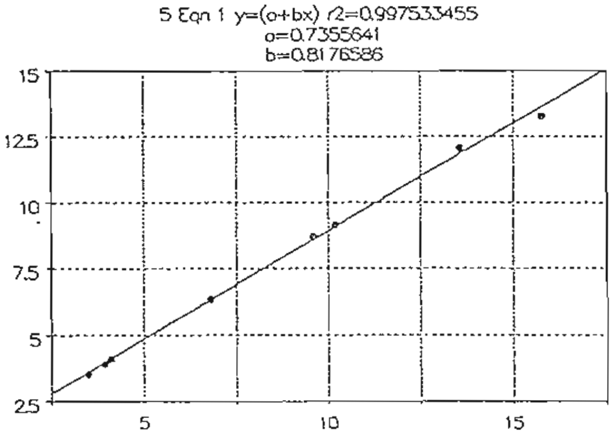
is first order in nitramide but is catalyzed by acetate ion. The tabulated data are cited by Laidler (Reaction Kinetics, volume two, 1963). Formulate the dependence of k on the acetate ion concentration.

The data are plotted and are represented by the equation

$$10^5 k = 0.736 + 0.818(10^3)[CH_3COO^-]$$

The number 0.736 is the specific rate of the uncatalyzed reaction.

$10^3[CH_3COO^-]$	10^5k, 1/s
3.55	3.53
3.97	3.90
4.14	4.10
6.83	6.35
9.61	8.76
10.20	9.20
13.60	12.1
15.80	13.3



P3.07.03. GLUCOSE MUTAROTATION

The following results refer to the mutarotation of glucose in aqueous hydrochloric acid solutions at 20 C:

10^3[HCl], mol/liter	20.05	40.25	60.20	80.26
10^4k, 1/sec	3.841	5.090	6.616	7.854

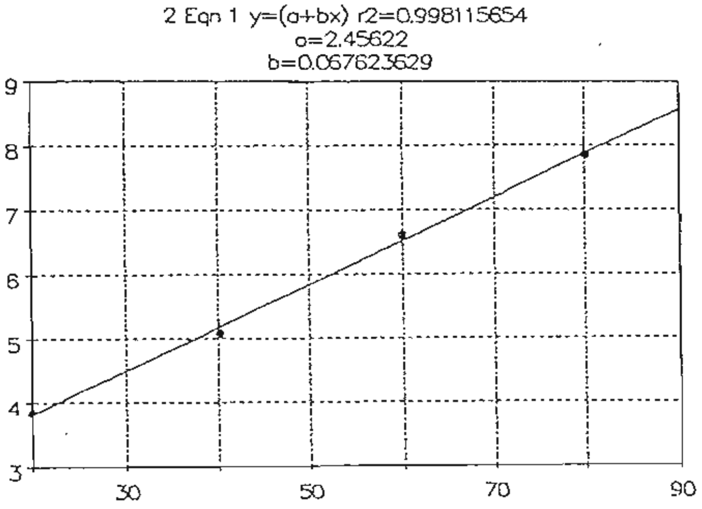
Find the catalytic coefficient for the hydrogen ions and the specific rate of the uncatalyzed reaction.

The plot of k against [HCl] is linear, with equation,

$$10^4k = 2.456 + 0.0676(10^3)[HCl]$$

The second constant on the right is called the catalytic coefficient. The specific rate of the uncatalyzed reaction is

$$k = 2.456(10^{-4}),\ 1/sec$$



P3.07.04. GLUCOSE DECOMPOSITION

The following data were obtained for the decomposition of 0.056 mol/liter glucose at 140 C at various concentrations of HCl catalyst:

10^3k, 1/h	3.66	5.80	8.18	10.76
$[H_2O^+]$, mol/liter	0.0108	0.0197	0.0295	0.0394

Find the catalytic coefficient.

The data are plotted two ways and both appear to give acceptable linear behavior in the experimental range, with equations,

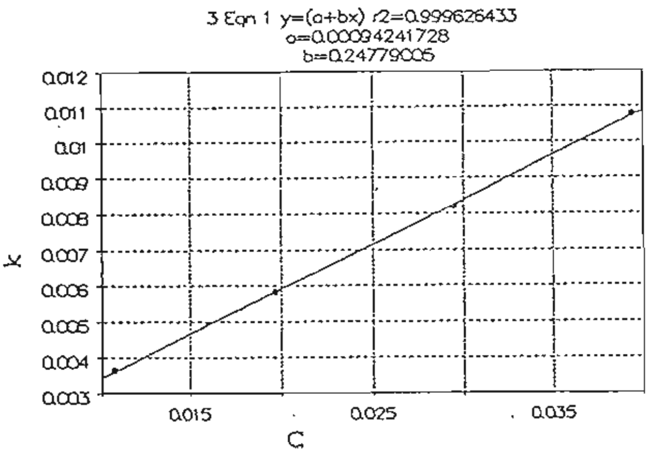
$$k_1 = 0.00094 + 0.238[H_3O^+]$$

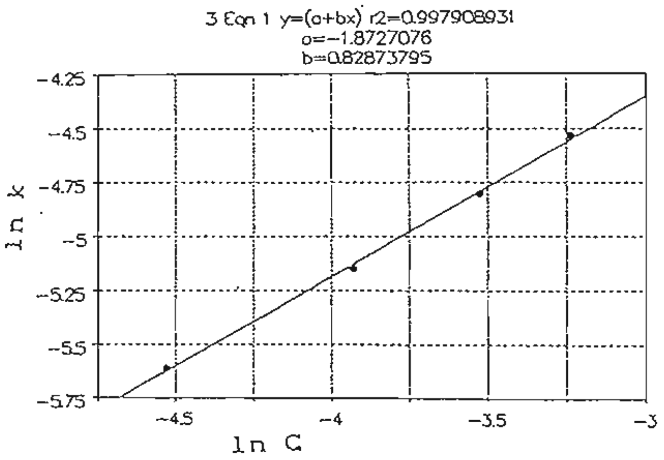
$$\ln k_2 = -1.8727 + 0.8287 \ln[H_3O^+]$$

or

$$k_2 = 0.1537\ [H_3O^+]$$

However, k_2 predicts zero rate at zero concentration of hydrogen ion which is not correct.





P3.07.05. ORDER WITH RESPECT TO CATALYST

The irreversible decomposition of a reagent A in solution is catalyzed by a material B. The time of half completion of the batch reaction was determined by varying the initial concentrations of A and B. From the results estimate the reaction orders with respect to A and B and the specific rate.

$$A + B(\text{catalyst}) \Rightarrow \text{Products}$$

$$-\frac{dA}{dt} = kA^aB^b$$

During reaction the amount of B does not change. Integrating,

$$kB^bt = \frac{1}{a-1}(A^{1-a} - A_0^{1-a})$$

When A + 0.5 A_0,

$$kB^bt_{1/2} = \frac{2^{a-1}-1}{(a-1)}A_0^{1-a} \qquad (1)$$

Accordingly

$$t_{1/2}A_0^{a-1}B^b = \text{Constant}$$

Take the points in pairs.

$$17(1)^{a-1}(0.001)^b = 8.5(2)^{a-1}(0.004)^b$$

$$12(1)^{a-1}(0.002)^b = 9.8(2)^{a-1}(0.003)^b$$

$$b = 0.5$$

Similarly for the other pair. Also,

$$17(1)^{a-1}(0.001)^{0.5} = 8.5(2)^{a-1}(0.004)^{0.5}$$

$$12(1)^{a-1}(0.002)^{0.5} = 9.8(2)^{a-1}(0.003)^{0.5}$$

$$a = 1.0$$

For first order, Eq (1) becomes

$$k = \frac{\ln 2}{B^{0.5}t_{1/2}} \qquad (2)$$

The four values calculated from this equation are recorded in the fourth column of the data table.

A_0	B_0	t	k
1.0	0.001	17.0	1.289
1.0	0.002	12.0	1.292
2.0	0.003	9.8	1.291
2.0	0.004	8.5	1.289

P3.07.06. OXIDATION OF CARBON MONOXIDE

Catalytic oxidation of carbon monoxide was studied at constant volume at 300 C and initial pressure of 204 torr. Data of time against drop in total pressure (Prettre & Claudel, 26, 1970) are tabulated. They are fitted to a cubic polynomial,

$$P = 204.03 - 1.211t + 0.0121t^2 - 4.384(10^{-5})t^3$$

and differentiated to give r = dP/dt. Then r is curve fitted by

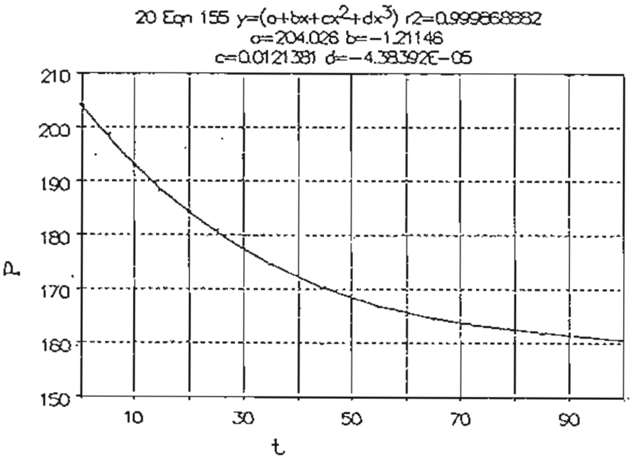
$$r = 5.534 - 877.4/P = \frac{-887.4 + 5.534P}{P}$$

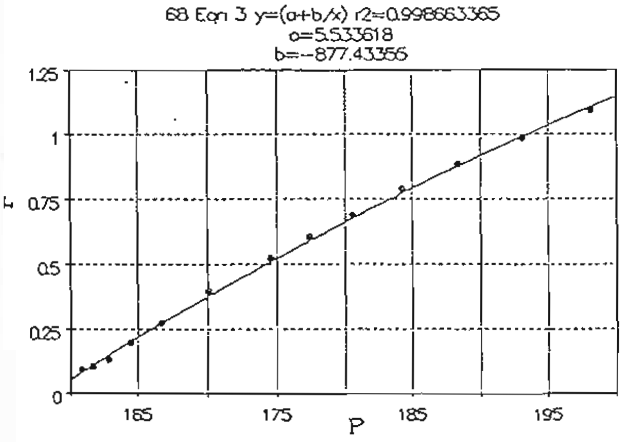
The possible applicability of a power law, $r = kP^q$, is checked in the third figure. The very poor linear fit is represented by

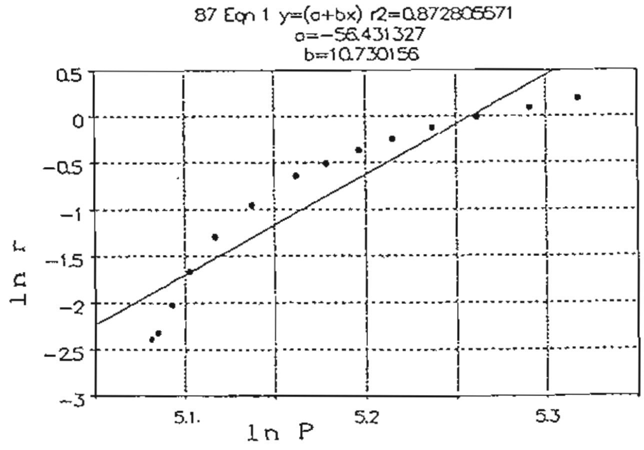
$$\ln(-r) = -56.43 + 10.730 \ln P, \quad \text{or } r = -3.11(10^{-25})P^{10.7}$$

Prettre & Claudel say q = 0.8, but do not give the coefficient.

t	$-\Delta P$	$-r$
0	0	1.211
5	5.4	1.093
10	11.1	0.982
15	15.8	0.877
20	19.9	0.779
25	23.2	0.687
30	26.5	0.602
35	29.4	0.523
45	33.7	0.385
55	37.2	0.274
65	39.5	0.189
75	41.1	0.131
85	42.3	0.098
95	43.0	0.092







P3.07.07. AN AUTOCATALYTIC REACTION

A reaction, $2A \Rightarrow B + C$, proceeds with the formation of a short lived intermediate, P, according to the sequence,

$$2A \overset{1}{\Rightarrow} B+C, \quad A + B \overset{2}{\Rightarrow} P, \quad 2P \overset{3}{\Rightarrow} 3B + C$$

The steady state hypothesis for P gives

$$\frac{dP}{dt} = k_2AB - 0.5k_3P^2 = 0$$

whence

$$P^2 = (2k_2/k_3)AB$$

Then the rate of formation of component C becomes

$$\frac{dC}{dt} = k_1A^2 + k_3P^2 = k_1A^2 + 2k_2AB \qquad (1)$$

Since the rate increases as the amount of product B goes up, this is an instance of an autocatalytic reaction. A typical plot of an autocatalytic rate as a function of product concentration has a maximum.

Some data of the rate as a function of the concentration of C are represented by the graph, when starting with pure reactant $A_0 = 3$. Two points off this curve are

$$(C, r) = (0.24, 6.50), (1.12, 5.00)$$

After application of stoichiometric balances, Eq (1) becomes

$$r = k_1(3 - 2C)^2 = 2k_2(3-2C)C$$

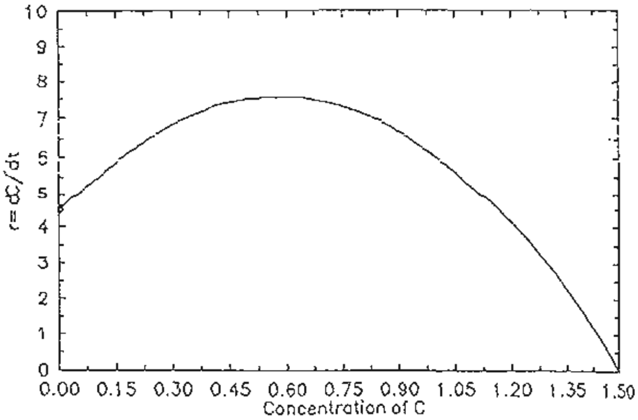
Substituting numbers,

$$6.5 = k_1(3-0.48)^2 + 2k_2(3-0.24)(0.24)$$

$$5.0 = k_1(3-2.24)^2 + 2k_2(3-1.12)(1.12)$$

from which

$k_1 = 0.496$, $k_2 = 2.769$



P3.07.08. CATALYSIS OF SEBACIC ACID

The reaction between dibasic acids and alcohols is catalyzed by hydrogen ions,

$$-\frac{d[COOH]}{dt} = k[H^+][COOH][OH]$$

The hydrogen ion concentration also is necessarily in accordance with the ionization constant of the dibasic acid.

Consider the tabulated data on the reaction between sebacic acid and 1,6-hexandiol at 170 C with equimolar quantitites $C_0 = 6.2418$ gmol/kg (Tang & Yao, Int Chem Eng 2 39, 1962). Find the overall order of the reaction and the rate equation.

Ionic equilibrium of the dibasic acid,

$$[H^+] = K^{1/2}[COOH]^{1/2}$$

The rate of reaction is

$$-\frac{d[COOH]}{dt} = k[H^+][COOH][OH] = kK^{1/2}[COOH]^{3/2}[OH]$$

Let

$$C = C_0(1-x)$$

so with equimolal concentrations initially,

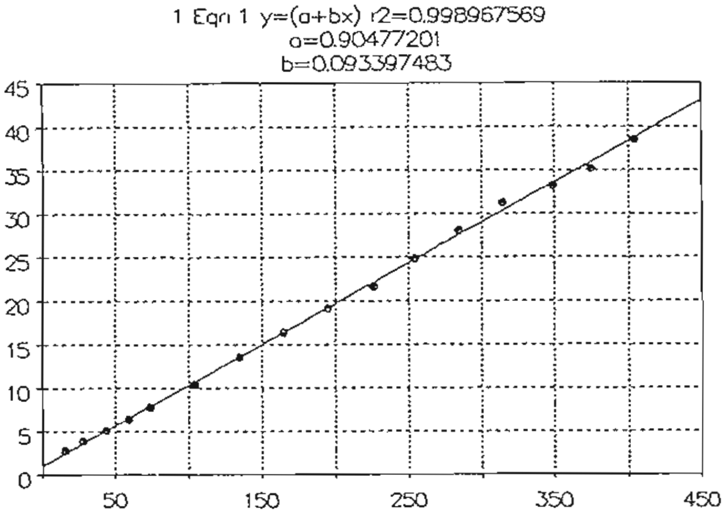
$$\frac{dx}{dt} = kK^{1/2}C_0^{5/2}(1-x)^{5/2}$$

The integral is

$$kK^{5/2}C_0^{5/2}t = \int_0^x (1-x)^{-5/2}dx = (1-x)^{-3/2} + 1$$

The plot is of $y = (1-x)^{-3/2}$ against t. Its linearity confirms the assumed mechanism. The overall order is 5/2.

t, min	x
18	0.4839
30	0.5928
45	0.6658
60	0.7085
75	0.7435
105	0.7902
135	0.8235
165	0.8438
195	0.8605
225	0.8713
255	0.8826
285	0.8921
315	0.8993
346	0.9033
375	0.9070
405	0.9122



P3.07.09. AUTOCATALYTIC REACTION

The gas phase reaction, A ⇒ B + D, is catalyzed by the reaction product. The rate equation is

$$r_a = kC_aC_d^{0.5}$$

Initially, $A_0 = 0.5$ mols, $B_0 = 0$ and $D_0 = 0.05$. The reaction is run at constant pressure and temperature. Given the data of the first two columns beteen the rate and the fractional conversion, confirm that the assumed rate equation is correct. Also check if the plot of rate against concentration has the peak that is characteristic of many autocatalytic reactions.

$$D = A_0+D_0-A = = 0.55 - A$$

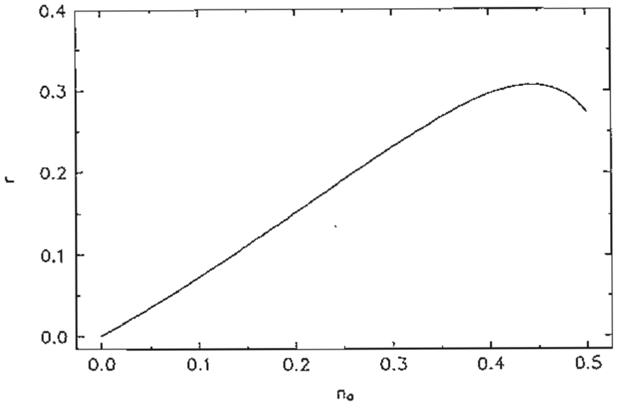
$$V = \frac{n_tRT}{P} = \frac{RT}{P}(1.05 - A)$$

$$r = k(\frac{A}{V})(\frac{D}{V})^{0.5} = k(\frac{P}{RT})^{1.5}\frac{A(0.55-A)^{0.5}}{(1.05-A)^{1.5}} = k'y$$

$$y = \frac{A(0.55-A)^{0.5}}{(1.05-A)^{1.5}}$$

The value of r/y is calculated and recorded in the last column of the table. Since it is nearly constant, the assumed rate equation is confirmed. The plot of r against the amount of reactant is drawn and does display a peak value.

x	r	A	y	r/y
0	0.86	0.5	0.860	1.00
0.2	0.30	0.4	0.298	1.01
0.4	0.23	0.3	0.231	0.995
0.6	0.15	0.2	0.152	0.985
0.8	0.072	0.1	0.0727	0.990
0.9	0.035	0.05	0.0353	0.992



P3.07.10. AUTOCATALYTIC AND NON CATALYTIC

An autocatalytic reaction may be able to proceed in the absence of the catalyst. In some cases the catalytic product may be removed as it forms, by distillation, extraction, precipitation, or some other means. The process, A ⇒ B + P, may have the rate equation

$$r = k_0A(1 + k_1P) = k_0A[1+k_1(A_0-A)] \qquad (1)$$

Given the tabulated data of time and concentration, find the constants of this rate equation. Note that $A_0 = 1$.

The tabulated data are curve fitted as

$$A = 0.9986 - 0.6951t + 0.1927t^2 - 0.0203t^3 \qquad (2)$$

from which the derivative is

$$r = dA/dt = -0.6951 + 0.3854t - 0.0609t^2 \qquad (3)$$

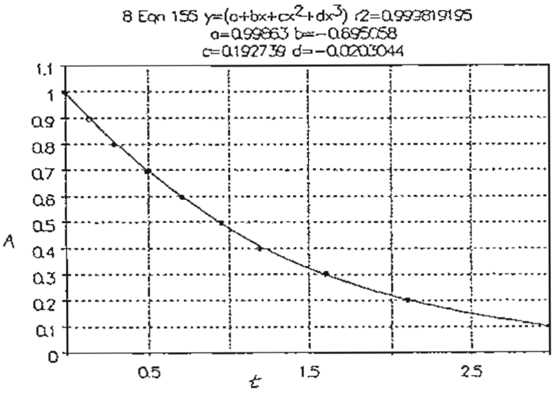
From the linearized plot,

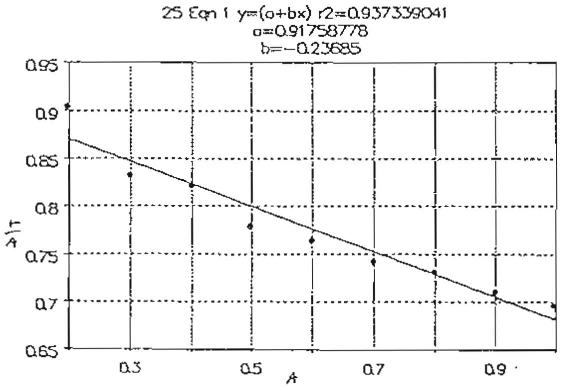
$$y = r/A = k_0(1+k_1A_0) - k_0k_1A$$
$$= 0.9176 - 0.2369\ A$$

Finallly

$$r = A(0.9176 - 0.2369A) = A[0.9176 - 0.2369(1-P)]$$
$$= 0.6807\ A(1 + 0.3480P)$$

t	A	-r	-r/A
0	1	0.6951	0.6951
0.15	.9	0.6388	0.7098
0.30	.8	0.5855	0.731
0.50	.7	0.5191	0.741
0.70	.6	0.4581	0.763
0.95	.5	0.3893	0.778
1.2	.4	0.3290	0.822
1.6	.3	0.2497	0.832
2.1	.2	0.1808	0.903
3.0	.1	0.1410	1.41





P3.07.11. TOLUENE CHLORINATION.

The chlorination of toluene at 17 C is catalyzed by acids.

$C_6H_5CH_3 + Cl_2 \Rightarrow ClC_6H_4CH_3 + HCl$

Case (a). With a catalyst concentration, $[CF_2ClCOOH] = 0.117$ mol/liter, the data of first table were obtained. Determine the order with respect to chlorine.

Case (b). Determine the order with respect to catalyst from the data of the second table.

Case (c). In toluene with CCl_3COOH as the catalyst data were obtained at 6 C and 32 C. Determine the order with respect to catalyst at each temperature. What are the possible causes of the difference?

(a) The values of

$$k = \frac{1}{t} \ln \frac{0.0775}{C} = 0.1060, \text{ mean value.}$$

are tabulated and confirm first order.

(b) The loglog plot is

$\ln k = \ln k_0 + q \ln \ln C_{cat}$ $1.3115 + 1.635 \ln C_{cat}$

$k = 3.712C_{cat}^{1.635}$

(c) The log log plots for the two temperatures are on the second figure. The order is 1.15 at 6 C and 1.57 at 32 C. The mechanism probably involves several steps that are affected in different ways by temperature.

Case (a)

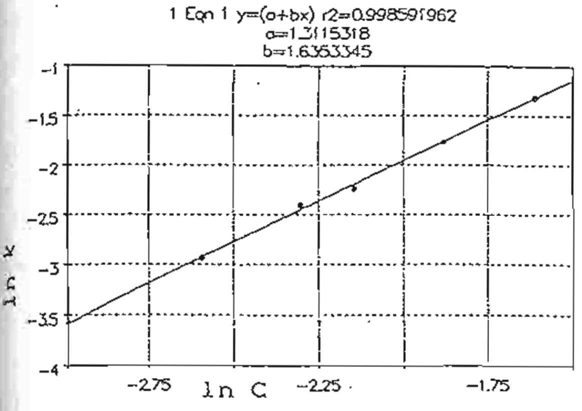
t	$[Cl_2]$	k
0	0.0775	
3	0.0565	0.1053
6	0.0410	0.1061
10	0.0265	0.1073
14	0.0175	0.1063
20	0.0095	0.1049
25	0.0055	0.1058

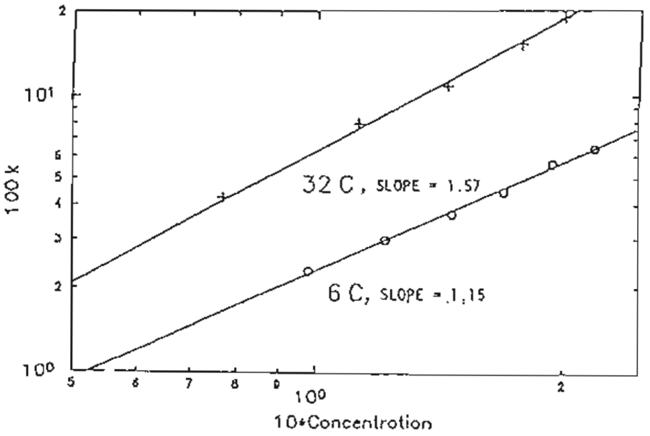
Case (b)

[cat]	k, 1/min
0.050	0.0278
0.075	0.0530
0.100	0.090
0.117	0.1060
0.153	0.172
0.200	0.270

Case (c)

[cat]	k_6			[cat]	k_{32}
0.098	0.023			0.0485	0.0195
0.122	0.030			0.077	0.0425
0.147	0.0372			0.113	0.0795
0.170	0.0448			0.145	0.109
0.195	0.0565			0.178	0.153
0.220	0.0645			0.200	0.190





P3.07.12. AUTOCATALYTIC HYDROLYSIS OF METHYL ACETATE

The hydrolysis of methyl acetate (A) is catalyzed by the reaction product acetic acid (B). In one experiment, when the initial concentration of acetate was 0.5 and that of the acid was 0.05 gmol/liter, 60% conversion was attained in one hour. Find the time at which the reaction velocity became a maximum and the value of this maximum.

Neglect the slight variation in the amount of water and incorporate its initial concentration in the proportionality constant. The rate of the reaction is postulated to be

$$r_a = -\frac{dA}{dt} = k'[H_2O]AB = kAB = kA(0.55-A)$$

$$kt = -\int_o^A \frac{dA}{A(0.55-A)} = \frac{1}{0.55}\ln\frac{10(0.55-A)}{A}$$

At 60% conversion, $t = 1$, $A = 0.4A_0 = 0.4(0.5) = 0.2$

$$k = \frac{1}{0.55}\ln\frac{10(0.35)}{0.55} = 5.204$$

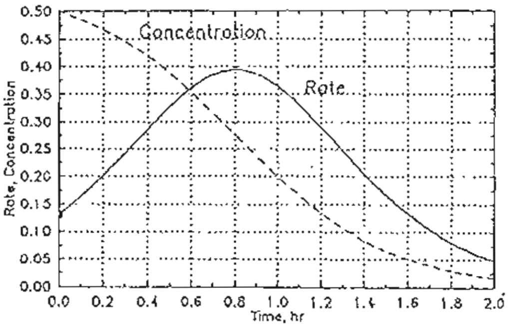
At the maximum rate,

$$\frac{dr_a}{dt} = k(0.55 - 2A) = 0$$

$$A = 0.275$$

$$t = \frac{1}{0.55(5.204)}\ln\frac{10(0.275)}{0.275} = 0.805 \text{ hr}$$

The rate and concentration profiles are drawn.



P3.07.13. GAS PHASE AUTOCATALYSIS

The gas phase reaction, $A \Rightarrow B + C$, is catalyzed by the reaction product C, with a rate proportional to the concentration of A and to the square root of the concentration of C. Initial concentrations are $A_0 = 0.5$, $B_0 = 0$ and $C_0 = 0.05$. With the tabulated data of fractional conversion and rate, find a rate equation.

$$n_c = n_{a0}+n_{c0}-n_a = 0.55-n_a$$
$$n_t = n_{t0}+n_{a0}-n_a = 1.05-n_a$$
$$V = n_tRT/\pi = (1.05-n_a)RT/\pi$$

$$r_a = kC_aC_b^{1/2} = \frac{k}{V^{3/2}}n_an_b^{1/2} = k(\frac{\pi}{RT})^{3/2}\frac{n_a(0.55-n_a)^{1/2}}{(1.05-n_a)^{3/2}}$$

The values of $k' = k(\pi/RT)^{3/2}$ are calculated and tabulated. Their mean value is 1.01.

x	r_a	n_a	k'
0	0.86	0.5	1.00
0.2	0.30	0.4	1.01
0.4	0.23	0.3	0.995
0.6	0.15	0.2	0.985
0.8	0.07	0.1	0.963
0.9	0.04	0.02	1.13

P3.08.01. SUGAR HYDROLYSIS WITH YEAST

Cane sugar is hydrolyzed by the action of yeast. The tabulated data are of concentration, mol/liter, and rate of inversion, polarimeter degrees/min. Find the constants of the rate equation

$$r = \frac{k_1C}{1+k_2C}$$

using these three linearized forms

$$\frac{C}{r} = \frac{1}{k_1} + \frac{k_2}{k_1}C \qquad (1)$$

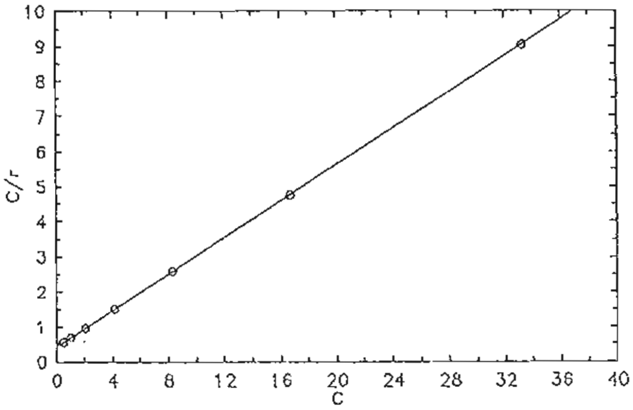
$$\frac{r}{C} = \frac{k_1}{k_2} - \frac{r}{k_2} \qquad (2)$$

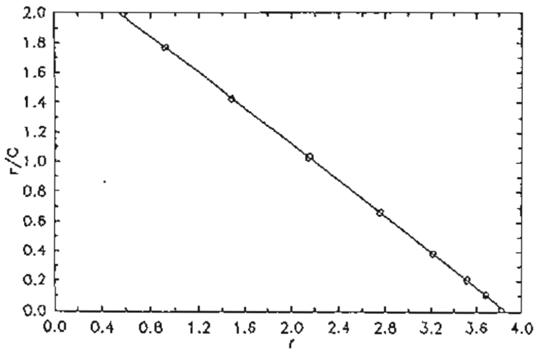
$$\frac{1}{r} = \frac{1}{k_1}\left(\frac{1}{C}\right) + \frac{k_2}{k_1} \qquad (3)$$

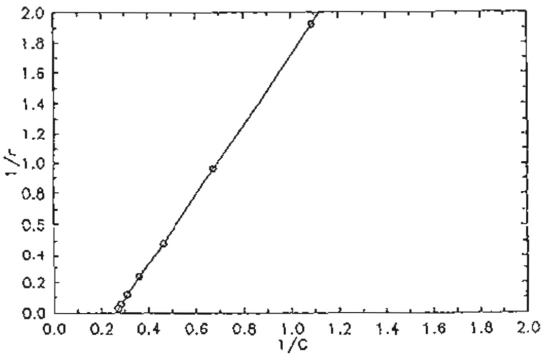
The plots are all made with 100 r. They are all linear and give the same result,

$$r = \frac{2.317C}{1 + 59.88C}$$

C	100r
0.0052	0.919
0.0104	1.485
0.0208	2.15
0.0416	2.76
0.0833	3.22
0.167	3.52
0.333	3.685







P3.08.02. INHIBITION OF YEAST GROWTH BY SULFANILAMIDE

Data were obtained on the rate of absorption of oxygen by yeast, r_1 without sulfanilamide and r_2 with 20 mg/ml of added sulfanilamide. Oxygen partial pressure is in torr, the rates are microliters of oxygen per hour per mg of cells. Find the constants of the rate equations of the two cases.

Assume $r = k_1p/(1+k_2p)$ or in linearized form,

$$\frac{1}{r} = \frac{1}{k_1}\left(\frac{1}{p}\right) + \frac{k_2}{k_1}$$

$= 0.02 + 0.0188/P,$ with SA

$0.02 + 0.0110/P,$ without SA

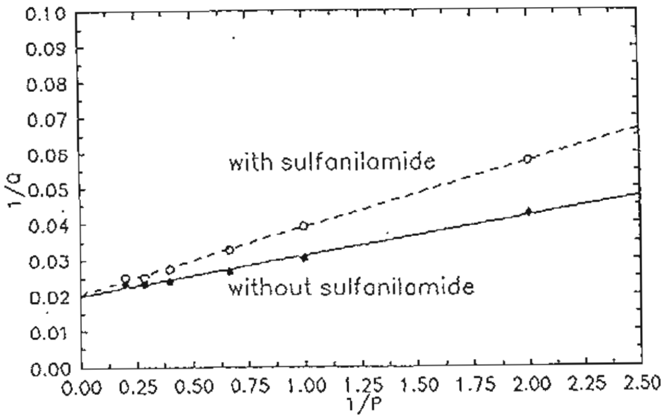
$k_1 = 1/0.0188 = 53.2,$ with SA

$1/0.0110 = 90.9,$ without SA

$k_2 = 0.02k_1 = 1.064,$ with SA

$1.818,$ without SA

p	r_1	r_2
0	0	0
0.5	23.5	17.4
1.0	33.0	25.6
1.5	37.5	30.8
2.5	42.0	36.4
3.5	43.0	39.6
5.0	43.0	40.0



P3.08.03. ENZYMATIC DECOMPOSITION OF UREA

The rate of enzymatic decompostion of urea, $\text{kmol/m}^3\text{-hr}$, is given in terms of the concentration, kmol/m^3. Find the constants of the Michaelis-Menten equation.

The data are plotted as

$$\frac{1}{r} = \frac{1}{k_1} + \frac{k_2}{k_1 C}$$

$$= 0.7550 + \frac{0.02072}{C}$$

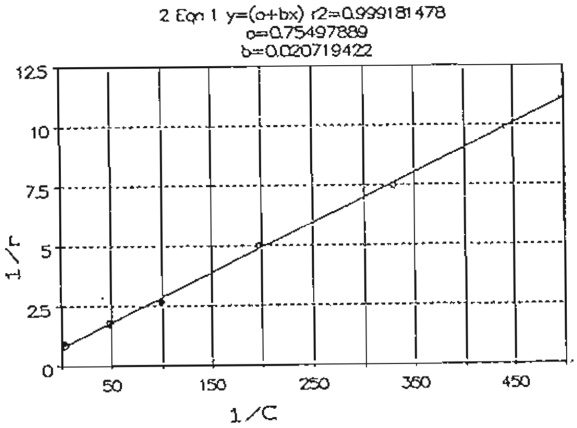
whence

$k_1 = 1.325,\ k_2 = 0.0274$

and

$$r = \frac{1.325C}{1 + 0.0274C}$$

C	-r
0.20	1.08
0.02	0.55
0.01	0.38
0.005	0.20
0.002	0.09



P3.08.04. ENZYME HYDROLYSIS WITH INHIBITION

The enzyme pepsinase catalyzes the hydrolysis of the substrate (S) carbobenzoxy-L-tyrosine to yield L-tyrosine and a second product (P) carbobenzoxy-L-glutamic acid:

$$E + S \underset{2}{\overset{1}{\Leftrightarrow}} ES \overset{3}{\Rightarrow} E + P + \text{L-tyrosine}$$

The hydrolysis rate is measured manometrically by decarboxylating the L-tyrosine produced. The product P competes for the enzyme, thus inhibiting the hydrolysis reaction:

$$E + P \overset{4}{\underset{5}{\rightleftharpoons}} EP$$

The rate equation is expected to be

$$r = \frac{k_aS}{1+k_bP+k_cS}$$

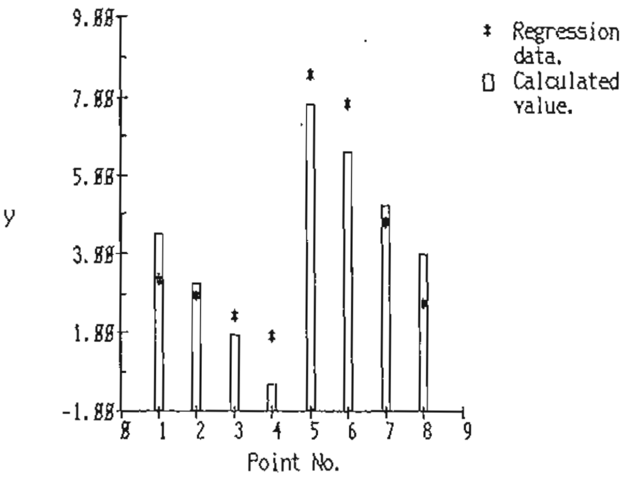
In linearized form,

$$\frac{1}{r} = \frac{k_c}{k_{a1}} + \frac{k_b}{k_a}P + \frac{1}{k_a}\left(\frac{1}{S}\right)$$

$$= -0.00959 + 0.001096P + \frac{0.2184}{S}$$

or

$$r = \frac{4.579\ S}{1 + 0.00502\ P - 0.0439\ S}$$



The numbers are obtained by POLYMATH multilinear regression. The plot indicates only poor fit of the data. The negative constant in the denominator also casts doubt on the correlation.

Point	S	P	r
1	4.7	0	43.4
2	6.5	0	52.6
3	10.8	0	71.3
4	30.3	0	111.1
5	4.7	30.3	13.3
6	6.5	30.3	14.7
7	10.8	30.3	26.6
8	30.3	30.3	58.1

P3.08.05. HYDROLYSIS OF METHYL HYDROCINNAMATE

Hydrolysis of methyl hydrocinnamate is catalyzed by the enzyme chymotripsin. Data were obtained at 25 C with pH k7.6 and a constant enzyme concentration. These are of initial reaction rate, mol/liter-sec, and corresponding initial substrate concentrations. Find the Michaelis-Menten constants.

Take the first and last points and solve the linearized equations simultaneously and compare with linear regression of all the points

$$r_0 = \frac{kC_0}{k_m+C_0}$$

By linear regression,

$$\frac{C_0}{r_0} = k_m/k + C_0/k$$

$$= 0.2016 + 0.0483\ C_0$$

$$k = 20.70,\ k_m = 3.88$$

By TABLECURVE plotting, shown here, the constants are slightly different.

By simultaneous solution,

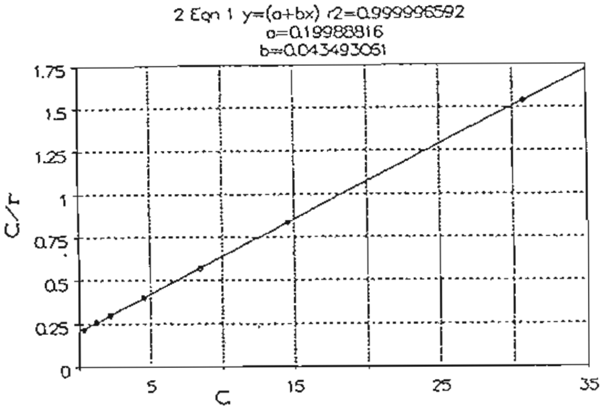
$$14.6/17.5 = k_m/k + 14.6/k$$

$$2.24/7.5 = k_m/k + 2.24/k$$

$$k_m/k = 0.2016,\ 1/k = 0.0433,\ k = 23.09,\ k_m = 4.66.$$

The agreement is not good.

10^3C_0	10^8r_0	$10^5C_0/r_0$
30.8	20	1.54
14.6	17.5	0.834
8.57	15.0	0.571
4.6	11.5	0.40
2.24	7.5	0.299
1.28	5.0	0.256
0.32	1.5	0.213



P3.08.06. EADIE'S PLOT OF THE M-M EQUATION

The tabulated data of initial rates and concentrations were obtained for enzyme conversion of a substrate at 37 C, pH 6.5.

Eadie (J Biol Chem 146 85, 1942) rearranges the M-M equation.

$$r = \frac{kC}{k_m + C}$$

becomes

$$\frac{r}{C} = \frac{k}{k_m} - \frac{r}{k_m}$$

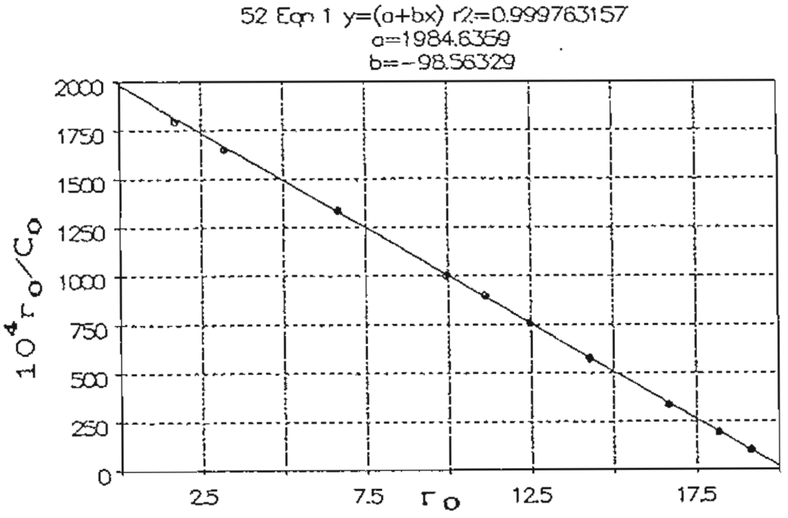
The plot of the data is

$$\frac{10^4 r_0}{C_0} = 1984.6 - 98.56\ r_0$$

from which

$$r_0 = \frac{20.14 C_0}{101.5 + C_0}$$

C_0	r_0
5	19.2
10	18.2
20	16.7
40	14.3
60	12.5
80	11.2
100	10.0
200	6.7
500	3.3
1000	1.8



P3.08.07. SUCROSE HYDROLYSIS. TIME-CONCENTRATION DATA

Sucrose hydrolysis is catalyzed by an enzyme. Time- concentration data are given in the first two columns. The applicability of the M-M equation, r = kC/(M+C), is to be checked.

Method (a). Integrate the equation,

$$kt = \int_C^{C_0} (1+M/C)dC = C_0 - C + M\ \ln(C_0/C) \qquad (1)$$

The plot is made of the linearized form,

$$\frac{t}{C_0 - C} = \frac{1}{k} + \frac{M}{k} \frac{\ln(C_0/C)}{C_0 - C}$$

$$= 5.03 + 0.99 \frac{\ln(C_0/C)}{C_0-C} \qquad (2)$$

whence

$$k = 0.1988,\ M = 4.98 \qquad (3)$$

Method (b). The (C,t) data are fitted by a fourth degree polynomial on the second graph, from which the derivative is

$$-r \approx dC/dt = -\ 0.1383 - 0.0241t + 0.0080t^2 - 0.00043t^3 \quad (4)$$

The rate equation is rearranged and plotted on the third graph as

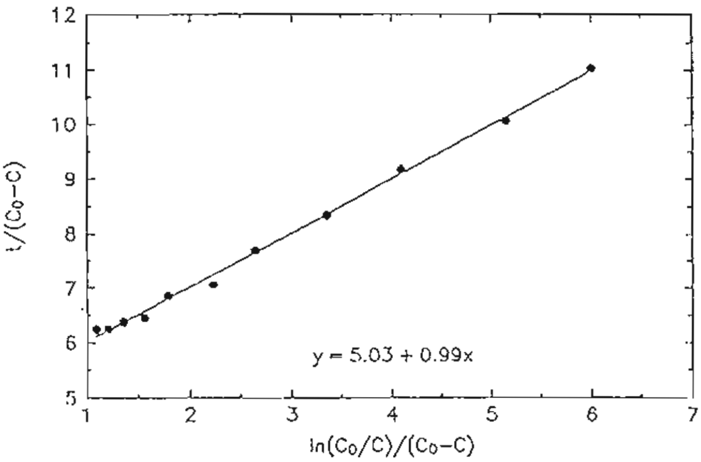
$$\frac{C}{r} = \frac{M}{k} + (\frac{1}{k})C = 0.72 + 5.73\ C \qquad (5)$$

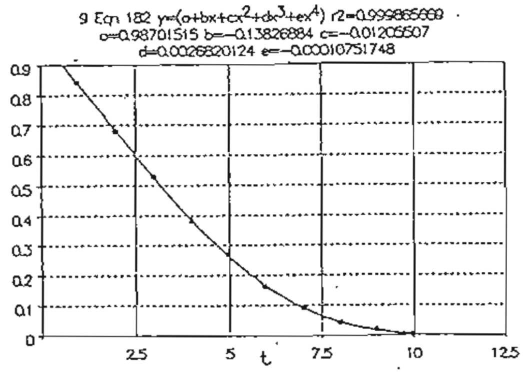
whence

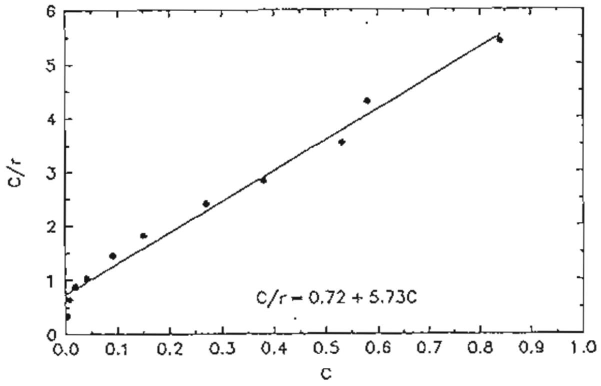
$$k = 0.1745,\ M = 4.126 \qquad (6)$$

The agreement between lines (3) and (6) is not particularly good.

t	C	$\frac{t}{1-C}$	$\frac{\ln(1/C)}{1-C}$	-r	C/r
0	1			0.1383	
1	0.84	6.25	1.090	0.1548	5.426
2	0.68	6.25	1.205	0.1579	4.307
3	0.53	6.383	1.351	0.1502	3.529
4	0.38	6.452	1.561	0.1342	2.832
5	0.27	6.849	1.794	0.1126	2.400
6	0.15	7.059	2.232	0.0878	1.822
7	0.09	7.692	2.646	0.0625	1.440
8	0.04	8.333	3.353	0.0393	1.018
9	0.018	9.165	4.091	0.0207	0.870
10	0.006	10.06	5.147	0.0093	0.645
11	0.0025	11.03	6.007	0.0077	0.325







P3.08.08. BIOCHEMICAL RATE DATA

Find the constants of the rate equation

$$r = k_1C/(1+k_2C)$$

given these data:

C	1.5	0.8
1/r	3.889	5.833

Set up the simultaneous equations,

$$3.889 = k_2/k_1 + 1/1.5k_1$$
$$5.833 = k_2/k_1 + 1/0.8k_1$$
$$k_1 = \frac{1.25-0.667}{5.833-3.889} = 0.300$$
$$k_2 = 3.889k_1 - 1/1.5 = 0.500$$

so that

$$r = \frac{0.3C}{1+0.5C}$$

P3.08.09. AMMONIA DECOMPOSITION ON TUNGSTEN

Measurements of total pressure, torr, at various times, seconds, were made for the decomposition of ammonia on a tungsten wire at 856 C. The rate equation is to be found.

$$2\ NH_3 \Rightarrow N_2 + 3\ H_2$$
$$\pi = n_tRT/V = (2n_{a0}-n_a)RT/V$$
$$n_a = 2n_{a0} - \pi V/RT = (2\pi_0-\pi)RT/V$$

Assume a power law rate equation,

$$-\frac{1}{V}\frac{dn_a}{dt} = k(n_a/V)^q$$

$$\frac{1}{RT}\frac{d\pi}{dt} = \frac{k}{(RT)^q}(2\pi_0-\pi)^q \tag{1}$$

Second order,

$$\frac{k_2}{RT} = \frac{1}{t-200}\left(\frac{1}{456-\pi} - \frac{1}{228}\right) \tag{2}$$

First order,

$$k_1 = \frac{1}{t-200}\ln\frac{228}{456-\pi} \tag{3}$$

Zero order,

$$k_0RT = \frac{1}{t-200}(\pi - 228) \tag{4}$$

These values are tabulated and show the reaction to be of zero order. This indicates that at these pressures the surface is always saturated with ammonia. Experiments at lower pressure indicate that the surface is not saturated, and a different rate mechanism applies.

t	π	$10^6k_2/RT$	10^4k_1	k_0RT
200	228			
400	250	2.34	5.07	0.1100
600	273	2.70	5.50	0.1125
1000	318	3.58	6.28	0.1125

P3.08.10. AMMONIA DECOMPOSITION ON QUARTZ.

Measurements were made of the decomposition of ammonia on quartz at two temperatures (Hinshelwood & Burk, J Chem Soc 127 1105, 1925). Find the order of the reaction and the activation energy.

The half time relation is

$$t_{1/2} = \frac{2^{q-1}-1}{k(q-1)P_0^{q-1}},\quad q / 1$$

Take the pairs of points:

$43/44 = (137.5/53.5)^{q-1}$, $q = 0.9783$ at 1267 K

$196/191 = (298/117)^{q-1}$, $q = 1.0276$ at 1220 K

The order appears to be unity. The specific rates are

$k = \ln(2)/t_{1/2} = 0.693/43.5 = 0.01593$ at 1267 K

$0.693/193.5 = 0.00358$ at 1220 K

The activation energy is

$$\frac{E}{R} = \ln(k_2/k_1)/(\frac{1}{T_1} - \frac{1}{T_2}) = \ln\frac{0.00358}{0.001593} / (\frac{1}{1220} - \frac{1}{1267})$$

$$= 49078$$

P3.08.11. AMMONIA DECOMPOSITION. TWO DIFFERENT INITIAL PRESSURES.

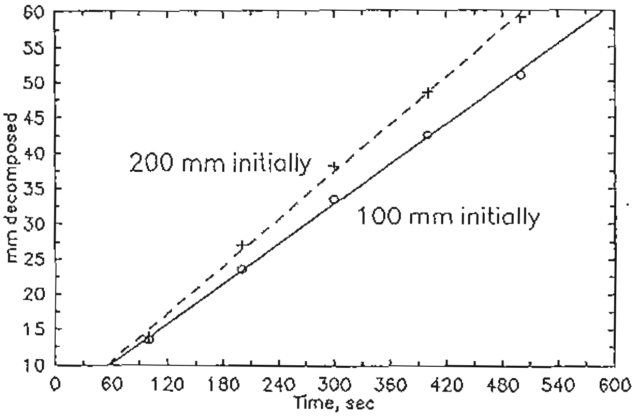
Data were taken of the decomposition of ammonia on a tungsten wire at 856 C with two different starting pressures (Hinshelwood & Burk, J Chem Soc 127 1105, 1925). Time is tabulated against the change in partial pressure, torr. Find the order of the reaction.

The plots are practically linear and show that the rates are constant. Consequently the order of reaction is zero at both initial pressures. If a Langmuir-Hinshelwood rate equation,

$$r = \frac{k_1P}{1+k_2P}$$

were tried, it would be found that $k_2P >> 1$ and r would be constant.

t, sec	Δp $p_0=100$	Δp $p_0=200$
100	13.5	14.0
200	23.5	27.0
300	33.5	38.0
400	42.5	48.5
500	51.0	59.0



P3.08.12. ETHYL CHLORIDE FORMATION

For the formation of ethyl chloride using a catalyst of zirconium oxide on silica gel in the presence of inert methane, data were taken of the rate, lbmol/(h)(lb catalyst), and partial pressures of the participants in atm. Temperature was 350 F. The equilibrium constant is 35.

$C_2H_4 + HCl \Leftrightarrow C_2H_5Cl$

The controlling mechanism is surface reaction between adsorbed ethylene and adsorbed HCl. Find the rate equation.

A = ethylene, B = HCl, C = ethylchloride, D = methane.

The controlling mechanism is

$A\sigma + B\sigma \Leftrightarrow C\sigma + \sigma$

and the rate equation is

$$r = k(\vartheta_a\vartheta_b - \vartheta_c/K_e) = k\vartheta_v^2(p_ap_b - p_c/K_e)$$
$$= \frac{k(p_ap_b - p_c/K_e)}{(1+k_ap_a+k_bp_b+k_cp_c+k_dp_d)^2}$$

In linear form,

$$y = \left(\frac{p_ap_b-p_c/35}{r}\right)^{1/2} = (1+k_ap_a+k_bp_b+k_cp_c+k_dp_d)/\sqrt{k}$$
$$= ap_a + bp_b + cP_c + dp_d + e \qquad (1)$$

There are 5 unknowns and 5 sets of data. Solution of the linear system by Gaussian elimination gives the values of the coefficients as

$a = 13.293$, $b = 16.449$, $c = 16.709$, $d = 0.9766$, $e = 0.4451$.

10^4r	p_a	p_b	p_c	p_d	y
2.71	0.300	0.370	0.149	7.005	19.85
2.63	0.416	0.215	0.102	7.090	18.14
2.44	0.343	0.289	0.181	7.001	19.62
2.58	0.511	0.489	0.334	9.889	30.52
2.69	0.420	0.460	0.175	10.169	26.45

P3.08.13. METHANE FROM ETHANE

Data have been obtained for the rate of the heterogeneous reaction with catalyst of nickel on silica at 191 C (Yates et al, JACS 86 2996,1964):

$C_2H_6 + H_2 \Leftrightarrow 2\ CH_4$

The problem is to find the constants of a proposed rate equation,

$$r = kp_{Et}^m p_{H_2}^n$$

The partial pressures are in atm. r_0 is the rate when the two partial pressures are 0.03 and 0.2 respectively.

The linearized rate equation is

$$\ln(r/r_0) = \ln k + m \ln p_{Et} + n \ln p_{H_2} \qquad (1)$$

The constants could be found by multilinear regression. In this case, however, the special nature of the data permits solution by simultaneous equations. Thus

$$\ln(r/r_0) - \ln(1) = m \ln(p_{Et}/0.03) + n \ln(p_{H_2}/0.20) \qquad (2)$$

Substitute the data.

$\ln 3.1 = n \ln(0.1/0.2)$

$\ln 0.2 = n \ln(0.4/0.2)$

$n = \ln(3.1/0.2)/\ln(0.25) = -1.9771$, say -2.0

$\ln(0.29) - \ln(2.82) = m[\ln(0.01/0.03) - \ln(0.10/0.03)]$

$m = 0.9909$, say 1.0

The values of k/r_0 are calculated at each of the 5 data points from

$$k/r_0 = (r/r_0)/p_{Et}p_{H_2}^{-2}$$

These values are recorded in the table, but they are not all quite the same.

POLYMATH multilinear regression gives $m = 0.9898$, $n = -1.9771$, and $k/r_0 = 0.879$.

r/r_0	p_{Et}	p_{H_2}	k/r_0
3.10	0.03	0.10	1.033
1.00	0.03	0.20	1.333
0.20	0.03	0.40	1.067
0.29	0.01	0.20	1.160
2.84	0.10	0.20	1.136

P3.08.14. ETHYLENE OXIDE

Ethylene can be oxidized to ethylene oxide over a silver-alumina catalyst. Experimental data were obtained at 260 C and atmospheric pressure (Wan, Ind Eng Chem 45 234, 1951). Selected data are tabulated. Inlet composition was 80% ethylene (A) and 20% oxygen (B). Evaluate the constants of the rate equation

$$r = kp_a^m p_b^n$$

The stoichiometric equation is

$C_2H_4 + 0.5\ O_2 \Rightarrow C_2H_4O$

x = fraction converted to oxide.

$$p_a = \frac{n_a x}{n_t} = \frac{1-x}{1.25-0.5x}$$

$$p_b = \frac{0.25-0.5x}{1.25-0.5x}$$

$$p_c = 1 - p_a - p_b$$

These partial pressures are recorded.

The POLYMATH multilinear regression is

$$\ln r = \ln k + m \ln p_a + n \ln p_b$$
$$= 54.356 - 151.83 \ln p_a + 58.174 \ln p_b$$

or

$$r = 4.04(10^{23})\ p_a^{-151.83} p_b^{58.174} \qquad (1)$$

The POLYMATH graph show the fit to be good, but the large values of the constants do not seem to have physical significance.

Wan, in the paper cited, states

$$r = 0.0141\ p_a^{0.316}\ p_b^{0.677} \qquad (2)$$

which appears plausible, but the fit to the data is not as good as Eq (1).

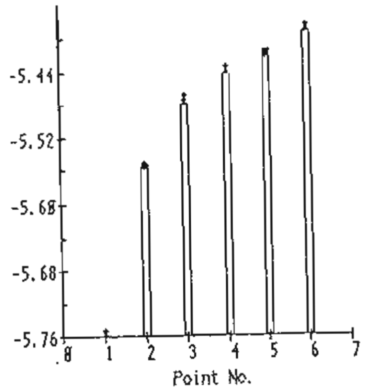
Two Langmuir-Hinshelwood type equations also were tried.

$$y = p_a p_b/r = 172 - 238p_a + 265\ p_b + 122\ p_c \qquad (3)$$

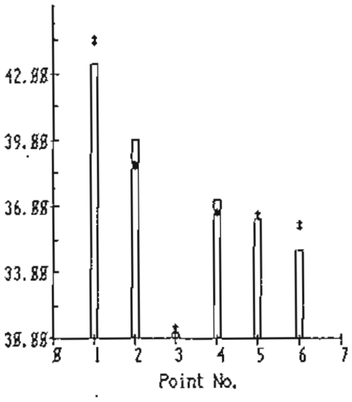
$$y = (p_a p_b/r)^{1/2} = 17.2 - 19.9p_a + 22.5p_b + 9.8p_c \qquad (4)$$

The graphs show that these fits are not as good as Eq (1). Moreover one of the constants is negative in each case, which rules out a plausible mechanism.

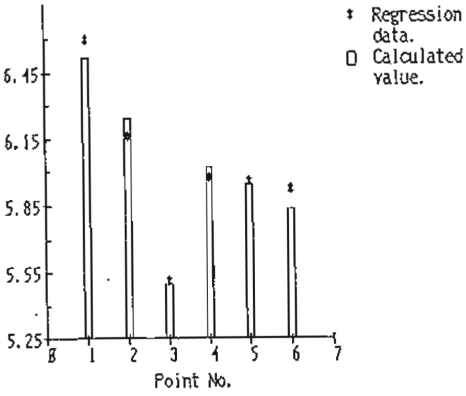
x	$10^3 r$	p_a	p_b	p_c
0.065	3.16	0.76796	0.17864	0.0534
0.0392	3.87	0.78088	0.18725	0.0319
0.0258	4.20	0.78748	0.19165	0.0286
0.0177	4.34	0.79144	0.19430	0.0143
0.00902	4.42	0.79564	0.19710	0.00742
0	4.57	0.8	0.2	0



Eq (1).



Eq (3).



Eq (4).

P3.08.15. PHOSGENE OVER CARBON CATALYST

Rate data of the reaction for the synthesis of phosgene, $CO + Cl_2 \Rightarrow COCl_2$, over activated carbon are given. Although a Langmuir-Hinshelwood mechanism may be preferred, a power law rate is asked for.

$$r = k\{CO\}^a[Cl_2]^b[COCl_2]^c$$

or in linear form

$$\ln r = \ln k + a \ln[CO] + b \ln[Cl_2] + c \ln[COCl_2]$$

POLYMATH multilinear regression gives

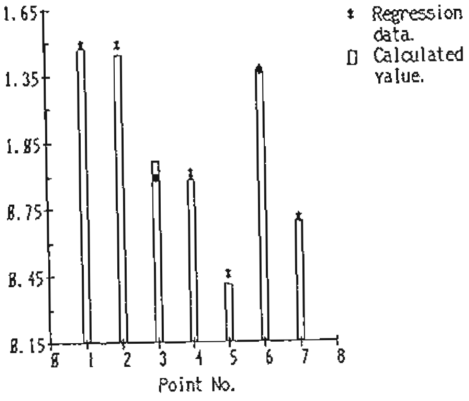
$$\ln (1000r) = 2.9702 + 1.3311 \ln[CO] + 0.5771 \ln[Cl_2] - 0.1871 \ln [COCl_2]$$

$$r = 0.0195 [CO]^{1.3311}[Cl_2]^{0.5771}[COCl_2]^{-0.1871}$$

The quality of the fit is indicated by the graph. By some other linear regression procedure, Carberry (1976) finds

$$r = 0.00356[CO]^{0.619}[Cl_2]^{0.277}[COCl_2]^{-0.683}$$

which seems to represent the data equally well.



$10^3 r$	p_{CO}	p_{Cl_2}	p_{COCl_2}
4.41	0.406	0.352	0.226
4.40	0.396	0.363	0.231
2.41	0.31	0.32	0.356
2.45	0.287	0.333	0.376
1.57	0.253	0.218	0.522
3.90	0.61	0.113	0.231
2.00	0.179	0.608	0.206

P3.08.16. HYDROGENATION OF ACETONE AND CYCLOHEXENE

Concurrent hydrogenation of acetone (A) and cyclohexene (B) in cyclohexane occurs with Raney nickel catalyst at 25 . Catalyst concentration was 2 g/liter and the product compositions also are in g/liter. Determine the orders and relate the amounts of the reactants.

[acetone]	91.5	76.5	69.5	63.8	42.8	27.8	11.0
[cyclohexane]	95	70	59	49	27	10	2

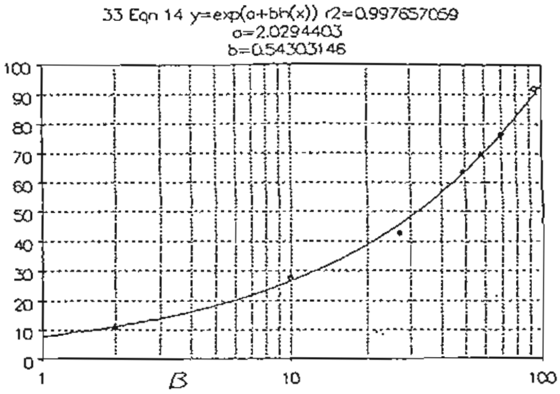
Assume the rate equations,

$$-\frac{dA}{dt} = k_a[H_2]A^a$$

$$-\frac{dB}{dt} = k_b[H_2]B^b$$

and

$$\frac{dA}{dB} = \frac{k_aA^a}{k_bB^b} \qquad (1)$$



The plot of (A, B) is well fitted by the equation

$$\ln A = 2.029 + 0.543,\ \ln B$$

from which

$$\frac{dA}{dB} = 0.543\,\frac{A}{B} \qquad (2)$$

Comparison of lines (1) and (2) reveals that

$$a = b = 1 \text{ and } k_a/k_b = 0.543$$

and that

$$A = 7.6055\ B^{0.543}$$

P3.08.17. NICKEL AMMONIUM CHLORIDE DECOMPOSITION. ZERO ORDER

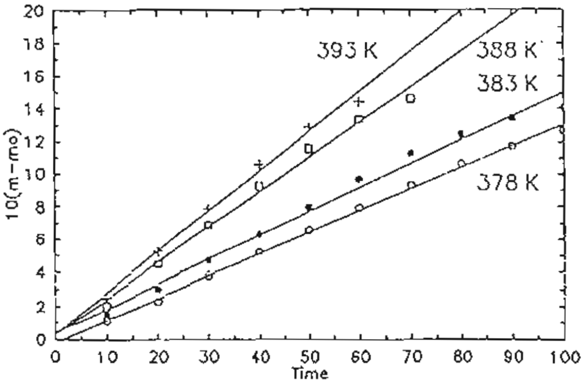
The thermal decomposition of nickel ammonium chloride powder,

$$[Ni(NH_3)_4]Cl_2 \Rightarrow [Ni(NH_3)_2]Cl_2 + 2NH_3$$

with particle size 0.75 - 0.06 mm diameter, was studied in a gas stream of flow rate 8-9 liters/hr with the tabulated results for an initial weight of 0.5 g.

WEIGHT LOSS IN GM. AT

Time in min.	378°*K*	383°*K*	388°*K*	393°*K*	398°*K*
10	0·0112	0·0148	0·0204	0·0249	0·0325
20	0·0231	0·0299	0·0447	0·0521	0·0690
30	0·0375	0·0471	0·0685	0·0787	0·1052
40	0·0520	0·0629	0·0926	0·1060	0·1350
50	0·0654	0·0799	0·1155	0·1288	0·1440
60	0·0793	0·0967	0·1332	0·1443	
70	0·0932	0·1123	0·1462		
80	0·1062	0·1245			
90	0·1170	0·1343			
100	0·1269	0·1407			



Let m = fraction decomposed and assume the rate equation

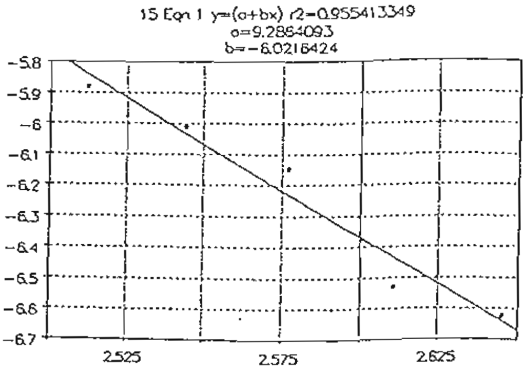
$$\frac{dm}{dt} = km^q$$

The data are plotted and m is revealed to vary linearly with time. Thus the reaction is zero order, with these specific rates at the various temperatures.

T	378	383	388	393	398
10^3k	1.33	1.46	2.14	2.45	2.79

The Arrhenius equation is

$$k = \exp(9.286 - 6021/T)$$



P3.09.01. ISOPROPYL ISOCYANATE IN A DIFFERENTIAL REACTOR

Data of time-temperature-rate were obtained in a differential packed reactor for the thermal decomposition of isopropyl isocyanate (Fogler, 1992). Find a rate equation.

In a differential flow reactor the contact time and the conversion are small so the reaction rate is $r = \Delta n/\Delta t$. Assume a rate equation

$$r = \exp(A-B/T)\ C^q$$

or

$$\ln r = A - \frac{B}{T} + q \ln C$$

POLYMATH multilinear regression gives

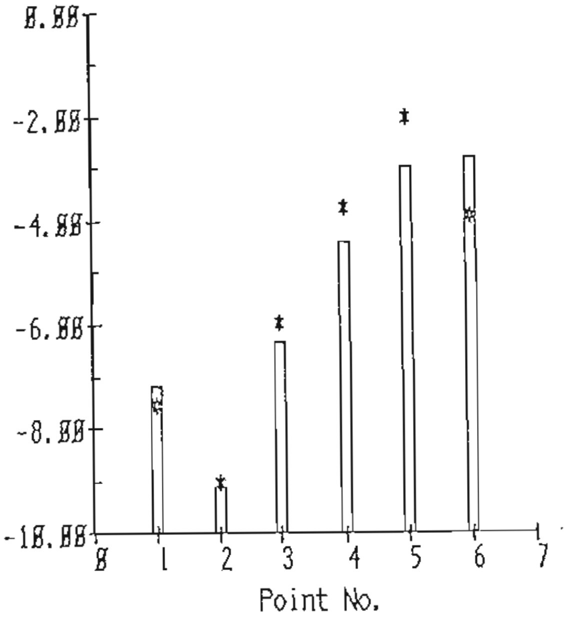
$$\ln r = 18.912 - 16532/T + 1.5259 \ln C$$

or

$$r = \exp(18.912-16532/T)\ C^{1.5259}$$

Not all the data points are well represented by this equation.

Run	$10^4 r$ mol/s-liter	C mol/liter	°K
1	4.9	0.2	700
2	1.1	0.02	750
3	24.0	0.05	800
4	220	0.08	850
5	1180	0.10	900
6	182	0.06	950



P3.09.02. ACETONE PYROLYSIS

Conversion data were obtained in a tubular flow reactor for the pyrolysis of acetone at 520 C and 1 atm to form ketene. The reactor was 3.3 cm ID and 80 cm long. Find a rate equation.

$$(CH_3)_2CO \Rightarrow CH_2CO + CH_4$$

$$n_t = 2n_{a0}-n_a$$

Assume a rate equation,

$$r_a = k\left(\frac{n_a}{V'}\right)^q = k\left(\frac{P}{RT}\right)^q \left(\frac{n_a}{2n_{a0}-n_a}\right)^q = k\left(\frac{P}{RT}\right)^q \left(\frac{1-x}{1+x}\right)^q \qquad (1)$$

$$x = 1-n_a/n_{a0}$$

The flow reactor equation is

$$-dn_a = n_{a0}dx = r_a dV_r \qquad (2)$$

$$y = k\left(\frac{P}{RT}\right)^q \left(\frac{V_r}{n_{a0}}\right) = \int_0^x \left(\frac{1+x}{1-x}\right)^q dx \qquad (3)$$

Values of y for q = 1 and for q = 2 are tabulated and confirm that the reaction is more nearly second order. The mean value of y is 8.170.

$$V_r = 80(3.3)^2(\pi/4) = 684.2 \text{ cc}$$
$$RT/P = 82.05(773)/58.08 = 1090 \text{ cc/gm acetone}$$

The mean value of k is

$$k = \frac{8.170}{684.2}(1090)^2 = 14200, \ 1/h$$

$$r_a = 14200\ C_a^2 \quad g/h\text{-}cc \qquad (4)$$

V' g/h	x	y q=1	y q=2
130	0.05	6.836	7.196
50	0.13	7.426	8.532
21	0.24	6.486	8.514
10.8	0.35	5.524	8.432

P3.09.03. OXYGEN AND CHLORINE.

A flow study of the reaction between oxygen atoms and chlorine at high pressures (Bradley et al, J Chem Soc Trans Faraday Soc 1 1251, 1973) produced data of oxygen concentration along the tube, columns 1 and 2 of the table. The velocity was 666 cm/sec, the initial concentration of oxygen was 3.3(10^{-8}) mol/liter and that of chlorine was 25.4(10^{-8}). Find a rate equation.

Let $y = 10^8[O]$
$t = L/666$

Try second order.

$$-\frac{d[O]}{dt} = k[O][Cl_2]$$

$$-\frac{dy}{dL/666} = 10^{-8}k\ y(25.4-3.3+y)$$

$$\frac{10^{-8}k}{666} = \frac{1}{L}\int_0^{2.519}\frac{dy}{y(22.1+y)} = \frac{1}{22.1L}\ln\frac{22.1+y}{9.773y} \qquad (1)$$

Values of k obtained from this equation are tabulated and have a mean value

$$k = 5.25(10^7) \text{ liters/mol-sec}$$

L, cm	y	$10^{-7}k$
0	2.519	
2	2.420	5.439
4	2.349	4.744
6	2.257	4.980
8	2.104	6.142
10	2.083	5.190
12	2.002	5.237
14	1.904	5.481
16	1.885.	4.970
18	1.811	5.036

P3.09.04. DI-t-BUTYL PEROXIDE

The data of the table are of the decomposition of di-t-butyl peroxide to acetone and ethane at 188 C in a tubular flow reactor of 82.4 cc volume. The concentrations are in mol/liter and flow rate is in cc/sec. A carrier gas was used, and any volume change resulting from the reaction may be taken negligible. Find the rate equation.

$$(CH_3)_2CO_2 \Rightarrow 2(CH_3)_2CO + C_2H_6$$

Try a first order reaction. Because of the large excess of carrier gas, the residence time is simply

$$t = V_r/V' = 82.4/V'$$

and

$$k = \frac{V'}{82.4} \ln \frac{C_{a0}}{C_a} \qquad (1)$$

The values are tabulated in the last column. The mean value is

$$k = 7.493(10^{-3}),\ 1/\text{sec}$$

V'	10^4C_{a0}	10^4C_a	10^3k
2.31	8.17	6.35	7.065
1.20	9.25	5.41	7.811
1.00	8.71	4.67	7.564
0.88	5.90	2.82	7.883
0.66	10.17	4.00	7.474
0.56	6.58	2.24	7.323
0.51	6.00	1.80	7.451
0.44	4.81	1.21	7.369

P3.09.05. GAS OIL CRACKING

Cracking of a gas oil was done in a pilot coil 15 ft long by 0.209 inch ID (0.0356 cuft) immersed in a lead bath. The oil entered at 200 F and 475 psig at the rate of 1.6 gal/hr (0.00347 lb/sec). Conversion to gas plus gaoline was 12.2 wt%. The heat transfer coefficient was figured as 31. The density of the mixture is expressed by the equation

$$1/\rho = 0.0229 + 0.317x$$

where x is the wt fractional conversion. Hydrocarbon cracking is a first order reaction. Find the specific rate.

Heat transfer calculations show that when 15% of the coil has been traversed, the oil temperature is within 5°F of the lead bath. It will be assumed that no significant conversion has occurred in the preheat section and that the reaction is substantially isothermal in the remaining 85% of the reactor volume.

$$W' = 0.00347 \text{ lb/sec}$$

$$V' = W'/\rho = \frac{0.00347}{0.0299+0.317x},\ \text{cuft/sec}$$

$$V_r = 0.85(0.0356) = 0.0303 \text{ cuft}$$

The flow reactor material balance is

$$-dn_a = n_{a0}dx = r_a dV_r = \frac{kn_{a0}(1-x)}{V'}\, dV_r$$

$$k = \frac{W'}{V_r}\int_0^x \frac{dx}{\rho(1-x)} = \frac{0.00347}{0.0303}\int_0^{0.122} \frac{0.0229+0.317x}{1-x}\, dx$$

$$= 0.00068,\ 1/\text{sec}$$

The result may be compared with an approximate solution, taking an average reciprocal density.

$$1/\rho_{in} = 0.0229,\ 1/\rho_{out} = 0.0229+0.317(0.122) = 0.0616,$$

$$1/\rho_{mean} = 0.5(0.0229+0.0616) = 0.0423$$

$$k = \frac{0.00347(0.0423)}{0.0303} \ln \frac{1}{1-0.122} = 0.00058$$

P3.09.06. CHLORINATION OF OLEIC ACID

Chlorination of oleic acid dissolved in carbon tetrachloride was tested in a flow reactor. The data are at 12.8 C (Roper, Chem Eng Sci 227, 1953). The reactants were dissolved separately and mixed in the liquid phase at the inlet to the reactor. Show that the reaction is second order.

A = chlorine, B = oleic acid

At constant density,

$$-dn_a = V'dC_a = kC_aC_bdV_r$$

$$k = \frac{V'}{V_r}\int_{C_a}^{C_{a0}} \frac{dC_a}{C_a(C_{b0}-C_{a0}+C_a)} = \frac{V'/V_r}{C_{b0}-C_{a0}} \ln \frac{C_{a0}(C_{b0}-C_{a0}+C_a)}{C_{b0}C_a}$$

The values are tabulated and have a mean value

k = 132.7 liters/gmol-sec

V_r/V'	C_{a0}	C_{b0}	C_a	k
0.054	0.0208	0.0242	0.0181	112.97
0.093	0.0208	0.0242	0.0162	123.71
0.258	0.0186	0.0242	0.0097	133.26
0.350	0.0186	0.0242	0.0072	159.27
0.573	0.0186	0.0242	0.0056	133.99

P3.09.07. ETHYLBENZENE TO STYRENE

Pyrolysis of ethyl benzene was carried out at 950 F in a flow reactor (Rase & Kirk, Chem Eng Prog 30 35, 1954) with the tabulated results at two pressures. Find a power law rate equation for this process.

Ethylbenzene ⇒ Styrene + Hydrogen

The material balance on the flow reactor,

$$-dn_a = W_0'\,dx = r_a dW_r = k\left(\frac{n_a}{V'}\right)^q dW_r = k\left(\frac{\pi}{RT}\right)^q\left(\frac{n_a}{n_t}\right)^q dW_r$$

$$= k\left(\frac{\pi}{RT}\right)^q \left(\frac{1-x}{1+x}\right)^q dW_r$$

$$k/(RT)^q = \frac{W'}{W_r\pi^q}\int_0^x \left(\frac{1+x}{1-x}\right)^q dx$$

The values for both first and second order are tabulated. Neither set is the same for both pressures. An adjustment of the first order constants for pressure can be made by assuming that the specific rate depends on some power of the pressure. Taking the average values at the two pressures,

$$2.110(0.97)^\alpha = 1.578(3.15)^\alpha$$

$$\alpha = 0.247$$

making the specific rate

$$k = 0.00211\ \pi^{0.247},\quad \text{1/hr, with } \pi \text{ in atm.}$$

π	W_r/W'	x	$10^3k_1/RT$	$10^3k_2/(RT)^2$
0.97	0	0		
	5	0.009	1.870	1.80
	10	0.021	2.211	2.10
	15	0.031	2.198	2.07
	20	0.040	2.147	2.00
	25	0.049	2.123	1.96
3.15	5	0.025	1.628	5.00
	10	0.047	1.564	4.70
	15	0.068	1.542	4.53

P3.09.08. ACETALDEHYDE DECOMPOSITION

Acetaldehyde vapor was passed through a plug flow reactor at atmospheric pressure and 600 C. The fraction remaining, $f = n_a/n_{a0}$, was measured as a function of V_r/n_{a0} measured in seconds.
What power law rate equation fits the data?

$CH_3CHO \Rightarrow CH_4 + CO$, $A \Rightarrow B + C$

$V' = n_tRT/\pi = (2n_{a0}-n_a)RT/\pi$

The flow reactor material balance is

$$-dn_a = -n_{a0}df = r_a dV_r = k(n_a/V')^q\, dV_r = k\left(\frac{\pi}{RT}\right)^q \left(\frac{n_a}{2n_{a0}-n_a}\right)^q dV_r$$

$$k_q = k\left(\frac{\pi}{RT}\right)^q = \frac{n_{a0}}{V_r}\int_f^1 \left(\frac{2-f}{f}\right)^q df \qquad (1)$$

$f = n_a/n_{a0}$

The result of integration is tabulated for q = 1, 1.5 and 2. The value q = 1.5 is the best fit to the data., although there is still some drift in $k_{1.5}$.

V_r/n_{a0}	n_a/n_{a0}	k_1	$k_{1.5}$	k_2
10	0.917	0.00903	0.00943	0.00984
20	0.842	0.00930	0.01012	0.01104
40	0.733	0.00886	0.01030	0.01204
80	0.577	0.00846	0.01097	0.0144
160	0.401	0.00768	0.01164	0.0182
320	0.254	0.00623	0.01134	0.02192

P3.09.09. PROPYLENE POLYMERIZATION

Polymerization of propylene was done in a packed tower with the gas flowing countercurrently to 98% liquid phosphoric acid
(Bethea & Karchmer, Ind Eng Chem 48 370, 1956). % composition of the charge was 58.0 propylene, 41.0 propane, 0.5 butylene and 0.5 butane. On an average, 1 mol of polymer required 3.4 mol propylene. Selected data at 360 F are:

Pressure, psig	400	500	702	700
Olefin feed, mol/liter-h, n_{a0}/V_r	3.25	7.10	7.22	13.12
Olefin % conversion	88.6	70.6	86.6	60.5
Average compressibility, z	0.83	0.81	0.67	0.72

Find the first order specific rate for each run.

$3.4\ C_3H_6 \Rightarrow \text{Polymer}$

n_{a0} = mols entering propylene, x = fraction converted

$n_t = n_{inert} + n_a + n_p = (0.42/0.58)n_{a0} + n_a + (n_{a0}-n_a)/3.4$

$\quad = 1.0182\ n_{a0} - 0.7059\ n_a = n_{a0}(1.7241 - 0.7059\ x) \qquad (1)$

$R = 0.67$ psi(liters)/(gmol)($^\circ$R)

$V' = zn_tRT/\pi = 0.67(820)zn_t/\pi = 550\ zn_t/\pi \qquad (2)$

$r_a = k(n_a/V') = kn_{a0}(1-x)/V' \qquad (3)$

Material balance on the flow reactor,

$$-dn_a = n_{a0}dx = r_a dV_r = kn_{a0}\frac{1-x}{V'}\,dV_r$$

$$k = \frac{550\ z}{\pi}\left(\frac{n_{a0}}{V_r}\right)\int_0^x \frac{1.7241 - 0.7059\ x}{1 - x}\,dx \qquad (4)$$

Substitute data from the table and integrate. The four values of k corresponding to the data are: 10.52, 11.04, 12.18, and 10.19.

These results are not correct because the polymer will not be in the vapor phase. The correct values of n_t, the integrand of Eq (4) and k will be,

$n_t = n_{a0}(0.42/0.58 + 1-x) = n_{a0}(1.7241-x)$

Integrand = $(1.7241-x)/(1-x)$

k = 9.12, 10.07, 8.80 and 9.483.

P3.09.10. ETHYLAMINE DECOMPOSITION

Ethylamine gas, when passed over an alumina catalyst at 120 C and 1 atm, is decomposed according to the equation

$C_2H_5NH_2 \Rightarrow C_2H_4 + NH_3$

Experiments were performed at two flow rates in a vessel containing 7760 liters of catalyst.

liters/hr input	11200	5700
liters/hr output	15700	9140

Verify that the reaction is first order and find the specific rate.

$n_t = 2n_{a0} - n_a$

Molal input rates,

$$n_{a0} = \frac{11200(273.2)}{22.4(393.2)} = 347.4 \text{ gmol/hr, Case 1}$$

$$\frac{5700)273.2)}{22.4(393.2)} = 176.8 \text{ gmol/hr, Case 2}$$

Conversions,

$$\frac{2n_{a0}-n_a}{n_a} = \frac{15700}{11200} = 1.4018,\ n_a/n_{a0} = 0.5982, \text{ Case 1}$$

$$\frac{9140}{5700} = 1.6035,\ n_a/n_{a0} = 0.3965, \text{ Case 2}$$

Volumetric flow rate,

$$V' = \frac{(2n_{a0}-n_a)RT}{\pi} \qquad (1)$$

Plug flow reactor,

$$-dn_a = r_a dV_r = k(n_a/V')dV_r = \frac{k\pi}{RT}\left(\frac{n_a}{2n_{a0}-n_a}\right)dV_r$$

$$\frac{k\pi V_r}{RT} = \int_{n_a}^{n_{a0}} \frac{n_{a0}-n_a}{n_a}\, dn_a = 2n_{a0}\ \ln(n_{a0}/n_a) - (n_{a0}-n_a)$$

$$= 347.4[2\ \ln(1/0.5982) - (1-0.4018)] = 217.4,\ \text{Case 1}$$

$$176.8[2\ \ln(1/0.3965) - (1-0.6035)] = 220.4,\ \text{Case 2}$$

Substantial agreement between these two values confirms the first order mechanism. The factor,

$$\frac{\pi V_r}{RT} = \frac{1(7760)}{0.082(393.2)} = 240.7$$

P3.09.11. ION EXCHANGE REACTOR

A 0.01 M solution of an ester is passed through an ion exchange catalyst bed where it is decomposed into a monobasic acid and an alcohol. The amount of acid, mols/liter, produced at different flow rates, liters/hr, are tabulated. The quantity of resin catalyst was 120 kg, the bulk density was 1.10 and the true density was 1.25 g/cc. Confirm that the reaction is first order.

Free volume:

$V_{total} = 120/1.1 = 109.1$ liters

$V_{resin} = 120/1.25 = 96.0$

$V_r = 109.1 - 96 = 13.1$ liters

from which the contact time for a given flow rate V' is

$t = 13.1/V'$

A = ester, B = acid product

$$\frac{dB}{dt} = kA = k(A_o-B) = k(0.01-B)$$

Integrating,

$$k = \frac{1}{t}\ \ln\frac{0.01}{0.01-B} = \frac{V'}{13.1}\ \ln\frac{0.01}{0.01-B}$$

The six values of k are tabulated. They are nearly constant and thus confirm the first order mechanism.

V'	10^4B	k
730	2.5	1.411
249	7.0	1.379
110	15	1.365
25.2	51	1.372
14.1	72	1.370
9.5	85	1.376

P3.09.12. METHYL ACETATE WITH AN ACID CATALYST

An aqueous solution of 0.02 M methyl acetate at 25 C was passed through a column of trioctyl phosphate (on a cellulose base) which acted as an acid catalytst. The reaction is

$CH_3COOCH_3 + H_2O \Rightarrow CH_3COOH + CH_3OH$

The effective free volume of the bed is 16.7 liters. The flow rate, liters/hr, and acid product, mols/liter, are tabulated. Confirm that the reaction is first order.

Since the solution is quite dilute, the reaction is expected to be pseudo first order

$t = V_r/V' = 16.7/V'$

$$k = \frac{1}{t}\ln\frac{0.02}{0.02-C_b} = \frac{V'}{16.7}\ln\frac{0.02}{0.02-C_b}$$

The tabulated values of k confirm first order.

V'	C_b	k
1020	0.00015	0.460
121.8	0.0012	0.451
16.5	0.0073	0.449
9.0	0.0113	0.449
5.7	0.014	0.453

P3.09.13. CARBON DISULFIDE

Methane and sulfur form carbon disulfide by the reaction

$CH_4 + 2\ S_2 \Rightarrow CS_2 + 2\ H_2S, \quad A + B \Rightarrow C + D$

Data of the reaction at 600 C and 1 atm with two mols of sulfur per mol of methane are tabulated (Fisher & Smith, Ind Eng Chem 42 704, 1950). The reactor volume, V_r, is given in cc, the feed rate of methane is n_{a0} gmol/hr, conversion is a fraction x of the methane.

Volumetric flow rate is

$$V' = \frac{n_tRT}{\pi} = 3n_{a0}RT/\pi$$

The rate equation is

$$r_a = kC_aC_b = 2kC_a^2 = 2k(n_a/V')^2 = \frac{2}{9}(\frac{\pi}{RT})^2k(\frac{n_a}{n_{a0}})^2 \qquad (1)$$

$n_a/n_{a0} = 1-x$

For a plug flow reactor,

$-\ dn_a = n_{a0}dx = r_adV_r$

Integrating,

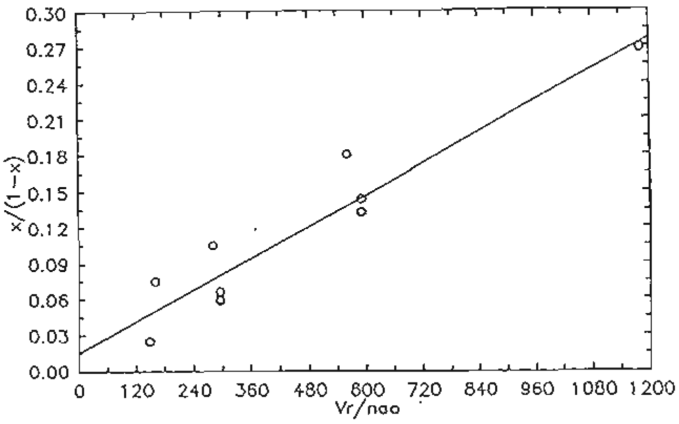
$$\frac{2}{9}(\frac{\pi}{RT})^2k = \frac{n_{a0}}{V_r}\int_0^x\frac{dx}{(1-x)^2} = \frac{n_{a0}}{V_r}(\frac{x}{1-x}) \qquad (1)$$

The plot of x/(1-x) against V_r/n_{a0} is fitted roughly with a straight line whose slope is

$$\text{Slope} = 2.125(10^{-4}) = \frac{2}{9}(\frac{\pi}{RT})^2k$$

$$k = 2.125(10^{-4})(4.5)[\frac{82.05(823.2)}{1}]^2 = 4.36(10^6)\ \text{cc/gmol-hr}$$

V_r, cc	n_{ao}	x_a
67	0.238	0.105
67	0.417	0.075
67	0.119	0.180
35.2	0.0595	0.133
35.2	0.02975	0.269
35.2	0.119	0.058
35.2	0.0298	0.268
35.2	0.238	0.025
35.2	0.119	0.066
35.2	0.0595	0.144
35.2	0.119	0.060



P3.09.14. CRACKING OF PENTENE-2

Cracking of pentene-2 was investigated at 670 C and 1 atm in a plug flow reactor (Kunzru et al, IECPDD 2 339, 1963). The product was a mixture of substances and was characterized simply by the number of mols produced per mol of reactant transformed.

Two sets of data were taken:

$S = V'_0/V_r$	3.85	1.15
x = fraction converted	0.088	0.22
β = mols product/mol converted	1.712	1.945

Try a first order rate equation.

$$V' = n_t RT/\pi = n_{a0}(1 + \beta x)\ RT/\pi$$

At the inlet,

$$S = V'_0/V_r = \frac{n_{a0}RT}{V_r\pi} = 3.85,\ \text{Case 1}$$

$$1.15,\ \text{Case 2}$$

For a plug flow reactor,

$$-\ dn_a = n_{a0}dx = r_a dV_r = k(\frac{n_a}{V'})\ dV_r = \frac{k\pi}{RT}\ \frac{1-x}{1+\beta x}\ dV_r$$

Integrating,

$$k = \frac{n_{a0}RT}{V_r\pi} \int_0^x \frac{1+\beta x}{1-x}\ dx = S \int_0^x \frac{1+\beta x}{1-x}\ dx$$

For the two cases,

S	3.85	1.15
β	0.712	0.945
k	0.366	0.317

The two values of k are only roughly the same, and constitute a weak confirmation of first order mechanism.

P3.09.15. LAMINAR FLOW REACTOR. SPECIFIC RATE DATA.

In a laminar flow reactor the concentration varies both radially and axially and depends on the specific rate. Along a stream line, the material balance is

$$2u_m(1-\beta^2)\frac{dC}{dL} + kC^q = 0$$

where the radial position is $\beta = r/R$, u_m is the mean velocity, L is the axial position and q is the order of the reaction. The concentration ratio along a stream line, $(C/C_0)_{SL}$, is obtained readily by integration.

What is of interest is the mean value over the cross section. In problem P4.08.01 it is shown that the mean value is related to the stream line values by

$$(C/C_0)_m = 0.5\,\bar{t}^2 \int_{0.5\bar{t}}^{\infty} \frac{(C/C_0)_{SL}}{t^3}\,dt$$

$$= 0.5\int_{0.5}^{\infty} \frac{(C/C_0)_{SL}}{t_r^3}\,dt_r \qquad (1)$$

where $\bar{t} = L/u_m$ is the mean residence time in the reactor, and $t_r = t/\bar{t}$. For first order,

$$(C/C_0)_m = 0.5 \int_{0.5}^{\infty} \frac{\exp(-kt)}{t_r^3}\,dt_r$$

$$= 0.5 \int_{0.5}^{\infty} \frac{\exp(-k\bar{t}t_r)}{t_r^3}\,dt_r \qquad (2)$$

For second order,

$$(C/C_0)_m = 0.5 \int_{0.5}^{\infty} \frac{1}{t_r^3(1+kC_0\bar{t}t_r)}\,dt_r \qquad (3)$$

The results of numerical integration of Eqs (2) and (3) are plotted.

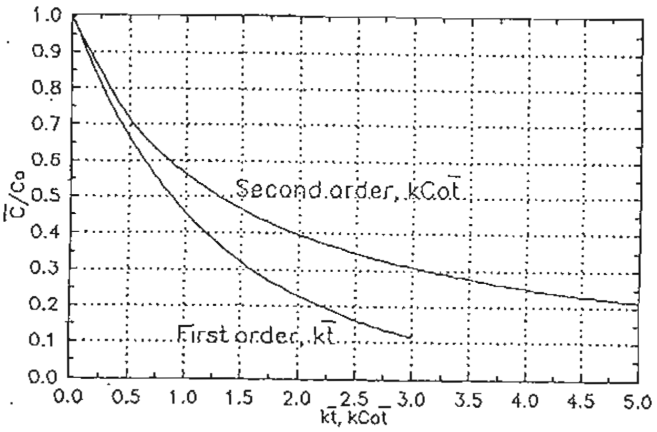
For a given order, specified conversion and residence time $\bar{t}$, the specific rate can be read off these plots. EXAMPLE: A first order reaction has $\bar{t} = 1$, $C/C_0 = 0.2$ and specific rate

$$k_{laminar} = 2.2$$

For comparison,

$$k_{plug\ flow} = \frac{\ln(C_0/C)}{\bar{t}} = 1.61$$

$$k_{CSTR} = \frac{(C_0/C - 1)}{\bar{t}} = 4.0$$



P3.10.01. CONVERSION AS A FUNCTION OF TIME

Data on the reaction, 2A ⇔ B, were taken with a CSTR with the tabulated time-conversion results in the table. Feed concentrations were $C_{a0} = 1.5$ and $C_{b0} = 0.5$ lbmol/cuft. Find the rate equation.

Try a rate equation corresponding to the stoichiometry.

$$r_a = k(C_a^2 - C_b/K_e) = k\left(C_a^2 - \frac{C_{a0}+2C_{b0}-C_a}{2K_e}\right)$$

$$K_e = \frac{1.5+2(0.5)-0.3}{2(0.3)^2} = 12.22$$

Material balance on the CSTR,

$$C_{a0} = C_a + \bar{t}k(C_a^2 - \frac{2.5-C_a}{24.44})$$

$$k = \frac{C_{a0}-C_a}{\bar{t}(C_a^2 - \frac{2.5-C_a}{24.44})} \qquad (1)$$

The values of k are tabulated. Their mean value is

$k = 0.752$ cuft/(lbmol)(hr)

$\bar{t}$	C_a/C_{a0}	k
0	1.0	
0.11	0.9	0.768
0.29	0.8	0.746
0.58	0.7	0.744
1.07	0.6	0.753
2.04	0.5	0.749
∞	0.2	

P3.10.02. DATA AT TWO TEMPERATURES.

A reaction, $A \Rightarrow 2R$, is conducted in a 5 liter CSTR with an inlet concentration $C_{a0} = 1.0$ mol/liter. Data of temperature, flow rate and product concentration are in the first three columns of the table. Find the rate equation to fit.

$C_a = C_{a0} - 0.5C_r$

Material balance is

$$C_{a0} = C_a + \bar{t}\ k\ C_a^q$$

$$k = \frac{C_{a0}-C_a}{\bar{t}C_a^q} \qquad (1)$$

$$= \exp(A-B/T) \qquad (2)$$

The two runs at 13 C establish that the order is $q = 2.0$, and that $k_{13} = 0.036$ liters/(gmol)(sec). The tabulations shows that first order does not fit. At 84 C,

$$k = \frac{1-0.1}{(0.1)^2(333)} = 0.2703$$

To find the Arrhenius constants,

$\ln(0.036) = A - B/286.2$

$\ln(0.2703) = A - B/357.2$

$A = 6.813,\ B = 2901.2$

The rate equation is

$$r_a = \exp(6.813-\frac{2901.2}{T})\ C_a^2$$

°C	V', cc/sec	C_R	$\bar{t}$	k_1	k_2
13	2	1.8	2500	0.0036	0.036
13	15	1.5	333	0.0090	0.036
84	15	1.8	333		0.270

P3.10.03. ARRHENIUS SPECIFIC RATE

Conversion data are obtained in a CSTR at several residence times and two temperatures. Verify that the reaction is second order and find the Arrhenius constants.

$f = C/C_0$

The material balance is

$$C_0 = C + k\bar{t}C^q$$

or

$$1 = f+k\bar{t}C_0^{q-1}f^q$$

$$kC_0^{q-1} = \frac{1-f}{\bar{t}f^q} \qquad (1)$$

These values are tabulated for 315 K and confirm that the order is q = 2. The average value is 0.1255. The value at 360 K is

$$k = \frac{1-0.388}{10(0.388)^2} = 0.4065$$

For the Arrhenius constants,

$\exp(A-B/315) = 0.1255$

$\exp(A-B/360) = 0.4065$

$A = 7.3268,\ B = 2961.7$

$\bar{t}$	T	f	k_1	k_2C_0
10	315	0.580	0.0724	0.1249
15		0.510	0.0641	0.1256
20		0.460	0.0587	0.1276
30		0.400	0.0500	0.1250
60		0.302	0.0385	0.1276
100		0.248	0.0303	0.1266
Average				0.1255
10	360	0.388		0.4065

P3.10.04. THREE STAGE CSTR

A second order reaction conducted in a three stage CSTR undergoes 88% conversion. Inlet concentration is $C_0 = 2$ and the residence time per stage is 6 minutes. The specific rate is to be found.

$f_1 - C_1/C_0$

Material balances:

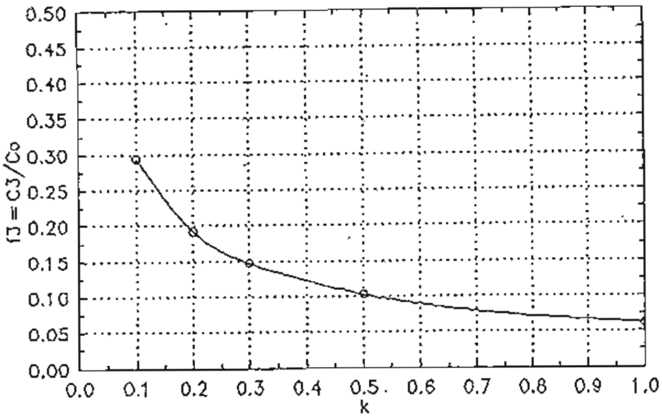
$$1 = f_1 + k\bar{t}C_0f_1^2 = f_1 + 12kf_1^2$$

$$f_1 = f_2 + 12kf_2^2$$

$$f_2 = f_3 +12kf_3^2 = 0.12 + 12(0.12)^2k$$

Solution method (a): Assume values of k, calculate corresponding values of f_3 and interpolate to $f_3 = 0.12$. From the graph, k = 0.40.

Solution method (b): Solve the three nonlinear equations simultaneously. The result is $k = 0.4025$, $f_1 = 0.3631$, $f_2 = 0.1896$, $f_3 = 0.12$.



P3.10.05. GAS PHASE CSTR

The gas phase reaction, $2A \Rightarrow B+C$, was studied in a well stirred reactor. Pure A was charged at 600 K and 40 atm. The experimental data are of fractional conversion against V_r/n_{a0} in the units liters/(mol)(sec) and are given in the first two columns of the table. Equilibrium conversion was 90%. Find the specific rate.

Try the rate equation

$$r_a = k[C_a^2 - \frac{(C_{a0}-C_a)^2}{K_e}]$$

$$K_e = (\frac{C_{a0}-0.1C_{a0}}{0.1C_{a0}})^2 = 81$$

$$C_a = C_{a0}(1-x)$$

$$r_a = kC_{a0}^2[(1-x)^2 - x^2/81]$$

Material balance:

$$V'C_{a0} = V'C_a + r_aV_r$$

$$V'(C_{a0}-C_a) = V'C_{a0}x = kV_rC_{a0}^2[(1-x)^2 - x^2/81]$$

$$V' = n_{a0}RT/\pi$$

$$k' = kC_{a0}n_{a0}\pi/RT = (\frac{n_{a0}}{V_r})\frac{x}{(-x)^2-x^2/81}$$

Substitute n_{a0}/V_r and x from the table. The resulting values of k' are tabulated and appear to be nearly constant, thus confirming the assumed rate equation.

V_r/n_{a0}	x	k'
0.017	0.05	3.26
0.065	0.15	3.20
0.139	0.25	3.20
0.260	0.35	3.52
0.633	0.50	3.20
1.21	0.60	3.19
2.61	0.70	3.19
7.80	0.80	3.20
19.62	0.85	3.19

P3.10.06. GAS PHASE REACTION WITH VOLUME CHANGE

A gas phase reaction, $2A \Rightarrow B$, is conducted in a CSTR. Two runs were made, with the results:

n_{a0}/V_r	0.10	0.15
$f = n_a/n_{a0}$	0.20	0.30

Find the constants of the rate equation.

$$V' = n_t RT/\pi = (n_{a0}+n_a)RT/2\pi$$

The material balance is

$$n_{a0} = n_a + kV_r(n_a/V')^q = kV_r\left(\frac{2\pi}{RT}\right)^q \left(\frac{n_a}{n_{a0}+n_a}\right)^q$$

$$1 = f + k\left(\frac{2\pi}{RT}\right)^q \left(\frac{V_r}{n_{a0}}\right)\left(\frac{f}{1+f}\right)^q$$

$$k\left(\frac{2\pi}{RT}\right)^q = (1-f)\left(\frac{1+f}{f}\right)^q \qquad (1)$$

Substitute the two sets of data.

$$(1-0.2)(1.2/0.2)^q(0.1) = (1-0.3)(1.3/0.3)^q(0.15)$$

$$q = \ln(0.08/0.105)/\ln(4.333/6) = 0.836 \qquad (2)$$

$$k\left(\frac{2\pi}{RT}\right)^{0.836} = (1-0.2)(6)^{0.836}(0.1) = 0.3578 \qquad (3)$$

To find k itself, pressure and temperature are needed.

P3.10.07. L-H TYPE RATE EQUATION

A gas phase reaction, $2A \Rightarrow B$, is conducted in a CSTR. The rate equation is of the form

$$r_a = k_1C_a/(1+k_2C_a)$$

Two runs were made in order to find the constants:

V_r/n_{a0}	3.0	1.8
$f = n_a/n_{a0}$	0.2	0.3

Transforming the variables,

$$C_a = n_a/(n_tRT/\pi) = \left(\frac{n_a}{n_{a0}+n_a}\right)\left(\frac{2\pi}{RT}\right) = \left(\frac{f}{1+f}\right)\left(\frac{2\pi}{RT}\right)$$

$$r_a = \frac{k_1(2\pi/RT)\left(\frac{f}{1+f}\right)}{1+k_2(2\pi/RT)\left(\frac{f}{1+f}\right)} = \frac{k_1'f}{1+f+k_2'f}$$

Material balance,

$$n_{a0} = n_a + r_aV_r = n_a + \frac{k_1'f}{1+f+k_2'f}\ V_r$$

$$(1-f)(1+f+k_2'f) = k_1'f(V_r/n_{a0})$$

Substitute the two sets of data,

$$0.7(1.3+0.3k_2') = 1.8(0.3)k_1'$$

$$0.8(1.2+0.2k_2') = 3.0(0.2)k_1'$$

$$k_1' = k_1(2\pi/RT) = 1.9561$$

$$k_2' = k_2(2\pi/RT) = 0.6957$$

P3.10.08. ETHYL ACETATE AND BARIUM HYDROXIDE

In an experiment conducted by Stead et al (Discuss Faraday Soc, No 2, 263, 1947) solutions of ethyl acetate (B) and barium hydroxide (A) were introduced into a vessel of volume $V_r = 0.602$ liters at flow rates V'_a and V'_b, liters/s, through capillary inlet tubes and were thoroughly mixed on entering the vessel. Overflow was at a steady rate. Find the rate equation.

Stoichiometric balance,

$$V' = V'_a + V'_b$$

$$V'_a A_0 - V'A = V'_b B_0 - V'B$$

$$B = (V'_b B_0 - V'_a A_0 + V'A)/V'$$

The rate equation is

$$r_a = kAB = kA(V'_b B_0 - V'_a A_o + V'A)/V'$$

Material balance on the steady reactor operation,

$$V'_a A_0 = V'A + kV_r A(V'_b B_0 - V'_a A_0 + V'A)/V'$$

Solving for k,

$$k = \frac{(V'_a A_0 - V'A)V'}{(V'_a A_0 - V'_b B_0 + V'A)V_r}$$

Substitute $V_r = 0.602$ liters and data from the table. The four values of k are quite close to each other, confirming the assumed rate equation. The average value is k = 0.0995 liters/mol-sec.

$10^2 A_0$	$10^2 B_0$	$10^4 V'_a$	$10^4 V'_b$	$10^2 A$	k
0.511	3.94	3.18	3.32	0.0917	0.099
0.587	3.89	3.22	3.32	0.1094	0.099
0.767	3.88	2.91	3.34	0.1268	0.102
0.965	10.40	3.18	3.33	0.0866	0.098

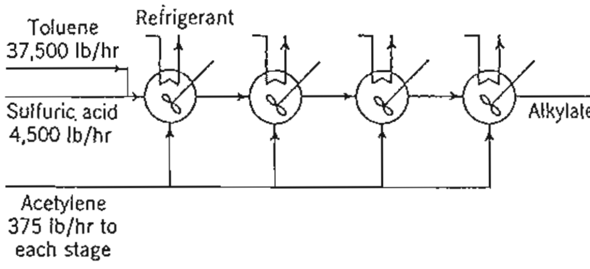
P3.10.09. ALKYLATION IN FOUR STAGES

Alkylation of toluene and acetylene in the presence of sulfuric acid is accomplished in the four-stage reactor of the sketch. Retention time in each stage is 10 min, temperature is 41 F and pressure is 50 psig. On the assumption that the liquid always is saturated with acetylene, the reaction is first order with respect to toluene. At the conditions shown, the reaction is estimated 95% complete. Find the specific reaction rate.

$$f = n_a/n_{a0}$$

The rate equation is

$$r_a = -\frac{df}{dt} = kf$$



Material balances on successive stages are

$$f_{n-1} = f_n + k\bar{t}f_n \ , \ n = 1, 2, 3, 4$$

$$f_4 = \frac{f_0}{(1+k\bar{t})^4} = \frac{1}{(1+10k)^4} = 0.05$$

$$k = 0.1115$$

P3.10.10. HYDROGENOLYSIS OF ETHANE

Hydrogenolysis of ethane over a commercial nickel catalyst was studied in a rotating basket reactor containing 40 g of catalyst.

$$H_2 + C_2H_6 \Rightarrow 2CH_4, \quad A + B \Rightarrow C$$

Data at 300 C are cited by Fogler (1992) and are tabulated in the first four columns. Find the constants of the rate equation,

$$r_c = 2kp_a^a p_b^b \qquad (1)$$

Define these terms,

n_t = feed rate, gmol/hr

x = mol fraction CH_4 in the product stream

$p_a = p_{a0} - (p_{a0}+p_{b0})(x/2)$

$p_b = p_{b0} - (p_{a0}+p_{b0})(x/2)$

These values are recorded in the table. Material balance on methane,

$$0 = n_t x + W_r r_c$$

$$r_c = \frac{n_t x}{0.04}, \text{ gmol/(h)(kg catalyst)}$$

These values are tabulated in column 7. In linearized form the rate equation is

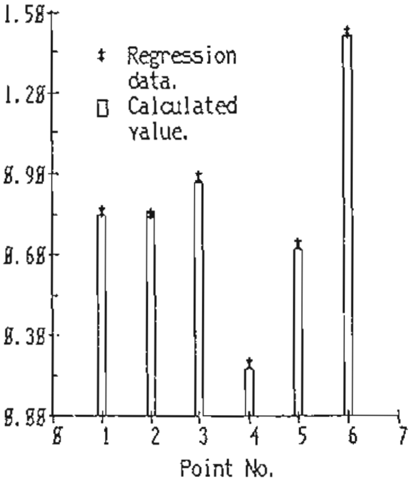
$$\ln r_c = \ln 2k + a \ln p_a + b \ln p_b$$
$$= 0.02253 + 0.9845 \ln p_a - 1.9575 \ln p_b$$

or

$$r_c = 2(0.5114)p_a^{0.9845}\ p_b^{-1.9575}$$

The numbers are found by POLYMATH multilinear regression.

n_t	p_{a0}	p_{b0}	x	p_a	p_b	r_c
1.7	0.5	0.5	0.05	0.475	0.475	2.125
1.2	0.5	0.5	0.07	0.465	0.465	2.100
0.6	0.5	0.5	0.16	0.420	0.420	2.400
0.3	0.4	0.6	0.16	0.320	0.520	1.200
0.75	0.6	0.6	0.10	0.540	0.540	1.875
2.75	0.6	0.4	0.06	0.570	0.370	4.125



P3.10.11. DI-t-BUTYL PEROXIDE DECOMPOSITION

The decomposition of gaseous di-t-butyl peroxide in the presence of a nitrogen carrier gas (D) has been studied near 481 K in a CSTR (Mulcahy & Williams, Austral J Chem 14 534, 1961).

$$(CH_3)_3CO \Rightarrow 2(CH_3)_2CO + C_2H_6, \quad A \Rightarrow 2B + C$$

Reactor volume was 0.276 liters. Data are presented of P in torr, n_{a0} mols/sec of entering reactant, $y = n_d/n_{a0}$ mols carrier gas per mol of reactant, and x fractional conversion. Check a first order rate equation.

$$n_a = n_{a0}(1 - x)$$

n_t = exit mols/sec

$$= n_d + 3n_{a0} - 2n_a = yn_{a0} + 3n_{a0} - (1-x)n_{a0}$$
$$= (y+1+2x)n_{a0} \qquad (1)$$

Material balance on the reactor,

$$n_{a0} - n_a = n_{a0}x = kV_r(\frac{n_a}{V'}) = kV_r(\frac{\pi}{RT})(\frac{n_a}{n_t})$$

$$= kV_r(\frac{\pi}{RT})(\frac{1-x}{1+y+2x})$$

$$RT/V_r = 62.3(481)/0.276 = 108600$$

$$k = \frac{RT}{V_r}\ (\frac{n_{a0}}{\pi})(\frac{x(1+y+2x)}{1-x} = 108600(\frac{n_{a0}}{\pi})(\frac{x(1+y+2x)}{1-x})$$

The values are tabulated and are roughly constant, except for the sixth entry which does not appear to be part of this family.

°K	π	$10^6 n_{a0}$	y	x	k
481.5	8.2	8.82	48.5	0.009	0.0526
481.8	1.11	8.65	45.4	0.014	0.0591
477.5	8.0	35.8	3.8	0.017	0.0404
476.7	6.7	52.1	0	0.041	0.0462
479.9	12.0	5.21	18.4	0.048	0.0463
480.4	9.5	40.4	4.1	0.066	0.1706
480.2	9	43.8	0	0.076	0.0500
480.5	9	43.7	0	0.079	0.0524
482.5	9.2	42.7	0	0.091	0.0599
481.5	27	6.97	7.8	0.158	0.0480
481.8	12.8	17.3	0	0.219	0.0593
482.0	7.2	7.73	0	0.226	0.0496
482.6	11.8	4.64	0	0.428	0.0594
482.8	18.7	2.34	0	0.640	0.0532

P3.11.01. DINITROBENZENE.

One mol of nitrobenzene (a) and 3 mols of nitric acid (B) react to form the meta (C) and ortho (D) dinitro derivatives. After 20 minutes, half of the nitrobenzene disappears and the product consists of 93% meta and 7% ortho. Find the specific rates.

$$A + B \overset{1}{\Rightarrow} C, \quad A + B \overset{2}{\Rightarrow} D$$

$$-\frac{dA}{dt} = (k_1+k_2)AB = (k_1+k_2)A(2+A)$$

$$k_1+k_2 = \frac{1}{t}\int_A^{A_0}\frac{dA}{A(2+A)} = 0.05\int_{0.5}^{1}\frac{dA}{A(2+A)} = 0.01277 \qquad (1)$$

$$\frac{dC}{dt} = k_1AB$$

$$\frac{dD}{dt} = k_2AB$$

$$\frac{k_1}{k_2} = \frac{dC}{dD} = \frac{C-C_0}{D-D_0} = \frac{C}{D} = \frac{93}{7} \qquad (2)$$

Between lines (1) and (2),

k_1 =0.01188, k_2 = 0.00894

P3.11.02. CONSECUTIVE REACTIONS.

For the set of reactions,

$$A \overset{1}{\Rightarrow} B, \quad B + C \overset{2}{\Rightarrow} D$$

with $A_0 = C_0 = 1$ and $B_0 = 0$, these data are known: when t = 10, B = 0.2 and dB/dt = 0.028; when t = 20, B = 0.4 and dB/dt = 0.012.
Find the specific rates.

The stoichiometric balance gives

$$C + C_0+A+B-(A_0+B_0) = A+B$$

$$\frac{dA}{dt} = -k_1A,$$

$$A = A_0\exp(-k_1t) = \exp(-k_1t) \qquad (1)$$

$$\frac{dB}{dt} = k_1A - k_2BC = k_1A - k_2A(A+B)$$

$$= \exp(-k_1t)(k_1-k_2B) - k_2B^2 \qquad (2)$$

Substitute numerical values.

$$0.028 = \exp(-10k_1)[k_1-k_2(0.2)] - (0.2)^2k_2$$

$$0.012 = \exp(-20k_1)[k_1-k_2(0.4)] - (0.4)^2k_2$$

The solution is $k_1 = 0.05387$, $k_2 = 0.02138$ (3)

P3.11.03. THREE DINITROBENZENES.

Dinitrobenzene was prepared from mononitrobenzene by addition of three equivalents of nitric acid. After 20 minutes the mono was half used up and the o-, m- and p- forms of the dinitrobenzene were present in the proportions 6.4, 93.5 and 0.1. Find the second order specific rates of the three reactions.

$A = HNO_3$, B = mono, C = ortho, D = meta, E = para

At 50% conversion,

$A = 2.5,\ B = 0.5,\ C = 0.032,\ D = 0.4675,\ E = 0.0005$

The rate equations are

$$-\frac{dA}{dt} = -\frac{dB}{dt} = (k_1+k_2+k_3)AB = (k_1+k_2+k_3)(B+A_0-B_0)B$$

$$(k_1+k_2+k_3)t = \frac{1}{A_0-B_0}\ln\frac{B_0(B+A_0-B_0)}{A_0B}$$

Substituting $t = 20$ and 50% conversion,

$$k_1+k_2+k_3 = \frac{1}{20(3-1)}\ln\frac{0.5+3-1}{3(0.5)} = 0.0128 \qquad (1)$$

Since $dC/dt = k_1AB$, $dD/dt = k_2AB$ and $dE/dt = k_3AB$,

$dC/dD = k_1/k_2$

$C-C_0 = (k_1/k_2)(D-D_0) = (k_1/k_3)(E-E_0)$

But $C_0 = D_0 = E_0 = 0$, so

$k_1:k_2:k_3 = C:D:E = 0.032:0.4675:0.0005$ (2)

From lines (1) and (2),

$k_1 = 0.000815,\ k_2 = 0.0119,\ k_3 = 0.0000127$ (3)

P3.11.04. SELECTED PAIRS OF POINTS

The rate equation

$$\frac{dC}{dt} = 1.5k_1\exp(-k_1t) - k_2C$$

has the integral,

$$C = \frac{1.5k_1}{k_2-k_1}[\exp(-k_1t) - \exp(-k_2t)]$$

Given the following data, find the numerical values of k_1 and k_2:

t	20	30	40	50
C	0.698	0.520	0.351	0.226

The proper way is to use nonlinear regression with all four points simultaneously, by which method the values found are $k_1 = 0.100$ and $k_2 = 0.050$. Alternatively, take arbitrary pairs of points and solve the simultaneous equations. The tabulation shows that all pairs give about the same result, but this is not generally true.

Points	k_1	k_2
1,2	0.10022	0.049986
1,3	0.10018	0.049980
1,4	0.10017	0.049978
2,3	0.10005	0.049999
2,4	0.10003	0.050011
3,4	0.09938	0.050015

P3.11.05. CHLORINATION OF METHANE

Chlorination of methane results in the replacement of one, two, three or four atoms of hydrogen by chlorine. Data of product compositions obtained with various reaction times are tabulated (Gorin et al, *Ind Eng Chem* 40 2135, 1948). Estimate the ratios of the specific rates for the first three substitutions.

$A = CH_4$, $B = CH_3Cl$, $C = CH_2Cl_2$, $D = CHCl_3$, $E = CHCl_4$, $F = Cl_2$. The stoichiometric balance is

$$F = F_0 - A_0 + A$$

The ratios of rate equations are

$$\frac{dB}{dA} = \frac{dB/dt}{dA/dt} = -1 + \frac{k_2 B}{k_1 A}$$

$$\frac{dC}{dA} = \frac{k_2 B - k_3 C}{k_1 A}$$

$$\frac{k_2}{k_1} = \left(1 + \frac{dB}{dA}\right)\left(\frac{A}{B}\right)$$

$$\frac{k_3}{k_1} = \left(1 + \frac{dB}{dA} + \frac{dC}{dA}\right)\left(\frac{A}{C}\right)$$

The data are plotted as (B,A) and (C,A) and fitted with cubic polynomials, although the fits are poor. Then they are differentiated to obtain the derivatives,

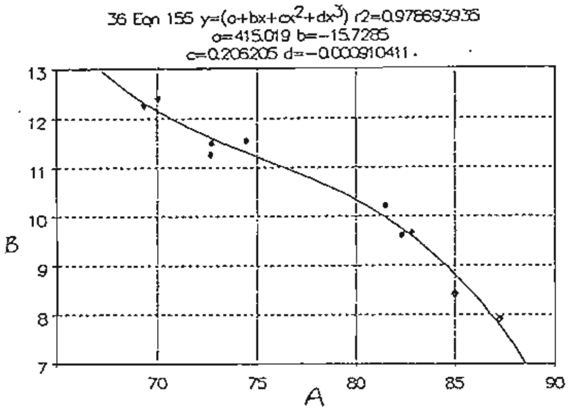
$$dB/dA = -15.73 + 0.4125A - 0.00273A^2$$

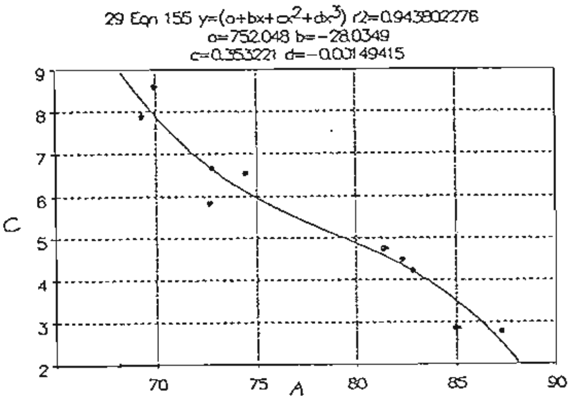
$$dC/dA = -28.035 + 0.7064A - 0.00450A^2$$

The values of the derivatives and of the ratios of the specific rates are tabulated. The first two entries are ignored in taking the averages of the ratios. The ratios are only roughly constant, with

$k_2/k_1 = 0.110$, $k_3/k_1 = 0.028$

A	B	C	D	E	dB/dA	dC/dA	k_2/k_1	k_3/k_1
87.3		2.76	0.90	0.30			0.04273	-0.00158
85.1	8.43	2.85	1.50	0.00			0.06302	0.00868
82.4		4.47	1.76	0.00			0.8631	0.02361
82.9	9.66	4.21	1.81	0.41			0.08223	0.02091
81.5		4.72	1.83	0.20			0.09330	0.02824
74.5	11.53	6.53	4.59	1.56			0.12933	0.04522
72.7		5.84	3.49	0.49			0.13292	0.04145
72.8	11.48	6.64	5.47	1.69			0.13278	0.04179
69.4		7.89	3.64	1.19			0.13306	0.01716
70.0	12.39	8.58	3.81	1.32			0.13370	0.02392





P3.11.06. RATE EQUATION OF A CHAIN REACTION

A reaction, A + B ⇒ 2C, has a rate equation of the same form as that of the hydrogen-bromine reaction studied in problem P2.03.15, namely,

$$r = \frac{dC}{dt} = \frac{k_1(A_0-C)^{5/2}}{A_0+(k_2-1)C}$$

Data are $A_0 = B_0 = 1$, $C_0 = 0$; $r = 0.5$ when $C = 0.2$; $r = 0.15$ when $C = 0.5$. Find the specific rates.

The simultaneous equations,

$$0.5 = \frac{(1-0.5)^{2.5}k_1}{1+0.2(k_2-1)}$$

$$0.15 = \frac{(1-0.5)^{2.5}k_1}{1+0.5(k_2-1)}$$

have the solutions $k_1 = 0.891$, $k_2 = 1.100$.

P3.11.07. HYDROGEN-BROMINE REACTION

The reaction between hydrogen and bromine was studied by Bodenstein & Lind (Z physik Chem 57 168, 1907). Data were obtained at 277.5 C of time, minutes, against mols reacted per 22.4 liters, x. Initial concentrations were $[H_2] = 0.5637$ and $[Br_2] = 0.2947$ mols/ 22.4 liters. They proposed the rate equation

$$r = \frac{dC}{dt} = \frac{k_1AB^{1/2}}{1+k_2C/B} \tag{1}$$

See problem P2.03.15 for the derivation. The constants k_1 and k_2 are to be found.

The (x, t) data are fitted by the 4th degree polynomial on the graph. Then

$$\frac{d[HBr]}{dt} = 2\frac{dx}{dt} = 2(b + 2ct + 3dt^2 + 3et^3) \tag{2}$$

$$A = [H_2] = 0.5637-x \tag{3}$$
$$B = [Br_2] = 0.2947-x \tag{4}$$
$$C = [HBr] = 2x \tag{5}$$

Equation (1) in linearized form is

$$\frac{AB^{1/2}}{r} = \frac{1}{k_1} + \frac{k_2}{k_1}\left(\frac{C}{B}\right)$$

or

$$y = \frac{(0.5637-x)(0.2947-x)^{1/2}}{r}$$
$$= \frac{1}{k_1} + \frac{k_2}{k_1}\left(\frac{2x}{0.2947-x}\right)$$

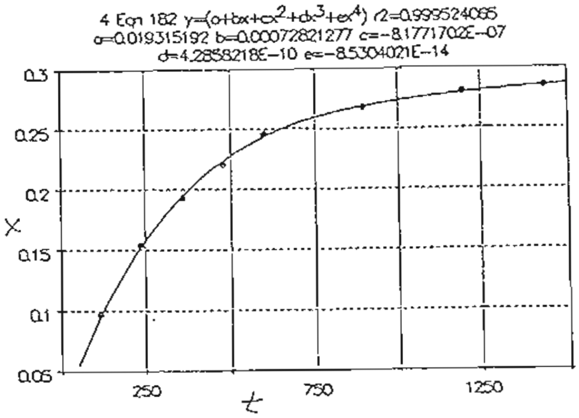
The constants of the last equation are obtainable by straight line plotting,

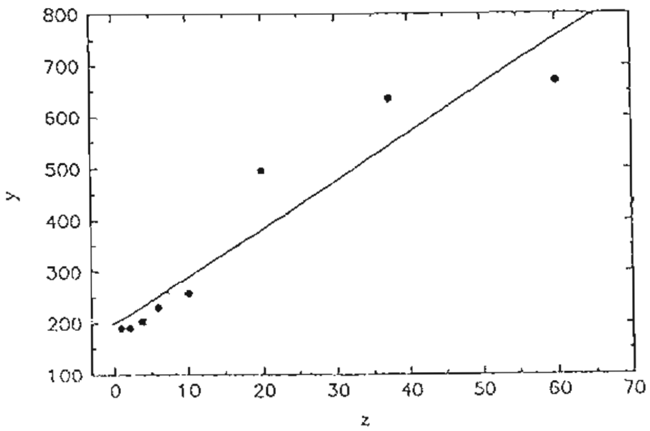
$$y = a + bz = 200 + 9.23z$$

Therefore,

$$k_1 = 0.005,\ k_2 = 0.0462$$

t	x	$10^4 r$	y	z
120	0.0953	10.0	380.5	0.96
240	0.1538	8.10	380.1	2.18
360	0.1936	5.80	405.8	3.83
480	0.2210	4.03	461.7	6.00
600	0.2460	2.72	515.8	10.10
900	0.2679	0.976	991.4	20.00
1200	0.2797	0.547	1271.1	37.30
1440	0.2852	0.405	1339.2	60.04





P3.11.08. PARALLEL REACTIONS

The kinetics of coupling a diazonium salt (D) with naphthol (N) to form a dye (A) is complicated to a minor extent by spontaneous decomposition of D to form inert products P. Data of A, but not of other participants, are in the table (Hanna et al, JACS 96 7222, 1974). Temperature was 0 C, $N_0 = 0.01$ mols/liter, $D_0 = 0.0001$. Find the specific rates.

$$D + N \overset{1}{\Rightarrow} A + H,\quad D \overset{2}{\Rightarrow} P$$

The rate equations are

$$\frac{dA}{dt} = k_1 DN = k_1 D(N_0-A) \tag{1}$$

$$\frac{dD}{dt} = -k_1 DN - k_2 D = -D[k_1(N_0-A) + k_2] \tag{2}$$

These equations could be integrated, but both k_1 and k_2 could not be evaluated unless data about D or P were available. Since the second reaction is said to be minor, consider only the first rate equation.

$$\frac{dA}{dt} = -\frac{dx}{dt} = k_1(0.0001-x)(0.01-x)$$

$$k_1 = \frac{1}{t-8.33}\int_{2(10^{-5})}^{x}\frac{dx}{(0.0001-x)(0.01-x)}$$

The five values are tabulated and have a mean value,

k_1 = 2.08 liters/mol-sec. Their rough constancy implies that the decomposition rate of D into inerts is relatively small.

10^3t, s	10^5A	k_1
8.33	2.00	
10.89	2.45	2.27
14.15	2.90	2.06
16.99	3.25	1.9
19.08	3.60	2.08
24.36	4.23	2.04
∞	6.4	

P3.11.09. THREE SERIES REACTIONS

Data for the consecutive first order reactions

$$C_0 \overset{1}{\Rightarrow} C_1 \overset{2}{\Rightarrow} C_2 \overset{3}{\Rightarrow} C_3$$

are: When $t = 0$, $C_0 = 1$; when $t = 2$, $C_0 = 0.2$, $C_1 = 0.4$, $C_2 = 0.3$ and $C_3 = 0.1$. Find the specific rates.

The rate equations and their integrals found by Laplace transformation,

$$dC_0/dt = -k_1C_0$$

$$dC_1/dt = k_1C_0-k_2C_1$$

$$dC_2/dt = k_2C_1-k_3C_3$$

$$C_0 = \exp(-k_1t) = 0.2 \text{ when } t = 2$$

$$C_1 = \frac{k_1}{k_2-k_1}\exp(-k_1t) + \frac{k_1}{k_1-k_2}\exp(-k_2t) = 0.4 \text{ when } t = 2$$

$$C_2 = \frac{k_1k_2}{(k_2-k_1)(k_3-k_1)}\exp(-k_1t) + \frac{k_1k_2}{(k_1-k_2)(k_3-k_2)}\exp(-k_2t)$$

$$+ \frac{k_1k_2}{(k_1-k_3)(k_2-k_3)}\exp(-k_3t) = 0.3 \text{ when } t = 2$$

The last three equations are solved in succession, for one variable at a time.

$k_1 = 0.8047$, $k_2 = 0.5948$, $k_3 = 0.3652$

P3.11.10. ISOPROPYL BENZENES

Data of the product compositions in the reaction between benzene and a large excess of propylene are on the figure and in the table. The subscripts 0, 1, 2, 3, 4 refer to benzene, the mono, the di, the tri and tetra isopropyl benzenes. The maxima on the curves are at t = 1.11 for the mono, t = 3.13 for the di, and t = 7.06 for the tri derivative. The compositions in the table are at these key times.

t	B	mono	di	tri	tetra	k_1
0	100	0	0	0	0	
1.11	32.8	41.0	22.9	3.2	0.1	1.004
3.13	4.4	19.0	47.6	24.6	4.4	0.998
7.06	0.1	1.3	23.1	46.3	29.1	0.978

The values of k_1 are obtained by integrating the differential equation for benzene,

$$dn_0/dt = -k_1n_0$$

at each of the three times in the table. They differ slightly, and have an average $k_1 = 0.993$. The other specific rates are found from the differential equations equated to zero at the times of the peak values.

$$dn_1/dt = k_1n_0 - k_2n_1 \Rightarrow 0 \text{ when } t = 1.11$$

$$dn_2/dt = k_2n_1 - k_3n_2 \Rightarrow 0 \text{ when } t = 3.13$$

$$dn_3/dt = k_3n_2 - k_4n_3 \Rightarrow 0 \text{ when } t = 7.06$$

Substitute values from the table.

$k_1 = 0.993$

$32.8k_1 - 41.0k_2 = 0$

$19.0k_2 - 47.6k_3 = 0$

$23.1k_3 - 46.3k_4 = 0$

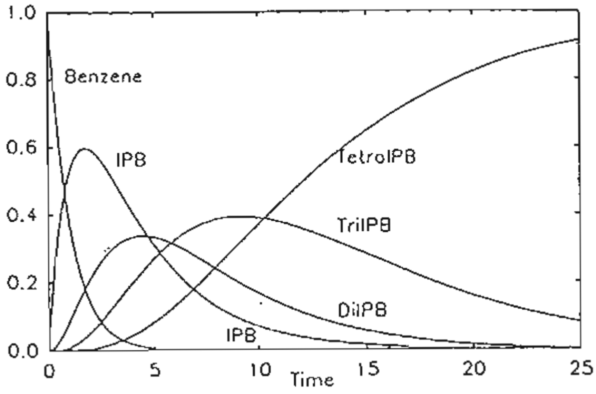
The solutions are

$k_1 = 0.993$

$k_2 = 0.8k_1$

$k_3 = 0.32k_1$

$k_4 = 0.16k_1$



P3.11.11. SECOND AND FIRST ORDER IN SERIES

The reaction system, $2A \xrightarrow{1} B \xrightarrow{2} C$, has been studied in a constant volume, batch reactor with the tabulated results. Assuming the orders conform to the stoichiometry, find the specific rates.

The rate equations are

$$\frac{dA}{dt} = k_1A^2 \qquad (1)$$

$$\frac{dB}{dt} = k_1A^2 - k_2B = \frac{k_1A_0}{1+2k_1A_0t} - k_2B \qquad (2)$$

$$\frac{dC}{dt} = k_2B \qquad (3)$$

Integrating the first equation,

$$k_1 = \frac{1}{2t}\left(\frac{1}{A} - 1\right) = 5.04,\ \text{average}$$

The values are tabulated in column 6 and have the average shown.

The third equation can be integrated with the trapezoidal rule. Values are shown in the last column and have the average shown.

$$k_2 = \frac{1}{t-0.03}\int_{0.02}^{C}\frac{dC}{B} = 10.86,\ \text{average}$$

Equation (2) is not needed for evaluation of the specific rates. It is a first order linear equation that could be integrated with the found specific rates and the resulting (B, t) could be compared with the given data for consistency.

t	A	B	C	1/B	k_1	k_2
0	1.0	0	0			
0.03	0.76	0.098	0.02	10.20	5.26	
0.06	0.63	0.122	0.06	8.20	4.89	12.26
0.1	0.51	0.140	0.10	7.143	4.80	9.64
0.15	0.39	0.120	0.17	8.333	5.21	10.13
0.2	0.33	0.10	0.24	10	5.08	10.93
0.3	0.25	0.05	0.32	20	5.00	11.33

P3.11.12. CONSECUTIVE SAPONIFICATIONS

Glycol diacetate (A) and glycol monoacetate (B) saponify in dilute aqueous solution with production of acetic acid (C). The reactions are irreversible pseudo first order.

$A + H_2O \xrightarrow{1} B + C,\ B + H_2O \xrightarrow{2} C + D$

Two sets of experiments are reported (Meyer, Z physik Chem 66 81, 1909) at 18 C in a 0.01 N HCl medium: The first starting with pure monoacetate, the second with pure diacetate. The given concentrations are of the acetic acid produced, mol/liter. The specific rates are to be found.

The reactions are assumed to go to completion, so the starting values are given by the limiting amounts of acetic acid produced, as given in the table.

$B_0 = 0.1110$ mol/liter, starting with pure mono

$A_0 = 0.5(0.1765) = 0.\ 0883$, starting with pure di

For the monoacetate experiment,

$$\frac{dB}{dt} =- k_2B$$

$$k_2 = \frac{1}{t}\ \ln(B_0/B) = \frac{1}{t}\ \ln\ \frac{0.1110}{0.111-C}$$

The values are tabulated and have a mean of

$$k_2 = 1.480(10^{-3})/\text{hr}$$

For the diacetate experiment,

$$C = 2(A_0-A) - B \tag{1}$$

$$A = A_0 - 0.5(B+C) = 0.0883 - 0.5(B+C)$$

$$\frac{dA}{dt} = -k_1A$$

$$A = A_0\exp(-k_1t)= 0.0883\ \exp(-k_1t)$$

$$\frac{dB}{dt} = k_1A - k_2B$$

$$= k_1A_0\exp(-k_1t) - k_2B$$

This is a first order linear equation with integrating factor, $\exp(k_2t)$ and solution

$$B\ \exp(k_2t) = k_1A_0\int \exp[(k_2-k_1)t]dt + I$$

with B = 0 when t = 0. The final form is

$$B = \frac{k_1A_0}{k_2-k_1}[\exp(-k_1t) - \exp(-k_2t)] \tag{2}$$

$$= 2(A_0-A) - C$$

$$= 2A_0[1-\exp(-k_1t)] - C$$

$$= 2(0.0883)[1 - \exp(-k_1t)] - C \tag{3}$$

Substitute $k_2 = 0.00148$ and sets of (t, C) data from the table, and solve (2) and (3) simultaneously for k_1. The values are tabulated in the last column and have a mean of

$$k_1 = 0.00296/\text{hr}$$

t, hr	C_{mono}	C_{di}	10^3k_2	10^3k_1
0	0	0		
47	0.0074		1.468	
47.5		0.0121		2.993
96	0.0149	0.0233	1.502	2.950
192	0.0274	0.0429	1.477	2.894
288	0.0384	0.0618	1.474	3.002
∞	0.1110	0.1765		

P3.11.13. A REVERSIBLE REACTION.

A reversible reaction is expected to have the rate equation,

$$r = k_1C^a - k_2(C_0-C)^b$$

Data were taken of the initial rates at several initial concentrations and of the variable rate with initial concentration $C_0 = 2$. Find the constants.

The initial rate equation

$$r_0 = k_1C_0^a$$

is plotted in linearized form as

$$\ln r_0 = \ln k_1 + a \ln C_0$$
$$= -0.693 + 1.498 \ln C_0$$

from which $k_1 = 0.50$ and $a = 1.50$.

With the variable rate data form a variable y,

$$-y = r - 0.5\ r^{1.5}$$

Tabulate these values and plot the function

$$\ln(-y) = \ln[k_2(2-C)^b] = \ln k_2 + b \ln(2-C)$$
$$= -1.566 + 1.981 \ln(2-C)$$

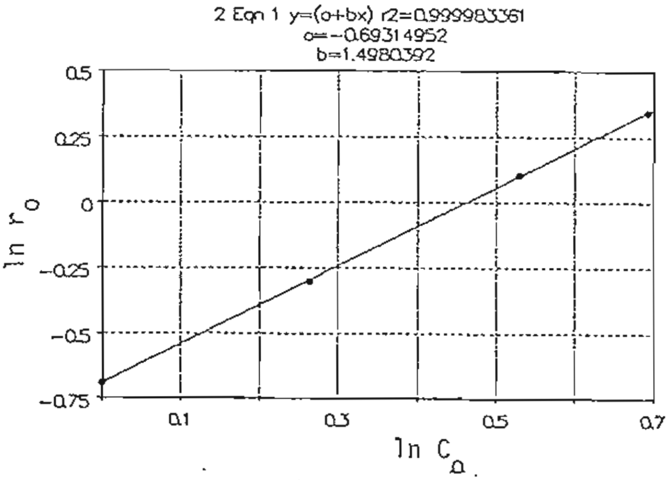
from which the constants of the rate equation are

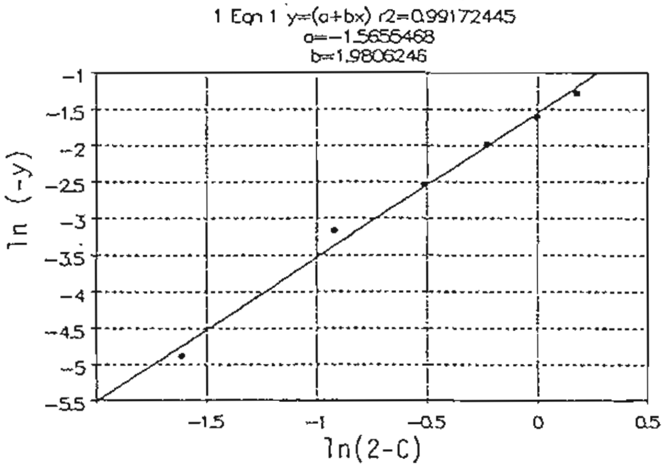
$k_2 = 0.209$ and $b = 1.981$.

Accordingly the complete rate equation is

$$r = 0.50\ C^{1.50} - 0.209\ (2-C)^{1.981}$$

C	r_0	r	-y
1.0	0.50		
1.3	0.74		
1.7	1.11		
2.0	1.41	1.41	0
1.8		1.20	0.0075
1.6		0.97	0.0419
1.4		0.75	0.0783
1.2		0.52	0.1373
1.0		0.30	0.2000
0.8		0.08	0.2778





CHAPTER 4
IDEAL REACTORS

THEORY

PROBLEMS

A useful classification of types of chemical reactors is in terms of their concentration patterns. Certain limiting or ideal types are represented by Figure 4.1 which illustrates batch reactors, continuous stirred tanks and tubular flow reactors. This chapter is concerned with the sizes, performances and heat effects of these ideal types. They afford standards of comparison and are often as close enough to the truth as available information allows.

In a batch vessel, the reactants are loaded at once, then the concentration changes with time, but at any one time it is uniform throughout. The horizontal portion of Fig 4.1(b) corresponds to a period before reaction starts, before injection of catalyst, say, or before the temperature has been adjusted properly.

In an ideal continuous stirred tank reactor, CSTR, the composition and temperature are uniform throughout and the condition of the effluent is the same as that of the tank. When a battery of such vessels is employed in series, the concentration profile is step shaped if the abscissa is total residence time or the stage number.

In another kind of ideal flow reactor, all portions of the fluid have the same residence time. It is called a plug flow reactor, PFR, or a tubular flow reactor, TFR, because this flow pattern is characteristic of tubes and pipes. As the reaction proceeds, the concentration falls off with distance.

Complete mixing often cannot be approached for economic reasons. Inactive or dead zones, bypassing and limitations of energy input are common causes. Packed beds usually are preponderantly in plug flow but they may also have superimposed small mixing zones in series or parallel. In tubular reactors for

viscous fluids, laminar or non-Newtonian behavior gives rise to variation of residence times. More general cases of nonideality are studied in later chapters

4.1. EQUILIBRIUM CONSTANTS

As a reversible reaction approaches equilibrium its rate slows down and for a given extent of conversion the required size of the reactor goes up. For practical reasons, it may be feasible to operate only to within some percentage of equilibrium, say 95 or 99%, and either discard unconverted material or recover and recyle it, depending on the economics.

For a reaction,

$$aA + bB \Leftrightarrow cC + dD \tag{4.1}$$

the equilibrium constant in terms of concentrations is

$$K_c = \frac{C_c^c C_d^d}{C_a^a C_b^b} \tag{4.2}$$

The concentrations are related by stoichiometric coefficients,

$$\frac{C_{a0}-C_a}{a} = \frac{C_{b0}-C_b}{b} = -\frac{C_{c0}-C_c}{c} = -\frac{C_{d0}-C_d}{d} = \varepsilon \tag{4.3}$$

Thus the equilibrium condition is expressible in terms of the initial concentrations and the single variable, ε, which is called the degree of advancement. Also, all concentrations can be expressed in terms of a single one of the others, say,

$$C_b = C_{b0} - \frac{b}{a}(C_{a0}-C_a), \text{ and so on.} \tag{4.4}$$

When several reactions occur simultaneously a degree of advancement is associated with each stoichiometric equation. Problem P4.01.26 is a application of this point. Some processes, for instance cracking of petroleum fractions, involve many substances. Then a correct number of independent stoichiometric equations must be formulated before equilibrium can be calculated. Another technique is to apply the principle that equilibrium is at a minimum of Gibbs free energy. This problem, however, is beyond the scope of this book.

Gaseous equilibria are expressed in terms of fugacities which can be regarded as partial pressures corrected for nonideality. Several other thermodynamic terms are involved in that definition.

$\hat{f}_i$ = partial fugacity

$= y_i f_i$, the Lewis & Randall Rule

$$= y_i \phi_i \pi \qquad (4.5$$

$\phi_i = f_i/\pi$, fugacity coefficient of pure component

$$K = K_{\hat{f}} = \hat{f}_c^c \hat{f}_d^d / \hat{f}_a^a \hat{f}_b^b \tag{4.6}$$

$$= K_y K_\phi \pi^{c+d-a-b} \tag{4.7}$$

$$K_y = y_c^c y_d^d / y_a^a y_b^b \tag{4.8}$$

$$K_\phi = \phi_c^c \phi_d^d / \phi_a^a \phi_b^b \qquad (4.9$$

In terms of partial pressures, $p_i = y_i \pi$,

$$K_p = p_c^c p_d^d / p_a^a p_b^b = K_y \pi^{c+d-a-b} \qquad (4.10)$$

In all these cases, stoichiometry is invoked to reduce the number of variables on the right to a single one.

Fugacity coefficients are empirical quantities and are calculable from correlations such as equations of state. They differ appreciably from unity at high pressures or near the critical state.

Pressure affects the composition of an equilibrium mixture, but the equilibrium constant itself is independent of pressure. It does, however, depend on temperature..

4.2. TEMPERATURE CHANGE AND HEAT OF REACTION

Heat effects accompanying chemical reaction influence equilibrium constants and compositions as well as rates of reaction. The enthalpy change of reaction, ΔH_r, is the difference between the enthalpies of formation of the participants. It is positive for endothermic reactions and negative for exothermic ones. This convention is the opposite of that for heats of reaction, so care should be exercised in applications of this quantity. Enthalpies of formation are empirical data, most often known at a standard temperature, frequently at 298 K. The Gibbs energies of formation, ΔG_f, likewise are empirical data.

These quantities are related to the equilibrium constant by

$$\Delta G_r = -RT \ln K \qquad (4.11)$$

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{RT^2} \qquad (4.12)$$

The heat of reaction at a particular temperature is

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p dT \qquad (4.13)$$

$$\Delta C_p = cC_{pc} + dC_{pd} - aC_{p_a} - bC_{pb} \qquad (4.14)$$

$$= \alpha + \beta T + \gamma T^2 + \delta T^3 + \ldots$$

Accordingly,

$$\ln K = \ln K_{298} + \frac{1}{R}\int_{298}^{T} \frac{\Delta H_{r298} + \int_{298}^{T} \Delta C_p dT}{T^2} dT \qquad (4.15)$$

Problems P4.02.05, P4.02.06 and P4.02.11 are brief applications of these formulas.

In terms of an average heat of reaction over a modest temperature range, the often adequate equation is

$$K = \exp(A+B/T) \qquad (4.16)$$

Figure 4.2 shows the goodness of fit of this result for some common reactions.

P4.3. BATCH REACTORS.

Batch reactors are tanks usually provided with agitation and some mode of heat tranfer to maintain temperature within a desirable range. They are employed primarily for relatively slow reactions, of several hours duration since downtime for filling and emptying large equipment may be an hour or so by itself. Agitation is for maintenance of uniformity and for improvement of heat transfer. A pumparound system through an external heat exchanger also may be used to provide agitation and heat transfer. Filling and emptying modes are described in Section 2.6.1.

Except in the laboratory, batch reactors are mostly liquid phase. In semi-batch operation, some participants are preloaded and the others then are charged gradually. This is necessary when some of the reactants are gases of limited solubility and in other cases to keep the temperature within the capability of the heat transfer. Batch reactors are popular in practice because of their great flexibility with regard to reaction time and the kinds and quantities of reactants they can process.

Material and energy balances of a nonflow reactor are summarized in Table 2.3. The main problems to be solved are:

1. What is the size of a reactor to obtain a specified daily production?
2. What conversion or yields are obtainable in a reactor of specified size? This may involve establishing temperature or rate of heat transfer.
3. With complex or multiple reactions, what product distribution can be obtained in comparison with that from a flow reactor?

The rate equations of batch reaction and their integration are discussed in the previous chapter, notably Section 2.1-2.2. For the stoichiometric process , Eq 4.1, the rate equation is

$$r_a = -\frac{dC_a}{dt} = k_1C^aC_b^b - k_2C_c^cC^d \qquad (4.17)$$

This becomes integrable after the replacements,

$$C_b = C_{b0} - \frac{b}{a}(C_{a0}-C_a)$$

$$C_c = C_{c0} + \frac{c}{a}(C_{a0}-C_a)$$

$$C_d = C_{d0} + \frac{d}{a}(C_{a0}-C_a) \qquad (4.18)$$

Section P2.4 has integrals of many batch equations. Numerical integration sometimes is more convenient than analytical.

Gas phase reactions usually are at nearly constant pressure. For them the concentrations are replaced by the ratio of mols to reactor volume,

$$C_i = n_i/V_r$$

The total number of mols present is given by Eq. 2.14,

$$n_t = n_{t0} + \delta_a(n_{a0}-n_a) \qquad (4.19)$$

By the ideal gas law the reaction volume is

$$V_r = \frac{n_tRT}{\pi} \qquad (4.20)$$

An example of a rate equation in these units is

$$r_a = -\frac{1}{V_r}\frac{dn_a}{dt} = kC_a^\alpha = k\left(\frac{\pi n_a}{n_tRT}\right)^\alpha \qquad (4.21)$$

and

$$-\frac{dn_a}{dt} = k\left(\frac{\pi}{n_tRT}\right)^{\alpha-1}n_a^\alpha \qquad (4.22)$$

Such equations are used in the analysis of experimental data in Section P3.3.

An example with a nonideal gas is in problem P3.03.06

4.4. CONTINUOUS STIRRED TANK REACTORS (CSTR)

Flow reactors are used for larger production rates, when reaction time is comparatively short, when uniform temperature is necssary, when labor costs are high, and so on. CSTRs are used singly or in multiple units in series, either in separate vessels or in compartmented single shells.

Material and energy balances of CSTRs are derived by the general conservation rule, Inputs = Outputs + Sinks + Accumulations

In the operation of liquid phase reactions at steady state, the input and output flow rates are constant so the holdup is fixed. The usual control of the discharge is on liquid level in the tank. When the mixing is adequate, concentration and temperature are uniform, and the effluent has these same properties. The steady material balance on a reactant A is

$$V'_0C_{a0} = V'C_a + V_rr_a \tag{4.23}$$

Usually changes in density because of reaction or temperature changes are small enough to be ignored. Then the volumetric flow rate is constant and the balance becomes

$$C_{a0} = C_a + \tau r_a \tag{4.24}$$

where the residence time is

$$\tau = V_r/V' \tag{4.25}$$

A useful rearrangement

$$r_a = \frac{C_{a0}-C_a}{\tau} \tag{4.26}$$

emphasizes how CSTR measurements can provide data for the development of rate equations.

During startup or discharge the unsteady form of the material balance applies,

$$V'_0C_{a0} = V'C_a + V_rr_a + \frac{d(V_rC_a)}{dt} \tag{4.27}$$

where the reactor volume V_r may be a function of time. Usually this equation must be integrated numerically.

For a power law rate equation,

$$C_{a0} = C_a + k\tau C_a^{\alpha} \tag{4.28}$$

A summary of material and energy balances is in Table 2.4.

For each vessel of a series,

$$C_{a,n-1} = C_{an} + k_n\tau_nr_{an} \tag{4.29}$$

These equations are to be solved simultaneously. The simplest problem is when all stages have the same $k\tau$. Then one of the three variables--$k\tau$, n or C_{an}--can be found when the others are specified.

For first order reactions

$$C_{an}/C_{a0} = \frac{1}{(1+k_1\tau_1)(1+k_2\tau_2)\ldots(1+k_n\tau_n)} \tag{4.30}$$

$$\Rightarrow \frac{1}{(1+k\tau_{total}/n)^n} \tag{4.31}$$

Closed form solutions are not possible or are quite complex algebraically in most other cases.

For multiple reactions, material balances must be made for each stoichiometry. An example is the consecutive reactions, A ⇒ B ⇒ C, for which problem P4.04.52 develops a closed form solution. Other cases of sets of first order reactions are solvable by Laplace Transform, and of course numerically.

CSTRs often are operated in multiple. The total volume drops off sharply with the number of stages. An economical number often is only 3 to 6, since the benefit of reduced volume may be outweighed by increased cost of multiple agitators, pumps and controls. Problems P4.04.29 and P4.12.13 show typical variations of stage volumes with number of stages. When all stages are enclosed in a single shell, the economics are different, but the single shell arrangements lose some of the flexibility of the multiple tank designs. Five or six stages sometimes may be taken as equivalent to a plug flow unit. Eq 4.31 for instance reduces to the plug flow equation as $n \Rightarrow \infty$.

4.5. TUBULAR AND PACKED FLOW REACTORS

Reactions in which all portions of the flow have essentially the same residence time are conducted in single or multiple tubes in parallel of less than a hundred or so millimeters in diameter. In packed beds of larger diameters, large scale convection may be inhibited to such an extent that plug flow is approached. Continuous gas reactions are largely done in such units, and so are many liquid reactions. Immiscible liquids are best reacted in stirred tanks, although inline mixers have facilitated such reactions in pipes. Reaction times are mostly short, the temperature being elevated to make this possible. In large scale operations such as oil cracking the tubes are several hundred meters long, in a trombone-like arrangement. Temperature control is through the vessel wall. In the extreme, a multitubular arrangement like a shell and tube heat exchanger is employed. Product distribution of complex reactions is like that of batch reactors, but different from CSTRs. Problems P4.04.57 and P4.04.60 make such comparisons.

As a matter of convenience the loading on a flow reactor is expressed as a size of reactor per unit of flow rate, and is called the <u>space velocity</u>. Various units for both these quantities are in common use. Some of these are stated in problem P4.05.03 as well as in P3.01.04 and P3.01.05. How to find the actual contact time of a given operation is illustrated in problem P4.05.02 as well as in P3.01.02 and P3.01.03.

Material and energy balances on plug flow and packed bed reactors are summarized in Tables 2.5 and 2.6. They are formulated on a differential reactor volume. When n_a is the molal flow rate of reactant A the flow reactor equation is

$$-dn_a = n_{a0}dx = -V'dC_a = r_a dV_r \tag{4.32}$$

$$V_r = -\int_{n_{a0}}^{n_a} \frac{dn_a}{r_a} = n_{a0}\int_{x_0}^{x} \frac{dx}{r_a} \tag{4.33}$$

In a rate equation the concentrations are replaced by ratios of molal and volumetric flows,

$$C_i = n_i/V'$$

and the volumetric flow rate is based on the ideal gas law or other equation of state,

$$V' = n_t RT/\pi = \frac{[n_{t0}+\delta(n_{a0}-n_a)]RT}{\pi} \tag{4.34}$$

A typical power law rate equation in these units is,

$$r_a = kC_a^\alpha = k\left(\frac{n_a}{V'}\right)^\alpha = k\left[\frac{n_{a0}(1-x)}{V'}\right]^\alpha = k\left(\frac{\pi}{RT}\frac{n_a}{n_t}\right)^\alpha \tag{4.35}$$

A number of specific rate equations of this type are considered in problem P4.05.01.

Plug flow reactors mostly operate at essentially constant pressure but sometimes pressure drop due to friction is appreciable. Thus problems P4.05.30 and P4.05.29 reveal a significant effect of friction on conversion and reactor size. For flow in pipelines, the pressure drop is given by

$$-dP = \frac{f\rho u^2}{2gD}\,dL \tag{4.36}$$

A good approximation to the friction factor in the turbulent range is

$$f = 0.046(Re)^{-0.2} = 0.044\left(\frac{\mu D}{W}\right)^{0.2} \qquad (4.37)$$

The mass flow rate is

$$W = 0.7854D^2\rho u$$

For ideal gases the density in terms of the molecular weight M is

$$\rho = \frac{M}{V} = \frac{PM}{RT} = \frac{PM_0n_{t0}}{RTn_t}$$

Also,

$$dV_r = 0.7854D^2dL$$

Putting these together,

$$-dP = \frac{0.046W^{1.8}\mu^{0.2}RT[n_{t0}+\delta(n_{a0}-n_a)]}{gD^{6.8}M_0n_{t0}P}\,dV_r \qquad (4.38)$$

This is to be solved simultaneously with the flow reactor Eq 4.32. Also, dV_r can be eliminated from Eq 4.38 for a direct relation between P and n_a.

4.6. RECYCLE AND SEPARATION MODES

All reactor modes sometimes can be operated advantageously with recycle of part of the product or intermediate streams. When the recycle is heated or cooled appropriately it can serve to moderate undesirable temperature travel. This function is well served with pumparound from a stirred tank through an external heat exchanger. Recycle streams also can be processed for changes in composition before return.

As the recycle ratio through a PFR is increased, changes in temperature and composition across the reactor itself become smaller. Eventually it can be regarded as a differential reactor with approximately constant temperature. Between the fresh inlet to the system and the product withdrawal, substantial differences will develop. The differential operation at virtually constant temperature thus eliminates the main objection to the PFR as a device for obtaining data from which a rate equation can be determined.

Notation and material balances for recycle operation are stated in problems P4.06.01 and P4.06.02. An adiabatic operation is studied in P4.06.08.

With reversible reactions, sufficient improvement in conversion sometimes can be realized from removing the product to warrant a recycle operation. This can be done by sending the product to a separator and returning only unconverted material. Some systems, moreover, lend themselves to continuous removal of product in equipment integrated with the reactor. Extraction is thus employed in problem P4.06.13 and azeotropic distillation in problems P4.06.14 and P4.06.15. The gasoline additive, methyl-*tert*-butyl ether, is made in a distillation column where reaction and simultaneous separation take place.

4.7. TEMPERATURE CHANGES

The heat balance of a reactor is made up of three terms,

Heat of reaction + Heat transfer = Gain of sensible and latent heats.

This establishes the temperature as a function of the composition,

$$T = f(n_a)$$

which may be substituted into the specific rate and equilibrium constant,

$$k = \exp\left[A + \frac{B}{f(n_a)}\right]$$

$$K_e = \exp[C + \frac{D}{f(n_a)}]$$

With these substitutions the rate equation remains a function only of the comnposition.

Heat balances for the several types of reactors are summarized in Tables 2.3-2.6.

Enthalpy changes of processes depend only on the end states. Normally the enthalpy change of reaction is known at some standard temperature, T_b = 298 K for instance. The simplest formulation of the heat balance, accordingly, is to consider the reaction to occur at this temperature, to transfer whatever heat is required and to raise the enthalpy of the reaction products to their final values.

For batch reaction,

$$-(\Delta H_r)_{T_b}(n_{a0}-n_a) + Q = \Sigma n_i(H_{iT} - H_{iT_b}) \qquad (4.39)$$

The solvent and any other inerts are included in this summation. The heat exchange through a jacket or coils at temperature T_m is

$$Q = UA(T_m - T) \qquad (4.40)$$

When phase changes are absent,

$$-(\Delta H_r)_{T_b}(n_{a0}-n_a) + UA(T_m - T) = \Sigma n_i \int_{T_b}^{T} C_{pi}dT \qquad (4.41)$$

When the mixture can be characterized by an overall heat capacity,

$$-(\Delta H_r)_{T_b}(n_{a0}-n_a) + UA(T_m-T) = V_r\rho C_p(T-T_b) \qquad (4.42)$$

or

$$-(\Delta H_r)_{T_b}(C_{a0}-C_a) + (UA/V_r)(T_m-T) = \rho C_p(T-T_b) \qquad (4.43)$$

For CSTR reaction,

The quantities n_i are molal flow rates. The heat balance in unit time is,

$$-(\Delta H_r)_{T_b}V_r r_a + Q = \Sigma n_i(H_{iT} - H_{iT_b}) \qquad (4.44)$$

$$\Rightarrow \Sigma n_i \int_{T_b}^{T} C_{pi}dT \qquad (4.45)$$

Eq 4.45 applies when phase changes are absent.

For plug flow reaction,

Differential relations in a cylindrical vessel are

$$dA = (4/D)dV_r$$

$$-\Delta H_{rT}dn_a + \frac{4UA}{D}\, dV_r = \Sigma n_i C_{pi}dT \qquad (4.46)$$

$$\Rightarrow n_t C_{pt}dT \qquad (4.47)$$

Note that the enthalpy change of reaction is a function of temperature, but approximations often are adequate.

The various heat balance results are to be solved simultaneously with the appropriate material balances, but when the temperatures can be solved for explicitly their equivalents are simply substituted into the equations of k and K_e as indicated at the beginning of this section.

4.8. LAMINAR AND POWER LAW FLOW

Plug flow is an idealization. Deviations arise with viscous or non-Newtonian fluids. A mathematically simple deviation from the plug flow pattern is that of power law fluids whose velocity in a tube depends on the radial position, $\beta = r/R$, according to the equation,

$$u = \bar{u}\left[\frac{2n+1}{n+1}\left(1-\beta^{(n+1)/n}\right)\right] \qquad (4.46)$$

where $\bar{u}$ is the average velocity. Fluids are classified by the magnitude of the parameter n:

$n = 0$, normal fluids
$n = 1$, laminar fluids
$0<n<1$, pseudoplastic fluids
$1<n<\infty$, dilatant fluids

The corresponding velocity profiles between parallel plates are in Figure 4.3.

Along any particular radial position, all molecules have the same residence time, that is, plug flow conversion is achieved on that streamline. The average over the cross section will be different.

The equation for conversion in laminar flow is developed in problem P4.08.01 which also compares the performance with that in plug flow when the rate equation is first or second order. The residual concentration is higher (the conversion is lower) with laminar flow. A similar result is found in problem P4.08.09 which is for straight line radial variation or $n \Rightarrow \infty$. Numerical magnitudes of the variation of concentration over a cross section are found in problem P4.08.07. Other problems point out the errors in calculated specific rates when the data are assumed to be plug flow instead of laminar.

4.9. UNSTEADY CONDITIONS WITH ACCUMULATION TERMS

Unsteady material and energy balances of reacting systems are formulated with the conservation law,

Inputs = Outputs + Sinks + Accumulations

The sink term of a material balance is $V_r r_a$ and the accumulation term is the time derivative of the content of reactant in the vessel, or $d(V_r C_a)/dt$, where both V_r and C_a depend on time. An unsteady condition in the sense used in this section always has an accumulation term. This sense of unsteadiness excludes the batch reactor where the conditions do change with time but are taken account of by the sink term. Startup and shut down periods of batch reactors , however, are classified as unsteady.

When a batch tank is being filled with reacting liquid, the material balance is

$$V'C_{a0} = 0 + V_rC_a + \frac{d(V_rC_a)}{dt}, \quad V_r=V_{r0}, \quad C = C_{a0} \text{ when } t = 0 \qquad (4.47)$$

where V_r depends on time. While it is being emptied,

$$0 = V'C_a + V_r r_a + \frac{d(V_rC_a)}{dt}, \quad V_r = V_{rt}, \quad C_a=C_{a1} \text{ when } t = 0 \qquad (4.48)$$

For a semibatch operation in which some of the ingredients are preloaded and the others are fed in gradually, the equations are developed in problem P4.09.09.

Similarly the unsteady material balance of a CSTR has an accumulation term added to it, for example,

$$V'C_{a0} = V'C_a + V_r r_a + \frac{d(V_rC_a)}{dt} \qquad (4.49)$$

Enthalpy balances also will have accumulation terms.

Conditions that may give rise to unsteadiness are changes in feed rate, composition or temperature. In problem P4.09.34, sinusoidal variations of these three properties are forced on the CSTR. The resulting outlet conditions likewise are cyclic, with the same period but with amplitudes that are lower as the specific rates are increased.

If a sinusoidal variation of the temperature of the heat transfer medium in the jacket or coil occurs, say

$T_m = T_{m0}(1 + \alpha \sin \beta t)$

the unsteady balances will be

$$-\Delta H_r V_r r_a + UA[T_{m0}(1+\alpha \sin \beta t)-T] = V'\rho C_p(T-T_0) + \rho V_r C_p \frac{dT}{dt} \qquad (4.50)$$

$$V'C_{a0} = V'C_a + V_r r_a + V_r \frac{dC_a}{dt} \qquad (4.51)$$

Since each input of mass to a perfect plug flow unit is independent of what has been input previously, its condition as it moves along the reactor will be determined solely by its initial condition and its residence time, independently of what comes before or after. Practically, of course, some interaction will occur at the boundary between successive inputs of different compositions or temperatures. This is governed by diffusional behaviors which are beyond the scope of the present work.

4.10. MULTIPLE STEADY STATES

A phenomenon that arises particularly with continuous stirred reactors is the occurrence of more than one steady state. This becomes apparent from the heat and material balances. "Heat generation" is made up of the heat of reaction plus any heat transfer, and the "heat removal" is the sensible and latent heat change of the reaction products. In problem P4.10.13, for instance, both the heat generation and the heat removal are plotted against the temperature. The two lines intersect at three points which represent the steady states. A point at which the slope of the heat generation line is greater than that of the heat removal line is unstable; and where it is less the point is stable. At an unstable point, any fluctuation in conditions will cause the temperature to change towards that of a neighboring point. This is also true of plots of material balance and energy balance separately as functions of temperature. Problem P4.10.07, for instance reveals that the shapes and orientations of the two sets of curves are similar. Problem P4.10.02 has a case where the energy balance line is not quite straight, as it need not be.

Endothermic reactions are always stable. On the figure of P4.10.13, for instance, when the slope of the heat generation line is negative, evidently only one intersection with the other curve is possible.

Which particular steady state will prevail can be established by choice of inlet conditions. As problem P4.10.11 shows adjustment of either temperature or pressure may ensure uniqueness.

Control systems may produce small fluctuations of the process variables, as in the sinusoidal cases of problem P4.09.34. When they occur while the system is at an unstable point, the temperature will migrate to that at a neighboring steady condition. In problem P4.10.01, as the unstable condition is approached (T = 280, C = 2.4), the profiles of temperature and concentration become erratic and eventually degenerate to the conditions at the stable point to the right.

Particular forms of the rate equation can give rise to multiple steady states even under isothermal conditions, as in problem P4.10.09 where uniqueness could be established by adjusting the inlet concentration or the residence time.

Plug flow reactors with recycle exhibit some of the characteristics of mixed reactors, including the possibility of multiple steady states. This topic is explored in other books (Perlmutter, Stability of Chemical Reactors, Chapter 9, 1972).

4.11. OPTIMA

The best quality to be found may be a temperature, a temperature program or profile, a concentration, a conversion, a yield of preferred product, kind of reactor, size of reactor, daily production, profit or cost -- a maximum or minimum of some of these factors. Examples of some of these cases are in this group of problems. When mathematical equations can be formulated, peaks or valleys are found by elementary mathematics or graphically. With several independent variables quite sophisticated mathematical procedures are available to find optima. Here a case of two variables occurs in problem P4.12.11 that is solved graphically. The application of Lagrange Multipliers for finding constrained optima is made in problem P4.11.19.

Reversible reactions particularly may need to be optimized. Often equilibrium composition becomes less favorable and rate of reaction more favorable as the temperature increases, so a best condition may exist. If the temperature is adjusted at each composition to make the rate a maximum, then a minimum reactor size or a maximum conversion will result. This kind of problem is a favorite of this collection, beginning with problem P4.11.01.

The other problems include finding best individual temperatures, preferred yields from complex reactions, best arrangements of reactor elements, and so on.

4.12. ECONOMIC BALANCE

The overall cost of any process is made up of the fixed investment costs and operating costs. An engineering project is evaluated by balancing these.

Detailed and accurate costs of equipment, overhead, labor, utilities, materials and products are at least a voluminous matter. The problems here are necessarily simplified but they do compare pertinent kinds of factors. Some of the data are in MU (money units) rather than dollars, since the latter have varied greatly in recent years, and the specific problems have arisen over some time.

The cases included are of batch, tubular and CSTR battery reactors in which are conducted simple or complex reactions.

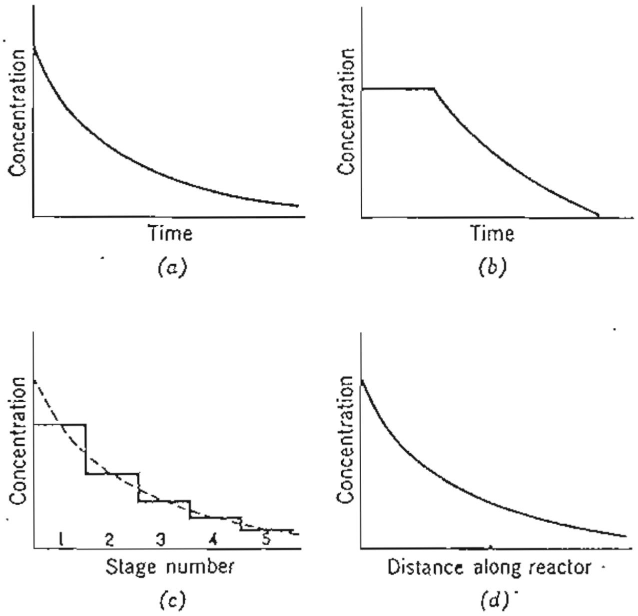


Figure 4.1. Progression of concentration in reactors. (a) Batch; (b) batch with preloading; (c) staged; (d) tubular flow.

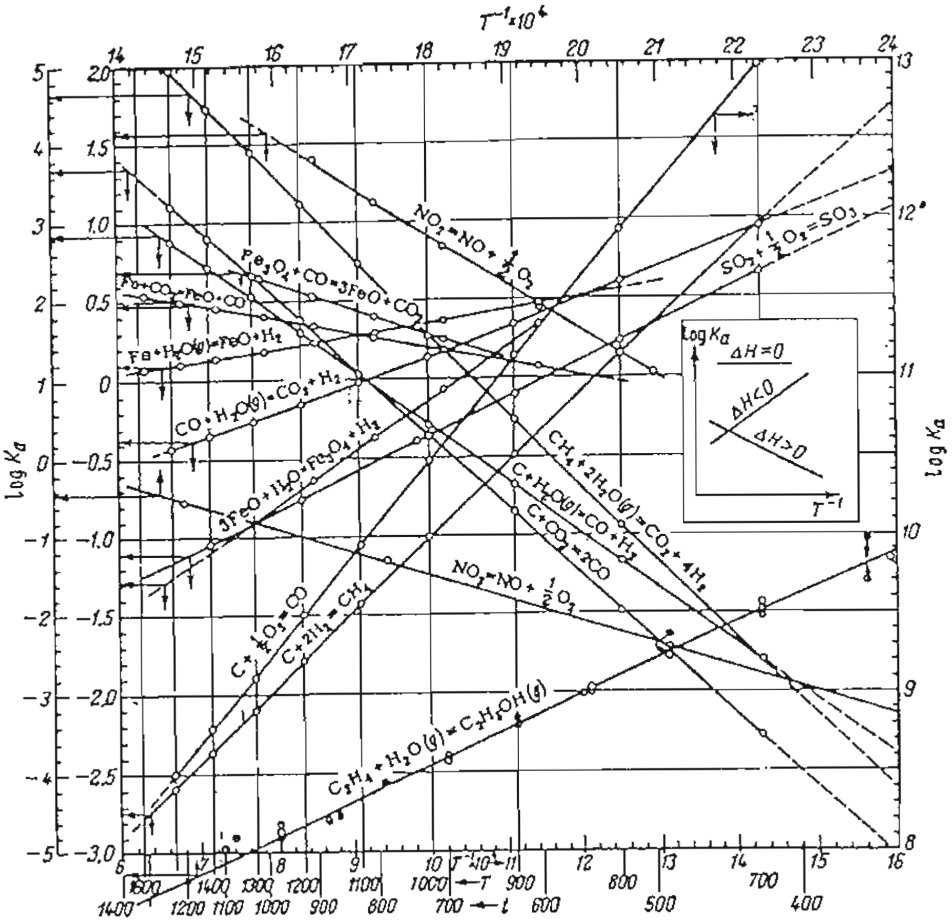


Figure 4.2. Equilibrium constants of some reactions as functions of temperature (Karapetyants, Physical Chemistry, Mir Publishers, Moscow, 1974).

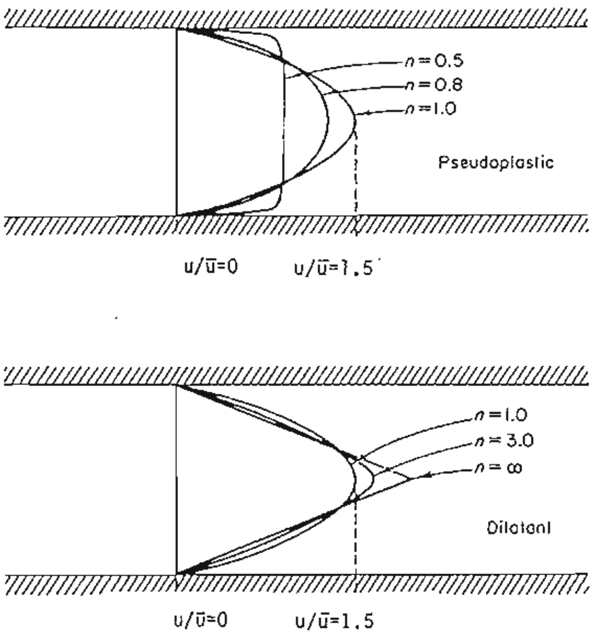


Figure 4.3. Velocity profiles of a power law fluid flowing between parallel plates. $\bar{u}$ is the mean velocity.

P4.01.01. BUTADIENE FORMATION.

For the reaction

acetylene (A) + acrolein (B) ⇒ butadiene-1,3 (C)

$1-x \quad 1-x \quad x \quad \Sigma = 2-x$

the equilibrium constant at 1500 F and 2 atm is $K_p = 4.25$. Find the composition of a mixture that originally contained equal amounts of the reactants.

$$K_p = \frac{p_c}{p_a p_b} = \frac{y_c\pi}{(y_a\pi)(y_b\pi)} = \frac{x(2-x)}{2(1-x)^2} = 4.25$$

$x = 0.676$

$y_a = y_b = 0.245$, $y_c = 0.510$ mol fractions.

P4.01.02. BUTADIENE AND STEAM

Butadiene is made by the gas phase catalytic deydrogenation of 1-butene. In order to suppress side reactions and to maintain the temperature level, high temperature steam is added to the feed. The reactor pressure is 2 atm and the feed consists of 12 mol of steam per mol of butene. The equilibrium constant as a function of temperature is

$K = \exp(14.3417 - 13997/T)$

Find the equilibrium temperature at which 30% of the butene is converted to butadiene.

$$C_4H_8 \overset{steam}{\Leftrightarrow} C_4H_6 + H_2$$

$1-x \quad x \quad x \quad \Sigma = 13+x$

$$K = K_y\pi = \frac{x^2\pi}{(1-x)(13+x)}$$

When $x = 0.3$ and $\pi = 2$, $K = 0.004833$.

$$T = \frac{13997.3}{14.3417-\ln(0.004833)} = 711.5$$

P4.01.03. METHANOL SYNTHESIS.

Methanol can be manufactured by the gas phase reaction

$CO + 2H_2 \Leftrightarrow CH_3OH$, $A + 2B \Leftrightarrow C$

For one feed composition, the equilibrium gas at 400 K and 1 atm contains 40 mol% H_2 and the only other species present are CO and CH_3OH. The equilibrium constant is 1.52 and $\Delta H^\circ = -22{,}580$ cal/(mol CO). (a) What is the complete composition of the equilibrium gas?; (b) For the same feed composition would the equilibrium gas at 500 K and 1 atm contain more or less hydrogen?

$$K = K_yK_p = \frac{y_c}{y_a(y_b)^2} \quad \frac{y_c}{y_a(0.4)^2} = 1.52 \qquad (1)$$

$y_b = 0.4$

$$y_a + y_c = 1 - 0.4 = 0.6 \qquad (2)$$

Solving simultaneously, $y_a = 0.482$, $y_b = 0.4$, $y_c = 0.118$.

Part (b). The effect of temperature is

$$\frac{d \ln K}{dt} = \frac{\Delta H^\circ}{RT^2} = -\frac{22580}{RT^2}$$

Because of the negative sign, K will be smaller at the higher temperature, methanol will be less and hydrogen will be more than at 400 K.

P4.01.04. METHANOL SYNTHESIS. VARIOUS EQUILIBRIUM CONSTANTS.

The equilibrium constant for the methanol synthesis reaction is K_p = 0.00928 at 300 C and 1 atm. The fugacity coefficient of methanol is ϕ = 0.97 at 10 atm and 0.86 at 50 atm, and all other fugacity coefficients involved are unity. What are the numerical values of the following quantities at this temperature?

(a) K at 1 atm
(b) K_p at 10 atm and at 50 atm.
(c) K at 10 and at 50 atm total pressure
(d) K_y at 1, 10 and 50 atm total pressure.

The reaction is $CO + 2H_2 \Leftrightarrow CH_3OH$. For the reaction $aA + bB \Leftrightarrow cC + dD$, the various forms of the equilibrium constant are:

$$K = (f_c)^c(f_d)^d/(f_a)^a(f_b)^b = K_yK_\phi\pi^{c+d-a-b}$$

$$K_y = (y_c)^c(y_d)^d/(y_a)^a(y_b)^b$$

$$K_p = K_y\pi^{c+d-a-b} = K/K_\phi$$

$$\phi_i = f_i/\pi$$

The answers are:

(a) $K = K_pK_\phi = 0.00928(1)$, since $K_\phi = 1$ at $\pi = 1$

(b) $K_\phi = 0.97/(1)^2(1)^2 = 0.97$ at 10 atm
0.86 at 50 atm
$K_p = K/K_\phi = 0.00928/0.97 = 0.00957$ at 10 atm
0.0108 at 50 atm.

(c) K = 0.00928, independent of pressure

(d) $K_y = (K/K_\phi)\pi^2 = 0.00928\pi^2/K_\phi = 0.00928$ at 1 atm
$0.00928(100)/0.97= 0.957$ at 10 atm
$0.00928(50)^2/0.86 = 27.0$ at 50 atm

P4.01.05. DECOMPOSITION OF METHANOL.

Find the degree of advancement and the equilibrium compostion in the decomposition of methanol at 200 C and 5 atm. The equilibrium constant is K_p = 42. For the reaction, $aA \Leftrightarrow bB$
the degree of advancement is

$$\varepsilon = \frac{n_{a0}-n_a}{a} = \frac{n_b-n_{b0}}{b}$$

For the reaction,

$CH_3OH \Leftrightarrow CO + 2H_2$, $A \Leftrightarrow B + 2C$

take $n_{a0} = 1$, $n_{b0} = n_{c0} = 0$

$\varepsilon = 1-n_a = n_b = 0.5n_c$

$n_t = n_{t0} + 2\varepsilon = 1 + 2\varepsilon$

Substitute into the equation for equilibrium,

$$K_p = \frac{n_b(n_c)^2}{n_a(n_t)^2}\pi^2 = \frac{\varepsilon(2\varepsilon)^2(5)^2}{(1-\varepsilon)(1+2\varepsilon)^2} = 42$$

$\varepsilon = 0.81410$

$n_t = 2.6282$

$y_a = (1-\varepsilon)/n_t = 0.07073$

$y_b = \varepsilon/n_t = 0.30976$

$y_c = 2\ y_b = 0.61951$

P4.01.06. DIMETHYL ETHER FROM METHANOL

Dimethyl ether is formed from methanol by the reaction

$2\ CH_3OH \Leftrightarrow (CH_3)_2O + H_2O, \quad 2\ A \Leftrightarrow B + C$

The Gibbs energy changes of the reaction are given at the temperatures in the table. The units are cal/gmol dimethyl ether. Confirm the tabulated values of the equilibrium constant, K, and of the fractional conversion, x, of the methanol.

The equilibrium constants are found from,

$K = \exp(-\Delta G^\circ/RT) = \exp[2950/(1.987)(500)] = 19.472$ at 500 K

When starting with pure methanol,

$$K = \frac{(0.5x)^2}{(1-x)^2}$$

$T^\circ K$	500	600	700
$-\Delta G^\circ$	2950	2560	2180
K	19.472	8.560	4.793
x	0.898	0.854	0.814

$$x = \frac{K^{1/2}}{0.5 + K^{1/2}}$$

P4.01.07. TEMPERATURE OF MAXIMUM CONVERSION

A reaction, $A + 2B \Leftrightarrow C$, is conducted with several starting ratios, $r = n_{b0}/n_{a0}$. The equilibrium constant is $K_x = 5$. At what value of the ratio is the conversion of substance A a maximum?

$A \quad + \quad 2B \quad \Leftrightarrow \quad C$

$1-x \quad r-2x \quad x \quad \Sigma = 1+r-2x$

$$K_x = \frac{x(1+r-2x)^2}{(1-x)(r-2x)} = 5$$

$f(x,r) = -5 + K_x$

The extremum can be found after making the derivative zero.

$$\frac{\partial x}{\partial r} = -\ (\partial f/\partial r)/(\partial f/\partial x) \Rightarrow 0$$

Here it is found by trial. The tabulated trials show that the maximum is x = 0.5555 when r = 2.1.

r	1.5	1.9	2.0	2.1	2.2	2.5
x	0.5193	0.5523	0.5547	0.5555	0.5551	0.5485

P4.01.08. EQUILIBRIUM TEMPERATURE

For the ideal gas reaction, $A \Leftrightarrow 2B$, data are

$\Delta H^o_{298} = 3000$ cal/ gmol A

$\Delta G^0_{298} = -400$ cal/gmol A

$\Delta C_p = 3.5$ cal/(gmol A)(K)

The pressure is 1.2 atm. Find the temperatures at which the conversions of are 25%, 50%, 75% and 95%.

$A \quad \Leftrightarrow \quad 2B$

$1-x \quad 2x \quad \Sigma = 1+x$

$$K = \frac{y_b^2\pi}{y_a} = \frac{(2x)^2 1.2}{(1-x)(1+x)} = \frac{4.8x^2}{(1-x^2)} \qquad (1)$$

$$K_{298} = \exp[400/(298)(1.987)] = 1.9651$$

$$\ln\frac{K}{K_{298}} = \frac{1}{R}\int_{298}^{T} \frac{1}{T^2}(\Delta H_{298}^0 + \int_{298}^{T}\Delta C_p dT\ )dT$$

$$= \frac{1}{R}\int_{298}^{T} \frac{1}{T^2}[3000 + 3.5(T-298)]dT$$

$$= \frac{1}{R}\int_{298}^{T} (\frac{1957}{T^2} + \frac{3.5}{T})dT$$

$$\ln\frac{K}{1.9651} = \frac{1}{R}\ [1957(\frac{1}{298} - \frac{1}{T}) + 3.5\ \ln\frac{T}{298}] \qquad (2)$$

For the specified values of x, solve equations (1) and (2) for T.

x	K	T
0.25	0.32	216.2
0.50	1.60	286.3
0.75	6.1714	380.2
0.95	44.43	640.8

P4.01.09. RATES OF CHANGE AWAY FROM EQUILIBRIUM

Some data for the gas phase reaction , 2A ⇔ B, are: π = 10 atm, T = 1260 R, n_{a0} = 1 lbmol, n_{b0} = 0, K = 0.46, K_ϕ = 0.7 and the rate of reaction

$$r_a = \frac{0.005p_a^2}{1+2.2p_a}$$

(a) Find the composition of the equilibrium mixture.

(b) When the conversion is 90% of that at equilibrium, find the values of r_a, dn_a/dt and dV/dt.

$$\begin{array}{lll} 2A & \Leftrightarrow & B \\ 1-x & & x/2 \quad \Sigma = 1-x/2 \end{array}$$

$$K_y = \frac{x(2-x)}{4(1-x)^2} = \frac{K\pi}{K_\phi} = \frac{0.4(10)}{0.7} = 6.571 \qquad (1)$$

The equilibrium values of x and the mol fractions are

$$x_e = 0.8086$$

$$y_a = (1-x)/(1-x/2) = 0.3213$$

$$y_b = 0.6713$$

At 90% of equilibrium conversion,

$$x = 0.9(0.8086) = 0.7277$$

$$n_a = 1-0.7277 = 0.2723$$

$$n_t = 0.5(n_{a0}+n_a) = 0.5(1.2723) = 0.63615$$

$$p_a = \frac{n_a\pi}{n_t} = \frac{0.2423(10)}{0.63615} = 4.280 \text{ atm}$$

$$V = \frac{n_tRT}{\pi} = \frac{0.63615(0.729)(1260)}{10} = 58.43 \text{ cuft}$$

$$r_a = \frac{0.005(4.28)^2}{1+\ 2.2(4.28)} = 0.0088 \text{ lbmol/(hr)(cuft)}$$

$$\frac{dn_a}{dt} = -Vr_a = -58.43(0.0088) = -0.5142 \text{ lbmol/hr}$$

$$\frac{dV}{dt} = -\frac{RT}{\pi}\frac{dn_t}{dt} = -\frac{RT}{2\pi}\frac{dn_a}{dt} = -\frac{0.729(1260)}{20}\,0.5142$$

$$= -23.6 \text{ cuft/hr}$$

P4.01.10. NONIDEAL GASES. GIVEN FREE ENERGY DATA.

The gas phase reaction, A ⇔ 2B, is maintained at 800 R and 10 atm. The reaction started with 1 lbmol of pure A. The heat of reaction is $\Delta H_r = 2500$ Btu/lbmol at 520 R, and $\Delta G^o = -100$. Heat capacities of A and B are 20 and 12 Btu/(lbmol)(R), and the fugacity coefficients, 0.97 and 0.49. Find the equilibrium composition.

$$K_{520} = \exp(-\Delta G^o/RT) = \exp(\frac{100}{1.987(520)}) = 1.1016$$

$$\Delta H_r = \Delta H_{r0} + \int_{T_0}^{T} \Delta C_p dT = 2500 + \int_{520}^{T} 4dT = 4T + 420$$

$$\ln\frac{K_{800}}{1.1016} = \int_{520}^{800} \frac{4T+420}{RT^2}\, dT = 1.00947$$

$$K_{800} = 3.02302$$

$$K_\phi = \phi_b^2/\phi_a = (0.49)^2/0.97 = 0.24753$$

$$K_y = y_b^2/y_a = \frac{n_b^2}{n_a n_t} = \frac{4(n_{a0}-n_a)^2}{n_a(2n_{a0}-n_a)} = \frac{4(1-f)^2}{f(2-f)}$$

$$f = n_a/n_{a0}$$

$$K = K_\phi \pi^{2-1} K_y$$

$$3.02302 = 0.24753(10)\,\frac{4(1-y)^2}{f(2-f)}$$

$$f = 0.51636$$

$$y_a = \frac{n_a}{2n_{a0}-n_a} = \frac{f}{2-f} = 0.34804,\ y_b = 0.65196$$

P4.01.11. REVERSIBLE SPECIFIC RATES

A second order reversible reaction, A + B ⇔ C + D, has forward specific rates of $k_f = 10.4$ liter/g mol-s at 230 C and 45.4 at 260 C. The standard state entropy and enthalpy changes of the overall reaction are approximately independent of temperature and are given by $\Delta S° = -2.31$ cal/g mol-K and $\Delta H° = 8400$ cal/g mol. Find expressions for the forward and reverse specific rates functions of temperature.

At a particular temperature,

$$\Delta G° = \Delta(H^o - TS^o) = \Delta H^o - T\Delta S^o = 8400 + 2.31T$$

$$K = \exp(-\Delta G^o/RT) = \exp[-\frac{8400/T+2.31}{1.987} = \exp(-1.1626 - \frac{4227.5}{T})$$

Apply the Arrhenius equation to the two values of k_f

$$10.4 = \exp(A-B/503.2),\quad 45.4 = \exp(A-B/533.2)$$

Therefore,

$$k_f = \exp(28.52 - 13170/T)$$

The reverse rate is

$$k_{-f} = k_f/K = \frac{\exp(28.52-13170/T)}{\exp(-1.1626-4227.5/T)} = \exp(29.68-8943/T)$$

P4.01.12. DISSOCIATION KNOWN AT ONE T AND P

The gas phase reaction, $A \Leftrightarrow B + C$, started with pure A. Suppose that 50% dissociation of A occurred at 1000 K and 10 atm as well as at 500 K and 0.1 atm. Also, $\Delta C_p = 0$. Find the % dissociation (a) at 250 K and 1 atm; (b) at 250 K and 0.01 atm.

$n_{a0} = 1,\ n_a = 1-x,\ n_b = n_c = x,\ n_t = 1 + x$

$$K = \frac{y_b y_c \pi}{y_a} = \frac{x^2\pi}{(1-x)(1+x)} \qquad (1)$$

Substitute x = 0.5 and the two pressures.

$$K = \frac{0.5^2\pi}{1-0.25} = 3.33 \text{ at 10 atm at 1000 K}$$

$$0.0333 \text{ at 0.1 atm and 500 K}$$

$$\Delta H_r = \Delta H_{r0} + \int \Delta C_p dT = \Delta H_{r0}$$

Apply

$$\frac{d\ln K}{dT} = -\frac{\Delta H_r}{RT^2}$$

$$\Delta H_r = \frac{R\ \ln(K_2/K_1)}{1/T_1-1/T_2} = \frac{1.987\ \ln(3.33/0.0333)}{1/500-1/1000} = 9150.5$$

Equilibrium constant at 250 K is

$$K = 3.33 \exp[-\frac{9150.5}{1.9870}(\frac{1}{250} - \frac{1}{1000})] = 3.33(10^{-6}) \qquad (2)$$

From Eq (1),

$$x = \sqrt{\frac{K}{K+\pi}} = 0.00182 \text{ at 1 atm}$$

$$0.0182 \text{ at 0.01 atm}$$

P4.01.13. ETHANE PYROLYSIS

For the reaction,

$C_2H_6 \Leftrightarrow C_2H_4 + H_2$, $\quad A \Leftrightarrow B + C$

the standard thermodynamic data at 298 K are

C_2H_6 $\Delta H = -20236$, $\Delta G = -7860$ cal/mol

C_2H_4 $\Delta H = +12496$, $\Delta G = +16282$ cal/mol

A mixture initially 85% C_2H_6, 5% C_2H_4 and 10% H_2 is kept at 2 atm and 900 C. If ΔH_r is assumed independent of temperature, find the equilibrium conversion.

For the reaction at 298 K,

$\Delta H_r = 12496 - (-20236) = 32732$

$\Delta G_r = 16282-(-7860) = 24142$

$$K_{298} = \exp[-\frac{24142}{1.987(298)}] = -40.77$$

At 1173 K,

$$\ln K_{1173} = \ln K_{298} + \int_{298}^{1173} \frac{32732}{RT^2}\,dT$$

$$= -40.77 + \frac{32732}{1.987}\left(\frac{1}{298} - \frac{1}{1173}\right) = 0.4652$$

$K_{1173} = 1.5924$

Material balances and prtial pressures,

$0.85 - n_a = n_b - 0.05 = n_c - 0.1$

$n_t = n_a+n_b+n_c = 1.85-n_a$

$$p_a = \frac{2n_a}{1.85-n_a},\quad p_b = \frac{2(0.9-n_a)}{1.85-n_a},\quad p_c = \frac{2(0.95-n_a)}{1.85-n_a}$$

$$K = \frac{2(0.9-n_a)(0.95-n_a)}{n_a(1.85-n_a)} = 1.5924$$

Finally,

$n_a = 0.309$

P4.01.14. EQUILIBRIUM FROM ΔH_r AND ΔG

An ideal gas reaction, $A \Leftrightarrow 2B$, occurs at 5 atm and 500 K, starting with pure A. The rate equation is

$$-dC_a/dt = 0.7[p_a-(5-p_a)^2/K_e] \quad \text{gmol/liter-min}$$

Thermodynamic data for the reaction are

$$\Delta G^o_{298} = -500 \text{ cal/mol}$$

$$\Delta H_r = -1000 + \int_{298}^{T}(6 + 0.02T)dT$$

Find the following:

(a) The equilibrium partial pressures at 500 K

(b) The value of $-dC_a/dt$ when the change in p_a is 90% of the change at equilibrium.

$$\ln K_{298} = -\frac{\Delta G^o}{RT} = \frac{500}{1.987(298)} = 0.844$$

$$\Delta H_r = -1000 + \int_{298}^{T} (6+0.02T)dT = -3676 + 6T + 0.01T^2$$

$$\ln K_{500} = 0.844 + \int_{298}^{500} \frac{-3676 + 6T + 0.01T^2}{RT^2}\,dT = 0.9753$$

$$K_{500} = 2.652 = \frac{(5-p_{ae})^2}{p_{ae}}$$

$p_{ae} = 2.451,\ p_{be} = 2.549$

When $p_a = 5 - 0.9(5-2.451) = 2.706$ atm.

$$-dC_a/dt = 0.7[2.706-(5-2.706)^2/2.652] = 0.5047 \text{ mol/liter-min.}$$

P4.01.15. EQUILIBRIUM CONSTANT WHEN THE COMPOSITION IS KNOWN

When starting with pure A the equilibrium composition resulting from the two reactions, $A \Leftrightarrow 2B + C$ and $2B \Leftrightarrow D$, is $y_a = 0.25$ and $y_d = 0.40$. Find the equilibrium constants, K_y.

$A \Leftrightarrow 2B + C$

$1-e_1 \quad 2e_1 \quad e_1$

$2B \Leftrightarrow D$

$2(e_1-e_2) \quad e_2$

$n_a = 1-e_1$

$n_b = 2e_1-2e_2$

$n_c = e_1$

$n_d = e_2$

$n_t = 1+2e_1-e_2$

$$y_a = \frac{1-e_1}{1+2e_1-e_2} = 0.25 \qquad (1)$$

$$y_d = \frac{e_2}{1+2e_1-e_2} = 0.40 \qquad (2)$$

Solving simultaneously,

$e_1 = 0.5588$, $e_2 = 0.3539$

The equilibrium constants are

$$K_{y1} = \frac{y_b^2 y_c}{y_a} = \frac{4(e_1-e_2)^2 e_1}{(1-e_1)(1+2e_1-e_2)} = 0.0660$$

$$K_{y2} = \frac{y_d}{y_b^2} = \frac{e_2(1+e_1-e_2)}{4(e_1-e_2)^2} = 3.9010$$

P4.01.16. EQUILIBRIUM OF A PAIR OF REACTIONS

Consider the two simultaneous reactions, $A + B \Leftrightarrow C + D$ and $A + C \Leftrightarrow 2E$, with equilibrium constants $K_{p1} = 2.667$ and $K_{p2} = 3.200$. The initial mixture consisted of 2 mols of A and 1 mol of B. Find the equilibrium composition.

First the material balances:

$A \quad + \quad B \quad \Leftrightarrow \quad C \quad + \quad D$

$2-x \quad 1-x \quad x \quad x$

$A \quad + \quad C \quad \Leftrightarrow \quad 2E$

$2-x-y \quad x-y \quad 2y$

$A = 2-x-y$ 0.70605 mols

$B = 1-x$ 0.16584 mols

$C = x-y$ 0.37437 mols

$D = x$ 0.83416 mols

$E = 2y$ 0.91958 mols

$\Sigma = 3.0$

The equilibrium constants are

$$K_{p1} = \frac{x(x-y)}{2-x-y)(1-x)} = 2.667 \qquad (1)$$

$$K_{p2} = \frac{4y^2}{(2-x-y)(x-y)} = 3.200 \qquad (2)$$

This pair of equations has two solutions,

$x = 0.73817$, $y = -8.4336$

$x = 0.83416$, $y = 0.45979$

but only the second is physically possible. The numbers of mols present at equilibrium are tabulated alongside the formulas for the amounts.

P4.01.17. PARTIAL ANALYSIS OF A TWO REACTION EQUILIBRIUM

A reaction has the stoichiometry, $A + 2B \Leftrightarrow C$ and $A + C \Leftrightarrow D$. The initial mixture consisted of 1 mol of A and 2 mols of B. The equilibrium mixture contains 30% of B and 10% of D. What is the complete analysis of the equilibrium mixture?

$$A + 2B \Leftrightarrow C$$
$$1-\alpha \quad 2-2\alpha \quad \alpha$$
$$A + C \Leftrightarrow D$$
$$1-\alpha-\beta \quad \alpha-\beta \quad \beta$$

$A = 1-\alpha-\beta$

$B = 2-2\alpha$

$C = \alpha-\beta$

$D = \beta$

$\Sigma = 3-2\alpha-\beta$

$$y_a = \frac{1-\alpha-\beta}{3-2\alpha-\beta}$$

$$y_b = \frac{2(1-\alpha)}{3-2\alpha-\beta} = 0.3 \qquad (1)$$

$$y_c = \frac{\alpha-\beta}{3-2\alpha-\beta}$$

$$y_d = \frac{\beta}{3-2\alpha-\beta} = 0.1 \qquad (2)$$

From equations (1) and (2),

$\alpha = 0.8125$, $\beta = 0.1250$

and the complete composition is

$y_a = 0.05$, $y_b = 0.30$, $y_c = 0.55$, $y_d = 0.10$

P4.01.18. OPTIMUM STARTING COMPOSITION FOR AMMONIA SYNTHESIS

For the synthesis of ammonia according to

$0.5\ N_2 + 1.5\ H_2 \Leftrightarrow NH_3$, $\qquad 0.5A + 1.5B \Leftrightarrow C$

The equilibrium constant is $K = 0.0091$ and $K_\phi = 1.00$. The conditions are 700 K and 300 atm. Find the initial ratio , r = hydrogen/nitrogen, that gives the highest concentration of ammonia at equilibrium.

In terms of the degree of advancement, e, the material balance is

$C_0-C = 2(A-A_0) = (2/3)(B-B_0) = e$

Let $C_0 = 0$, $A_0 = 1$, $B_0 = rA_0 = r$

$n_c = e$

$n_b = B_0-1.5e = r - 1.5e$

$n_a = n_{a0} - 0.5e = 1 - 0.5e$

$n_t = n_{t0}-e = 1+r-e$

$$y_{NH_3} = \frac{e}{1+r-e} \qquad (1)$$

The equilibrium constant is

$K = K_yK_\phi/\pi = 0.0091$

$$K_y = \frac{n_c n_t}{n_a^{1/2} n_b^{3/2}} = \frac{e(1+r-e)}{(1-0.5e)^{1/2}(r-1.5e)^{1.5}} = 0.0091(300) \qquad (2)$$

Solve Eqs (1) and (2) at specified values of r. The tabulation shows that the peak mol fraction of ammonia is obtained with r = 3.

r	e	y_{NH_3}	
1	0.3954	0.2278	
2	0.7618	0.3404	
2.5	0.9206	0.3569	
3	1.060	0.3605	Maximum
3.5	1.186	0.3579	
4	1.294	0.3492	
5	1.464	0.3228	

P4.01.19. METHANE-STEAM REACTIONS

The simultaneous reactions

$CH_4 + H_2O \Leftrightarrow CO + 3H_2$

$CO + H_2O \Leftrightarrow CO_2 + H_2$

are conducted at atmospheric pressure with two mols of water per mol of methane. Equilibrium constants as functions of temperature in °F are

$\ln K_{p1} = 30.079 - 48295/(T+460)$

$\ln K_{p2} = -4.098 + 7925/(T+460)$

Prepare a tabulation of the fractional conversion of methane as a function of the temperature at which the concentrations of carbon monoxide and carbon dioxide are equal.

$$\begin{array}{llll} CH_4 + & H_2O & \Leftrightarrow CO & + 3H_2 \\ 1-x & 2-x & x & 3x \\ CO & + H_2 & \Leftrightarrow CO_2 & + H_2 \\ x-y & 2-x-y & y & 3x+y \end{array}$$

$CH_4 = 1-x \quad \Rightarrow 1-x$

$H_2O = 2-x-y \quad \Rightarrow (4-3x)/2$

$CO = x-y \quad \Rightarrow x/2$

$CO_2 = y \quad \Rightarrow x/2$

$H_2 = 3x+y \quad \Rightarrow 7x/2$

$\Sigma = 3+2x$

When $[CO] = [CO_2]$, $x-y = y$ and $y = x/2$. Formulate the equilibrium constants.

$$K_1 = \frac{x(7x)^3}{4(1-x)(4-3x)(3+2x)^2}$$

$$K_2 = \frac{x(7x)}{x(4-3x)}$$

$$\frac{K_1}{K_2} = \frac{6.125x^3}{(1-x)(3+2x)^2} = \exp(34.177-\frac{56220}{T+460})$$

Some of the values are tabulated.

x	0.1	0.3	0.5	0.7	0.9
T	894.9	1012.4	1079.2	1137.4	1217.4

P4.01.20. METHANE AND STEAM AT 600 C

At 600 C the principal reactions between steam and methane are

$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad K_{p1} = 0.574$

$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad K_{p2} = 2.21$

Find the equilibrium composition when 1 mol of methane is mixed with 5 mols of steam at 1 atm.

Make the material balances.

$CH_4 + H_2O \Leftrightarrow CO + 3H_2$

$1-x \quad 5-x \qquad x \quad 3x$
$CO \quad + H_2O \qquad CO_2 + H_2$
$x-y \quad 5-x-y \quad y \qquad 3x+y$
$CH_4 = 1-x$
$H_2O = 5-x-y$
$CO = x-y$
$H_2 = 3x+y$
$CO_2 = y$
$\Sigma = 6+2x$

Formulate the equilibrium constants.

$$K_{p1} = \frac{(x-y)(3x+y)^3}{(1-x)(5-x-y)(6+2x)^2} = 0.574 \qquad (1)$$

$$K_{p2} = \frac{y(3x+y)}{(x-y)(5-x-y)} = 2.21 \qquad (2)$$

The solution by the Newton-Raphson method is

$x = 0.9121,\ y = 0.63284$

The molal composition is

$y_{CH_4} = (1-x)/(6+2x) = 0.0112$, and so on.

P4.01.21. PROPANE DECOMPOSITION

Find the composition of the equilibrium mixture resulting from the decomposition of propane according to the following reactions at 1400 F and one atm.

$C_3H_8 \Leftrightarrow C_3H_6 + H_2 \qquad K_{p1} = 7.88$
$1-x \qquad x \qquad x$
$C_3H_8 \Leftrightarrow C_2H_4 + CH_4 \qquad K_{p2} = 755$
$1-x-y \quad y \qquad y$

The material balances are formulated.

$C_3H_8 = 1-x-y$ mol fraction = 0.0007
$C_3H_6 = x$ 0.0463
$H_2 = x$ 0.0463
$C_2H_4 = y$ 0.4534
$CH_4 = y$ 0.4534
$\Sigma = 1+x+y$

Write the equilibrium constants.

$$K_{p1} = \frac{x^2}{(1+x+y)(1-x-y)} = 7.88 \qquad (1)$$

$$K_{p2} = \frac{y^2}{(1+x+y)(1-x-y)} = 755 \qquad (2)$$

These are solved as

$x = 0.092642,\ y = 0.906814$

and the mol fractions as

$y_{C_3H_8} = (1-x-y)/(1+x+y) = 0.00027$, and so on. The values are tabulated preceding.

P4.01.22. A GRAPHICAL SOLUTION

The simultaneous gas phase reactions take place at 1 atm, beginning with stoichiometric proportions of A and B. Find the equilibrium composition of the mixture.

$2A \ + B \ \Leftrightarrow 2C \qquad K_1 = 2$

$2-2x \quad 1-x \quad 2x$
$A \ + \ C \Leftrightarrow D \qquad K_2 = 0.5$
$2-2x-y \quad 2x-y \quad y$

$A = 2-2x-y$ mol fraction = 0.4158
$B = 1-x$ 0.2377
$C = 2x-y$ 0.2868
$D = y$ 0.0597
$\Sigma = 3-x-y$

$$K_1 = \frac{(2x-y)^2(3-x-y)}{(2-2x-y)^2(1-x)} = 2.0 \qquad (1)$$

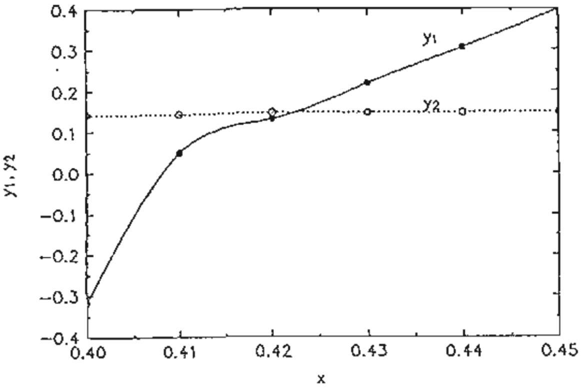
$$K_2 = \frac{y(3-x-y)}{(2-2x-y)(2x-y)} = 0.5 \qquad (2)$$

The solution of the simultaneous equations is accomplished by assuming a series of values of x, then calculating corresponding values of y from equations (1) and (2), then interpolating on a graph to find the correct values. The correct values are

$x = 0.42146$, $y = 0.14510$

Some of the values from which the plot is made are tabulated.

x	y_1	y_2
0.40	-0.3174	0.1417
0.41	0.0495	0.1433
0.42	0.1328	0.1488
0.43	0.2182	0.1463
0.44	0.3065	0.1476
0.45	0.3983	0.1488



P4.01.23. SOLUTION BY ITERATION

At 600 K and 1 atm the equilibrium constants of the reactions between methyl chloride and water are $K_1 = 0.00154$ and $K_2 = 10.6$. The initial composition was one mol each of methyl chloride and water. Find the composition of the equilibrium mixture.

$CH_3Cl + H_2O \Leftrightarrow CH_3OH + HCl$
$1-e_1 \quad 1-e_1 \quad e_1 \quad e_1$
$2CH_3OH \Leftrightarrow (CH_3)_2O + H_2O$
$e_1-2e_2 \quad e_2 \quad 1-e_1+e_2$

The material balances are:

$CH_3Cl = 1-e_1$ mol fraction = 0.4759
$H_2O = 1-e_1+e_2$ 0.4807
$HCl = e_1$ 0.0241
$CH_3OH = e_1-2e_2$ 0.0146
$(CH_3)_2O = e_2$ 0.0047
$n_t = 2$

The equilibrium constants are

$$K_1 = \frac{(e_1-2e_2)(e_1}{(1-e_1)(1-e_1+e_2)} = 0.00154$$

$$K_2 = \frac{e_2(1-e_1+e_2)}{(e_1-2e_2)^2} = 10.6$$

Rearrange these equations for solution by iteration.

$$e_1 = \frac{0.00154(1-e_1)(1-e_1+e_2)}{e_1-2e_2} \qquad (1)$$

$$e_2 = \frac{10.6(e_1-2e_2)^2}{1-e_1+e_2} \qquad (2)$$

The solution procedure is to assume a value of e_2. Substitute into Eq (1) and try values of e_1 until the RHS equals the LHS. Substitute that value of e_1 into the RHS of Eq (2) and find another value of e_2. Repeat until convergence. The final values are

$e_1 = 0.04815$, $e_2 = 0.009442$

The corresponding mol fractions are tabulated preceding.

P4.01.24. REACTION BETWEEN H_2S AND SO_2. GRAPHICAL SOLUTION

The initial mixture contains 35% H_2S, 15% SO_2 and 50% inert N_2 at 1500 K and 0.8 atm. Two independent reactions and their equilibrium constants are

$H_2S \Leftrightarrow H_2 + 0.5S_2 \qquad K_1 = 0.334$

$2H_2S + SO_2 \Leftrightarrow 2H_2O + 1.5S_2 \qquad K_2 = 30.2$

In terms of the individual degrees of advancement the material balances are

$H_2S =$	$0.35-e_1-2e_2$	mol fraction = 0.0584
$H_2 =$	e_1	0.0507
$S_2 =$	$0.5e_1+1.5e_2$	0.1854
$SO_2 =$	$0.15-e_2$	0.0315
$H_2O =$	$2e_2$	0.2134
$N_2 =$	0.5	0.4606
$n_t =$	$1+0.5e_1+0.5e_2$	

The equilibrium equations are

$$f_1 = -0.334 + \frac{e_1(0.5e_1+1.5e_2)^{0.5}(0.8)^{0.5}}{(0.35-e_1-2e_2)(1+0.5e_1+0.5e_2)^{0.5}} = 0$$

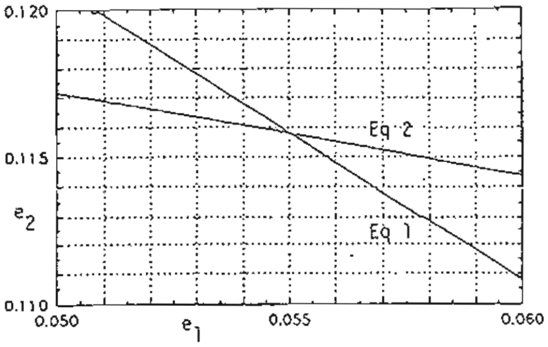
$$f_2 = -30.2 + \frac{(2e_2)^2(0.5e_1+1.5e_2)^{1.5}(0.8)^{0.5}}{(0.35-e_1-2e_2)^2(0.15-e_2)(1+0.5e_1+0.5e_2)^{0.5}} = 0$$

The two equations are solved by first specifying e_1 and then finding e_2 by single variable Newton-Raphson. The intersection of the two plots is at

$e_1 = 0.05500$, $e_2 = 0.11579$

The mol fraction of H_2S is

$$y = \frac{0.35-e_1-2e_2}{1+0.5e_1+0.5e_2} = 0.0584,$$ and so on for the others. These values are tabulated alongside the material balances.



P4.01.25. METHANOL FROM CO_2 AND H_2

The simultaneous reactions in this process are

$$\underset{1-e_1}{CO_2} + \underset{3-e_1}{H_2} \Leftrightarrow \underset{e_1}{CO} + \underset{e_1}{H_2O} \qquad K_1 = 0.05$$

$$\underset{e_1-e_2}{CO} + \underset{3-e_1-2e_2}{H_2} \Leftrightarrow \underset{e_2}{CH_3OH} \qquad K_2 = 4.458(10^{-5})$$

The starting mixture contained 3 mols hydrogen per mol CO_2. The temperature is 1073 K and the pressure is 500 atm. The degrees of advancement are recorded below the chemical symbols in the equations above. The material balances are,

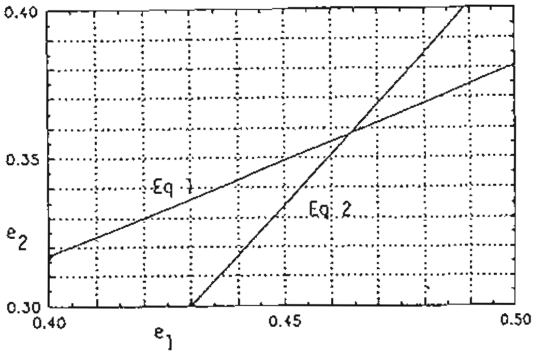
$CO_2 = 1-e_1$ mol fraction = 0.1633
$H_2 = 3-e_1-2e_2$ 0.5539
$CO = e_1-e_2$ 0.0320
$H_2O = e_1$ 0.1414
$CH_3OH = e_2$ 0.1094
$n_t = 4-2e_2$

The equilibrium constants are,

$$K_1 = \frac{(e_1-e_2)e_1}{(1-e_1)(3-e_1-2e_2)} = 0.05 \qquad (1)$$

$$K_2 = \frac{e_2(4-2e_2)^2}{(e_1-e_2)(3-e_1-2e_2)^2(500)^2} = 4.458(10^{-5}) \qquad (2)$$

The equations are solved graphically. Values of e_1 are assumed and corresponding values of e_2 are calculated from each equation by the Newton-Raphson method. The intersection of the curves is at $e_1 = 0.46402$ and $e_2 = 0.35903$. The corresponding mol fractions are tabulated alongside the material balances.



P4.01.26. A PAIR OF REACTIONS

The feed to a reactor contains A and B in the ratio 3:1 and the reactions are

$A + B \Leftrightarrow C + D \qquad K_1 = 0.15$

$A + C \Leftrightarrow 2E \qquad K_2 = 1.60$

Consider a total mixture of 4 mols, with e_1 mols converted by the first reaction and e_2 by the second. Then the mols of the various components of the mixture are

	mol fraction
$A = 3-e_1-e_2$	= 0.50
$B = 1-e_1$	0.10
$C = e_1-e_2$	0.05
$D = e_1$	0.15
$E = 2e_2$	0.20
Total = 4, constant	

Hence,

$$K_1 = \frac{e_1(e_1-e_2)}{(1-e_1)(3-e_1-e_2)} = 0.15$$

$$K_2 = \frac{(2e_2)^2}{(e_1-e_2)(3-e_1-e_2)} = 1.6$$

Elimination of e_2 between these equations gives

$$385e_1^4 + 24e_1^3 + 342e_1^2 - 432e_1 + 81 = 0$$

from which $e_1 = 0.6$. By back substitution, $e_2 = 0.4$. The mol fractions of all components are tabulated alongside the material balances.

P4.01.27. COAL GASIFIER OPERATION

Feed to a coal gasifier consists of 1 mol of steam, 1.88 mols of N_2 and 0.5 mols of O_2 at 20 bar. The net reactions are

$$\begin{array}{llll} C + CO_2 & \Leftrightarrow & 2CO & \\ \quad 0.5-e_1 & & 2e_1 & \\ H_2O \; + C & \Leftrightarrow & H_2 & + CO \\ 1-e_2 & & e_2 & 2e_1+e_2 \end{array}$$

The equilibrium constants are $K_1 = 53.155$ at 1200 K and 584.85 at 1400 K; $K_2 = 38.609$ at 1200 K and 268.76 at 1400 K. The material balances in terms of the degrees of advancement are

			1200 K	1400 K
$H_2 =$	e_2	mol fraction =	0.1879	0.2013
$CO =$	$2e_1+e_2$		0.3271	0.3978
$H_2O =$	$1-e_2$		0.0318	0.0059
$CO_2 =$	$0.5-e_1$		0.0402	0.0054
$N_2 =$	1.88		0.4130	0.3896
Total =	$3.38+e_1+e_2$			

The expressions for the equilibrium constants are

$$K_1 = \frac{20(2e_1+e_2)^2}{(0.5-e_1)(3.38+e_1+e_2)} = 53.155 \text{ or } 584.85$$

$$K_2 = \frac{20(e_2(2e_1+e_2)}{(1-e_2)(3.38+e_1+e_2)} = 38.609 \text{ or } 268.76$$

The solutions are

$e_1 = 0.3168$, $e_2 = 0.8551$ at 1200 K

$e_1 = 0.4739$, $e_2 = 0.9713$ at 1400 K

The mol fractions are tabulated alongside the material balances.

P4.01.28. NITRIC OXIDE EQUILIBRIUM

A gas enters the space between trays in an absorber with the component partial pressures shown in column 2 of the table. The rate equation for the reaction, $2NO + O_2 \Rightarrow 2NO_2$, is

$$-\frac{dp_{NO}}{dt} = 11.75\ p_{NO}^2 p_{O_2}$$

Equilibrium for the reaction, $2NO_2 \Leftrightarrow N_2O_4$, is established very rapidly and is represented by

$$P_{N_2O_4}/P_{NO_2}^2 = 4.5$$

(a) For a contact time of 2 seconds, find the partial pressures of the mixture leaving the vapor space, assuming that there is no substntial change in total mols of the system during this process.

(b) Find the partial pressures at equilibrium.

Let A = NO, B = O_2. Using the data from the second column of the table,

$B + B_0 + 0.5(A_0-A) = 0.42 + 0.5(0.061-A) = 0.3895 - 0.5A$

$$-\frac{dA}{dt} = 11.75A^2(0.3895-0.5A)$$

Integration shows that A = 0.040 when t = 2. The composition immediately after reaction is shown in column 3.

The equilibrium reaction is

$2NO_2 \quad \Leftrightarrow \quad N_2O_4$

$0.173-x \quad 0.105+0.5x$

The expression for the equilibrium constant is, neglecting the change in mols,

$$\frac{0.105+0.5x}{(0.173-x)^2} = 4.5$$

Whence

$x = 0.0149$

$NO_2 = 0.173 - 0.0149 = 0.1581$

$N_2O_4 = 0.105 + 0.5(0.0149) = 0.1125$

The complete partial pressures at equilibrium are in the last column.

Component	Inlet p	after reaction	at equilib
NO	0.061	0.040	0.040
NO_2	0.152	0.173	0.1581
N_2O_4	0.105	0.105	0.1125
O_2	0.420	0.4095	0.4095
N_2	6.262	6.262	6.262
Total	7.000	6.9895	6.9821

P4.01.29. CHLORINATION OF SOLID MgO

The rate of chlorination of small particles of MgO suspended in a molten mixture of $MgCl_2$ and KCl has been measured by Savinkova et al (J Applied Chem USSR 40 734, 1967) and they proposed this rate equation for 500 C,

$$-\frac{dn}{dt} = 24.3(10^{-5})n^{2/3}\ \text{gmol/min}$$

For a particle that is originally 1 mg, or 0.001/40.32 gmol, find how long it takes for the diameter of the particle to be halved.

$MgO + Cl_2 \Rightarrow MgCl_2 + ?$

$$t = \frac{1}{24.3(10^{-5})} \int_n^{n_0} n^{-2/3} dn = \frac{3n_0^{1/3}}{24.3(10^{-3})} [1-(n/n_0)^{1/3}]$$

$$= \frac{3n_0^{1/3}}{24.3(10^{-5})}(1-d/d_0)$$

For $n_0 = 0.001/40.32$ and $d/d_0 = 0.5$,

$$t = \frac{3(0.001)}{40.32(24.3)(10^{-5})} (1-0.5) = 179.9 \text{ min}$$

P4.02.01. DEHYDROGENATION OF BUTENE-1

For the dehydrogenation of butene-1 to butadiene the heat of reaction at 298 K is $\Delta H_{r,298} = +26360$ cal/gmol and the heat capacity difference is

$$\Delta C_p = 5.97-5.85(10^{-6})T^2, \quad 298 \le T \le 900$$

Accordingly the heat of reaction at temperature is

$$\Delta H_r = 26360 + \int_{298}^{T} \Delta C_p dT$$

$$= 26360 + 5.97(T-298) - \frac{5.85(10^{-6})}{3}(T^3 - 298^3)$$

$$= 24633 + 5.97T - 1.95(10^{-6})T^3$$

P4.02.02. REACTION ENTHALPY CHANGE

A reaction, $A \Leftrightarrow 2B$, reaches equilibrium with 73% conversion at 450 K and 1 atm. The Gibbs free energy of reaction at 298 K is +500 cal/gmol and the heat capacity difference is $\Delta C_p = 3.5$ cal/gmol-K. Find the enthalpy change of reaction at 298 K.

$$\Delta H_T = \Delta H_{298} + 3.5(T-298) = \Delta H_{298} - 1043 + 3.5T \qquad (1)$$

With x = 0.73, the equilibrium constant is

$$K_{450} = \frac{(2x)^2 2}{(1-x)(1+x)} = 9.127, \quad \ln K_{450} = 2.211$$

$$\ln K_{298} = -\frac{\Delta G}{298R} = -\frac{500}{1.987(298)} = -0.8444$$

$$\ln K_{450} - \ln K_{298} = \int_{298}^{450} \frac{\Delta H_T}{RT^2} dT$$

$$2.211 + 0.8444 = \frac{1}{R} [(\Delta H_{298} - 1043)(\frac{1}{298} - \frac{1}{450}) + 3.5 \ln \frac{450}{298}]$$

$$\Delta H_{298} = 5250 \text{ cal/gmol.}$$

P4.02.03. ETHANOL EQUILIBRIUM AND HEAT REMOVAL

For the reaction,

$$C_2H_4 + H_2O \Leftrightarrow C_2H_5OH, \quad A + B \Leftrightarrow C$$

thermodynamic data at 418 K are $\Delta G^\circ = +1685$ and $\Delta H^\circ = -10400$ cal/gmol. A feed of 2.5 mol H_2O per mol C_2H_4 produces 300 kg C_2H_5OH per hour. The reaction is at 418 K and 2 atm. Find the fractional conversion and the hourly heat removal.

300 kg/hr = 6.51 kmol/hr ethanol

$$K = \exp(-\frac{\Delta G^{\circ}}{RT}) = \exp(-\frac{1685}{1.987(418)}) = 0.1315$$

Material balances are,

$$n_{a0}-n_a = n_{b0}-n_b = n_c = 6.51$$

$$n_t = n_{a0}-6.51 + 2.5n_{a0}-6.51 + 6.51 = 3.5n_{a0} - 6.51$$

$$K = \frac{n_c n_t}{n_a n_b \pi} = \frac{6.51(3.5n_{a0}-6.51)}{2(n_{a0}-6.51)(2.5n_{a0}-6.51)} = 0.1315$$

Solving,

n_{a0} = 41.82 kmol/hr, ethylene feed

$x = 6.51/41.82 = 0.1557$, fractional conversion of ethylene

Heat removal,

$$Q = -\Delta H(n_c) = 10.4(6.51) = 67.7 \text{ kcal/hr}$$

P4.02.04. ETHYLENE OXIDE.

Ethylene oxide is made from ethylene by the reaction

$$C_2H_4 + 0.5O_2 \Leftrightarrow C_2H_4O$$

The heat of reaction at 291 K is $\Delta H = -28.611$ kcal/gmol. The oxide is made at the rate of 5000 kg/day by feeding oxygen at 423 K with 10% in excess and ethylene at 463 K. The products leave at 548 K. Calculate the hourly heat removal from the reactor for converting 80% of the ethylene feed. Equations for the specific heats in cal/gmol-K are,

$$C_p = a + bT + cT^2 + dT^3$$

	a	10^2b	10^5c	10^9d
C_2H_4	0.944	3.735	-1.993	4.22
C_2H_4O	-1.12	4.925	-2.389	3.149
O_2	6.732	0.1505	-0.01791	

n_{a0} = ethylene feed

$n_{b0} = 1.1(0.5)n_{a0}$ = oxygen feed

$0.8n_{a0}$ = oxide produced = 5000/44 = 113.64 kgmol/day

Therefore,

n_{a0} = 113.64/0.8 = 142.05 kgmol/day

Input and output conditions are tabulated following. The enthalpies are with reference to 291 K.

Component	n, in	T	H	n, out	T	H
C_2H_4	142.05	463	2129.5	28.41	548	3427.4
C_2H_4O				113.64	548	3973.0
O_2	78.13	423	956.5	21.3	548	1884.0

The amount of heat removed is

$$Q = 28611(113.64) + 2129.5(142.05) + 956.5(78.13) - 3427.4(28.41) - 1884(21.3) - 3973(113.64) = 3.040(10^6) \text{ kcal/day}$$

P4.02.05. ETHYLBENZENE FORMATION

Ethylbenzene is made from benzene and ethylene in the gas phase at 260 C and 40 atm.

$C_6H_6 + C_2H_4 \Leftrightarrow C_6H_5C_2H_5$

Equimolal proportions of the reactants are used. Thermodynamic data at 298 are tabulated. The specific heats are averages. Find (a) the enthalpy change of reaction at 298 and 573 K; (b) equilibrium constant at 298 and 573 K; (c) fractional conversion at 573 K.

	C_p	ΔH_f	ΔG_f
C_6H_6	28	19820	30989
C_2H_4	5	12496	16282
$C_6H_5C_2H_5$	38	7120	31208
Δ	-5	-25196	-16063

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p dT = -25196 - 5(T-298)$$

$$= -26576 \text{ at } 573 \text{ K} \qquad \text{(a)}$$

$$\ln K_{298} = -\Delta G_{298}/298R = 16063/(1.987)(298) = 26.90$$

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} = -\frac{23706}{RT^2} - \frac{5}{RT}$$

$$\ln K_{298} = 26.9 - \int_{298}^{573} \left(\frac{11854}{T^2} + \frac{2.50}{T}\right)dT = 6.17 \qquad \text{(b)}$$

$$K = 485$$

$$= \frac{x(2-x)}{40(1-x)^2}$$

$x = 0.9929$, fraction converted (c)

P4.04.06. AMMONIA HEAT OF FORMATION

Find the enthalpy change of the ammonia reaction at 423 K.

$N_2 + 3H_2 \Leftrightarrow 2NH_3$

The heat of reaction at 298 is $\Delta H_{298} = 2(-11020) = -22040$ cal. Heat capacities have the equations

$$C_p = a + bT + cT^2$$

$$\Delta C_p = 2C_{NH_3} - C_{N_2} - 3C_{H_2}$$

	a	10^3b	10^6c
H_2	6.946	-0.196	0.476
N_2	6.457	1.39	-0.069
NH_3	5.92	8.963	-1.764
Δ	-15.46	17.12	-4.89

Accordingly the enthalpy change of reaction for two gmol of ammonia temperature is given by

$$\Delta H_{423} = -22040 + \int_{298}^{423} [15.46 + 17.12(10^{-3})T - 4.89(10^{-6})T^2]\, dT$$

$$= -23280 \text{ cal}$$

P40207. OXIDATION OF SO_2

A reactor for the oxidation of SO_2 is operated adiabatically with heat interchange between feed and product streams in countercurrent. Inlet concentrations are 10% each of SO_2 and O_2 and the balance N_2. Preheat temperature is to be 725 K, equilibrium is attained at the outlet and the conversion of SO_2 is 70%. Pressure is atmospheric. Find the temperatures of the feed and of the outlet.

Data: $\ln K_y = -11.2755 + 11794/T$

$C_p = 6.66 + 0.00105T$, cal/gmol-K

$\Delta H_r = -23250 - 1.45T + 0.0021T^2$ cal/(gmol SO_2 made)

As a basis, take 10 mols of feed.

$SO_2 + 0.5O_2 \Leftrightarrow SO_3$

$1-e \quad 1-0.5e \quad e \qquad n_t = 10- 0.5e$

$$K_y = \frac{e(10-0.5e)^{0.5}}{(1-e)(1-0.5e)^{0.5}}$$

$= 8.9905$ when $e = 0.7$

$$\ln K_y = \ln 8.9905 = -1102755 + \frac{11794}{T_1}$$

$T_1 = 875.5$, outlet equilibrium temperature (1)

The heat of reaction at 725 K raises the the temperature of the feed (10 mols/hr) from T_0 to 725 and of the products (9.65 mols/hr) from 725 to 875.5.

$$\Delta H_{725} = -23250 - 1.45(725) \quad 0.0021(725)^2 = -23197.5$$

$$= 10 \int_{T_0}^{725} (6.66 + 0.\ 00102T)dT$$

$$+ 9.65 \int_{725}^{875.5} (6.66 + 0.00102T)dT$$

$1233.5 = 6.66(725-T_0) + 0.00051(725^2 - T_0^2)$

$T_0 = 556.3$, feed temperature (2)

Lines (1) and (2) are the required temperatures.

P4.02.08. AMMONIA CONVERSION

For the ammonia reaction, $0.5N_2 + 1.5H_2 \Leftrightarrow NH_3$, find the conversion at 773 K and 250 atm with starting ratios , R = mol hydrogen/mol nitrogen = 3 or 4.5. The heat capacity difference is

$\Delta C_p = -6.085 - 0.00438T$ cal/gmol ammonia-K

Other data are:

$\Delta H_{298} =-11020$ cal/gmol

$\ln K_{298} = 6.7148$

$K_\phi = 0.8$

Make the stoichiometric balance.

$0.5\ N_2 + 1.5\ H_2 \Leftrightarrow NH_3$

$1-e \qquad R-3e \qquad 2e \qquad \Sigma = R+1-2e$

$$K_y = \frac{2e(R+1-2e)}{(R-3e)^{1.5}(1-e)^{0.5}} \qquad (1)$$

The heat of reaction,

$$\Delta H_T = -11040 + \int_{298}^{T} (-6.085 - 0.00438T)dT$$

$$= -9032.2 - 6.085T - 0.00219T^2 \qquad (2)$$

The equilibrium constant,

$$\ln K_T = \ln K_{298} + \frac{1}{R}\int_{298}^{T}\frac{\Delta H_T}{T^2}\,dT$$

$$= 6.7148 + \frac{1}{1.987}[9032.2(\frac{1}{T} - \frac{1}{298}) - 6.085 \ln\frac{T}{298} - 0.00219(T-298)] \qquad (3)$$

$$K_{773} = 0.002240$$

$$= \frac{K_y K_\phi}{\pi} = \frac{2e(R+1-2e)(0.8)}{(R-3e)^{1.5}(1-e)^{0.5}(250)} \qquad (4)$$

Several solutions for e are tabulated.

R	K_ϕ	e
3	1	0.2392
4.5	1	0.3176
3	0.8	0.2763
4.5	0.8	0.3664

The assumption of ideality, $K_\phi = 1$, underpredicts the yield of ammonia.

P4.02.09. METHANOL CONVERSION

The reaction is, $CO + 2H_2 \Leftrightarrow CH_3OH$. Stoichiometric proportions of reactants are used. Find the conversion at 500 and 600 K , each at 200 and 300 atm. Data are:

$\Delta H_{298} = -21660$ cal/gmol

$\Delta G_{298} = -6030$ cal/gmol

$\Delta C_p = -15.287 + 0.01558T + 6.113(10^{-6})T^2 + 6.195(10^{-9})T^3$

$\ln K_{298} = 6030/(1.987)(298) = 10.1836$

$K_{298} = 26467$

Heat of reaction as a function of temperature,

$$\Delta H = \Delta H_{298} + \int_{298}^{T}\Delta C_p dT$$

$$= -17862 - 15.287T + 0.00779T^2 + 2.038(10^{-6})T^3 + 1.549(10^{-9})T^4$$

Equilibrium constant as a function of temperature,

$$\ln\frac{K}{26467} = \int_{298}^{T}\frac{\Delta H}{RT^2}\,dT$$

$$= 8989.4(\frac{1}{T} - \frac{1}{298}) - 7.965 \ln\frac{T}{298} + .00392(T-298)$$

$$+0.5128(10^{-6})(T^2-298^2) + 0.2599(10^{-9})(T^3-298^3)$$

In terms of fractional conversion, the equilibrium constant is

$$K = \frac{x(3-2x)^2}{(1-x)(2-2x)^2\pi^2}$$

At the requested conditions,

T	K	π	x
400	18.87		
500	0.3318	200	0.9726
		300	0.9792
600	0.0265	200	0.9340
		300	0.9506

P4.02.10. HYDRATION OF ETHYLENE

Hydration of ethylene produces ethanol, $C_2H_4 + H_2O \Leftrightarrow C_2H_5OH$. The equilibrium constant is known at two temperatures: $K_{418} = 0.068$ and $K_{593} = 0.0019$. The heat capacity difference for the reaction is

$$\Delta C_p = -3.096 + 0.008842T - 3.483(10^{-6})T^2$$

Find the values of ΔH_{298} and K_{298}.

$$\Delta H = \Delta H_{298} + \int_{298}^{T} \Delta C_p dT$$

$$= \Delta H_{298} - 3.096(T-298) + 0.00442(T^2-298^2)$$

$$-1.161(10^{-6})(T^3-298^3)$$

$$= \Delta H_{298} + 1344.7 - 3.096T + 0.00442T^2 - 1.161(10^{-6})T^3 \quad (1)$$

$$\ln K_T = \ln K_{298} + \int_{298}^{T} \frac{\Delta H}{RT^2} dT$$

$$= \ln K_{298} + \frac{1}{1.987}[(-\Delta H_{298} - 1344.7)(\frac{1}{T} - \frac{1}{298})$$

$$- 3.096 \ln \frac{T}{298} + 0.00442(T-298)$$

$$-0.581(10^{-6})(T^2-298^2) \quad (2)$$

Equation (2) has the unknowns K_{298} and ΔH_{298}. Substitute the two known values (K_T, T) = (0.068, 418) and (0.0019, 593) and solve simultaneously. The resulting equations are

$$-6.0718 = 1.987 \ln K_{298} + 0.000963 \Delta H_{298}$$

$$-13.7219 = 1.987 \ln K_{298} + 0.00167 \Delta H_{298}$$

whence

$$\Delta H_{298} = -10820 \text{ cal/gmol}$$

$$K_{298} = 10.64$$

P4.02.11. SULFUR DIOXIDE EQUILIBRIUM

For the oxidation of SO_2,

$$SO_2 + 0.5O_2 \Leftrightarrow SO_3$$

the thermodynamic data are

$$\Delta G_{298} = -16730 \text{ cal/gmol}$$

$$\Delta H_{298} = -94450 - (-70960) = -23490 \text{ cal/gmol}$$

$$C_p = a + bT + cT^2$$

	a	10^3b	10^6c
SO_2	7.116	9.512	3.511
SO_3	6.077	25.537	-0.687
O_2	6.148	3.102	-0.923
Δ	-4.113	12.474	-3.7365

Find the enthalpy change of reaction and the equilibrium constant as functions of temperature.

$$\Delta H_T = -23490 + \int_{298}^{T} \Delta C_p dT$$

$$= -22785 - 4.113T + 6.237(10^{-3})T^2 - 1.245(10^{-6})T^3 \quad (1)$$

$$\ln K_{298} = -\Delta G_{298}/298R = 16730/(298)1.987) = 28.25$$

$$\ln K_T = \ln K_{298} + \int_{298}^{T}(\Delta H_T/RT^2)dT$$

$$= 28.254 + \frac{1}{1.987}\int_{298}^{T}(\Delta H_T/T^2)dT \qquad (2)$$

Substitute from (1) into (2) and complete the integration. At 749 K, for instance, numerical integration gives $K_T = 4.44$.

P4.0.12. AMMONIA. IDEAL AND REAL EQUILIBRIUM CONSTANTS

For the ammonia synthesis, $0.5\ N_2 + 1.5H_2 \Leftrightarrow NH_3$, the correction for nonideality at 700 K and 300 atm is given as $K_\phi = 0.72$ (Hougen & Watson, Thermodynamics p 1019, 1959). Use the given thermodynamic data to find the equilibrium composition.

$$\Delta C_p = -7.457 + 0.00738T^2 - 1.409(10^{-6})T^3 \text{ cal/gmol-K}$$

$$\Delta H = -9130 - 7.46T + 0.00369T^2 - 0.47(10^{-6})T^3 \text{ cal/gmol}$$

$$\Delta G = -9130 + 7.46T \ln T - 0.00369T^2 + 0.235(10^{-6})T^3 - 23.98T$$

At 700 K,

$$\Delta G = 6564$$

$$K = \exp\frac{6564}{1.987(700)} = 0.00892$$

$$= K_y K_\phi/\pi$$

The stoichiometric balance is

$$\begin{array}{llll} 0.5N_2\ + & 1.5H_2 \Leftrightarrow & NH_3 & \\ 0.5(1-x) & 1.5(1-x) & x & \Sigma = 2-x \end{array}$$

$$K_y = 0.00892(300)/0.72 = 3.717$$

$$= \frac{x(2-x)}{(0.5-0.5x)^{0.5}(1.5-1.5x)^{1.5}} = \frac{0.7698x(2-x)}{(1-x)^2}$$

$$x = 0.5858$$

Mol fraction of ammonia in the mixture is

$$y_{NH_3} = \frac{x}{2-x} = 0.4142$$

P4.02.13 CARBON-STEAM REACTION

Find the heat of the reaction between carbon and steam at 773 K

$$C + H_2O \Rightarrow CO + H_2$$

At 298 K,

$$\Delta H_{298} = -26416 - (-57798) = 31382 \text{ cal/gmol}$$

Heat capacities are represented by

$$C_p = A + bT + cT^2 + d/T^2$$

	a	10^3b	10^7c	10^{-5}d
C	4.100	1.020	0	-2.10
H_2O	7.219	2.374	2.67	0
CO	6.342	1.836	-2.80	0
H_2	6.947	-0.200	4.81	0
Δ	1.97	-1.758	-0.66	2.1

The heat of reaction at temperature is

$$\Delta H = \Delta H_{298} + \int_{298}^{T}\Delta C_p dT$$

$$= 31382$$

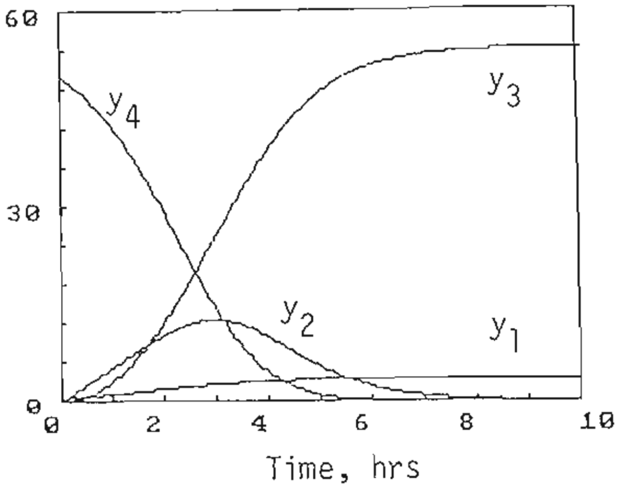
$$+ \int_{298}^{T} [1.97 - 0.001758T - 0.66(10^{-7})T^2 + 2.1(10^5)/T^2]dT$$

from which by numerical integration,

$$\Delta H_{773} = 32294 \text{ cal/gmol}$$

P4.03.01. GLUCONIC ACID BY FERMENTATION.

A mathematical model of the fermentation of the bacterium *Pseudomonas ovalis,* which produces gluconic acid, has been developed (Rai & Constantinides, *AIChE Symposium Series* 69 No 132, 114, 1973). This model which describes the dynamics of the logarithmic growth phase is summarized as follows.



Rate of cell growth,

$$\frac{dy_1}{dt} = b_1 y_1 (1 - \frac{b_1}{y_1})$$

Rate of gluconolactone formation,

$$\frac{dy_2}{dt} = \frac{b_3 y_1 y_4}{b_4 + y_4} - 0.9802 b_5 y_2$$

Rate of gluconic acid formation,

$$\frac{dy_3}{dt} = b_5 y_2$$

Rate of glucose consumption,

$$\frac{dy_4}{dt} = -1.011 (\frac{b_3 y_1 y_4}{b_4 + y_4})$$

where

y_1 = concentration of cells
y_2 = concentration of gluconolactone
y_3 = concentration of gluconic acid
y_4 = concentration of glucose
b_1 to b_5 = parameters of the system which depend on temperature and pH.

At the operating conditions of 30 C and pH = 6.6, the experimental values are

$b_1 = 0.949$, $b_2 = 3.439$, $b_3 = 18.72$, $b_4 = 37.51$, $b_5 = 1.169$

The initial conditions are,

$y_1 = 0.5$ UOD/ml, $y_2 = 0$ mg/mg, $y_3 = 0$ mg/mg, $y_4 = 50$ mg/mg.

The four concentration profiles are developed by solving this system of four first order differential equations. The concentrations of the cells and of the gluconic acid reach limiting values.

P4.03.02. A ZERO ORDER REACTION

A zero order gas reaction, A ⇒ rB, proceeds in a constant volume bomb, with 20% inerts, and the pressure rises from 1.0 to 1.3 atm in 2 min. If the same reaction takes place in a constant pressure batch reactor, what is the fractional change in volume in 4 min if the feed is at 3 atm and consists of 40% inerts?

Constant volume run:

$$-\frac{1}{V}\frac{dn_a}{dt} = k \quad (1)$$

$$n_t = n_a + n_b + n_I = n_a + r(n_{a0} - n_a) + 0.25 n_{a0} = (r+0.25)n_{a0} - (r-1)n_a$$

$$\pi = \frac{RT}{V}[(r+0.25)n_{a0} - (r-1)n_a]$$

$$\frac{d\pi}{dt} = -\frac{RT}{V}(r-1)\frac{dn_a}{dt} = -RT(r-1)k \qquad (2)$$

$$\pi - \pi_0 = kRT(r-1)(t-t_0)$$

$$1.3-1.0 = kRT(r-1)(2)$$

$$kRT(r-1) = 0.15 \qquad (3)$$

Constant pressure run:

$$n_t = n_a+r(n_{a0}-n_a) + \frac{2}{3}n_{a0} = (r+2/3)n_{a0}-(r-1)n_a$$

$$V = n_tRT/\pi$$

$$dV = -\frac{RT}{\pi}(r-1)dn_a$$

$$-\frac{1}{V}\frac{dn_a}{dt} = \frac{\pi}{RT(r-1)V}\frac{dV}{dt} = k = \frac{0.15}{RT(r-1)} \qquad (4)$$

$$\ln(V/V_0) = \frac{0.15(t-t_0)}{\pi} = \frac{0.15(4)}{3} = 0.2$$

$$V/V_0 = 1.221 \qquad (5)$$

P4.03.03. PHOSPHINE DECOMPOSITION

The decomposition of phosphine,

$4PH_3 \Rightarrow P_4 + 6H_2$

at 650 C in the gas phase is first order. The specific rate is given by

$\log_{10}k = -18963/T + 2\log_{10}T + 12.13$

$k = 0.0031/\text{sec}$

A closed vessel is charged to 1 atm initially. Find the pressure as a function of time.

$$n_t = n_a + 1.75(n_{a0}-n_a) = 1.75n_{a0}-0.75n_a$$

$$\pi/\pi_0 = n_t/n_{t0} = 1.75 - 0.75(n_a/n_{a0})$$

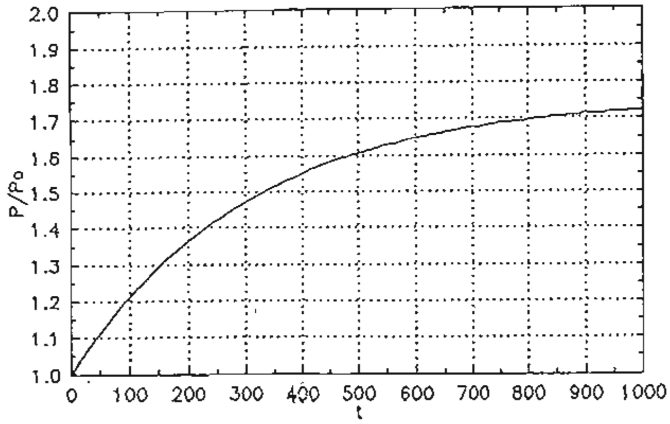
$$\frac{d(\pi/\pi_0)}{dt} = -0.75\frac{d(n_a/n_{a0})}{dt} = 0.75k(n_a/n_{a0})$$

$$= k(1.75 - \Pi/\Pi_0) \qquad (1)$$

Integrating,

$$kt = \int_1^{\pi/\pi_0}\frac{d(\pi/\pi_0)}{1.75-\pi/\pi_0} = \ln\frac{0.75}{1.75-\pi/\pi_0}$$

$$\pi/\pi_0 = 1.75 - 0.75\exp(-kt) = 1.75 - 0.75\exp(-0.00331t) \qquad (2)$$



P4.03.04. CONSECUTIVE REVERSIBLE REACTIONS.

For the two consecutive reversible reactions, $A \Leftrightarrow B \Leftrightarrow C$, the forward specific rates and equilibrium constants are

$k_1 = 0.001/\text{min}$, $k_2 = 0.01/\text{min}$, $K_1 = 0.8$, $K_2 = 0.6$.

Initial concentration of A is 1.0 molal.

(a) Find the concentration profiles of the three participants.

(b) How long does it take to reach 90% of equilibrium conversion of A? What will be the approaches to equilibrium of B and C at that time?

The stoichiometric balance is

$C = 1-A-B$

The rate equations are

$$\frac{dA}{dt} = -k_1(A-B/K_1) = -0.001(A-1.25B) \qquad (1)$$

$$\frac{dB}{dt} = k_1(A-B/K_1)-k_2(B-C/K_2)$$

$$= 0.001(A-1.25B)-0.01[B-(1-A-B)/0.6)] \qquad (2)$$

$$\frac{dC}{dt} = k_2(B-C/K_2) = 0.01(B-1.667C) \qquad (3)$$

The analytical solution of these three equations is attempted part way in problem P2.02.11. The numerical solution is plotted.

The equilibrium values are found by setting the rates to zero.

$A_e = 0.4386$, $B_e = 0.3509$, $C_e = 0.2105$.

At 90% of equilibrium conversion of A,

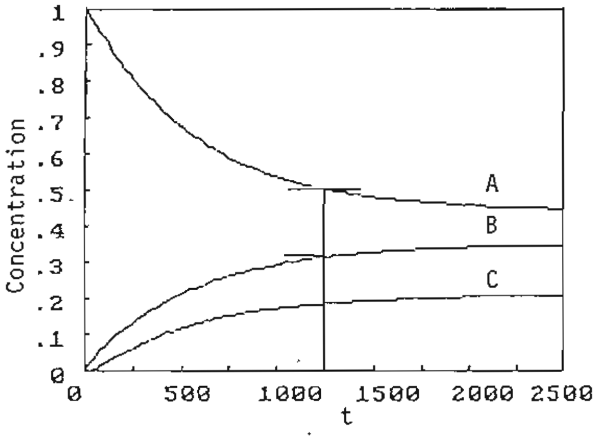
$A = 1-0.9(1-0.4386) = 0.495$

Reading off the graph,

$t = 1250$

$B = 0.31$, $100(1-0.3509)/(1-0.31) = 94.1\%$ equilibrium

$C = 0.195$, $100(1-0.2105)/(1-0.195) = 98.1\%$ equilibrium



P4.03.05. RATE OF A REVERSIBLE GAS PHASE REACTION

The reversible gas phase reaction, $A + B \overset{1}{\underset{2}{\Leftrightarrow}} 2C + D$, occurs at a constant volume of 1000 cuft. At time zero, the amounts of all participants are 1 lbmol each. Find the amount of substance converted and the time when the rate has fallen to half of its initial value. Data:

$k_1 = 8\ \text{cuft/(lbmol)(min)}$

$k_2 = 1500\ (\text{cuft})^2/(\text{lbmol})^2(\text{min})$

The stoichiometric balances are

$$1-n_a = 1-n_b = 0.5(n_C-1) = n_d-1$$

$$n_a = n_b\ ,\ n_c = 3-2n_a,\ n_d = 2-n_a$$

The rate of the reaction is assumed to follow the stoichiometry.

$$r_a = k_1 n_a n_b/V^2 - k_2 n_c^2 n_d/V^3$$

$$r_a' = V^2 r_a = k_1 n_a^2 - k_2(3-2n_a)^2(2-n_a)/V$$

$$= 8n_a^2 - 1.5(3-2n_a)^2(2-n_a)$$

When t = 0, $r_{ao}' = 6.5$

At half rate,

$$3.25 = 8n_a^2 - 1.5(3-2n_a)^2(2-n_a)$$

$$n_a = 0.8654$$

To find the time, use Simpsons Rule.

n_a	r_a'	$1/r_a'$	Simpson
1.0	6.5	0.154	0.154
0.9327	4.898	0.2042	0.8166
0.8654	3.25	0.308	0.308
Sum			1.279

$\left(\frac{0.6659}{2}\right) \frac{1}{3}\left[\frac{1}{6.5} + 4\cdot\frac{1}{\text{[illegible]}} + \frac{1}{\text{[illegible]}}\right]$

$$r_a' = V^2\left(\frac{1}{V}\frac{dn_a}{dt}\right)$$

$$t = V\int_{0.8654}^{1} \frac{dn_a}{r_a'} = 1000\left(\frac{0.0674}{3}\right)(1.279) = 28.73 \text{ min}$$

P4.03.06. ADDITION POLYMERIZATION

An activated monomer P_1 is produced from the monomer M according to

$$M \xrightarrow{0} P_1$$

Subsequently higher polymers are made in sequence, all with the same specific rate k,

$$M + P_1 \xrightarrow{1} P_2$$

so that

$$\frac{dP_1}{dt} = k_0 M - kP_1 = kM\left(\frac{k_0}{k} - P_1\right) \qquad (1)$$

Furthermore,

$$M + P_2 \Rightarrow P_3$$

$$\frac{dP_2}{dt} = kM(P_1-P_2)$$

For all subsequent processes,

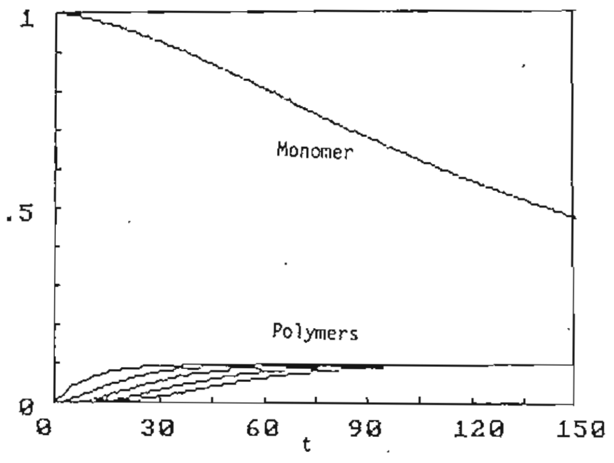
$$\frac{dP_n}{dt} = kM(P_{n-1}-P_n),\ n = 2,\ 3,\ 4,\ldots \qquad (2)$$

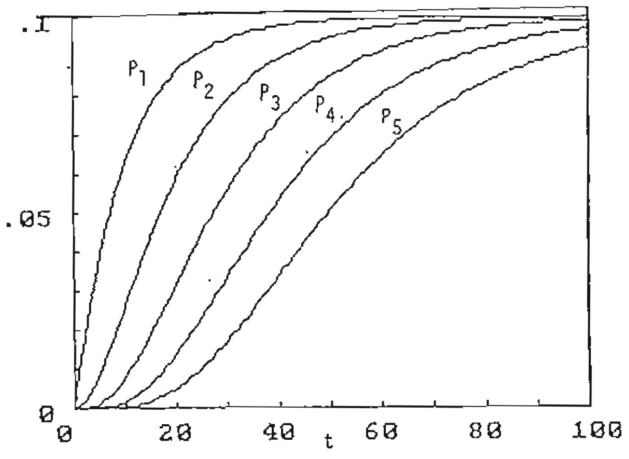
The overall conversion of monomer is

$$\frac{dM}{dt} = k_0 M - kM\sum_1^{\infty} P_n \qquad (3)$$

This system of second order rate equations is solved numerically for M and several values of P_n with these values:

$k_0 = 0.01$, $k = 0.1$, $M_0 = 1$, $n = 1\text{-}5$. Two scales are used for the ordinates.





P4.03.07. PARALLEL SECOND ORDER REACTIONS

Substances A and B react at constant volume with $A_0 = B_0$ according to

$$A + B \xrightarrow{1} C, \quad A + C \xrightarrow{2} D$$

Find the maximum conversion to C at several values of k_2/k_1. Is there an optimum selectivity, C/D?

The differential equations are,

$$\frac{dA}{dt} = -k_1(AB + \frac{k_2}{k_1}AC)$$

$$\frac{dB}{dt} = k_1AB = k_2\frac{k_1}{k_2}\,AB$$

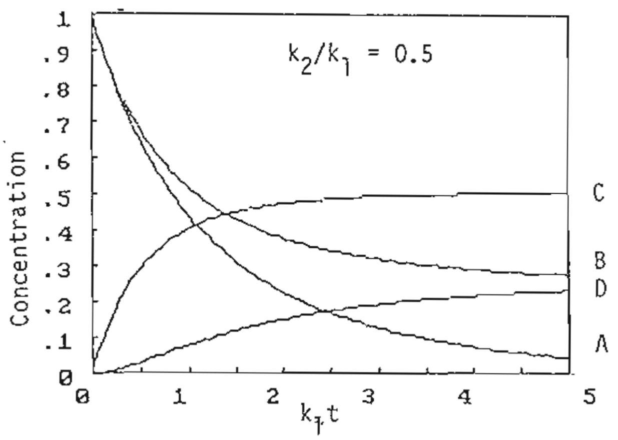
$$\frac{dC}{dt} = k_1(-\frac{k_2}{k_1}\,AC)$$

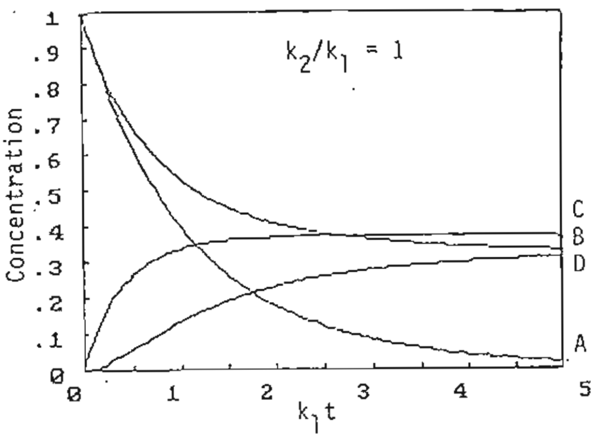
$$\frac{dD}{dt} = k_1\,\frac{k_2}{k_1}\,AC$$

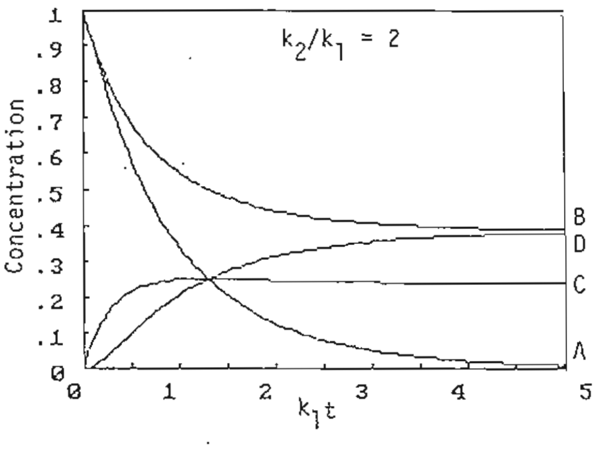
The equations are integrated with $A_0 = B_0 = 1$ and $C_0 = D_0 = 0$. The plots show that the maximum conversion to C depends on k_2/k_1:

k_2/k_1	0.5	1	2
C_{max}	0.48	0.38	0.25

The ratio C/D decreases continuously as the conversion to A proceeds.







P4.03.08. CRACKING OF BUTENES

Specific rate data for cracking butenes are reported as, (Watson, Chem Eng Progress 44 229, 1948):

$k = \exp(35.2-30203/T)$ gmol/(liter)(hr)(atm), °K

The reaction may be approximated as

$C_4H_8 \Rightarrow C_4H_6 + H_2$

The reaction is at 922 K, 1 atm and constant volume with a starting mixture of 10 mols of steam and 1 mol of butenes. Find the time and the reactor volume for 30% conversion.

At 922 K, k = 11.10, per hour; 11.10/3600, per sec

x = fractional conversion

$n_a = 1-x$

$n_t = 11 + x$

$V = n_tRT/\pi$

$$p_a = (n_a/n_t)\pi = \frac{1-x}{11+x} \quad (1)$$

The rate equation is,

$$-\frac{1}{V}\frac{dn_a}{dt} = kp_a$$

$$-\frac{dn_a}{dt} = kVp_a = kRTn_a$$

$$t = \frac{1}{kRT}\int_{0.7}^{1}\frac{dn_a}{n_a} = \frac{3600}{11.10(0.08205)(922)}\ln\frac{1}{0.7} = 1.53 \text{ sec}$$

$$V_r = n_tRT/\pi = 11.3(.08205)(922)/1 = 854.8 \text{ liters}$$

P4.03.09. OPTIMUM CYCLE PERIOD. FIRST ORDER REACTION

Find the optimum cycle period for a first order batch reaction with downtime of ϑ_d hrs/batch.

$$-\frac{dC}{d\vartheta} = kC$$

$$\vartheta = \frac{1}{k}\ln(C_0/C)$$

Number of daily batches,

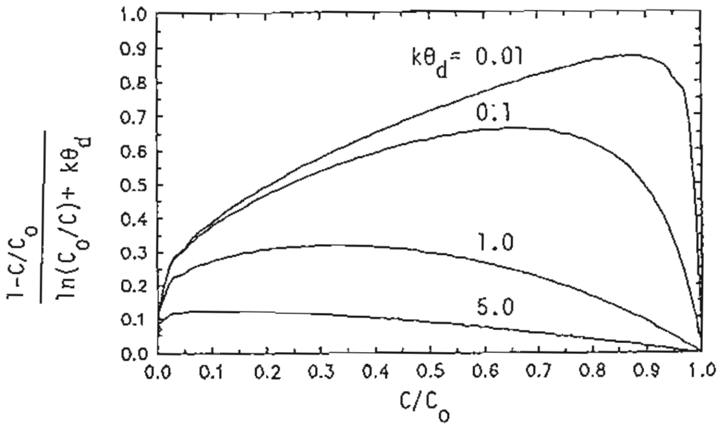
$$n = \frac{24}{\vartheta+\vartheta_d}$$

Daily yield

$$y = V_r(C_0-C)n = \frac{24V_r(C_0-C)}{\frac{1}{k}\ \ln(c_0/C) + \vartheta_d} = \frac{24kV_rC_0(1-C/C_0)}{\ln(C_0/C) + k\vartheta_d}$$

The ordinate of the plot is $y/24kV_rC_0$ which is proportional to the daily yield. The peaks in this curve are at these values of the parameters:

$k\vartheta_d$	0.01	0.10	1	5
C/C_0	0.87	0.65	0.32	0.12



P4.03.10. BATCH PROCESS WITH DOWNTIME

For the reaction, $A \Leftrightarrow B$, data are: $k_1 = 0.9$/hr, $K_e = 4$, $A_0 = 1.5$ lbmol/cuft, $B_0 = 0.1$. The downtime per batch is given by

$$t_d = 0.5 + 0.002V_r$$

in hours with reactor charge V_r in cuft. Each batch is to be run to 90% of equilibrium. Find V_r for an average conversion of A of 100 lbmols/hr.

Equilibrium concentration,

$$K_e = 4 = (1.6-A_e)/A_e$$

$$A_e = 0.32$$

Outlet concentration

$$A_f = A_0-0.9(A_2-A_e) = 1.5-0.9(1.5-0.32) = 0.438$$

$$-\frac{dA}{dt} = k(A-B/K_e) = k[(1+1/K_e)A - (A_0+B_00/K_e]$$

$$= 0.9(1.25A - 0.4)$$

$$t = \frac{1}{0.9}\int_{0.438}^{1.5} \frac{dA}{1.25A - 0.4} = 2.047 \text{ hr}$$

Conversion rate,

$$100 \text{ lbmol A/hr} = \frac{V_r(A_0-A_f)}{t_{react} + t_d} = \frac{V_r(1.5-0.438)}{2.047+0.5+0.002V_r}$$

$$V_r = 295.48 \text{ cuft.}$$

P4.03.11. PARALLEL REACTIONS OF BUTADIENE

Butadiene (B) reacts with acrolein (A) and also forms a dimer according to the reactions

$$C_4H_6 + C_3H_4O \overset{1}{\Rightarrow} C_7H_{10}O, \quad 2\ C_4H_6 \overset{2}{\Rightarrow} C_8H_{12}$$

The reaction is carried out in a closed vessel at 330 C, starting at 1 atm with equal concentrations of A and B, 0.010 gmol/liter each. Specific rates are $k_1 = 5.900$ and $k_2 = 1.443$ liters/(gmol)(min). Find (a) B as a function of A; (b) A and B as functions of t.

$$-\frac{dA}{dt} = k_1AB = 5.9AB \qquad (1)$$

$$-\frac{dB}{dt} = k_1AB + k_2B^2 = 5.9AB + 1.443B^2 \qquad (2)$$

Dividing these equations,

$$\frac{dB}{dA} - \frac{k_2B}{k_1A} = 1 \qquad (3)$$

This is a linear equation whose solution is

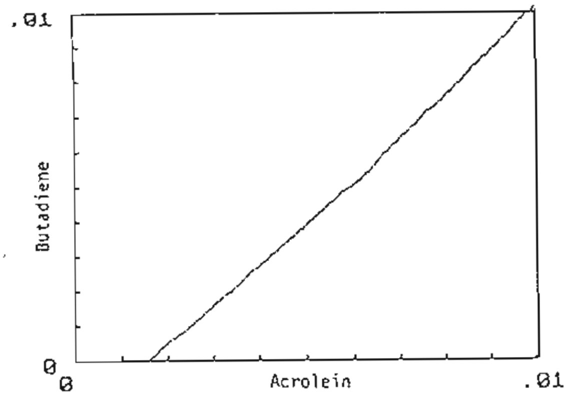
$$B = \frac{k_1}{k_1-k_2}A + IA^{k_2/k_1} = 1.32\ A - 0.010A^{0.245} \qquad (4)$$

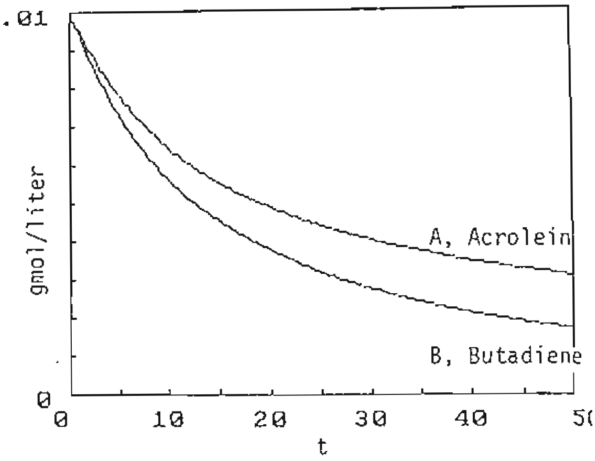
The integration constant was evaluated with $A_0 = B_0 = 0.010$.
Substitute (4) into (1)

$$-\frac{dA}{dt} = 5.9A(1.32A - 0.010A^{0.245}) \qquad (5)$$

The variables are separable, but an integration in closed form is not possible because of the odd exponent. Numerical integration followed by substitution into (4) will provide both A and B as fuctions of t.

However, the original differential equations are computer solved by Constantinides ODE and plotted here.





P4.03.12. REACTIONS A ⇒ B ⇒ C IN A BATCH REACTOR

For the set of reactions, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, data are: $k_1 = 0.35$, $k_2 = 0.13$, = 4 and $B_0 = C_0 = 0$. Plot the concentrations against the time.

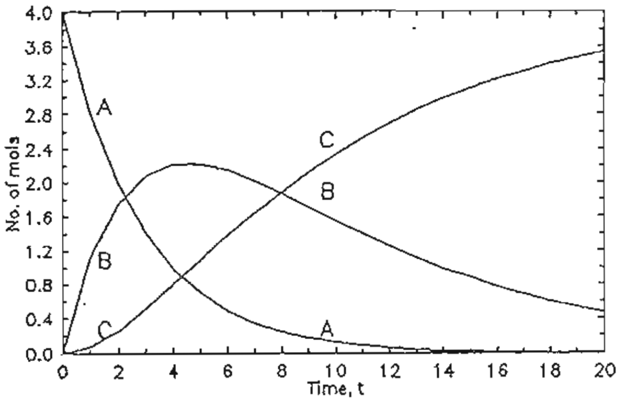
The differential equations are

$$\frac{dA}{dt} = -k_1A \qquad (1)$$

$$\frac{dB}{dt} = k_1A - k_2B = k_1A_0\exp(-k_1t) - k_2B \qquad (2)$$

$$C = A_0+B_0+C_0-A-B = 4-A-B \qquad (3)$$

The complete solution of these equations is worked out in problem P2.02.07. The plot is of the solution obtained numerically by program ODE. The peak value is B = 2.234 when t = 4.502.



P4.03.13. YIELD FROM BUTANE CRACKING

Under certain conditions the product from the thermal cracking of butane has the wt% composition given in the table. Find the mols of product per mol of butane converted.

The last three columns of the table give the yields of the compound, the carbon, and the hydrogen from 100 lb of butane or 1.75 mols of butane.

1.75 mols butane has 6.90 mols C and 17.25 mols H, whereas the tabulated numbers are 6.951 mols C and 16.595 mols H, not quite a perfect agreement. The product is

3.094/1.75 = 1.768 mols/mol butane charged

		Per 100 lbs butane		
Compound	Wt%	Mols	Mols C	Mols H
H_2	0.2	0.100	0	0.20
CH_4	10.8	0.675	0.675	2.70
C_2H_4	25.0	0.893	1.786	3.57
C_2H_6	10.0	0.333	0.667	2.00
C_3H_6	20.0	0.476	1.430	2.86
C_3H_8	3.0	0.068	0.205	0.545
C_4H_8	21.0	0.377	1.500	3.000
C_4h_{10}	10.0	0.1725	0.688	1.725
SUM	100.0	3.094	6.951	16.600

P4.03.14. CONSTANT PRESSURE OR CONSTANT VOLUME

The first order reaction, $A \Rightarrow 2.5B$, is carried out in a batch reactor at 2 atm with 20% inerts present, and the volume increases by 60% in 20 min. In a constant volume reactor, find the time required to reach 8 atm if the initial pressure is 5 atm, 2 atm of which consists of inerts.

$$-\frac{dn_a}{dt} = kn_a$$

Constant pressure run, $\pi = 2$.

$$n_t = n_a+n_b+n_i = n_a+2.5(n_{a0}-n_a)+0.25n_{a0} = 2.75n_{a0}-1.5n_a$$

$$n_{t0} = 1.25n_{a0}$$

$$V/V_0 = n_t/n_{t0} = 2.2-1.2n_a/n_{a0}$$

$$n_a/n_{a0} = \frac{2.2-V/V_0}{1.2} - \frac{1}{1.2}\frac{d(V/V_0)}{dt} = \frac{k}{1.2}(2.2-V/V_0)$$

$$kt = \int_1^{V/V_0} \frac{d(V/V_0)}{2.2-V/V_0} = \ln \frac{2.2}{2.2-V/V_0}$$

When t = 20, $V/V_0 = 1.6$, $k = 0.0347$.

Constant volume run.

$$n_t = n_a+2.5(n_{a0}-n_a)+ 0.667r_{a0} = 3.167n_{a0}-1.5n_a$$

$$\pi/\pi_0 = n_t/n_{t0} = \frac{3.167n_{a0}-1.5n_a}{1.667n_{a0}} = 1.90 - 2.5n_a/n_{a0}$$

$$n_a/n_{a0} = (1.9-\pi/\pi_0)/2.5 = 0.760 - 0.4\pi/\pi_0$$

$$d(n_a/n_{a0}) = -\ 0.4\ d(\pi/\pi_0)$$

$$0.4\frac{d(\pi/\pi_0)}{dt} = k(0.76-0.4\pi/\pi_0) = 0.0347(0.76-0.4\pi/\pi_0)$$

$$t = \frac{1}{0.0347}\int_1^{1.6}\frac{d(\pi/\pi_0)}{1.9-\pi/\pi_0} = 86.5$$

P4.03.15. VARIOUS RATES OF CHANGE

The reaction, $C_4H_{10} \Rightarrow 2C_2H_4+ H_2$, takes place at 1300 F and 3 atm, starting with 2 lbmol of butane. When the reaction is 50% complete, the partial pressure of the butane is changing at the rate of -2.4 atm/sec. At what rates are the following quantities changing? (a) partial pressure of ethylene; (b) number of mols of hydrogen present; (c) mol fraction of butane.

mols of butane = n_a

ethylene = $n_b = 2-n_a$

hydrogen = $n_c = 2-n_a$

$$n_t = 2(3-n_a)$$

$$p_a = \frac{n_a}{2(3-n_a)}\pi$$

$$p_b = \frac{2-n_a}{2(3-n_a)}\pi$$

$$dp_a = \frac{\pi}{2}d\left(\frac{n_a}{3-n_a}\right) = \frac{3\pi}{2(3-n_a)^2}dn_a$$

$$dp_b = \pi\ d\left(\frac{2-n_a}{3-n_a}\right) = -\frac{\pi}{(3-n_a)^2}dn_a$$

$$\frac{dp_b}{dt} = -\frac{2}{3}\frac{dp_a}{dt} = -(2/3)(-2.4) = +\ 1.6 \text{ atm/sec} \qquad \text{(a)}$$

$$dn_c = d(2-n_a) = -\ dn_a = -\frac{2(3-n_a)^2}{3\pi}dp_a$$

At 50% conversion, $n_a = 1$

$$dn_c/dt = -\ (8/9)(-2.4) = 2.13 \text{ mols/sec} \qquad \text{(b)}$$

mol fraction $N_a = p_a/\pi$

$$\frac{dN_a}{dt} = \frac{1}{\pi}\frac{dp_a}{dt} = -2.4/3 = -0.8 \text{ /sec} \qquad \text{(c)}$$

P4.03.16. RADIUM DECAY.

It is found that the number Q of radium atoms which break up per gram of radium in one second is, roughly, $Q = 3.7(10^{10})$. Find the time for 1/2 the radium to be changed. Avogadro's number is $6.023(10^{23})$ and atomic weight of radium is 226.

The reaction is first order. When $n_0 = 1$ gmol,

$$k = -\frac{1}{n}\frac{dn}{dt} = \frac{3.7(10^{10})(226)}{6.023(10^{23})} = 1.388(10^{-11}) \text{ /sec}$$

$$t_{1/2} = \frac{\ln 2}{k} = 4.994(10^{10}) \text{ sec, } 1583 \text{ yr} \qquad \text{(a)}$$

P4.03.17. RADIOACTIVE SERIES

In the series of 9 elements from radium to lead, inclusive, each element changes into its successor at a rate proportional to the amount of itself present. The half times and the corresponding specific rates are tabulated.

(a) Starting with pure Ra D, show how Ra E and Ra F build up and decay in the first year.

(b) Starting with pure radon, show how Ra A, Ra B, Ra C and Ra D build up and decay in the first hour.

(c) Starting with pure Ra A, show how Ra B, Ra C and Ra D build up and decay in the first two hours.

(d) Starting with pure radium, after how many days will the amount of Ra A be substantially constant.

(e) Starting with pure radon in considerable amount, shown that after a few weeks the rate of decay of the total amount of material is practically that of Ra D.

$Ra \overset{1}{\Rightarrow} R \overset{2}{\Rightarrow} A \overset{3}{\Rightarrow} B \overset{4}{\Rightarrow} C \overset{5}{\Rightarrow} D \overset{6}{\Rightarrow} E \overset{7}{\Rightarrow} F \overset{8}{\Rightarrow} Pb$

$dRa/dt = -k_1Ra$, $Ra = Ra_0\exp(-k_1t)$

$dR/dt = k_1Ra - k_2R$

$dA/dt = k_2R - k_3A$

$dB/dt = k_3A - k_4B$

$dC/dt = k_4B - k_5C$

$dD/dt = k_5C - k_6D$

$dE/dt = k_6D - k_7E$

$dF/dt = k_7E - k_8F$

$dPb/dt = k_8Pb$

		$t_{1/2}$,min	k
1	Radium	$842(10^{6})$	$8.24(10^{-12})$
2	Radon	$5.52(10^{3})$	$126(10^{-6})$
3	Ra A	3	$231(10^{-3})$
4	Ra B	26.8	$25.9(10^{-3})$
5	Ra C	19.7	$35.2(10^{-3})$
6	Ra D	$13.1(10^{6})$	$52.7(10^{-9})$
7	Ra E	$7.2(10^{3})$	$96.3(10^{-6})$
8	Ra F	$196(10^{3})$	$3.53(10^{-6})$
9	Pb	∞	0

The solution for consecutive first order reactions has been worked out by Rodiguin (1964).

$$C_0 = C_0^{(0)} e^{-k_1 t};$$

$$C_1 = C_0^{(0)}\left[\frac{k_1}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_1 - k_2} e^{-k_2 t}\right];$$

$$C_2 = C_0^{(0)}\left[\frac{k_1 k_3}{(k_2 - k_1)(k_3 - k_1)} e^{-k_1 t} + \frac{k_1 k_2}{(k_1 - k_2)(k_3 - k_2)} e^{-k_2 t} + \right.$$
$$\left. + \frac{k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} e^{-k_3 t}\right];$$

. . . .

$$C_{n-1} = C_0^{(0)}\left[\frac{k_1 k_2 \ldots k_{n-1}}{(k_2 - k_1)(k_3 - k_1)\ldots(k_n - k_1)} e^{-k_1 t} + \right.$$
$$+ \frac{k_1 k_2 \ldots k_{n-1}}{(k_1 - k_2)(k_3 - k_2)\ldots(k_n - k_2)} e^{-k_2 t} + \ldots$$
$$\left. \ldots + \frac{k_1 k_2 \ldots k_{n-1}}{(k_1 - k_n)(k_2 - k_n)(k_3 - k_n)\ldots(k_{n-1} - k_n)} e^{-k_n t}\right];$$

$$C_n = C_0^{(0)}\left[1 - \frac{k_2 k_3 k_4 \ldots k_n}{(k_2 - k_1)(k_3 - k_1)(k_4 - k_1)\ldots(k_n - k_1)} e^{-k_1 t} - \right.$$
$$- \frac{k_1 k_3 k_4 \ldots k_n}{(k_1 - k_2)(k_3 - k_2)(k_4 - k_2)\ldots(k_n - k_2)} e^{-k_2 t} -$$
$$- \frac{k_1 k_2 k_4 \ldots k_n}{(k_1 - k_3)(k_2 - k_3)(k_4 - k_3)\ldots(k_n - k_3)} e^{-k_3 t} - \ldots$$
$$\left. \ldots - \frac{k_1 k_2 \ldots k_{n-1}}{(k_1 - k_n)(k_2 - k_n)(k_3 - k_n)\ldots(k_{n-1} - k_n)} e^{-k_n t}\right] =$$
$$= C_0^{(0)} - (C_0 + C_1 + C_2 + \ldots + C_{n-1}).$$

where C_0 is the concentration of the first reactant and $C_0^{(0)}$ is its initial concentration.

(a) Start with pure D.

$$D/D_0 = \exp(-k_7 t) = \exp(-52.6(10^{-9})t]$$

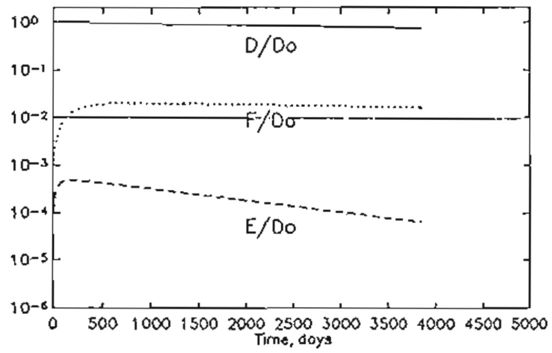
$$E/D_0 = \frac{k_6}{k_7 - k_6}\,[\exp(-k_6 t) - \exp(-k_7 t)]$$

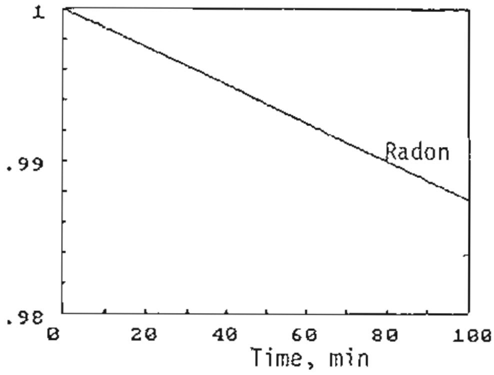
$$= 5.475(10^{-4})\{\exp[-52.7(10^{-9})t] - \exp[-96.3(10^{-6})t]\}$$

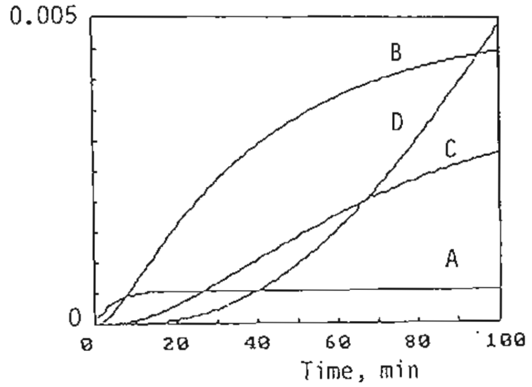
$$F/D_0 = 0.021285 \exp[-52.7(10^{-9})t] + 0.000562 \exp[-96.3(10^{-6})t] + 0.021847 \exp[-3.53(10^{-6})t]$$

The graph shows that the peak amount of E is reached in about 200 days. The plot of F falls off only slightly beyond t = 1000.

(b) With more than three participants, numerical integration of the differential equations is preferable. The results are plotted.







P4.03.18. APPROACHING EQUILIBRIUM?

(a) When transforming 49.3 gms acetochloranilid into parachloracetanilid, it was observed that 13.7 gms of para were formed during the first hour and 9.25 gms during the second hour.
Deduce the first order rate equation. (b) How much acetochloranilid would be expected after 8 hours? The amount actually found was 4.8 gms. What could be the reason for the discrepancy?

If first order,

$$k = \frac{1}{t} \ln \frac{n_0}{n} = \ln(49.3/35.6) = 0.3256$$

$$0.5 \ln(49.3/25.75) = 0.3247$$

When t = 8,

$$n = n_0 \exp[-0.325(8)] = 3.66$$

Since less conversion is obtained than predicted by a first order reaction, it may be that the reaction is reversible and equilibrium is being approached.

P4.03.19. CONSTANT P OR CONSTANT V. THIRD ORDER.

A gas containing 40% each of A and B and 20% of inerts undergoes the reaction, A+ 2B ⇒ C, with rate equation

$$-\frac{dC_a}{dt} = 12.5\ C_aC_b^2$$

the charge is 100 gmol and the temperature stays at 500 C. It is required to find the time when the content of B becomes 11.8% when (a) the pressure is constant at 10 atm; (b) at constant volume with initial pressure of 10 atm.

The stoichiometric balances are,

$$n_{a0}-n_a = 0.5(n_{b0}-n_b) = n_c$$
$$n_t = n_an_b+n_c+n_I = 0.5n_{a0} + 2n_a$$
$$n_{a0} = n_{b0} = 40$$

When

$$\frac{n_b}{n_t} = \frac{2n_a-40}{2n_a+20} = 0.118,\ n_a = 24.00$$

$$V = n_tRT/\pi = (2n_a+20)(0.8205)(773)/\pi = 63.426(2n_a+20)/\pi$$

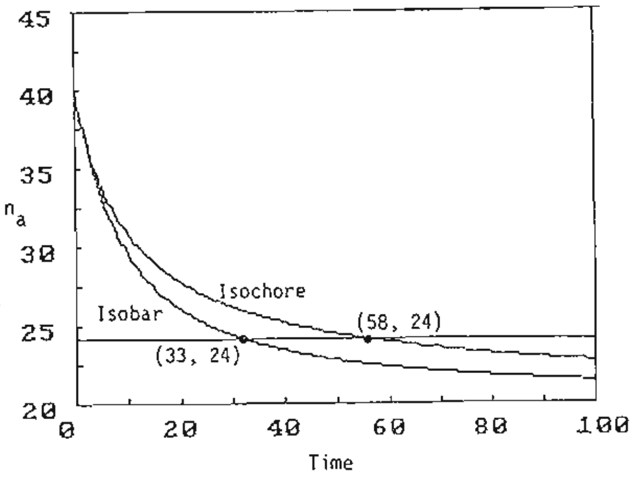
(a) At constant pressure,

$$-\frac{dn_a}{dt} = k\ \frac{n_an_b^2}{V^2} = 12.5\ \frac{n_a(2n_a-40)^2}{[6.346(2n_a+20)]^2} \qquad (1)$$

(b) At constant volume,

$$-\frac{dn_a}{dt} = \frac{12.5n_a(2n_a-40)^2}{(634.26)^2} \qquad (2)$$

Both integrals are evaluated numerically and plotted. When B = 11.8%, n_a = 24, t = 33.5 at constant pressure and t = 58.5 at constant volume.



P4.03.20. CELL GROWTH INHIBITION.

The dynamics of the growth of cells, A, is represented by the equation

$$\frac{dA}{dt} = k_1A(1 - \frac{A}{k_2}) \qquad (1)$$

(Constantinides et al, Biotech Bioeng 12 803, 1970). The second term on the right represents an inhibition. Also, the rate of growth of a penicillin producing organism, B, is represented by

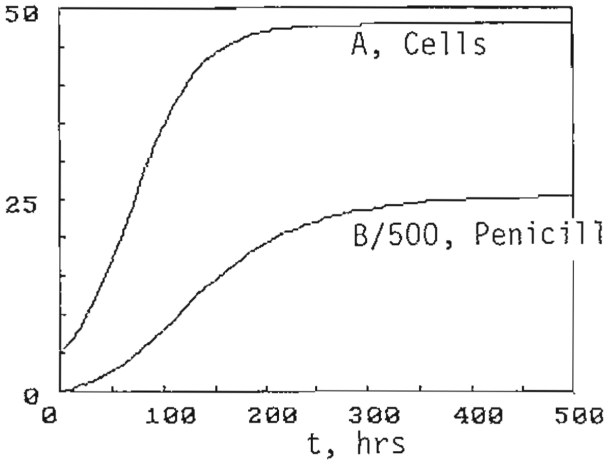
$$\frac{dB}{dt} = k_3A - k_4B \qquad (2)$$

The values of the constants are, with time in hours:

$k_1 = 0.03210,\ k_2 = 47.70,\ k_3 = 3.374,\ k_4 = 0.01268$

Integrate the equations with $A_0 = 5$ and $B_0 = 0$.

The first equation could be integrated analytically and the result substituted into the second equation which may not be integrable. Therefore, the plotted solution was obtained by numerical integration of the pair. Both the cells and the penicillin producing entity reach steady state in a few hundred hours



P4.03.21. VARIABLE TEMPERATURE

For a first order liquid phase reaction, the temperatures were recorded at values of the amount of reactant, starting with n = 2. The specific rate is,

$k = \exp(8.53-3250/T)$, $300 < T < 400$

$\exp(2.96-1022/T)$, $400 < T < 500$

Find the corresponding reaction times.

The time is given by trapezoidal integration, and tabulated.

$$t = \int_n^2 \frac{dn}{kn}$$

n	T	1/kn	t
2.00	300	5.00	0
1.64	320	3.03	1.445
1.34	340	2.10	2.215
1.10	360	1.52	2.649
0.92	380	1.11	2.886
0.67	400	1.00	3.149
0.58	420	1.03	3.241
0.44	440	1.20	3.397
0.26	460	1.83	3.670
0.21	480	2.07	3.767
0.10	500	4.00	4.101

P4.03.22. ETHYLACETATE SAPONIFICATION

A solution contains 5 g/liter of ethyl acetate and 0.1 mols/liter of NaOH. Second order specific rates are 23.5 at 0 C and 92.4 liter/gmol-min at 20 C. Find the time for 95% conversion at 40 C.

$k = \exp(a-b/T)$

$$b = \frac{\ln(k_2/k_1)}{1/T_1-1/T_2} = \frac{\ln(92.4/23.5)}{1/273.2-1/293.2} = 5482$$

$$a = \ln k_1 + 5482/T_1 = \ln (23.5) + 5482/293.2 = 23.22$$

$$k_{40} = \exp(23.22-5482/313.2) = 305.0$$
$$C_{a0} = 5/88.11 = 0.0567 \text{ gmol/liter}$$
$$C_b = C_{b0}-(C_{a0}-C_a) = 0.1 - 0.0567 + C_a = 0.0433 + C_a$$
$$-\frac{dC_a}{dt} = kC_a(0.0433+C_a)$$

For 95% conversion, $C_a = 0.05(0.0567) = 0.00284$

$$t = \frac{1}{305}\int_{0.00284}^{0.05} \frac{dC_a}{C_a(C_a+0.0433)} = 0.1683 \text{ min}$$

P4.03.23. BATCH PROCESS WITH DOWN TIME

A batch reaction process has a downtime of 0.5 hrs/batch. The specific rate is 0.2 liters/gmol-hr and the starting concentration is 8 gmol/liter. Find the fractional conversion at which a maximum daily production is obtained.

$$-\frac{dC}{dt} = 0.2C^2$$

$$t = \frac{1}{k}\left(\frac{1}{C} - \frac{1}{C_0}\right) = 5\left(\frac{1}{C} - 0.125\right)$$

Number of batches per day,

$$n = \frac{24}{t + t_d} = \frac{24}{t + 0.5}$$

Daily yield,

$$y = V_r(C_0-C)n = \frac{24V_r(C_0-C)}{5(\frac{1}{C} -0.125)+ 0.5}$$

The maximum is obtained when dy/dt = 0. The derivative reduces to

$$0.2C^2 - 16C + 64 = 0$$

$C = 4.223$ or 47.2% conversion

The time per batch,

$$t = 0.56 \text{ hr}$$

Yield,

$$y_{max} = 85.6V_r \text{ gmol/day}$$

P4.03.24. FILLING PERIOD OF A BATCH REACTOR.

A reactor is charged initially with 200 liters of solvent and 100 liters (400 mols) of reactant A. Then 100 liters (400 mols) of reactant B is charged over a 20 minute period. The volumes are additive. The specific rate of the second order reaction is 0.05. Find the variation of the content of A up to 20 minutes and beyond.

$V_r = 300 + 5\,t$, liters

$n_b = 20t - 400 + n_a$

The rate equation is

$$-\frac{dn_a}{dt} = \frac{kn_an_b}{V_r} = \frac{0.05n_a(20t-400+n_a)}{300+5t} \quad (1)$$

This is integrated numerically up to t = 20; the results are tabulated. Beyond t = 20 when the input of B is discontinued the rate equation is,

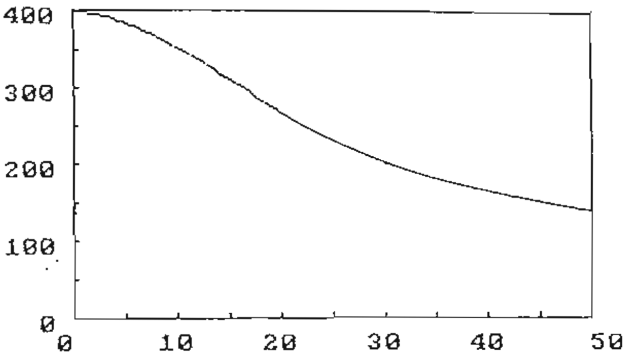
$$-\frac{dn_a}{dt} = \frac{0.05n_a^2}{400}, \text{ with } n_a = 266.9 \text{ when } t = 20$$

The integral is

$$n_a = \frac{266.9}{1+(0.05)(266.9)(t-20)/400} \tag{2}$$

Values of this integral between t = 20 and 100 are tabulated.

t	n_a
0	400
5	386.0
10	353.1
15	311.4
20	266.9
25	228.7
30	200.1
40	160.0
50	133.3
100	72.7



P4.03.25. STYRENE

Catalytic dehydrogenation of ethyl benzene to styrene is accompanied by the formation of benzene and some toluene, but the latter will be neglected in this problem (Wenner & Dybdal, Chem Eng Progress 44 275, 1948). The reactions and their rate equations are

$C_6H_5C_2H_5 \Leftrightarrow C_6H_5C_2H_3 + H_2$, $A \Leftrightarrow B + C$

$C_6H_5C_2H_5 \Rightarrow C_6H_6 + C_2H_4$, $A \Rightarrow D + E$

$$dn_b/dt = k_1(p_a - p_bp_c/K_e) \text{ , lbmol/hr-cuft} \tag{1}$$

$$dn_d/dt = k_2p_a \tag{2}$$

The constants k_1, k_2, K_e are known. Rewrite these equations exclusively in terms of the variables n_b and n_d and t.

The stoichiometric balances are,

$n_a = n_{a0}-n_b-n_d$

$n_c = n_b$

$n_e = n_d$

$n_t = n_a+n_b+n_c+n_d+n_e = n_{a0}+n_b+n_d$

Express the partial pressures in terms of n_b and n_d, using the ideal gas law.

$$p_a = (n_a/n_t)\pi = \frac{n_{a0}-n_b-n_d}{n_{a0}+n_b+n_d}\pi$$

$$p_b = p_c = \frac{n_b}{n_{a0}+n_b+n_d}\pi$$

Substitute into the rate equations.

$$\frac{dn_b}{dt} = \frac{k_1\pi}{n_{a0}+n_b+n_d}[n_{a0}-n_b-n_d - \frac{n_b^2\pi}{K_e(n_{a0}+n_b+n_d)}] \tag{3}$$

$$\frac{dn_d}{dt} = k_2\pi(\frac{n_{a0}-n_b-n_d}{n_{a0}+n_b+n_d}) \tag{4}$$

Equations (3) and (4) now are solvable numerically.

P4.03.26. METHANE CHLORINATION

Methane is chlorinated at temperatures in the range of 200-700 C. A mixture of mono, di, tri and tetra chlors is formed. Let the concentrations be: b = chlorine, c_0 = methane, c_1 = mono, c_2 = di, c_3 = tri, c_4 = tetra. The rate equations are,

$dc_0/dt = -k_1c_0b$
$dc_1/dt = (k_1c_0-k_2c_1)b$
$dc_2/dt = (k_2c_1-k_3c_2)b$
$dc_3/dt = (k_3c_2-k_4c_3)b$
$dc_4/dt = k_4c_3b$

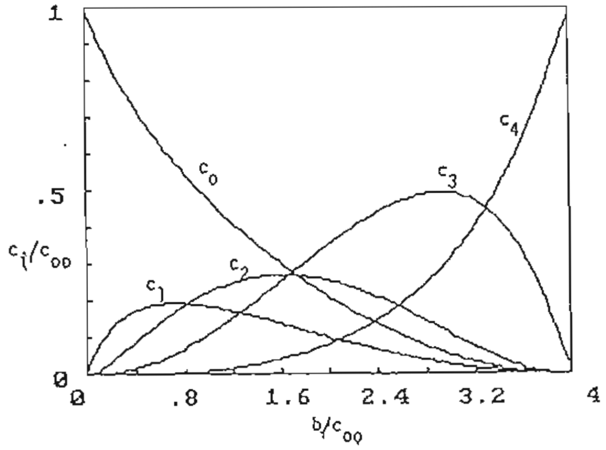
These are rearranged into,

$z = k_1c_0+k_2c_1+k_3c_2k_4c_3$
$dc_0/db = -k_1c_0/z$
$dc_1/db = (k_1c_0-k_2c_1)/z$
$dc_2/db = (k_2c_1-k_3c_2)/z$
$dc_3/db = (k_3c_2-k_4c_3)/z$
$dc_4/db = k_4c_3/z$

The specific rates are known as ratios (Kobelt & Troltenier, *Chem Ing Technik* 38 134-6, 1966):

$k_1:k_2:k_3:k_4 = 8:24:12:3$

Plot the ratios, $c_i/(c_0)_0$ against $b/(c_0)_0$, using ODE for the integration.



P4.04.01. RATE EQUATIONS FROM CSTR DATA.

For the consecutive reactions, 2A ⇒ B and 2B ⇒ C, concentrations were measured as functions of residence time in a CSTR. In all experiments, $C_{a0} = 1$ lbmol/cuft. Volumetric flow rate was constant. The data are tabulated in the first three columns. Check the proposed rate equations,

$$r_a = k_1 C_a^{\alpha}$$

$$r_b = -0.5k_1 C_a^{\alpha} + k_2 C_b^{\beta}$$

Write and rearrange the material balances on the CSTR.

$$C_{a0} = C_a + \bar{t}\, r_a$$

$$r_a = \frac{C_{a0}-C_a}{\bar{t}} = k_1 C_a^{\alpha} \qquad (1)$$

$$r_b = \frac{C_{b0}-C_b}{\bar{t}} = -0.5k_1 C_a^{\alpha} + k_2 C_b^{\beta} = -0.5r_a + k_2 C_b^{\beta} \qquad (2)$$

Numerical values of r_a, r_b and $r_b+0.5r_a$ are tabulated. The constants of the rate equations are evaluated from the plots of the linearized equations,

$$\ln r_a = \ln k_1 + \alpha \ln C_a = -2.30 + 2.001 \ln C_a$$

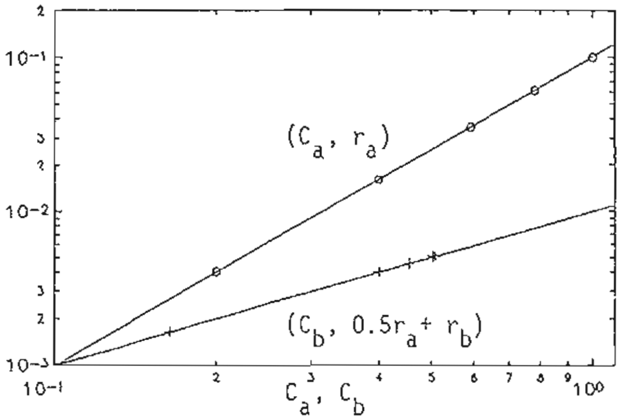
$$\ln(r_b+0.5r_a) = \ln k_2 + \beta \ln C_b = -4.606 + 0.9979 \ln C_b$$

which make the rate equations,

$$r_a = 0.1003 C_a^{2.00}$$

$$r_b = -0.0502 C_a^2 + 0.01 C_b^{0.998}$$

$\bar{t}$	C_a	C_b	r_a	$-r_b$	$r_b+0.5r_a$
10	1.000	0.4545	0.100	0.04545	0.00455
20	0.780	0.5083	0.061	0.02542	0.00508
40	0.592	0.5028	0.0352	0.01257	0.00503
100	0.400	0.400	0.0160	0.0040	0.0040
450	0.200	0.1636	0.0040	0.000364	0.00164



P4.04.02. SPECIFIC RATE AND REACTOR PERFORMANCE.

The liquid phase reaction, A+B ⇔ C+D, was tested in a laboratory CSTR with these results.

residence time, hrs	0.8	5.0
% conversion of A	50	60

Feed concentrations were $C_{a0} = 2$ mol/liter, $C_{b0} = 1.5$ and the others zero.

(a) Find the specific rates of the forward and reverse reactions.

(b) Find the time for 90% of equilibrium conversion in a batch reactor.

(c) A reactor is charged with 10 liters of a solution containing 30 mols of B. Then another solution containing 4 mol/liter of A is charged at the rate of 10 liters/hr to the same vessel with thorough stirring. Find C_a as a function of time, both with and without chemical reaction in the vessel.

Part (a):

$$r_a = \frac{C_{a0}-C_a}{\bar{t}} = k_1 C_a C_b - k_2 C_c C_d = k_1 C_a (C_a-0.5) - k_2 (2-C_a)^2$$

Substitute the data.

$$(2-1)/0.8 = 1(0.5)k_1 - k_2$$

$$(2-0.8)/5 = (0.8)(0.3)k_1 - (2-0.8)^2 k_2$$

whence,

$$k_1 = 3.25,\ k_2 = 0.375,\ K_e = k_1/k_2 = 8.667 \qquad \text{(a)}$$

Part (b):

Equilibrium conversion,

$$8.667C_{ae}(C_{ae}-0.5) = (2-C_{ae})^2$$

$$C_{ae} = 0.7444$$

Required final concentration,

$$C_{af} = 2 - 0.9(2-9.7444) = 0.8700$$

$$t = \int_{0.87}^{2} \frac{dC_a}{3.25C_a(C_a-0.5)-0.375(2-C_a)^2} = 0.4272 \qquad \text{(b)}$$

Part (c):

Unsteady material balance,

$$n_{af} = 0 + V_r r_a + \frac{d(C_a V_r)}{dt} = V_r r_a + C_a \frac{dV_r}{dt} + V_r \frac{dC_a}{dt} \qquad (1)$$

$$n_{af} = 40 \text{ mols/min}$$

$$V_r = 10(1+t)$$

$$\Delta n_a = \Delta n_b = -\Delta n_c = -\Delta n_d$$

$$n_{af} - V_r C_a = n_{b0} - V_r C_b = V_r C_c = V_r C_d$$

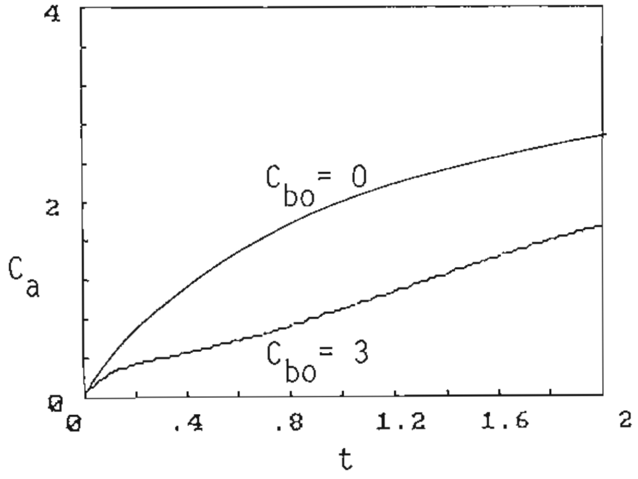
$$C_b = C_a + \frac{n_{b0}-n_{af}t}{V_r} = C_a + \frac{30-40t}{10(1+t)}$$

$$C_c = C_d = \frac{40t}{10(1+t)} - C_a$$

Substitute into Eq (1).

$$\frac{dC_a}{dt} = \frac{4-C_a}{1+t} - 3.25[C_a(C_a + \frac{3-4t}{1+t}) - (\frac{4t}{1+t} - C_a)^2/8.667] \qquad (2)$$

Integrate numerically with $C_{a0} = 0$ when $t = 0$. The plot shows the concentration of A with and without reaction with B.



P4.04.03. HEXAMINE SYNTHESIS

The reaction of ammonia and formaldehyde to make hexamine was studied at 36 C(Kermode & Stevens, Canad J Chem Eng 43 68, 1965) in a continuous flow vessel of 490 cc stirred at 1800 rpm. The reaction is

$4NH_3 + 6\ HCHO \Rightarrow (CH_2)_6 + 6H_2O$, $A + B \Rightarrow$ Products

and the rate equation is

$r_a = 0.0649C_aC_b^2$ mols/liter-sec

The reactants were fed in streams of 1.5 cc/s each with ammonia concentration 4.06 mol/liter and formaldehyde 6.32 mol/liter. Find the effluent concentrations.

The stoichiometric balance is

$(C_{a0}-C_a)/4 = (C_{b0}-C_b)/6$

$C_b = 6.32 - 1.5(4.02)+1.5C_a = 0.29 + 1.5C_a$

The residence time is

$\bar{t} = 490/(1.5+1.5) = 163.3$ sec

The CSTR material balance is

$C_{a0} = C_a + \bar{t}r_a$

$4.02 = C_a + 163.3(0.0649)C_a(0.29+1.5C_a)^2$

$C_a = 0.4124$

$C_b = 0.29 + 1.5(0.4124) = 0.9086$

P4.04.04. STYRENE AND BUTADIENE REACTION

Styrene (A) and butadiene (B) are to be reacted in a series of CSTRs, each of 26.5 m^3 capacity. The initial concentrations are A_0 0.795 and B_0 = 3.55 kgmol/m^3. Feed rate is 20 m^3/hr. The rate equation is

$r_a = 0.036AB$, kgmol/m^3-hr

Find the number of tanks in series needed to effect 90% conversion of the limiting reactant.

The required effluent concentration is

$A_f = 0.1(0.795) = 0.0795$

The rate equation is

$r_a = 0.036A(2.755+A)$

The residence time is

$\bar{t} = 26.5/20 = 1.325$ hr

Material balance on the first stage,

$$0.795 = A_1 + 0.036(1.325)A_1(2.755+A_1)$$

$$= 1.1314A_1 + 0.0477A_1^2$$

$$A_1 = \frac{-1.1314+\sqrt{1.2801+0.1908A_0}}{0.0954}$$

For subsequent stages,

$$A_n = \frac{-1.1314 + \sqrt{1.2801+0.1908A_{n-1}}}{0.0954}$$

Successive determinations show that between 17 and 18 tanks in series are needed.

n	A	n	A	n	A
0	0.7950				
1	0.6832	11	0.1733	21	0.0495
2	0.5893	12	0.1523	22	0.0438
3	0.5101	13	0.1340	23	0.0388
4	0.4427	14	0.1180	24	0.0344
5	0.3852	15	0.1040	25	0.0305
6	0.3359	16	0.0918		
7	0.2934	17	0.0810		
8	0.2567	18	0.0715		
9	0.2249	19	0.0632		
10	0.1973	20	0.0559		

P4.04.05. ESTERIFICATION IN TWO STAGES

The feed to a two stage CSTR contains ethanol (A_0 = 6.7 mols/liter) and acetic acid (10.5 mols/liter). The specific rates in the two tanks are $k_1 = 0.000476$ and $k_2 = 0.000163$ liter/mol-min. The residence times are 53 and 27 minutes. Find the concentrations of the effluents from the two stages.

The material balances are,

$$6.7 = A_1 + 53(0.000476)A_1(3.5+A_1)$$

$$A_1 = A_2 + 27(0.000163)A_2(3.5+A_2)$$

The solution of this pair is

$$A_1 = 5.462,\ A_2 = 5.260$$

These values are perhaps far enough from equilibrium to justify neglecting the back reaction of this normally reversible esterification.

P4.04.06. POLYOLEFINS

A scheme of Fontana et al (In Eng Chem 44 2955, 1952) for making polyolefins from butene employs four reactors in series with one fourth of the fresh butene charged to each reactor. A small stream containing catalyst is charged to the first reactor. The specific rate is k = 0.6/min. Feed concentration is 0.7. In this example the reactors are all of the same size.

Find the residence times, $\bar{t}_4$, of the last stage that will give the effluent concentration ratios C_4/C_0 = 0.1, 0.05 and 0.01.

F = total volumetric feed rate/ 100 cuft of reactor

$$\bar{t}_4 = F,\ \bar{t}_3 = (4/3)\bar{t}_4,\ \bar{t}_2 = 2\bar{t}_4,\ \bar{t}_1 = 4\bar{t}_4$$

Effluent from the first stage,

$$C_1 = \frac{C_0}{1+k\bar{t}_1} = \frac{C_0}{1+4k\bar{t}_4} \quad (1)$$

Feed to the second stage,

$$C_1' = [F/4)C_0+(F/4)C_1]/(F/2) = (C_0+C_1)/2$$

In the next stages,

$$C_2 = \frac{C_1'}{1+k\bar{t}_2} = \frac{C_0+C_1}{2(1+2k\bar{t}_4} \quad (2)$$

$$C_2' = [(F/4)C_0+(F/2)C_2]/(3F/4) = (C_0+2C_2)/3$$

$$C_3 = \frac{C_2'}{1+k\bar{t}_3} = \frac{C_0+2C_2}{3+4k\bar{t}_4} \quad (3)$$

$$C_3' = [(F/4)C_0+0.75FC_3]/F = 0.25(C_0+3C_3)$$

$$C_4 = \frac{C_3'}{1+k\bar{t}_4} = \frac{C_0+3C_3}{4(1+k\bar{t}_4)} \qquad (4)$$

In Eqs (1) to (4), substitute $k = 0.6$. Then specify $C_4/C_0 = C_4/0.7$ and find corresponding values of $\bar{t}_4$ and effluent concentrations from each stage.

C_4/C_0	0.1	0.05	0.01
$\bar{t}_4$	3.75	7.91	28.8

At the middle value, $C_1=0.1629$, $C_2=0.0411$, $C_3=0.0356$, $C_4=0.0350$.

P4.04.07. FIRST ORDER REVERSIBLE REACTION. UNSTEADY AND STEADY.

The first order reversible reaction, $A \underset{2}{\overset{1}{\rightleftharpoons}} B$, is carried out in a CSTR, with an inlet concentration A_0. Express the effluent ratio, A/A_0, in terms of the specific rates and the mean residence time, $\tau = V_r/F$.

(a) When the initial concentration in the tank is zero.
(b) When steady state is attained.
(c) For very rapid reactions.

Part (a):

The rate equation is

$$r_a = -r_b = k_1A - k_2B \qquad (1)$$

The unsteady material balances on the two participants are,

$$A_0 = A + \tau r_a + \tau \frac{dA}{dt} \qquad (2)$$

$$0 = B - \tau r_a + \tau \frac{dB}{dt} \qquad (3)$$

Adding these equations,

$$A_0 = A+B + \tau \frac{d(A+B)}{dt} \qquad (4)$$

The integral is

$$t/\tau = \int_0^{A+B} \frac{d(A+B)}{A_0-A-B} = \ln \frac{A_0}{A_0-A-B}$$

Solving for B,

$$B = -A + A_0[1-\exp(-t/\tau)]$$

Then Eq (1) becomes,

$$r_a = k_1A - k_2B = (k_1+k_2)A - k_2A_0[1-\exp(-t/\tau)]$$

and Eq (2) becomes,

$$A_0 = A + (k_1+k_2)\tau A - k_2\tau A_0[1-\exp(-t/\tau)] + \tau \frac{dA}{dt}$$

Rearrange into a standard form of first order linear equation,

$$\frac{d(A/A_0)}{dt} + \frac{k_1\tau+k_2\tau+1}{\tau}(A/A_0) = \frac{1}{\tau}[1+k_2\tau - k_2\tau \exp(-t/\tau)] \qquad (5)$$

The integrating factor is

$$z = \exp[(k_1\tau+k_2\tau+1)(t/\tau)]$$

The final integral is

$$\frac{A}{A_0} = \frac{1+k_2\tau}{1+k_1\tau+k_2\tau} - \frac{k_2}{k_1+k_2}\exp(-t/\tau)$$

$$- \frac{k_1}{(k_1+k_2)(1+k_1\tau+k_2\tau)} \exp\{-[1+k_1\tau+k_2\tau](t/\tau)\} \qquad (6)$$

Part (b), steady state, when $t \Rightarrow \infty$,

$$A/A_0 \Rightarrow \frac{1+k_2\tau}{k_1\tau+k_2\tau+1} \qquad (7)$$

Part (c):

For fast reactions, $k_1\tau >> 1$ and $k_2\tau >> 1$ and

$$A/A_0 \Rightarrow \frac{k_2\tau}{k_1\tau+k_2\tau} = \frac{1}{1+k_1/k_2} = \frac{1}{1+K_e} \qquad (8)$$

P4.04.08. RECYCLE TO A CSTR

A first order liquid phase reaction is taking place in a mixed reactor with 92% conversion. It has been suggested that a fraction of the product stream be recycled. If the fresh feed rate remains unchanged, what will be the effect on conversion?

$$V'_1 = V'_0(1+\alpha)$$

$$C_{a1} = \frac{V'_0C_{a0}+\alpha V'_0C_a}{V'_0(1+\alpha)} = \frac{C_{a0}+\alpha C_a}{1+\alpha}$$

The material balance is,

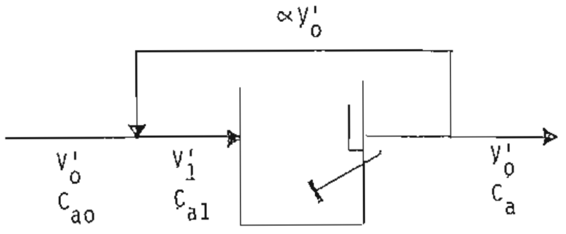
$$V'_1C_{a1} = V'_1C_a + kV_rC_a$$

$$C_a = \frac{C_{a1}}{1+kV_r/V'_1} = \frac{C_{a0}+\alpha C_a}{(1+\alpha)(1+\frac{kV_r}{V'_0(1+\alpha)}}$$

$$= \frac{C_{a0}}{1+\alpha+k\tau_0} + \frac{\alpha}{1+\alpha+k\tau_0}C_a = \frac{C_{a0}}{1+k(V_r/V'_0)}$$

$$\tau_0 = V_r/V'_0$$

Thus the conversion with the recycle is the same as without. There may be a justification for recycle if it is to be heated or cooled or modified in composition.



P4.04.09. DUMPING A CSTR BATTERY.

A two stage battery is operated with a feed rate of 75 cuft/hr, an inlet concentration $C_0 = 1.5$ lbmols/cuft and a rate equation, $-dC/dt = 0.4C$ lbmols/min-cuft. The product has a concentration $C = 0.1$. After several days operation input flow is stopped. The two reactors are dumped when the average of their concentrations is the same as the steady state effluent from the second reactor under normal operating conditions. Instantaneous discharge is to be assumed. How soon after the flow is stopped can the material be discharged?

Material balances on the two stages are

$$1 = C_1/C_0 + kC_0\tau\ (C_1/C_0)^2 = C_1/C_0 + 0.6\tau(C_1/C_0)^2 \qquad (1)$$

$$C_1/C_0 = C_2/C_0 + kC_0\tau\ (C_2/C_0) = (1/15) + 0.6\tau(1/15)^2 \qquad (2)$$

The solution is

$C_1/C_0 = 0.236$

$\tau = 22.75$

After input is stopped each vessel will function as a batch reactor.

$$-\frac{dC_1}{dt} = 0.4C_1^2$$

$$C_1 = \frac{C_{01}}{1+kC_{01}t} = \frac{0.236}{1+0.4(0.236)t} \qquad (3)$$

$$C_2 = \frac{0.1}{1+0.4(0.1)t} \qquad (4)$$

The average of these two concentrations is to be 0.1.

$$\bar{C} = 0.5(C_1 + C_2) = 0.1 \qquad (5)$$

The solution is

$t = 9.13,\ C_1 = 0.1268,\ C_2 = 0.0732,\ \bar{C} = 0.100$

P4.04.10. ALLOWABLE FEED RATE TO MULTIPLE STAGES.

Several reactors, each of 25 cuft capacity, are available for conducting the reaction, A + B ⇒ Products. These data apply:

C_{a0} = 1.5 lbmols/cuft
C_{b0} = 2.25 lbmols/cuft
k = 0.098 cuft/lbmol-min

Required conversion of A is 80%. Find the charge rates for one reactor, three reactors and five reactors in series.

The rate equation is

$$r_a = -\frac{dA}{dt} = 0.08A(0.75+A)$$

For the n-th stage,

$$A_{n-1} = A_n + \frac{V_r}{V'} r_{an} = A_n + \frac{2}{V'} A_n(0.75+A_n)$$

For one stage with $A_1 = 0.2A_0 = 0.3$

$$1.5 = 0.3 + \frac{2}{V'}(0.3)(0.75+0.3)$$

$V' = 0.525$ cfm

For three stages with $A_3 = 0.3$,

$1.5 = A_1 + 2A_1(0.75+A_1)/V'$
$A_1 = A_2 + 2A_2(0.75+A_2)/V'$
$A_2 = 0.3 + 2(0.3)(0.75+0.3)/V'$
$A_1 = 0.803,\ A_2 = 0.476,\ V' = 3.58$

Similarly for five stages with $A_5 = 0.3$,

$A_1 = 1.00,\ A_2 = 0.705,\ A_3 = 0.518,\ A_4 = 0.390,\ V' = 6.99$

P4.04.11. SECOND ORDER REACTION IN FOUR STAGES

A reaction with rate equation $r = kC^2$ is carried out in a four stage reactor with $kC_0\tau = 1.2$. Find the fractional conversion.

For the n-th stage,

$C_{n-1} = C_n + k\tau C_n^2$
$f_{n-1} = f_n + kC_0\tau f_n^2 = f_n + 1.2f_n^2$
$f_n = C_n/C_0 = 1 - x$

The solution of the quadratic equation is

$$f_n = \frac{-1+\sqrt{1+4.8f_{n-1}}}{2.4}$$

Solve for the four stages in succession

$f_0 = 1$

$f_1 = 0.4167(-1+\sqrt{1+4.8}) = 0.5868$

$f_2 = 0.4167[-1+\sqrt{1+4.8(0.5868)}] = 0.3974$

$f_3 = 0.4167[-1+\sqrt{1+4.8(0.3974)}] = 0.2938$

$f_4 = 0.4167[-1+\sqrt{1+4.8(0.2938)}] = 0.2302$

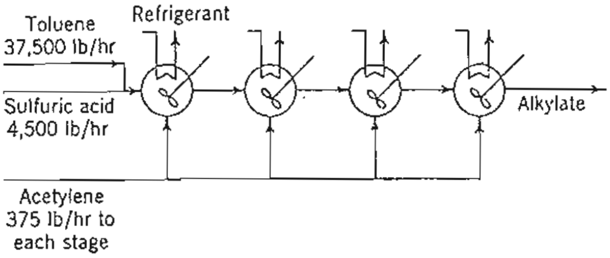
P4.04.12. TOLUENE ALKYLATION

Alkylation of toluene and acetylene in the presence of sulfuric acid is accomplished in the four stage reactor of the sketch. Retention time in each stage is 10 min, the temperature is 41 F and the pressure is 50 psig. On the assumption that the liquid is always saturated with acetylene, the reaction is first order with respect to toluene. Under the conditions shown, the reaction is estimated 95% complete. Find the specific rate.

For four stages,

$C_4/C_0 = 0.05 = 1/(1+k\tau)^4 = 1/(1+10k)^4$

$k = 0.1115$ /min



P4.04.13. STAGES AT DIFFERENT TEMPERATURES

Acetic anhydride is hydrolyzed in a four stage CSTR battery. Each stage is at a different temperature and specific rate, as tabulated.

°C	10	15	25	40
k, 1/min	0.0567	0.0806	0.1580	0.380

The inlet concentration is 1.5 lbmols/gal, the feed rate is 25 gpm, all vessels are the same size and the desired conversion is 95%. (a) Find the vessel size; (b) If all reactors are maintained at 15 C, how many vessels of the size found in part (a) will be needed?

Part (a):

$C_0/C_4 = 20 = (1+k_1\tau)(1+k_2\tau)(1+k_3\tau)(1+k_4\tau)$. Substitute the k-values and find $\tau = V_r/V' = 7.65$, $V_r = 25(7.65) = 191.2$ gal.

Part (b):

With all stages at 15 C,

$$C_0/C_n = 20 = [1+\frac{0.0806(191.2)}{25}]^n$$

$n = 6.24$ stages

P4.04.14. UNEQUAL INPUT AND OUTPUT VOLUMETRIC FLOW RATES

A vessel has a holdup of V_r gal of solution of concentration C_0. Another solution of concentration C_f flows into this vessel at rate R_1 and solution overflows at the rate R_2. The solute is well stirred. The solute undergoes a chemical reaction with rate $r = kC^q$.

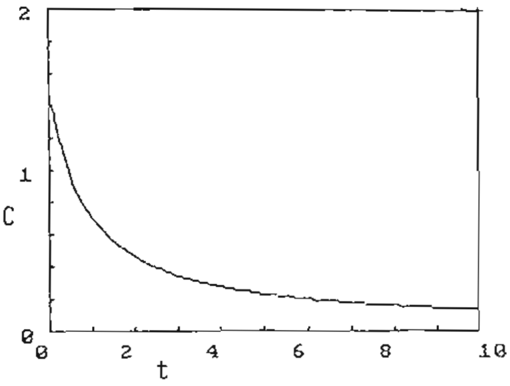
(a) Write the differential equation of the process.

(b) Integrate the equation for a second order reaction with these data:

$k = 0.75$ $\quad C_f = 0.5$

$V_{r0} = 200$ gal $\quad R_1 = 1.8$ gpm

$C_0 = 1.5$ lb/gal $\quad R_2 = 2.0$ gpm



Part (a):

$V_r = V_{r0} + (R_1-R_2)t$

$dV_r/dt = R_1-R_2$

Input $= C_fR_1dt$

Output $= CR_2dt$

Sink $= kV_rC^q$

$$\text{Accumulation} = \frac{d(V_rC)}{dt} = V_r\frac{dC}{dt} + C(R_1-R_2)$$

Putting it together and rearranging,

$$\frac{dC}{dt} + \frac{R_1}{V_{r0}+(R_1-R_2)t}(C - C_f) + kC^q = 0 \qquad (1)$$

Part (b):

With numbers, Eq (1) becomes

$$\frac{dC}{dt} = -\frac{1.8(0.5-C)}{200+0.2t} - 0.75C^2$$

Integration of this nonlinear equation is accomplished by ODE. Reading off the graph,

$t = 4.5$ when $C = 0.25\ C_0$

If the reaction were first order, the variables in Eq (1) would be separable.

P4.04.15. SINGLE AND MULTIPLE STAGES.

The reaction, $2A \Leftrightarrow C+D$, is conducted in a CSTR at a feed rate of 100 cfh with an inlet concentration C_{a0} = 1.5 lbmols/cuft. The specific rate in the forward direction is k = 10 amd the equilibrium constant is K_e = 16. 80% of equilibrium conversion is required. (a) Find the vessel size; (b) If vessels are limited to one-tenth the size found in part (a), how many such vessels are needed in series?

$C_b = C_c = 0.5(1.5-C_a)$

The rate equation is,

$$r_a = -\frac{dC_a}{dt} = k[C_a^2 - 0.25(1.5-C_a)^2/K_e]$$

$$= 10[(C_a^2 - (1.5-C_a)^2/64] \qquad (1)$$

At equilibrium,

$(1.5-C_{ae})^2 = 64C_{ae}^2$

$C_{ae} = 0.1667$

$C_{out} = 1.5-0.8(1.5-0.1667) = 0.4333$

In a single stage,

$1.5 = C + k\tau r_a \qquad (2)$

Substitute Eq (1) into (2) and C = 0.4333. The result is

$\tau = 0.6275,\ V_r = V'\tau = 100(0.6275) = 62.75$ cuft.

In successive stages with $\tau = 0.06275$

$$C_{n-1} = C_n + 0.06275(10)[C_n^2 - (1.5-C_n)^2/64] \qquad (3)$$

Numerical values are

n	C_n
0	1.5
1	0.9439
2	0.6694
3	0.5135
3.83	0.4333
4	0.4163

Interpolate to C_n = 0.4333 at n = 3.83.

P4.04.16. VARIABLE FLOW DENSITY

The specific volume of solutions flowing in a two stage CSTR depends on the concentrations according to

$V' = V'_s(1+0.1C)$

where V'_s is the volumetric flow rate of solvent. The inlet concentration is $C_0 = 1.5$ and the outlet of the second stage is $C_2 = 0.15$. Find the quantity $k(V_r/V'_s) = k\tau_s$. Compare this result with that by neglecting the variation of density.

The material balances are,

$V'_0C_0 = V'_1C_1 + kV_rC_1$

$C_0(1+0.1C_0) = 1.725 = C_1(1+0.1C_1) + k\tau_sC_1$ (1)

$C_1(1+0.1C_1) = C_2(1+0.1C_2) + k\tau_sC_2$

$= 0.15(1.015) + 0.15k\tau_s$ (2)

The solution of (1) and (2) is

$C_1 = 0.4941,\ k\tau_s = 2.4418$ (3

When the effect of C on the density is neglected,

$C_0/C_2 = 10 = (1+k\tau)^2$

$k\tau = 2.162,\ C_1 = 1/(1+2.162) = 0.4744$ (4)

P4.04.17. CHLORINATION OF BENZENE

Benzene (B) and chlorine (C)form the mono (M), di (D) and trichlor (T) derivatives of benzene. The reactions are

$B + C \overset{1}{\Rightarrow} M + HCl$

$M + C \overset{2}{\Rightarrow} D + HCl$

$D + C \overset{3}{\Rightarrow} T + HCl$

The ratio of chlorine to benzene in the feed is called α. The mass balance on the chlorine is

$\alpha B_0 = C + M + 2D + 3T$ (1)

The material balances on the individual component are

$B_0 = B + k_1\tau BC = B(1+k_1\tau C)$ (2)

$0 = M + \tau(-k_1BC+k_2MC)$, or $M(1+k_2\tau C) = k_1\tau BC$ (3)

$0 = D + \tau(-k_2MC+k_3DC)$, or $D(1+k_3\tau C) = k_2\tau MC$ (4)

$0 = T + \tau(-k_3DC)$ (5)

At 55 C, according to Cooper & Jeffreys (1971),

$k_1 = 8k_2$

$k_3 = k_2/30$

The case to be solved for numerically has

$B_0 = 11.2$ gmol/liter

$\alpha = 1.4$ mols chlorine/mol benzene

$k_2\tau = 1$

The numbered equations become,

$1.4(11.2) = C + M + 2D + 3T$

$11.2 - (1+8C)B = 0$

$(1+C)M - 8BC = 0$

$(1+C/30)D - MC = 0$

$T - DC/30 = 0$

The solution of this system of five equations by SEQS is

B = 1.3322

C = 0.9259

D = 4.6021

M = 5.1237

T = 0.1420

P4.04.18. TWO STAGES WITH KNOWN RESIDENCE TIME

The rate of a liquid phase reaction in a slurry of solid catalyst is represented by

$$r = \frac{0.6C}{(1+0.1\sqrt{C})^2}$$

A two stage battery is used, with residence time of 1 hr in each stage and feed concentration of $C_0 = 2$ lbmol/cuft. Find the fractional conversion.

Material balances on the two stages are

$$C_0 = 2 = C_1 + \tau r_1 = C_1[1 + \frac{0.6}{(1+0.1\sqrt{C_1})^2}]$$

$$C_1 = C_2[1 + \frac{0.6}{(1+\sqrt{C_2})^2}]$$

The solution is

$$C_1 = 1.3499,\ C_2 = 0.8995$$

P4.04.19. VARIATION IN VOLUMETRIC FLOW RATE

One gaseous feed stream at the rate of 1 liter/min and with $C_{a0} = 0.01$ mol/liter and a second stream of 3 liters/min with $C_{b0} = 0.02$ mols/liter enter a stirred reactor 1.5 liters in volume. Analysis of the outgoing stream of 6 liters/min shows $C_a = 0.0005$ mols/liter and for one of the products $C_c = 0.001$ mols/liter. All flow rates and concentrations are measured at uniform T and P. Find the rate of reaction of A and the rate of formation of C.

$$V'_0C_{a0} = V'C_a + V_r r_a$$

$$r_a = \frac{1(0.01)-6(0.0005)}{1.5} = 0.0047 \text{ mol/liter-min}$$

$$V'_0C_{c0} = 0 = V'C_c + V_r r_c$$

$$r_c = \frac{-6(0.001)}{1.5} = -0.004 \text{mol/liter-min}$$

P4.04.19. VARIATION IN VOLUMETRIC FLOW RATE

One gaseous feed stream at the rate of 1 liter/min and with $C_{a0} = 0.01$ mol/liter and a second stream of 3 liters/min with $C_{b0} = 0.02$ mols/liter enter a stirred reactor 1.5 liters in volume. Analysis of the outgoing stream of 6 liters/min shows $C_a = 0.0005$ mols/liter and for one of the products $C_c = 0.001$ mols/liter. All flow rates and concentrations are measured at uniform T and P. Find the rate of reaction of A and the rate of formation of C.

$$V'_0C_{a0} = V'C_a + V_r r_a$$

$$r_a = \frac{1(0.01)-6(0.0005)}{1.5} = 0.0047 \text{ mol/liter-min}$$

$$V'_0C_{c0} = 0 = V'C_c + V_r r_c$$

$$r_c = \frac{-6(0.001)}{1.5} = -0.004 \text{mol/liter-min}$$

P4.04.20. RESIDENCE TIMES IN TWO STAGES.

A CSTR battery has two stages of 25 cuft each. The reaction, A + B Products, is performed there, with $C_{a0} = 1.5$, $C_{b0} = 2.25$ lbmol/cuft and k 0.08 cuft/lbmol-min. Find the allowable charge rate for 80% conversion of A.

$$C_{a2} = 0.2C_{a0} = 0.3$$

$$C_{a0} = 1.5 = C_{a1} + k\tau C_{a1}(C_{a1}+ 0.75) \qquad (1)$$

$$C_{a1} = C_{a2} + k\tau C_{a2}(C_{a2}+0.75) = 0.3 + 0.3(1.05)k\tau \qquad (2)$$

Solve simultaneously.

$$C_{a1} = 0.4732$$

$k\tau = 1.4192$
$\tau = 1.4192/0.08 = 17.74$ min
$V' = V_r/\tau = 25/17.74 = 1.409$ cfm

P4.04.21. OPTIMUM TEMPERATURE. REVERSIBLE REACTION. TWO STAGE.

A reaction, $A \Leftrightarrow B$, is conducted in a two stage CSTR. The rate equation is

$$r = k[(1+1/K_e)C_a - C_{a0}/K_e]$$

with these data:

$C_{a0} = 4$ mol/liter
$C_{a2} = 0.2$ (95% conversion)
$k = \exp(17.2-5800/T)$, 1/min (1)
$K_e = \exp(-24.7+9000/T)$ (2)

Find the temperature that will result in the smallest residence time for the required conversion of 95%.

The material balances on the two stages,

$$C_{a0} = 4 = C_{a1} + k\tau[(1+1/K_e)C_{a1}-4/K_e] \quad (3)$$

$$C_{a1} = 0.2 + k\tau[(1+1/K_e)(0.2) - 4/K_e] \quad (4)$$

from which

$$\tau = \frac{4-C_{a1}}{k[(1+1/K_e)C_{a1}-4/K_e]} = \frac{C_{a1}-0.2}{k[(1+1/K_e)(0.2)=4/k_e]} \quad (5)$$

Specify T, find C_{a1} and τ from Eqs (1), (2) and (5). The tabulation shows that the residence time, τ, is a minimum when T = 318.

T	C_{a1}	τ	
310	0.8166	18.59	
315	0.7627	15.66	
316	0.7475	15.32	
317	0.7303	15.09	
318	0.7106	14.97	Minimum
319	0.6877	15.01	
320	0.6612	15.24	
321	0.6296	15.76	
322	0.5913	16.73	

P4.04.22. RESIDENCE TIME IN A THREE STAGE REACTOR

The reaction, $A+B \Rightarrow$ Products, is conducted in a three stage battery of equal sized vessels. Specific rate is k = 25 cuft/lbmol-hr. Inlet concentrations are $C_{a0} = 0.15$, $C_{b0} = 0.2$ lbmol/cuft. Conversion of 90% is required, that is $C_{a3} = 0.015$. Find the residence time in each vessel.

Material balances on A in the three stages are,

$$0.15 = C_{a1} + 25\tau C_{a1}(C_{a1}+0.05)$$

$$C_{a1} = C_{a2} + 25\tau C_{a2}(C_{a2}+0.05)$$

$$C_{a2} = C_{a3} + 25\tau C_{a3}(C_{a3}+0.05) = 0.015 + 25(0.015)0.065)\tau$$

These three equations are solved simultaneously, with the results

$C_{a1} = 0.0596$, $C_{a2} = 0.0285$, $\tau = 0.554$ hr in each stage.

P4.04.23. VARIABLE DENSITY.

A liquid phase reaction, $A \Rightarrow 2B$, is carried out in a CSTR. Input rate is W lb/hr with concentration $C_{a0} = 1.0$. The density of the solution depends on the concentrations,

$$\rho = 0.9 + 0.05C_a + 0.1C_b \quad (1)$$

The function $kV_r/W = 1.0$. Find the outlet concentration, and compare with the performance when the density remains 0.9.

The material balance on A is

$$n_{a0} = \frac{W}{\rho_0} C_{a0} = W/0.95 = \frac{W}{\rho} C_a + kV_rC_a$$

$$1.0526 = (1 + \frac{1}{\rho})C_a \qquad (2)$$

Balance on B is

$$n_b = 2(n_{a0}-n_a)$$
$$WC_b/\rho = 2(WC_{a0}/\rho_0 - WC_a/\rho)$$
$$C_b = 2(\frac{C_{a0}}{\rho_0} - C_a) = 2(1.0526 - C_a) \qquad (3)$$

Solve Eqs (1), (2) and (3) together.

$$C_a = 0.536,\ C_b = 1.1132,\ \rho = 1.0381 \qquad (4)$$

If the density were constant,

$$C_a/C_{a0} = C_a = \frac{1}{1+kV_r/W} = 0.500$$

P4.04.24. PROPIONIC ACID IN BATCH AND CSTR

Propionic acid is to be made from sodium propionate (A) and HCl at the rate of 24,000 lb/day according to the reaction

$$NaPr + HCl \Leftrightarrow C_2H_5COOH + NaCl,\ A + B \Leftrightarrow \text{Products}$$

The rate equation is

$$r = \frac{dx}{dt} = 0.41(0.938x^2 -0.34x +0.0289) \text{ lbmol/cuft-min} \qquad (1)$$

where

$$x = 0.17 - C_a$$

Initially, $C_{a0} = C_{b0} = 0.17$ lbmol/cuft. Required conversion of NaPr is 60%. Reactor sizes are to be found for three modes of operation: (a) A batch reactor with downtime of 30 minutes/batch; (b) A two stage CSTR to which the feed contains 0.17 lbmol/cuft of each reactant; (c) A single stage CSTR.

$$\text{Feed NaPr} = \frac{24000(96)}{0.6(74)} = 52000 \text{ lb/day}$$

$$\Rightarrow \frac{52000}{1440(96)} = 0.375 \text{ lbmol/min}$$

$$\Rightarrow \frac{0.375}{0.17} = 2.20 \text{ cuft/min of feed to the CSTRs}$$

Part (a): At 60% conversion, x = 0.6(0.17) = 0.102

Integrate the rate equation numerically.

$$t = \int_{0.17}^{0.102} \frac{dx}{r} = 22.7 \text{ min}$$

Batch time = 30 + 22.7 = 52.7 min

Number of batches/ day = 1440/52.7 = 27.4

Batch size, $V_r = 2.2(1440)/27.4 = 116$ cuft (a)

Part (b): Material balances for the two stages,

$$x_0 = 0 = x_1 -0.41\tau(0.938x_1^2 -0.34x_1 +0.0289) \qquad (2)$$

$$x_1 = x_2 -0.41\tau(0.938x_2^2-0.34x_2+0.0289)$$
$$= 0.102 - 0.0016\tau \qquad (3)$$

Solving (2) and (3),

$$x_1 = 0.0719,\ \tau = 18.83 \text{ min per stage} \qquad (b)$$

With a single stage substitute $x_1 = 0.102$ in Eq (2). Then,

$\tau = 62.5$ min (c)

P4.04.25. CSTR AND PFR IN SERIES.

The rate of the reaction, 2A ⇔ B, has the equation,

$$r_a = 0.752(C_a^2 - \frac{2.5-C_a}{24.44}) \text{ lbmol/cuft-hr}$$

A feed containing $C_{a0} = 1.5$ and $C_{b0} = 1.75$ lbmol/cuft is charged at the rate of 100 cuft/hr to a CSTR followed by a plug flow reactor with half the residence time of the CSTR. The concentration leaving the system is to be $C_{a2} = 0.4$. Find the composition C_{a1} leaving the CSTR and the sizes of the two reactors. Also, find the concentrations with the same sizes when the PFR is first.

In the CSTR,

$$C_{a0} = 1.5 = C_{a1} + \tau_s r_{a1} = C_{a1} + 0.752\tau_s(C_{a1}^2 - \frac{2.5-C_{a1}}{24.44})$$

$$\tau_s = \frac{32.5(1.5 - C_{a1})}{(24.44C_{a1}^2+C_{a1}-2.5)} \qquad (1)$$

In the plug flow reactor,

$$-\frac{dC_a}{dt} = 0.03077(24.44C_a^2 + C_a - 2.5)$$

$$\tau_p = 32.5\int_{0.4}^{C_{a1}} \frac{dC_a}{24.44C_a^2 + C_a - 2.5}$$

$$= 0.5\tau_s$$

$$= 2.075 \ln \frac{7.4109(C_{a1}-0.3000)}{C_{a1}+0.3409} \qquad (2)$$

Between Eqs (1) and (2),

$C_{a1} = 0.622$, $\tau_s = 3.766$ hr, $\tau_p = 1.883$

With the plug flow unit first with these calculated residence times,

$$\tau_p = 1.883 = 32.5\int_{C_{a1}}^{1.5} \frac{dC_a}{24.44C_a^2 + C_a - 2.5}$$

By trial, $C_{a1} = 0.5283$

In the CSTR,

$$\tau_s = 3.766 = \frac{32.5(0.5283-C_{a2})}{24.44C_{a2}+C_{a2}-2.5}$$

$$C_{a2} = 0.3754$$

P4.04.26. CSTR AND PFR IN SERIES.

A reactor system is a series arrangement of a PFR and a CSTR with 10 times the volume of the PFR. A process with rate equation $r = 2.4C^2$ is to be conducted to 96% conversion from an inlet $C_{a0} = 1$. Find the allowable residence times: (a) with the PFR first; (b) with the CSTR first.

With the PFR first:

$$C_{a1} = \frac{1}{1+kC_{a0}\tau_p} = \frac{1}{1+2.4\tau_p}$$

$$= C_{a2} + k\tau_s C_{a2}^2 = 0.04 + 22.4(10)\tau_p(0.04)^2$$

$\tau_p = 6.19,\ \tau_s = 61.9$

With the CSTR first:

$$C_{a0} = 1 = C_{a1} + 2.4(10)\tau_p C_{a1}^2$$

$$C_{a2} = \frac{C_{a1}}{1+2.4\tau_p C_{a1}} = 0.04$$

Solving these two equations,

$C_{a1} = 0.200,\ \tau_p = 8.333,\ \tau_s = 83.33$

Allowable feed rate is greater when the PFR is first in series, by a factor 8.333/6.19 = 1.206.

P4.04.27. TRANSFER LINE

Tests were made in a laboratory CSTR of conversions at several conditions with the following results. The values of k are calculated from the other data.

T	C_{ao}	C_a	k
40	2.5	1.000	1.350
40	2.0	0.873	1.348
40	1.5	0.727	1.353
60	2.5	0.750	2.872

Concentrations are in gmol/liter. Reactor volume was 0.5 liters and feed rate was 1.0 liters/min. Density is a function of the concentration according to the equation,

$$\rho = \frac{1}{0.9+0.1C_a}\ \text{g/cc}$$

The reaction is second order. In a commercial plant, feed containing 3 gmol.liter of reactant is charged at the rate of 5000 liters/min to a stirred tank with a volume of 10,000 liters and maintained at 50 C. Effluent from the stirred tank at concentration C_{a1} flows to storage through a long pipeline with a volume of 500 liters, where the reaction continues at 50 C until the storage tank is reached.

Find the following: (a) the specific rate at 50 C; (b) the concentration C_{a1} leaving the CSTR; (c) the concentration C_{a2} entering the storage tank; (d) the overall fractional conversion.

Part (a):

$$\text{Exit volumetric rate, } V' = \frac{V'_0\rho_0}{\rho} = \frac{0.9+0.1C_{a0}}{0.9+0.1C_a}(1.0)$$

$$\text{Material balance, } V'_0C_{a0} = V'C_a + kV_rC_a^2$$

Solve for k.

$$k = \frac{1}{C_a^2}\left[C_{a0} - \frac{(0.9+0.1C_{a0})C_a}{0.9+0.1C_a}\right]$$

The values of k are calculated and tabulated. Those at 40 C average k = 1.350. With this value and the value at 60 C,

$k = \exp(12.88-3939/T)$

from which $k_{50} = 2.00$.

Part (b):

$$V' = \frac{V'_0\rho_0}{\rho} = \frac{5000(1+0.3)}{0.9+0.1C_a} = \frac{6500}{0.0+0.1C_a}$$

Material balance,

$$C_{a0} = (V'/V'_0)C_{a1} + \frac{2V_r}{V'_0}C_{a1}^2$$

$$3 = \frac{1.3C_{a1}}{0.9+0.1C_{a1}} + \frac{2(10000)}{5000}C_{a1}^2$$

$$C_{a1} = 0.8485 \qquad (?)$$

Part (c):

In the pipeline,

$$VC_a = \frac{6500C_a}{0.9+0.1C_a}$$

$$d(VC_a) = CdC_a + C_adV = VdC_c + 6500[\frac{0.9}{(0.9+0.1C_a)^2}]dC_a$$

$$= 6500[\frac{1}{0.9+0.1C_a} + \frac{0.9}{(0.9+0.1C_a)^2}] \qquad (1)$$

Differential material balance

$$-dn_a = -d(VC_a) = kC_a^2\,dV_r$$

$$kV_r = 2(500) = \int_{C_{a2}}^{0.8485}\frac{d(VC_a)}{C_a^2} \qquad (2)$$

Substitute Eq (1) into (2), integrate and find the lower limit of integration by trial to equal the left hand side. The final result is

$$C_{a2} = 0.795 \qquad (c)$$

$$\rho_2 = 1/[0.9 + 0.1(0.795)] = 1.0209$$

Part d: Overall fractional conversion,

$$V'_2 = V'_0(\rho_0/\rho_2) = 5000(1.0753/1.0209) = 5266$$

$$x = 1 - \frac{V'_2C_{a2}}{V'_0C_{a0}} = 1 - \frac{5266(0.795)}{5000(3)} = 0.7209$$

P4.04.28. TWO SECOND ORDER REACTIONS

The pair of reactions, $A + B \xrightarrow{1} 2C$ and $A + C \xrightarrow{2} D$, have the rate equations

$$r_a = -\frac{dA}{dt} = 0.3AB + 0.15A(A-3B)$$

$$r_b = -\frac{dB}{dt} = 0.3AB$$

They are conducted in a four stage CSTR battery with $A_0 = 0.9$, $B_0 = 0.3$ and $C_0 = D_0 = 0$. The steady state material balances on the first stage are

$$C_{a0} - C_{a1} = \tau_1 r_{a1} = C_{a1}\tau_1[k_1C_{b1} + k_2(C_{a1}-3C_{b1})]$$

$$C_{b0} - C_{b1} = \tau_1 k_1 C_{a1} C_{b1}$$

The eight equations for the four stages are written in the simplified notation $C_{a1} = a_1$, $C_{b1} = b_1$, and so on. The residence time in each stage is $\tau = 10$. The equations are solved by the program SEQS. The solutions converge readily with an initial estimate of 0.1 for each unknown. The eight equations are

$a_1 + 10[0.3a_1b_1+0.15a_1(a_1-3b_1)] = 0.9$
$b_1 + 10(0.3)a_1b_1 = 0.3$
$a_2 + 10[0.3a_2b_2+0.15a_2(a_2-3b_2)] = a_1$
$b_2 + 3a_2b_2 = b_1$
$a_3 +10[(0.3a_3b_3+0.15a_3(a_3-3b_3)] = a_2$
$b_3 + 3a_3b_3 = b_2$
$a_4 + 10[(0.3a_4b_4+0.15a_4(a_4-3b_4)] = a_3$
$b_4 + 3A_4b_4 = b_3$

The answers are

$a_1 = 0.54599 \qquad b_1 = 0.11372$
$a_2 = 0.37027 \qquad b_2 = 0.00539$
$a_3 = 0.27166 \qquad b_3 = 0.02968$
$a_4 = 0.21077 \qquad b_4 = 0.01819$

P4.04.29. CSTR AND BATCH COMPARISON

A solution containing 0.5 lbmol/cuft of reactive component is to be treated at 25 cuft/hr. The rate equation is

$r = -dC/dt = 2.33C^{1.7}$ lbmol/(cuft-hr

(a) If the downtime is 45 min per batch, what size reactor is needed for 90% conversion?

(b) What percentage conversion is attained with a two stage CSTR, each vessel being 50 cuft?

(c) For 90% conversion, find the total reactor volumes needed with one, two, three or four stages.

Part (a):

The integral of the rate equation is solved for the time,

$$t = \frac{1}{0.7k}(C^{-0.7}-C_0^{-0.7}) = \frac{1}{0.7(2.33)}\left(\frac{1}{0.05^{0.7}} - \frac{1}{0.5^{0.7}}\right)$$

$= 4.00$ hr

Number of batches = 24/(4+0.75) = 5.053/day

Reactor volume, $V_r = 24(25)/5.053 = 118.7$ cuft

Part (b):

$\tau = 50/25 = 2$

$0.5 = C_1 + \tau r = C_1 + 2(2.33)C_1^{1.7}$

$C_1 = C_2 + 2(2.33)C_2^{1.7}$

The solution is,

$C_1 = 0.1994$, % conversion = 60.1
$C_2 = 0.1025$, % conversion = 79.5

Part (c):

The equations for four stages are,

$0.5 = C_1 + 2.33\tau C_1^{1.7}$

$C_1 = C_2 + 2.33\tau C_2^{1.7}$

$C_2 = C_3 + 2.33\tau C_3^{1.7}$

$C_3 = C_4 + 2.33\tau C_4^{1.7} = 0.05 + 2.33\tau(0.05)^{1.7}$

The solution is

$\tau = 1.624,\ C_1 = 0.2174,\ C_2 = 0.1177,\ C_3 = 0.0732,\ C_4 = 0.05$

And the total reactor volume is

$V_{rtotal} = nV'\tau = 4(25)1.624 = 162.4$ cuft

Part (c):

n	τ	V_{rtotal}
1	31.44	786
2	5.74	287
3	2.67	200
4	1.624	162
Batch	4.75	119

P4.04.30. CSTR AND TRANSFER LINE.

A mixture is fed at the rate of 100 cfh to a two stage CSTR. The effluent from the second stage continues to react in the line going to storage. This line is 0.864 sq in cross section and is 1000 ft long. The reaction is , $2A \Leftrightarrow C + D$, the inlet concentration is A_0 = 1.5 lbmols/cuft and the rate equation is

$$r_a = 10(A^2 - BC/16) \text{ lbmol/cuft-hr}$$

It is required to have 80% approach to equilibrium at the storage tank. What is the volume of each stage?

$$B = C = 0.5(1.5-A)$$

$$r = 10[A^2-(1.5-A)^2/64]$$

The equilibrium value is given by

$$A_e^2 = (1.5-A_e)^2/64$$

$$A_e = 0.167$$

$$A_{storage} = 0.2(1.5) + 0.8(0.167) = 0.433$$

Tubular reactor:

$$V_r = 0.864(1000)/144 = 6 \text{ cuft}$$

$$-V'dA = r\,dV_r$$

$$\tau_p = V_r/V' = 6/100 = 0.06$$

$$= \int_{0.433}^{A_2} \frac{dA}{10[A^2-(1.5-A)^2/64]}$$

By trial, the upper limit of the integral is

$$A_2 = 0.5715$$

The CSTR equations are

$$A_0 = 1.5 = A_1 + 10\tau[A_1^2 - (1.5-A_1)^2/64] \qquad (1)$$

$$A_1 = A_2 + 10\tau(A_2^2 -(1.5-A_2)^2/64]$$
$$= 0.5175 + 3.1314\tau \qquad (2)$$

The solution of Eqs (1) and (2) is

$$A_1 = 0.8528,\ \tau = 0.0898 \text{ hr in each stage}$$

$$V_r = \tau V' = 0.0898(100) = 8.98 \text{ cuft in each stage.}$$

P4.04.31. LEAD BATH REACTOR

Pyrolysis of propane was accomplished by bubbling the gas through a shallow bed of molten lead at 1400 F and 4 psig (Fair et al, Chem Eng Prog 53 433, 1953). The vessel was assumed to have no gradients of temperature or concentration. The rate equation was,

$$r = \frac{0.15\pi(1-x)}{1+0.95x}\ \frac{\text{lbmol propane converted}}{\text{(hr)(cuft lead)(psia)}} \qquad (1)$$

where π is the pressure and x is the fractional conversion.

Consider a reactor with a cross section of 4 sqin filled to a depth of 3ft in which there is no axial mixing. Density of lead is 685 lb/cuft, temperature is 1400 F and pressure above the lead surface is 2 psig. Charge rate of pure propane is equivalent to a suuperficial velocity at the surface of 2 ft/sec at temperature. Find the conversion, taking into account the variation in static head.

$$V_r = 4(3)/144 = 0.0833 \text{ cuft}$$

Pressure along the reactor,

$$\pi = 16.7 + \frac{685(0.0833-V_r)}{4} = 30.95 - 171.3V_r \qquad (2)$$

With 2 fps superficial velocity at the top,

$$W = \frac{2(4)(3600)(520)(16.7)}{144(379)(1860)(14.7)} = 0.1673 \text{ lbmol propane/hr}$$

PFR equation,

$$Wdx = rdV_r \qquad (3)$$

Substitute Eqs (1) and (2) into (3) and integrate

$$\frac{0.15}{W}\int_0^{0.0833} \pi dV_r = \frac{0.15}{0.1673}\int_0^{0.0833} (30.95-171.3V_r)dV_r$$

$$= 1.81$$

$$= \int_0^x \frac{1+0.95x}{1-x}dx = 0.95x + \ln\frac{1}{1-x}$$

$$x = 0.4966 \qquad (4)$$

Line (4) is the fractional conversion of propane.

P4.04.32. MICHAELIS-MENTEN RATE EQUATION

For a reaction with rate equation,

$$r = \frac{k_1C}{1+k_2C}$$

conducted in a CSTR, find the effluent concentration as a function of residence time.

The material balance is

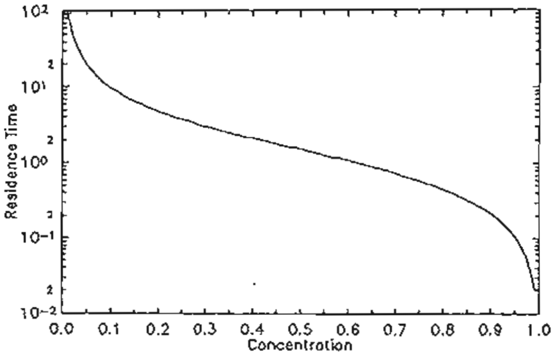
$$C_0 = C + \frac{\tau k_1 C}{1+k_2C}$$

Clearing of fractions,

$$k_2C^2 + (1+k_1\tau-k_2C_0)C = C_0$$

which is readily solvable for C.

The graph is for $C_0 = k_1 = k_2 = 1$, for which $\tau = 1/C - C$



P4.04.33. BYPASSING A STAGE.

An irreversible first order reaction reaches steady state in a three stage CSTR. Then the second stage is bypassed. Find the unsteady performance of the third stage.

The initial steady conditions are

$$C_1 = C_0/(1+k\tau),\ C_2 = C_0/(1+k\tau)^2,\ C_3 = C_0/(1+k\tau)^3$$

The performance of the first stage is not changed by the bypassing. The unsteady balance of the third stage is

Input = Output + Sink + Accumulation

$$C_1 = \frac{C_0}{1+k\tau} = C_3 + k\tau C_3 + \tau\frac{dC_3}{dt}$$

$$\frac{dC_3}{dt} = \frac{C_0}{\tau(1+k\tau)} - \frac{1+k\tau}{\tau} C_3$$

Integrate with the initial condition,

$$C_{3,o} = C_0/(1+k\tau)^3$$

The variables are separable so integration is straightforward.

P4.04.34. MULTIPLE REACTOR ARRANGEMENTS

A dilute aqueous solution of maleic anhydride is to be continuously hydrolyzed at 25 C. Because of the dilution the reaction is pseudo first order with k = 0.143 gmol/cc-min. A volumetric rate of 530 cc/min is to be processed with inlet concentration of 0.00015 gmol/cc. There are two 2.5 liter and one 5.0 liter stirred vessels available. Find the conversions for various arrangements of these vessels.

Material balance on a single stage,

$$C_n = \frac{C_{n-1}}{1+k\tau} = \frac{C_{n-1}}{1+0.1439V_r/0.53} = \frac{C_{n-1}}{1+0.27V_r}.$$

Part (a), 5 liter vessel.

$$C/C_0 = 1/[1+0.27(5)] = 0.881$$

Part (b), two 2.5 liter vessels

$$C/C_0 = 1/[1+0.27(2.5)]^2 = 0.356$$

Part (c), plug flow vessel of 5 liters

$$-V'dC = kCdV_r$$

$$C/C_0 = \exp(-k\tau) = \exp[-0.143(5000)/(530)] = 0.259$$

Part (d), 2.5 liter PFR in series with 2.5 liter CSTR

Out of the PFR, $C_p/C_0 = \exp[-0.143(2500)/(530)] = 0.5094$

Out of the CSTR, $C/C_0 = 0.5094/[1+0.143(2500)/530)] = 0.3040$

P4.04.35. RECYCLE IN A CSTR BATTERY

A first order irreversible reaction is carried out in three CSTRs of equal volumes. The feed rate is V'. A quantity $\alpha V'$ of the effluent from the last stage is recycled to the first stage. Find an expression for C_3/C_0 under recycle conditions.

The material balances on the three stages are,

$$V'C_0 + \alpha V'C_3 = (1+\alpha)V'C_1 + kV_rC_1$$

$$C_1 = \frac{C_0+\alpha C_3}{1+\alpha+k\tau}$$

$$C_2 = \frac{(1+\alpha)C_1}{1+\alpha+k\tau} = \frac{(1+\alpha)(C_0+\alpha C_3)}{(1+\alpha+k\tau)^2}$$

$$C_3 = \frac{(1+\alpha)C_2}{1+\alpha+k\tau} = \frac{(1+\alpha)^2(C_0+\alpha C_3)}{(1+\alpha+k\tau)^3} = \beta(C_0+\alpha C_3) = \frac{\beta C_0}{1-\alpha\beta}$$

$$\beta = \frac{(1+\alpha)^2}{(1+\alpha+k\tau)^3}$$

This reduces to the correct form when there is no recycle, $\alpha = 0$.

P4.04.36. CORROSION OF A CSTR

A stirred tank is used to accomplish a reaction that is catalyzed by hydrogen ions. Residence time is 0.2 hrs. Under normal conditions the inlet acid concentration is 0.002 N. The tank corrodes slowly in the acid environment. In contact with 0.001 N acid, laboratory results show that the corrsoion rate is 0.005 inches/yr or 0.006 gram equivalents of iron/hr. In the plant, the amount of exposed surface does not change appreciably as corrosion goes on.

Because of

operator negligence, inlet acid concentration changes suddenly to C_f =,0.01 N and stays at this value.

(a) What is the corrsosion rate at the original steady state?

(b) What is the corrosion rate at the steady condition following the upset?

(c) What is the acid concentration 0.1 hrs after upset?

(d) How long does it take to get within 5% of the new steady condition?

Part (a): The rate of reaction of the acid is first order. Using the laboratory data,

$$0.006 = 0.001k$$

$$k = 6\ /\text{hr}$$

The steady state concentration is

$$C_1 = C_0/(1+k\tau) = 0.002/[1+6(0.2)] = 0.00091$$

$$r_1 = kC_1 = 6(0.0091) = 0.00546\text{gm equivalents/liter-hr} \quad \text{(a)}$$

Part (b):

$$C_2 = C_0/(1+k\tau) = 0.01/2.2 = 0.00455$$

$$r_2 = kC_2 = 6(0.00455) = 0.0273 \quad \text{(b)}$$

Part (c):

Unsteady state balance,

$$C_{f2} = 0.01 = C + \tau(kC + \frac{dC}{dt})$$

$$\frac{dC}{dt} + (k+\frac{1}{\tau})C = \frac{C_{f2}}{\tau} = 0.01/0.2 = 0.05$$

with $C = C_1 = 0.00091$ when $t = 0$. The integral is

$$t = \int_{0.00091}^{C} \frac{dC}{0.05-11C} = \frac{1}{11} \ln \frac{0.05-0.0101}{0.05-11C}$$

When $t = 0.1$, $C = 0.00333$ (c)

Part (d):

At 95% of steady state concentration,

$$t = \frac{1}{11} \ln \frac{0.0399}{0.05-11(0.95)(0.00455)} = 0.252 \text{ hrs} \quad \text{(d)}$$

P4.04.37. INCOMPLETE MIXING

A reactor system consists of 2 CSTRs and a plug flow unit as shown on the sketch. In the CSTRs the change in concentration is 95% of the change in ideal units with the same residence times. The rate equation is $r = 0.4\ C^2$ lbmol/cuft-min. Other conditions are shown on the sketch. Find the concentrations at the outlets of the three reactors.

Let C_1^* and C_3^* be the concentrations leaving corresponding ideal CSTRs

$$C_0 = 0.5 = C_1^* + k\tau_1 C_1^{*2}$$

With $k\tau_1 = 0.8$,

$$C_1^* = 0.3828$$

$$C_1 = 0.5-0.95(0.5-0.3828) = 0.3886$$

In the plug flow unit,

$$-V' dC = r dV_r = kC^2 dV_r$$

$$V_r/V' = 0.4 = \int_{C_2}^{0.3886} \frac{dC}{0.4C^2} = \frac{1}{0.4}\left(\frac{1}{C_2} - \frac{1}{0.3886}\right)$$

$C_2 = 0.3658$

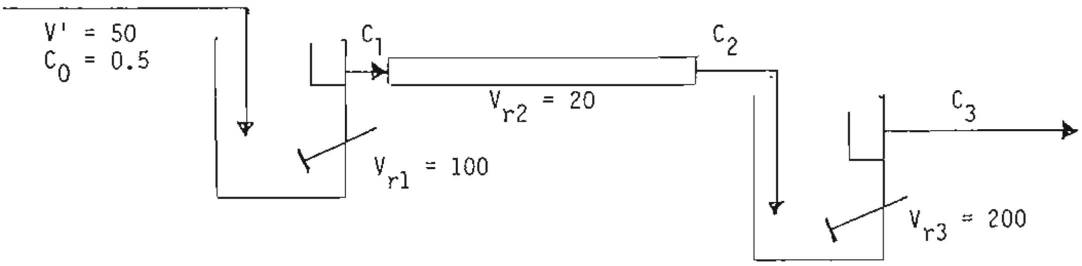
In the last reactor,

$\tau_3 = 200/50 = 4$

$C_2 = 0.3658 = C_3^* + 4C_3^{*2}$

$C_3^* = 0.2587$

$C_3 = 0.05(0.3658)+0.95(0.2587) = 0.2641$



P4.04.38. ISOTHERMAL AND ADIABATIC SEQUENCE

The simultaneous reactions

$2A \overset{1}{\Rightarrow} B$, $\Delta H_{r1} = -3000$ Btu/lbmol A

$2B \overset{2}{\Rightarrow} C$, $\Delta H_{r2} = -4000$ Btu/lbmol B

are conducted in a two stage battery of equal sizes. The first is operated at 130 F, the second adiabatically after the feed has been cooled to 110 F. Inlet condition is $C_{a0} = 0.1$ lbmol/cuft and the other concentrations are zero. Required conversion of A is 90%. Heat capacity is 15 Btu/cuft-F. Specific rates are

$k_1 = \exp(7.16-4416/T)$ (1)

$k_2 = \exp(4.86-4416/T)$, °R (2)

Find $\tau = V_r/V'$ for each stage, and the outlet temperature and composition out of the second stage.

First stage conditions,

$r_a = k_1C_{a1}^2 = 1.2C_{a1}^2$

$r_b = k_2C_{b1}^2 - 0.5k_1C_{a1}^2 = 1.12C_{b1} - 0.6C_{a1}^2$

$0.1 = C_{a1} + 1.2\tau C_{a1}^2$ (3)

$0 = C_{b1} + \tau(0.12C_{b1}^2 - 0.6C_{a1}^2)$ (4)

Second stage heat balance,

$C_{a2} = 0.1C_{a0} = 0.01$

$3000(C_{a1} - 0.01) + 4000(C_{b1} - C_{b2}) = 15(T_2 - 570)$ (5)

Material balances

$C_{a1} = C_{a2} + k_1\tau C_{a2}^2 = 0.01 + (0.01)^2k_1\tau$ (6)

$C_{b1} = C_{b2} + \tau[k_2C_{b2}^2 - 0.5(0.01)^2k_1]$ (7)

Solve Eqs (1) - (7) for the seven unknowns. SEQS was used. The concentration of C is found by stoichiometric balance,

$C_{c2} = 0.25(C_{a0}-C_{a2}) - 0.5C_{b2}$

$= 0.25(0.1-0.01) - 0.5(0.0249) = 0.01005$

$C_{a1} = 0.0198$ $\tau = 170.7$
$C_{b1} = 0.0261$ $T_2 = 572.3$
$C_{b2} = 0.0249$ $k_1 = 0.573$
$C_{c2} = 0.01005$ $k_2 = 0.0574$

P4.04.39. ADIABATIC REACTION

A reaction proceeds adiabatically in a CSTR of 50 liters. The rate equation is

$$r_a = C_a^{1.5}\exp(14 - 5000/T)\ \text{gmol/liter-hr}$$

Flow rate is 25 liters/hr or 100 gmol/hr of which 30% is reactant A. Inlet temperature is 350 K, heat capacity is 16 cal/gmol-K and enthalpy change of reaction is -2000 cal/gmol of A reacted. Find the outlet conditions.

Enthalpy balance,

$$(n_{a0}-n_a)(-\Delta H_r) = n_t C_p (T-T_0)$$

$$T = 350 + \frac{2000(30-n_a)}{100(16)} = 387.5-1.25n_a \qquad (1)$$

$$r_a = \exp(14 - 5000/T)\left(\frac{n_a}{25}\right)^{1.5}$$

$$= \exp\left(14 - \frac{5000}{387.5-1.25n_a}\right)\left(\frac{n_a}{25}\right)^{1.5} \qquad (2)$$

Material balance,

$$n_{a0} = n_a + V_r r_a$$

$$30 = n_a + 50\left(\frac{n_a}{25}\right)^{1.5}\exp\left(14 - \frac{5000}{387.5-1.25n_a}\right) \qquad (3)$$

The solution is

$n_a = 8.733$, $T = 376.6$, $k = 2.0601$

P4.04.40 CSTR AND BATCH COMPARISON

A process has the rate equation

$$r_a = -dC_a/dt = 0.008[C_a^2 - 1.5(2-C_a)^2]\ \text{kgmol/m}^3\text{-min}$$

with $C_{a0} = 2$ kgmol/m^3.

(a) In a CSTR, what residence time is needed to obtain 90% of equilibrium conversion?

(b) In a CSTR what % conversion is obtained when $\tau = 400$ min?

(c) For the conditions of part (a), how much of A is converted per day in a CSTR of 5 m^3?

(d) What is the reactin time for 90% of equilibrium conversion in a batch reactor?

(e) What volume of batch reactor is needed to convert 22.9 kgmols/day at 90% of equilibrium conversion, with a downtime of 2 hrs/batch?

Part (a):

At equilibrium, $C_{ae} = \sqrt{1.5}\,(2-C_{ae}) = 1.1010$

$C_a = 0.1C_{a0} + 0.9C_{ae} = 0.2+0.9(1.101) = 1.1909$

$$\tau = \frac{2-C_a}{r_a} = \frac{2-C_a}{0.008(-0.5C_a^2+6C_a-6)} = 231.8\ \text{min}$$

Part (b):

$2 = C_a + 0.008(400)(-0.5C_a^2+6C_a-6)$

$C_a = 1.1552$

$\Delta C_a = 2-1.1552 = 0.8448$

$\Delta C_a/\Delta C_{ae} = 0.8448/0.8990 = 0.9397$

Part (c):

$V' = V_r/\tau = 5/231.8 = 0.0216\ \mathrm{m^3/min},\ 1.2941\ \mathrm{m^3/hr}$

$$\text{Conversion} = \frac{24}{V'(2-C_a)} = \frac{24}{1.2941(2-1.1909)} = 22.92\ \text{kgmol/day}$$

Part (d):

$$\tau = \int_2^{1.1909} \frac{dC_a}{0.008(-0.5C_a^2+6C_a-6)} = 60.97\ \text{min}$$

Part (e):

With a downtime of two hours/batch, nearly 8 batches/day can be treated.

Conversion = 22.92/8 = 2.865 kgmol/batch

$$\text{Charge} = 2.865C_{a0}/\Delta C_a = \frac{2.865(2)}{0.8091} = 7.082\ \text{kgmol of A},\ 3.541\ \mathrm{m^3}\ \text{of solution.}$$

P4.04.41. CSTR WITH HEATED RECYCLE

A liquid phase reaction, 2A ⇒ 2B, is conducted in a CSTR with 20% recycle through a heater as shown. Fresh input is at 300 K and consists of 500 kg/hr of water and 20 kgmol/hr of substance A. The recycle is at 350 K. Heat capacity of the solute is 40 kcal/gmol-K, the reaction is endothermic with $\Delta H_r = +2000$ cal/gmol of A converted, reactor volume is 25,000 liters and the specific rate is

$$k = \exp(24.1-6500/T). \qquad (1)$$

Find the net fractional conversion and the reaction temperature. Compare with the performance without the heated recycle.

Heat balance: n_{a1} is the amount of A and T_1 is the temperature leaving the reactor.

$$[100(1)+4(40)](350-300) = [600(1)+24(40)](T_1-300) + 2000[20-(5/6)n_{a1}]$$

$$T_1 = 300 + \frac{13000 - 2000(20-0.833n_{a1})}{1560} \qquad (2)$$

Material balance:

$$20 + 0.167n_{a1} = n_{a1} + V_r r_a = n_{a1} + kV_r(n_{a1}/V')^2$$

$$= n_{a1} + \frac{25000}{(720)^2} n_{a1}^2 \exp(24.1-6500/T_1) \qquad (3)$$

The solution of equations (2) and (3) is

$n_{a1} = 7.216$

$x = 1-0.833n_{a1}/20 = 0.6993$

$T_1 = 290.40$

$k = 5.5693$

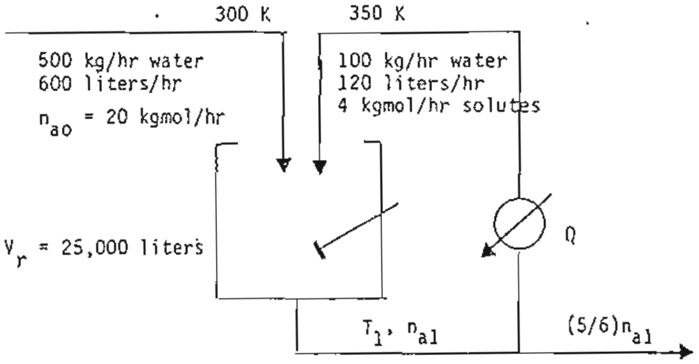
Without recycle,

$$-2000(20-n_{a1}) = [500(1) + 20(40)](T_1-300)$$

$$T_1 = 300-\frac{2000(20-n_{a1})}{1300} \qquad (4)$$

$$20 = n_{a1} + \frac{25000}{(600)^2} n_{a1}^2 \exp(24.1-6500/T_1)$$

$n_{a1} = 7.958$, $x = 0.6021$, $T_1 = 281.47$, $k = 2.738$



P4.04.42. ADIABATIC AND ISOTHERMAL STAGES

A two stage CSTR is used for a first order reaction. The first stage is adiabatic whereas the second is kept at the exit temperature of the first. These data are available.

$k = \exp[-2.5 -450/(T+460)]$, 1/min (1)
$\Delta H_r = -20{,}000$ Btu/lbmol
$V' = 50$ cuft/hr
$\rho = 50$ lb/cuft
$C_p = 0.75$ Btu/lb-F
$T_0 = 150$ F
$C_{a0} = 0.25$ lbmol/cuft
$C_{a2} = 0.05$ lbmol/cuft (80% conversion)

For 80% conversion in the system find: (a) the reaction temperature; (b) the size of each reactor (to be equal); (c) the heat removal in the second stage.

Heat balance on the first stage:

$$V'\rho C_p(T_1-T_0) = -\Delta H_r V_r k C_{a1}$$

$$T_1 = T_0 - \frac{\Delta H_r k\tau C_{a1}}{\rho C_p} \quad (2)$$

Material balances,

$$C_{a2} = \frac{C_{a0}}{(1+k\tau)^2}$$

$$k\tau = \sqrt{C_{a0}/C_{a2} -1} = \sqrt{5-1} = 2$$

$$C_{a1} = C_{a0}/(1+k\tau) = 0.25/3 = 0.0833$$

Substitute into Eq (2),

$$T_1 = 150 + \frac{20000(2)(0.0833)}{50(0.75)} = 238.9 \text{ F}$$

$k = \exp(-2.5-450/698.9) = 0.0431$, 1/min
$\tau = 2/0.0431 = 46.4$ min, 0.773 hr
$V_r = \tau V' = 0.773(50) = 38.7$ cuft

Heat removal in the second stage,

$$Q = -\Delta H_r k V_r C_{a2} = 20000(0.0431)(38.7)(0.05) = 1667 \text{ Btu/min}$$

P4.04.43. THREE STAGES AT DIFFERENT TEMPERATURES

A three stage battery is operated with $V'_0 = 100$ liters/hr of fresh feed and $V'_c = 50$ liters/hr of recycle from the second stage to the first stage. The fresh feed contains Cao = 2 gmol/liter of reactant. The rate equation is $r_a = kC_a^2$. The specific rates in the successive stages are 3.5, 6.0 and 10.5 liters/gmol-hr. Required conversion is 90%. Find the reactor sizes.

$$C_{a3} = 0.1C_{a0} = 0.2$$

$$V'_0C_{a0} + V'_cC_{a2} = (V'_0+V'_c)C_{a1} + k_1V_rC_{a1}^2$$

$$100(2) + 50C_{a2} = 150C_{a1} + 3.5V_rC_{a1}^2 \qquad (1)$$

$$150C_{a1} = 150C_{a2} + 6V_rC_{a2}^2 \qquad (2)$$

$$100C_{a2} = 100C_{a3} + k_3V_rC_{a3}^2$$

$$= 100(0.2) + 10.5V_r(0.2)^2 \qquad (3)$$

The solution of the numbered equations is,

$$C_{a1} = 0.7677,\ C_{a2} = 0.4150,\ C_{a3} = 0.2,\ V_r = 51.19 \text{ liters}$$

P4.04.44. SPLIT FLOW

A CSTR with two stages in series is operated adiabatically with one half of the fresh feed to each stage. The rate equation is

$$r_a = C_a^2 \exp(10-4000/T)\ ,\ \text{gmol/liter-hr}$$

Given the conditions on the sketch and the following data, find the temperature and composition out of each stage.

$\rho C_p = 900$/liter-°K

$\Delta H_r = 9000$ cal/gmol

$C_{a0} = 5$ gmol/liter

$T_0 = 400$ K

$V'_0 = 1000$ liters/hr

$V'_1 = 500$ liters/hr

$V_{r1} = V_{r2} = 250$ liters

Heat and material balances:

$$T_1 = T_0 - \frac{\Delta H_r(C_{a0}-C_{a1})}{\rho C_p} = 400 - \frac{9000(5-C_{a1})}{900} \qquad (1)$$

$$C_{a0} = C_{a1} + k_1\tau_1C_{a1}^2$$

$$5 = C_{a1} + 0.5C_{a1}^2\exp(10-4000/T_1) \qquad (2)$$

The solution of (1) and (2) is

$$C_{a1} = 2.7803,\ T_1 = 378.03$$

The properties of the mixed stream to the second stage are

$$C_{a1}^* = 0.5(5+2.803) = 3.9015$$

$$T_1^* = 0.5(400+378.03) = 389.02$$

Then,

$$T_2 = T_1^* - \frac{\Delta H_r(C_{a1}^*-C_{a2})}{\rho C_p} = 389.02 - 10(3.9015-C_{a2}) \qquad (3)$$

$$3.9015 = C_{a2} + 0.25C_{a2}^2\exp(10-4000/T_2) \qquad (4)$$

whence,

$$C_{a2} = 2.803,\ T_2 = 378.03$$

Without the flow split,

$$\tau_1 = \tau_2 = 0.25$$

$$T_1 = 400 - 10(5-C_{a1}) \qquad (5)$$

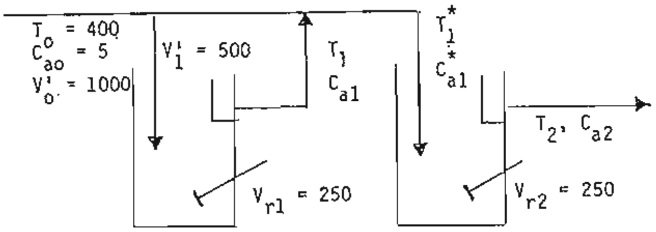
$$T_2 = T_1 - 10(C_{a1}-C_{a2}) \qquad (6)$$

$$5 = C_{a1} + C_{a1} + 0.25C_{a1}^2 \exp(10-4000/T_1) \tag{7}$$

$$C_{a1} = C_{a2} + 0.25C_{a2}^2 \exp(10-4000/T_2) \tag{8}$$

The solution of (5) to (8) is

$$C_{a1} = 3.2815,\ C_{a2} = 2.4888,\ T_1 = 382.82,\ T_2 = 374.89$$



P4.04.45. BATCH AND CSTR

A pair of reactions, $2A \overset{1}{\Rightarrow} B$ and $2B + C \overset{2}{\Rightarrow} D$, have the specific rates k_1 = 0.4 cuft/lbmol-hr and $k_2 = 0.2$. The starting concentration is $C_{a0} = 2$ lbmol/cuft and $C_{c0} = 1$. (a) For a batch process, find the concentrations of all participants as functions of time; (b) For a two stage CSTR with two hours in each stage, find the effluent concentrations.

Part (a): The stoichiometric balances are

$$C = 0.5(1+0.5A+B) \tag{1}$$

$$D = 1-C$$

The rate equations are

$$\frac{dA}{dt} = -k_1A^2 = -0.4A^2 \tag{2}$$

$$\frac{dB}{dt} = 0.5k_1A^2 - k_2B^2C = 0.2[A^2 - 0.5B^2(1+0.5A+B)] \tag{3}$$

The numerical solutions of Eqs (1), (2) and (3) are plotted.

Part (b): Reactor 1,

$$A_0 = 2 = A_1 + \tau r_{a1} = A_1 + 2(0.4)A_1^2 \tag{4}$$

$$B_0 = 0 = B_1 + \tau r_{b1}$$

$$= B_1 + 2(0.2)[A_1^2 - 0.5B_1^2(1+0.5A_1+B_1)] \tag{5}$$

From (4) and (5),

$$A_1 = 1.0752,\ B_1 = 0.4003$$

Reactor 2:

$$A_1 = 1.0752 = A_2 + 2(0.4)A_2^2$$

$$B_1 = B_2 + \tau k_2[A_2^2 - 0.5B_2^2(1+0.5A_2+B_2)]$$

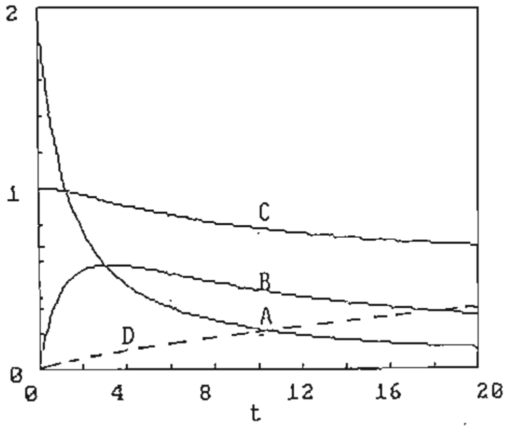
$$= B_2 + 2(0.2)[A_2^2 - 0.5(1+0.5A_2+B_2)]$$

from which

$$A_2 = 0.6920,\ B_2 = 0.4997$$

$$C_2 = 0.5(1+0.5A_2+B_2) = 0.9229$$

$$D_2 = 1-C_2 = 0.0771$$



P4.04.46. CSTR AND BATCH PERFORMANCES

For the simultaneous reactions, $2A \overset{1}{\Rightarrow} B$ and $2B + 2C \overset{2}{\Rightarrow} D$, the rate equations are

$r_a = 1.2A^2$ lbmol/cuft-hr (1)

$r_b = -0.6(A^2-0.5B^2C^2)$ (2)

$r_c = -0.3B^2C^2$ (3)

The starting concentrations are A_0 2.0 lbmol/cuft and $C_0 = 1.0$. Find the compositions as functions of time in a batch reactor and in a CSTR.

The stoichiometric balances are

$C = 0.5A + B$ (4)

$D = 0.5(C_0-C) = 0.5(1-C)$ (5)

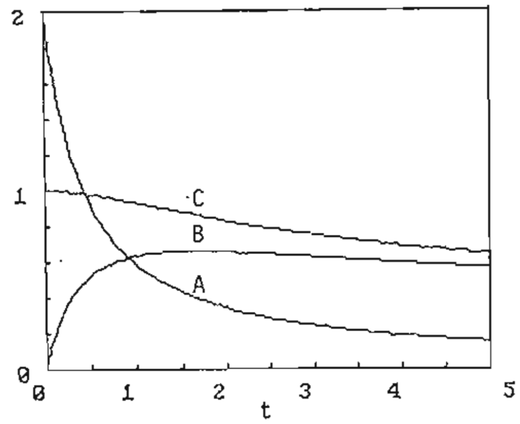
The CSTR equations are

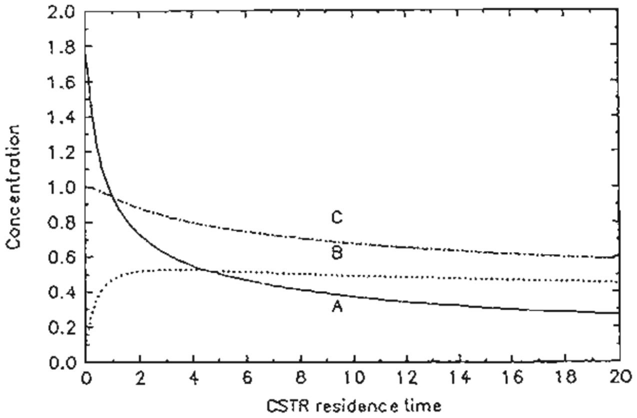
$A_0 = 2 = A_1 + 1.2\tau A_1^2$

$$A_1 = \frac{-1+\sqrt{1+9.6\tau}}{2.4\tau} \quad (6)$$

$B_0 = B_1 + 0.6\tau[A_1^2 - 0.5B_1^2(0.5A_1+B_1)]$ (7)

The differential equations are solved by ODE and plotted. Eqs (6) and (7) are solved at specified values of τ by "Root Solver". Both solutions are plotted.





P4.04.47. TWO STAGES WITH INTERCOOLING.

A reversible reaction, A ⇔ B, is conducted in a two stage CSTR with cooling between stages to 25 C which is also the fresh feed temperature. Inlet concentration $A_0 = 10$. Other data follow. Compare residence times and other operating conditions for 80% conversion with and without intercooling.

$\Delta H_r/C_p = -5$

$k = \exp(17.2-5800/T)$ (1)

$K_e = \exp(-24.7+9000/T)$ (2)

$r_a = k[(1+1/K_e)A - A_0/K_e]$

Heat and material balances are,

$C_p(T_1-T_0) = -\Delta H_r(A_0-A_1)$

$T_1 = T_0 + 5(A_0-A_1)$ (3)

$T_2 = T_0 + 5(A_1-A_2)$ (4)

$A_0 = 10 = A_1 + k_1\tau[(1+1/K_{e1})A_1 - 10/K_{e1})]$ (5)

$A_1 = A_2 + k_2\tau[(1+1/K_{e2})A_2 - 10/K_{e2}]$

$\quad = 2 + k_2\tau[(1+1/K_{e2})(2) - 10/K_{e2}]$ (6)

Without intercooling, Eq (4) is replaced by

$T_2 = T_0 + 5(A_0-A_2) = 338$ (7)

The solution of the six equations is obtained by SEQS.

	Cooled	Not cooled
T_1	332.8	326.9
T_2	303.2	338.0
A_1	3.041	4.226
τ	3.684	2.560
k_1	0.80	0.58
k_2	0.145	1.041
K_{e1}	1.04	1.701
K_{e2}	14.5	32.7

P4.04.48. ADDITION POLYMERIZATION

The reaction is of a monomer M producing a series of oligomers P_i,

$$M \Rightarrow P_1 + P_2 + \ldots + P_n$$

An initiation process has a specific rate k_0,

$$M \overset{k_0}{\Rightarrow} P_1, \quad r = k_0 M$$

where P_1 designates the activated monomer, and all subsequent steps have the same specific rate, k.

$$M + P_n \overset{k}{\Rightarrow} P_{n+1}, \quad r_n = kMP_n$$

The overall reaction rate of monomer is

$$r_m = k_0 M + \sum_1^\infty P_n \tag{1}$$

Part (a): In a CSTR with $\tau = V_r/V'$, for the monomer,

$$r_m = \frac{M_0 - M}{\tau} = k_0 M + \sum_1^\infty P_n \tag{2}$$

For individual oligomers,

$$r_1 = -k_0 M + kMP_1 = \frac{0 - P_1}{\tau}$$

$$P_1 = \frac{\tau k_0 M}{1 + \tau kM}$$

$$r_2 = kMP_1 - kMP_2 = \frac{0 - P_2}{\tau}$$

$$P_2 = \frac{kMP_1}{kM + 1/\tau} = \frac{k_0}{k}\left(\frac{\tau kM}{1 + \tau kM}\right)^2$$

For subsequent oligomers,

$$P_n = \frac{k_0}{k}\left(\frac{\tau kM}{1 + \tau kM}\right)^n = \frac{k_0}{k}\beta^n \tag{3}$$

$$\beta = \frac{\tau kM}{1 + \tau kM}$$

Part (b): Amount of unreacted monomer. Sum up all of the products.

$$\Sigma P_n = (k_0/k)\sum_1^\infty \beta^i$$

This a geometric series. When the last term goes to zero,

$$\Sigma P_n = (k_0/k)(1 + \tau kM) = k_0/k + k_0 \tau M \Rightarrow k_0 \tau M$$

since k_0/k is a relatively small number. Then,

$$k_0M = \frac{1}{\tau}\,\Sigma P_n \qquad (4)$$

In terms of fractional conversion, using Eq (2),

$$x = \frac{M_0-M}{M_0} = \frac{\tau}{M_0}\,(k_0M + kM\,\Sigma P_n) = \frac{\tau M}{M_0}\,(k_0+k_0\tau M)$$

$$= k_0\tau(1-x)[1+k\tau M_0(1-x)] \qquad (5)$$

This quadratic can be solved explicitly for x.

Part (c): Weight fractions , f_n, of individual oligomers.

W_0 = molecular weight of monomer

$$f_n = \frac{P_n n W_0}{(M_0-M)W_0} = \frac{nP_n}{M_0-M} = \frac{n}{(M_0-M)W_0}\left(\frac{k_0}{k}\right)\left(\frac{\tau kM}{1+\tau kM}\right)^n \qquad (6)$$

Part (d): A numerical example. These values are cited by J M Smith (1981),

$k_0 = 0.01/\text{sec}$, $k = 0.1$ liter/gmol-sec, $M_0 = 1.0$ gmol/liter

Eqs (5) and (6) become

$$x = 0.017t(1-x)[1+0.1\tau(1-x)]$$

$$f_n = \frac{0.1n}{x}\left[\frac{0.1\tau(1-x)}{1+0.1\tau(1-x)}\right\}^n$$

Some numerical values are tabulated.

τ	x	f_1	f_2	f_5	f_{10}
1	0.0109	0.8257	0.1486	0.0003	0.0000
10	0.1557	0.2940	0.2692	0.0646	0.0026
100	0.7683	0.0909	0.1270	0.1082	0.0360
1000	0.9734	0.0747	0.1085	0.1042	0.0422

P4.04.49. FRACTIONATED RECYCLE

The reversible reaction, 2A ⇔ B, is conducted in a three equal stage CSTR. Substances A and B have the same molal densities, ρ lbmol/cuft. A portion B_{21} of the content of substance B that leaves the second stage is recycled to the first stage. The inlet stream A_{01} and the product stream B_{30} are specified. The stream letters identify molal flow rates. Write the equations from which the various unspecified quantities labelled on the sketch and the reactor volume V_r can be found.

Stoichiometric balances:

$$A_{01} - A_{12} = 2(B_{12} - B_{21}) \qquad (1)$$

$$A_{12} - A_{23} = 2(B_{21}+B_{23}-B_{12}) \qquad (2)$$

$$A_{23} - A_{30} = (B_{30}-B_{23}) \qquad (3)$$

Rate equations for the three stages:

$$r_{a1} = k_1\left(\frac{\rho A_{12}}{A_{12}+B_{12}}\right)^2 - k_2\left(\frac{\rho B_{12}}{A_{12}+B_{12}}\right) \qquad (4)$$

$$r_{a2} = k_1\left(\frac{\rho A_{23}}{A_{23}+B_{21}+B_{23}}\right)^2 - k_2\left[\frac{\rho(B_{21}+B_{23})}{A_{23}+B_{21}+B_{23}}\right] \qquad (5)$$

$$r_{a3} = k_1\left(\frac{\rho A_{30}}{A_{30}+B_{30}}\right)^2 - k_2\left(\frac{\rho B_{30}}{A_{30}+B_{30}}\right) \qquad (6)$$

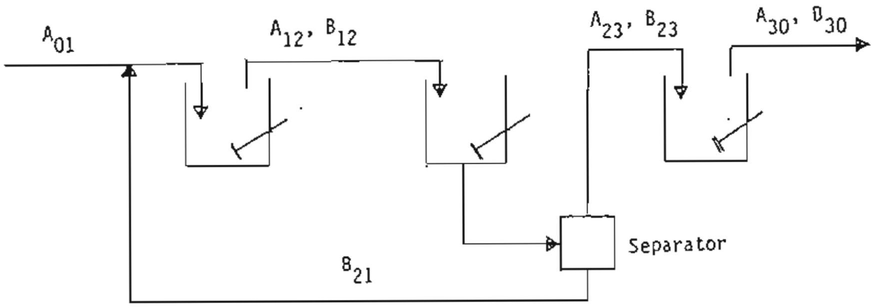
Material balances:

$$A_{01} = A_{12} + V_r r_{a1} \qquad (7)$$

$$A_{12} = A_{23} + V_r r_{a2} \qquad (8)$$

$$A_{23} = A_{30} + V_r r_{a3} \qquad (9)$$

The data to be specified are A_{01}, A_{30}, B_{21}, k_1, k_2, ρ. The nine remaining unknowns can be calculated from the nine equations.



P4.04.50. CSTR AND PFR SIZES

For a first order reaction, the volumes of a CSTR and of a plug flow reactor are to be compared for the same conversion.

For CSTR,

$$(C/C_0)_{stirred} = 1/(1+k\tau)$$

$$\tau_s = \frac{1}{k}(\frac{C_0}{C} - 1)$$

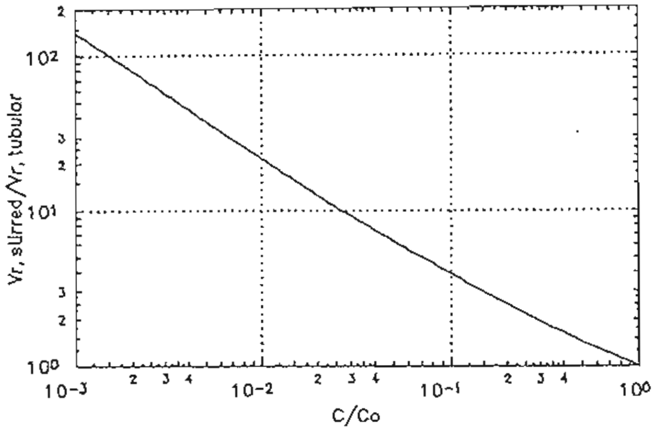
For plug flow,

$$-V'dC = rV_r = kCV_r$$

$$\tau_p = = \frac{1}{k} \ln \frac{C_0}{C}$$

The ratio of sizes is

$$\frac{V_{r,stirred}}{V_{r,pfr}} = \tau_s/\tau_p = \frac{C_0/C - 1}{\ln(C_0/C)}$$



The log-log plot is not quite linear.

P4.04.51. REACTIONS IN SERIES AND PARALLEL.

For the first order reactions,

$$A \overset{1}{\Rightarrow} R,\ R \overset{2}{\Rightarrow} S,\ R \overset{3}{\Rightarrow} T$$

the specific rates are

$$k_1 = \exp(9.21-3500/T)$$

$$k_2 = \exp(27.63-10500/T)$$

$$k_3 = \exp(18.42-7000/T)$$

Find the composition profiles at 325 and 350 K with $A_0 = 1$ and the other starting compositions zero, in batch and CSTR..

The rate equations are

$$\frac{dA}{dt} = -k_1A$$

$$\frac{dR}{dt} = k_1A -(k_2+k_3)R = k_1A_0 \exp(-k_1t) - (k_2+k_3)R$$

$$S = (k_2/k_3)T$$

These are integrated for a batch reactor by POLYMATH. The plots show that higher yields of R are obtained at the lower temperature.

For a CSTR the material balances are,

$A_0 = 1 = A+\tau k_1 A$

$$A = 1/(1+k_1\tau) \qquad (1)$$

$0 = R - \tau[k_1 A - (k_2+k_3)R]$

$$R = \frac{k_1\tau}{1+(k_2+k_3)\tau}A \qquad (2)$$

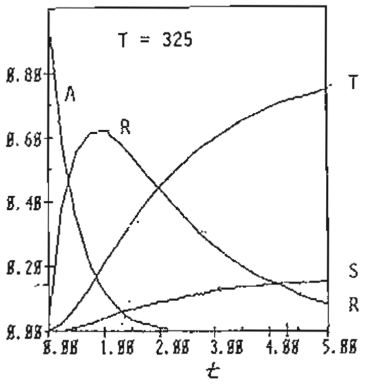
$0 = S - \tau k_2 R$

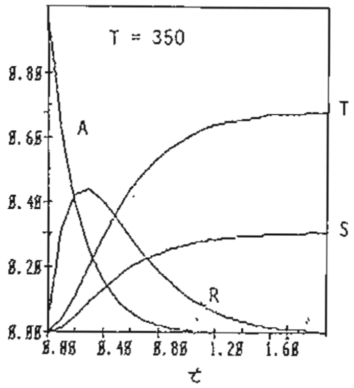
$$S = \tau k_2 R \qquad (3)$$

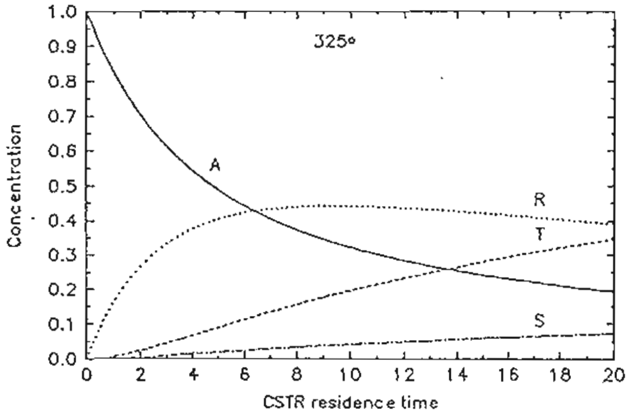
$$T = (k_3/k_2)S \qquad (4)$$

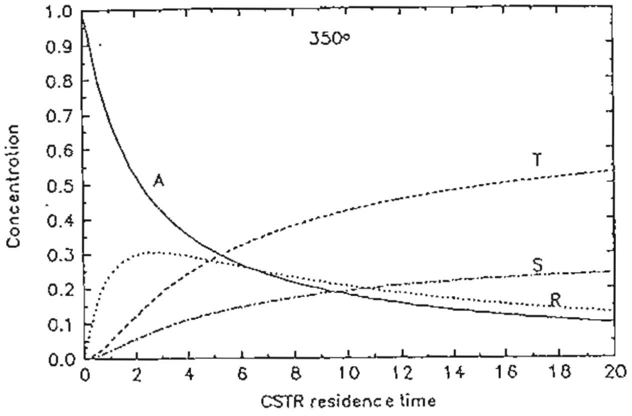
$$k_2/k_3 = \begin{cases} 0.00930/0.04423 = 0.210 \text{ at } 325\text{ K} \\ 0.09348/0.2059 = 0.454 \text{ at } 350\text{ K} \end{cases}$$

These results also are plotted. They show a peak value of $R_{max} = 0.44$ at 325 K compared with $R_{max} = 0.61$ in batch operation at the same temperature. The yield is higher at the lower temperature in both modes of operation.









P4.04.52. $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$

The relation between the number of stages, the residence time, and the concentrations of the consecutive first order reactions, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, will be found. $B_0 = C_0 = 0$.

n = number of stages

$\tau = (V_r/V')/n$ = residence time per stage

$\vartheta = k_1\tau A_0$

$\alpha = 1/(1+k_1\tau)$

$\beta = 1/(1+k_2\tau)$

The rate equations are,

$$\frac{dA}{dt} = -k_1A$$

$$\frac{dB}{dt} = k_1A-k_2B$$

In n stages,

$$A_n = A_0/(1+k_1\tau)^n = A_0\alpha^n \qquad (1)$$

In the first of n stages,

$$B_0 = B_1 + \tau(-k_1A_1+k_2B_1)$$

$$B_1 = \frac{B_0+k_1\tau A_1}{1+k_2\tau} = \alpha\beta\vartheta,\ \text{with } B_0 = 0$$

In subsequent stages,

$$B_2 = \beta(B_1+k_1\tau A_2) = \beta(\alpha\beta\vartheta+\alpha\vartheta) = \alpha\beta\vartheta(\beta+\alpha)$$

$$B_3 = \beta(B_2+k_1\tau A_3) = \beta[\alpha\beta\vartheta(\beta+\alpha)+\alpha^3)] = \alpha\beta\vartheta(\beta^2+\alpha\beta+\alpha^2)$$

$$.$$

$$B_n = \alpha\beta\vartheta(\beta^{n-1} + \alpha\beta^{n-2} + \alpha^2\beta^{n-3} + \ldots + \alpha^{n-1})$$

$$=(\alpha\beta\vartheta)\beta^{n-1}[1+(\alpha/\beta) + (\alpha/\beta)^2 + \ldots+(\alpha/\beta)^{n-1}]$$

This is a geometric series with ratio α/β. Introducing its sum results in

$$B_n = \frac{\alpha\beta\vartheta}{\alpha-\beta}(\alpha^n-\beta^n) \qquad (2)$$

For the remaining component,

$$C_n = A_0 - A_n - B_n \qquad (3)$$

Lines (1), (2) and (3) represent the concentrations of the three participants in terms of A_0, k_1, k_2 and τ, with $B_0 = C_0 = 0$.

When $n \Rightarrow \infty$, Eq (2) reduces to

$$B/A_0 = \frac{k_1}{k_2-k_1}[\exp(-k_1t) - \exp(-k_2t)] \qquad (4)$$

where t is the residence time in the whole battery. Advantage has been taken of the relationship

$$(1+kt/n)^n \Rightarrow \exp(kt) \text{ as } n \Rightarrow \infty.$$

This is the equation for a plug flow reactor.

Some numerical values are tabulated.

	$k_1 = 0.1$ $k_2 = 0.05$		$k_1 = 1$ $k_2 = 0.5$		$k_1 = 0.5$ $k_2 = 1$	
τ	A	B	A	B	A	B
0	1	0	1	0	1	0
1	0.7143	0.2381	.4	.343	.571	.171
2	0.6944	0.2640	.327	.405	.529	.202
3	.0687	0.2740	.296	.431	.512	.216
4	0.683	0.2794	.280	.446	.503	.223
5	0.6806	0.2827	.269	.456	.497	.228
6	0.6789	0.2849	.262	.462	.493	.231
7	0.6777	0.2866	.257	.467	.490	.234
8			.253	.471	.488	.235
9			.250	.474	.487	.237
10			.247	.476	.485	.238
∞	0.6703	0.2968	.223			

P4.04.53. PUMPAROUND SYSTEM

A stirred tank reactor with a pump-around heat exchanger is arranged as on the sketch. The first order reversible reaction , $A \Leftrightarrow B$, is to be carried to 80% conversion. The reaction temperature is to be kept at the value at which equilibrium conversion would be 90%. Temperature drop across the exchanger is to 60 K. Reaction in the exchanger circuit is neglected. Operating data are shown on the sketch and other data are:

$k = \exp(17.2-5800/T)$, 1/hr

$K_e = \exp(10000/T-24.7)$

$\Delta H_r = 19870$ cal/gmol

$C_p = 0.5$ cal/gm-K

Part (a): Find the reaction temperature, the heat load on the exchanger and the reactor volume.

Part (b): After leaving the heat exchanger, the net product goes to storage through a pipeline with a volume of 2500 liters. Reaction continues adiabatically. Find the conversion and temperature entering storage.

$K_e = B/A = 9 = \exp(10000/T-24.7)$

$T = 371.7$

$k = \exp(17.2-5800/371.7) = 4.933$/hr

Heat balance,

$Q + 10000(0.5)(371.7-60-300) = 50(0.8)19870)$

$Q = 736300$ kcal/hr, heat load on exchanger

$$\text{Circulation} = \frac{736300}{60(0.5)} = 24543 \text{ kg/hr}$$

Net recycle = 14543 kg/hr

$n_{a0} = 50$ kmol/hr, fresh feed

$n_{af} = 10$ kmol/hr, net reactor outlet

$n_{ar} = 14.543$

$n_{br} = 4n_{ar} = 58.172$

$n_a = n_{ar} + n_{af} = 24.543$

$n_{br} = 98.172$

The concentrations are the same in the tank, in the circulating line and to the transfer line.

$C_a = 10/5000$ kmol/liter

$C_b = 4C_a$

$$r_a = \frac{4.933}{5000}\left(10-\frac{40}{9}\right) = 0.00548 \text{ kgmol/liter-hr}$$

$n_{a0} = n_{af} + rV_r$

$$V_r = \frac{50-10}{0.00548} = 7299 \text{ liters.}$$

Part (b): Adiabatic heat balance on the transfer line,

$-\Delta H_r(n_{af}-n_a) = WC_p(T-T_0)$

$$T = 311.7 + \frac{19870(10-n_a)}{10000(0.5)} = 311.7 + 3.974(10-n_a)$$

$C_a = n_a/V'$

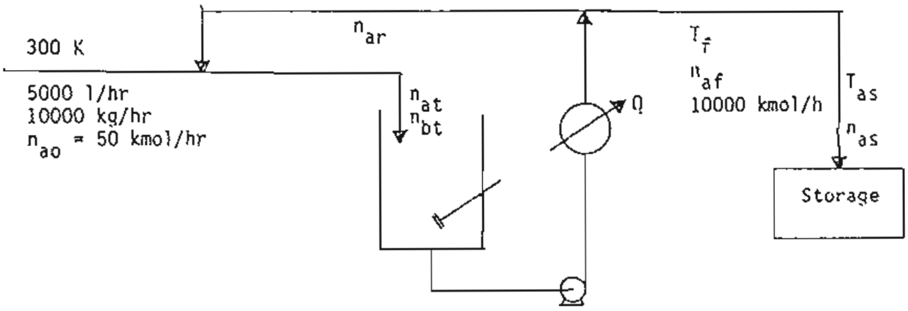
$C_b = (50-n_a)/V'$

$$V_r = \int_{n_a}^{10} \frac{dn_a}{r_a} = V' \int_{n_a}^{10} \frac{dn_a}{k[n_a-(50-n_a)/K_e]}$$

$$V_r/V' = \frac{2500}{5000} = 0.5 = \int_{n_a}^{10} \frac{dn_a}{k[n_a-(50-n_a)/K_e]}$$

Several trial values of n_a to storage are tabulated. The correct values are n_a = 8.67 and T = 317.0.

n_a	T	k	K_e	Integrand	∫
10	311.7	0.2447	1607	0.4097	0
9.5	313.7	0.2753	1309	0.3836	0.1983
9	315.7	0.3098	1073	0.3602	0.3842
8.67	317.0				0.5
8.5	317.7	0.3478	877	0.3102	0.5593



P4.04.54. PUMPAROUND HEAT EXCHANGER.

A second order reaction is conducted in a CSTR that is provided with a pumparound heat exchanger as sketched. Heat transfer rate in the exchanger is Q = $15000(\Delta T)_{lm}$ Btu/hr. The reactor is to be kept at 200 F. Other temperatures are shown on the sketch. Feed rate is V' = 100 cfh, inlet concentration is 0.5 lbmol/cuft Also ΔH_r= -50000, ρ = 50, C_p = 0.8.

Part(a): Find the circulation rate through the exchanger, the concentration in the reactor, and the magnitude of kV_r/V'.

Part (b): The effluent from a system like that of part (a) is at 200 F with A = 0.1955 lbmol/cuft. It proceeds to storage through a pipeline of 50 cuft volume under plug flow conditions. The specific rate as a function of temperature in °F is k = 4+0.2(T-200). Find the temperature and concentration at the exit of the pipeline.

In the exchanger,

$$(\Delta T)_{lm} = \frac{100-20}{\ln(100/20)} = 49.707$$

$$Q = 15000(49.707) = 745602 \text{ Btu/hr}$$

$$\text{Circulation, } R = Q/\rho C_p\Delta T = \frac{745602}{50(0.8)(200-100)} = 186.4 \text{ cfh}$$

Heat balance,

$$-\Delta H_r(A_0-A) = \rho C_p(T-T_0) + Q$$

$$A_0 - A = \frac{50(0.8)(200-80)+745602}{50000} = 0.2451$$

Material balance,

$$V'A_0 + RA = (V'+R)A + kV_rA^2$$

$$\frac{kV_r}{V'} = \frac{A_0-A}{A^2} = \frac{0.2451}{(0.5-0.2451)^2} = 3.773$$

Part (b): Heat balance,

$\rho C_p(T-T_0) = -\Delta H_r(A_0-A)$

$$T = 200 + \frac{50000(0.1955-A)}{50(0.8)} = 200 + 1250(0.1955-A)$$

$k = 4+0.2(1250)(0.1955-A) = 250(0.2115-A)$

The plug flow reactor equation is

$-V'dA = rdV_r$

$V_r/V' = 50/100 = 0.5$

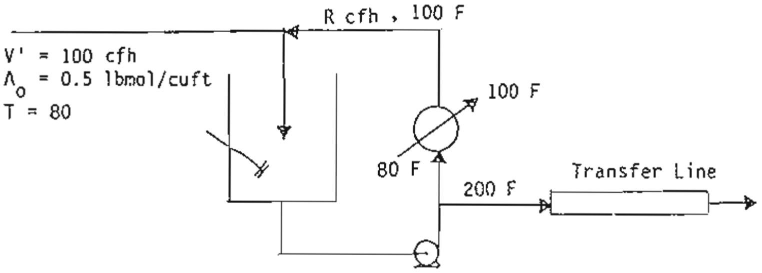
$$= \int_A^{0.1955} \frac{dA}{250A^2(0.2115-A)}$$

Numerical integration gives the lower limit as

$A = 0.0635$

Then

$T = 200+1250(0.1955-0.0635) = 365.0$



P4.04.55. CYCLOPENTADIENE DIMERIZATION

Cyclopentadiene in a hydrocarbon mixture is to be 75% dimerized in a three stage CSTR. Feed rate is 16000 kg/hr containing 16 wt% CPD which is equivalent to C_0 = 1.74 gmol/liter. Specific heat of the mixture is 550 cal/kg-K, density is 0.8 kg/liter and heat of reaction is ΔH_r = -9000 cal/gmol CPD and independent of temperature. Rate of dimerization is $r = kC^2$ with

$k = \exp(17.363-6876/T)$ (1)

(a) With an inlet temperature of 353.2 K and adiabatic conditions, find the residence time and conditions in the three reactors.

(b) Find the residence time under isothermal conditions of 93.3 C.

Part (A): Heat balance,

$-\Delta H_r(C_0-C_3) = \rho C_p(T_3-T_0)$

$9000(1.74)(0.75) = 0.8(550)(T_3-353.2)$

$T_3 = 379.9$,

$k_3 = 0.4786$

$$T_1 = T_0 + \frac{9000(1.74-C_1)}{0.8(550)} = 353.2 + 20.454(1.74-C_1) \qquad (2)$$

$$T_2 = T_3 - 20.454(C_2-C_3) = 379.9 - 20.454(C_2 - 0.435) \qquad (3)$$

Material balances,

$$C_0 = 1.74 = C_1 + k_1\tau C_1^2 \qquad (4)$$

$$C_1 = C_2 + k_2\tau C_2^2 \qquad (5)$$

$$C_2 = C_3 + k_3\tau C_3^2 = 0.435 + 0.4876(0.435)^2\tau$$
$$= 0.435 + 0.09055\tau \qquad (6)$$

The six numbered equations can be solved by trial. Assume C_1, find all the other unknowns in succession, and finally C_1 from Eq (5). Compare the assumed with the calculated values. The solution by SEQS is

$C_1 = 1.052$, $C_2 = 0.6538$, $C_3 = 0.435$

$T_1 = 367.26$, $T_2 = 375.42$, $T_3 = 379.9$

$k_1 = 0.2568$, $k_2 = 0.3859$, $k_3 = 0.4786$

$\tau = 2.417$

Part (b):

At 93.3 K, k = 0.2470

$$0.247\tau = \frac{1.74-C_1}{C_1^2} = \frac{C_1-C_2}{C_2^2} = \frac{C_2-0.435}{(0.435)^2} \tag{7}$$

The solution is

$\tau = 3.669$, $C_1 = 0.9398$, $C_2 = 0.6065$, $C_3 = 0.435$

P4.04.56. MAXIMUM YIELD OF CONSECUTIVE REACTIONS

For the consecutive reactions, $A \Rightarrow B \Rightarrow C$, the specific rates are equal and $B_0 = 0$. Find the maximum value of B/A_0 in (a) Batch reactor; (b) Two stage CSTR.

The rate equations are

$dA/dt = -k_1A$,

$dB/dt = k_1A-k_2B = k_1A_0\exp(-k_1t) - k_2B$

When $k_1 = k_2$, the solution by Laplace transform is

$B = kA_0t\exp(-kt)$

For the maximum, $dB/dt = 0$ and $kt = 1$

$$(B/A_0)_{max} = \exp(-1) = 0.3679 \tag{a}$$

in a batch or plug flow reactor.

Part (b):

$$A_n = A_0/(1+k\tau)^n$$

$$B_0 = 0 = B_1 + k\tau(-\frac{A_0}{1+k\tau} + B_1)$$

$$B_1 = \frac{k\tau A_0}{(1+k\tau)^2}$$

$$= B_2 + k\tau(-A_2 + B_2)$$

$$= B_2(1+k\tau) - \frac{k\tau A_0}{(1+k\tau)^2}$$

$$B_2 = \frac{2k\tau A_0}{(1+k\tau)^3}$$

Differentiation for a maximum gives

$$(1+k\tau)^3 - 3k\tau(1+k\tau)^2 = 0$$

$$k\tau = 0.5$$

$$(B/A_0)_{max} = 2(0.5)/(1.5)^3 = 0.296 \tag{b}$$

P4.04.57. YIELD OF INTERMEDIATE REACTANT

For the sequence, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, with $k_1 = 1$ and $k_2 = 0.5$, compare the profiles B/A_0 for one stage, two stage and batch reactors.

$$A_n = A_0/(1+k_1\tau)^n$$

$$B_0 = 0 = B_1 + \tau(-k_1A_1+k_2B_1)$$

$$B_1 = \frac{k_1\tau A_1}{1+k_2\tau} = \frac{k_1\tau A_0}{(1+k_1\tau)(1+k_2\tau)} \tag{1}$$

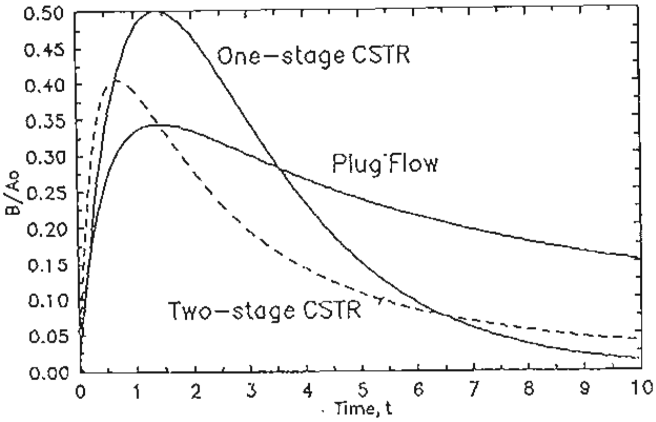
$$B_2 = \frac{k_1\tau A_2}{1+k_2\tau} + \frac{B_1}{1+k_2\tau}$$

$$= \frac{k_1\tau A_0}{(1+k_1\tau)(1+k_2\tau)}\left(\frac{1}{1+k_1\tau} + \frac{1}{1+k_2\tau}\right) \tag{2}$$

For a batch process, the integral is obtained in problem P2.02.07.

$$B/A_0 = \frac{k_1}{k_2-k_1}[\exp(-k_1\tau) - \exp(-k_2\tau)] \tag{3}$$

The three equations are plotted. The one stage CSTR gives the highest yield.



P4.04.58. REVERSIBLE CONSECUTIVE REACTIONS

For the reversible consecutive reactions, $A \underset{2}{\overset{1}{\Leftrightarrow}} B \underset{4}{\overset{3}{\Leftrightarrow}} C$, taking place in a CSTR, show that the concentration of B when the feed contains only A at a concentration A_0 is

$$\frac{B}{A_0} = \frac{\dfrac{k_1\tau}{1+k_1\tau}\left(1+\dfrac{k_2\tau}{K_b}\right)}{\left(\dfrac{k_1\tau}{1+k_1\tau}\dfrac{1}{K_a}+1\right)\left(1+\dfrac{k_2\tau}{K_b}\right)+k_2\tau}$$

where $K_a = k_1/k_2$ and $K_b = k_3/k_4$ are equilibrium constants.

Rates of reaction are,

$$r_a = -k_1A + K_2B$$

$$r_b = k_1A-(k_2+k_3)B + k_4C$$

$$r_c = k_3B-k_4C$$

In the CSTR,

$$A_0 = A + \tau(k_1A-k_2B) = (1+k_1\tau)A - k_2\tau B$$

$$A = \frac{A_0+k_2\tau B}{1+k_1\tau} \tag{1}$$

$$0 = B + \tau[-k_1A + (k_2+k_3)B - k_4C]$$

$$B = \frac{k_1\tau A+k_4\tau C}{1+k_2\tau+k_3\tau} \qquad (2)$$

$$0 = C + \tau(-k_3B + k_4C)$$

$$C = \frac{k_3\tau}{1+k_4\tau} B \qquad (3)$$

Rearrangement of Eqs (1) to (3) should give the stated result.

P4.04.59. REVERSIBLE SERIES REACTION

The reaction scheme, $A \xrightarrow{1} B \overset{2}{\underset{3}{\rightleftharpoons}} C$, is carried out in a CSTR with inlet concentration A_0. Find the outlet concentrations as functions of the residence time τ.

$$A = \frac{A_0}{1+k_1\tau} \qquad (1)$$

$$C_0 = 0 = C + \tau(-k_2B+k_3C)$$

$$C = \frac{k_2\tau B}{1+k_3\tau} \qquad (2)$$

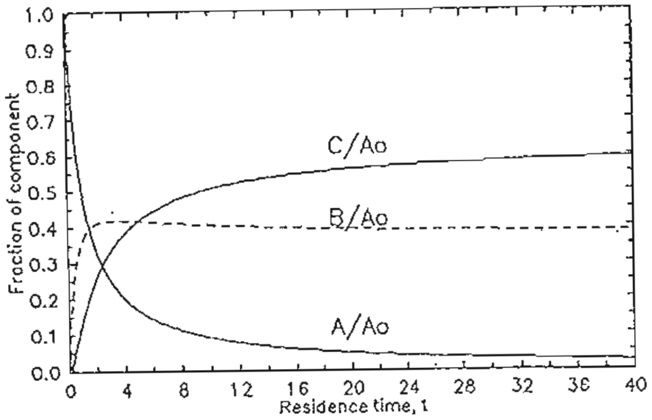
$$B_0 = 0 = B + \tau(-k_1A+k_2B-k_3C)$$

$$B = \frac{k_1\tau}{1+k_2\tau} A + \frac{k_3\tau}{1+k_2\tau} C$$

$$= \frac{k_1\tau A_0}{(1+k_1\tau)(1+k_2\tau)} + \frac{k_2k_3\tau^2}{(1+k_2\tau)(1+k_3\tau)} B$$

$$= \frac{k_1\tau(1+k_3\tau)}{(1+k_2\tau)(1+k_2\tau+k_3\tau)} A_0 \qquad (3)$$

To find C/A_0, substitute (3) into (2). The plots are for $k_1 = 1$, $k_2 = 0.5$ and $k_3 = 0.3$.



P4.04.60. CONSECUTIVE REACTIONS. BATCH AND CSTR

For the reactions, $A \xrightarrow{1} B \xrightarrow{2} C$, the specific rates are $k_1 = 2$ and $k_2 = 1$. Plot the concentration ratios as functions of residence time τ for a batch reactor and for one and two stage CSTRs.

Batch (see problem P2.02.07).

$$A/A_0 = \exp(-k_1\tau)$$

$$B/A_0 = \frac{k_1}{k_2-k_1}\,[\exp(-k_1\tau)-\exp(-k_2\tau)]$$

$$C/C_0 = 1 - A/A_0 - B/B_0$$

In a CSTR:

$$A/A_0 = 1/(1+k_1\tau)$$

$$B/B_0 = \frac{k_1\tau}{(1+k_1\tau)(1+k_2\tau)}$$

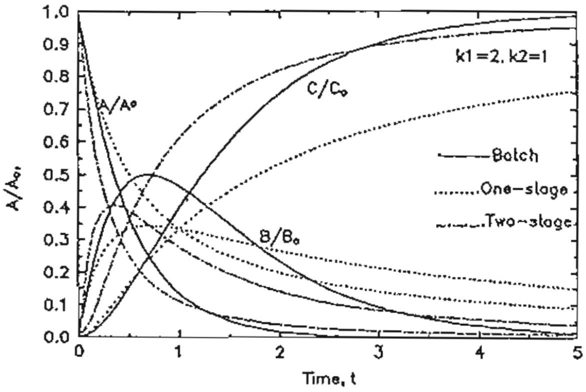
C/A_0 by Eq (3)

In a two stage battery (see problem P4.04.57):

$$A/A_0 = 1/(1+k_1\tau)^2$$

$$B/A_0 = \frac{k_1\tau}{(1+k_1\tau)(1+k_2\tau)}\left(\frac{1}{1+k_1\tau} + \frac{1}{1+k_2\tau}\right)$$

C/A_0 by Eq (3).



Comparison of the cases shows that as the number of stages increases, the product composition approaches the batch values, and the peak value of B is greatest for one stage.

P4.04.61. ADIABATIC CSTR WITH COOLED RECYCLE

The reaction A ⇒ B is conducted adiabatically in a CSTR but the product is cooled to $T_r = 320$ and recycled at a ratio R. Fresh feed is at $T_0 = 300$ with $C_{a0} = 1.0$. The specific rate is

$$k = \exp(17.2-5800/T) \tag{1}$$

and the outlet temperature is given by the heat balance as

$$T_2 = T_1 + 90(C_{a1} - C_{a2}) \tag{2}$$

(a) For a conversion of 80%, find the overall residence time V_r/V'_0 at several recycle ratios, R.

(b) With the residence time required for 80% conversion without recycle, find the fractional conversion at several recycle ratios, R.

Inlet temperature,

$$T_1 = \frac{T_0+RT_r}{R+1} = \frac{300+320R}{R+1} \tag{3}$$

Inlet concentration,

$$C_{a1} = \frac{C_{a0}+RC_{a2}}{R+1} = \frac{1+R(1-x)}{R+1} \tag{4}$$

$$C_{a2} = C_{a0}(1-x) = 1-x \tag{5}$$

Material balance,

$$(R+1)C_{a1} = (R+1)C_{a2} + k\tau C_{a2}$$

$$C_{a1} = (1-x)(1+\frac{k\tau}{R+1}) \tag{6}$$

Part (a):

1. Set x = 0.8
2. Specify R.
3. Find T_1, T_2, k, C_{a1} in succession
4. Find τ from Eq 5. The values are tabulated in the first part of the table.

Part (b):

From the table, τ = 0.8007 when R = 0. Keep this value for all values of R.

1. Specify R
2. Solve the numbered equations simultaneously for x and the other variables.

R	x	T_2	C_{a1}	τ
0	0.8	372	1.0	0.8007
1	0.8	346	0.6	2.584
2	0.8	337.3	0.467	3.975
5	0.8	328.7	0.333	6.255
0	0.8	372	1	0.8007
1	0.2584	321.6	0.871	0.8007
2	0.2496	320.8	0.834	0.8007
5	0.2445	320.3	0.796	0.8007

P4.05.01. FLOW REACTOR EQUATIONS AT CONSTANT PRESSURE.

Tubular flow reactors usually operate at nearly constant pressure. For a reactant A, the differential material balance is

$$-dn_a = n_{a0}dx = -V'dC_a = V'C_{a0}dx = r_a dV_r$$

One form of the integration is,

$$V_r/n_{a0} = \int_{x_0}^{x} dx/r_a, \text{ reactor volume/molal input rate}$$

$$n_t = n_{t0}+\delta_a(n_{a0}-n_a) = n_{t0}+\delta_a x$$
$$V' = n_t RT/\pi$$

$$C_a = n_a/V' = \left(\frac{\pi}{RT}\right)\left(\frac{n_a}{n_t}\right) = \left(\frac{\pi}{RT}\right)\left(\frac{n_{a0}-x}{n_{t0}+\delta_a x}\right)$$

The rate equations will be stated in these terms for a number of reactions. In all these cases, the integrands are ratios of second degree equations. The moderately complex integrations are accomplished with the aid of a table of integrals, or by MATHEMATICA, or numerically when the constants are known.

(a) $2A \Rightarrow M$
(b) $A+B \Rightarrow M$
(c) $2A \Leftrightarrow M$
(d) $A+B \Leftrightarrow M$

Part (a): $\delta_a = (1-2)/2 = -0.5$

$$V' = (RT/\pi)(n_{t0}-0.5x)$$

$$V_r/n_{a0} = \int dx/r_a = \frac{1}{k}\left(\frac{}{RT}\right)^2 \int_{x_0}^{x}\left(\frac{n_{t0}-0.5x}{n_{a0}-x}\right)^2 dx$$

Part (b): $\delta_a = (1-2)/1 = -1$

$$V' = (RT/\pi)(n_{t0}-x)$$

$$V_r/n_{a0} = \frac{1}{k}\left(\frac{\pi}{RT}\right)^2\int_{x_0}^{x} \frac{(n_{a0}-x)(n_{b0}-x)}{(n_{t0}-x)^2} dx$$

Part (c): $\delta_a = -0.5$

$$V' = (RT/\pi)(n_{t0}-0.5x)$$

$$r_a = k_1\left(\frac{RT}{\pi}\right)^2\left(\frac{n_{a0}-x}{n_{t0}-0.5x}\right)^2 - k_2\left(\frac{RT}{\pi}\right)\left(\frac{n_{m0}+0.5n_{a0}x}{n_{t0}-0.5x}\right)$$

Part (d): $\delta_a = -0.5$

$$r_a = k_1(RT/\pi)^2 \frac{(n_{a0}-x)(n_{b0}-x)}{(n_{t0}-0.5x)^2} - k_2(RT/\pi)\left(\frac{n_{m0}+0.5n_{a0}x}{n_{t0}-0.5x}\right)$$

P4.05.02. CONTACT TIME IN A PLUG FLOW REACTOR

The ratio V_r/V'_0 is of the volume of the reactor to the incoming volumetric rate and has the dimensions of time. It will be compared with the true residence time when the number of mols changes as reaction goes on, or P and T also change..

$$r_a = k(n_a/V')^q = k(\pi/RT)^q\left(\frac{n_a}{n_t}\right)^q$$

$$V' = n_t RT/\pi$$

The differential balance on the reactant is

$$-dn_a = r_a dV_r$$

$$dV_r = -\frac{1}{k}(\frac{RT}{\pi})^q(\frac{n_t}{n_a})^q\ dn_a$$

$$\frac{dV_r}{V'_0} = -\frac{1}{kn_{t0}}(\frac{RT}{\pi})^{q-1}(\frac{n_t}{n_a})^q\ dn_a \quad (1)$$

The definition of the rate of reaction and the law of mass action is

$$r_a = -\frac{1}{V'}\frac{dn_a}{dt} = k(\frac{n_a}{V'})^q$$

Rearrange to

$$dt = -\frac{1}{V'}\frac{dn_a}{r_a} = -\frac{1}{kV'}(\frac{V'}{n_a})^q\ dn_a = -\frac{1}{k}(\frac{RT}{\pi})^{q-1}(\frac{n_t^{q-1}}{n_a^q})\ dn_a \quad (2)$$

Lines (1) and (2) are the desired comparison. Before integrating, substitute

$n_t = n_{t0} + \delta_a(n_{a0}-n_a)$

<u>Example:</u> Take $q = 1$, $n_{t0} = n_{a0}$.

$$V_r/V'_0 = \int_{n_a}^{n_{a0}} \frac{(\delta_a+1)n_{a0}-\delta_a n_a}{n_a}\ dn_a = \frac{1}{k}\ [(\delta_a+1)\ \ln\frac{1}{1-x} - \delta_a x]$$

$$t = \frac{1}{k}\int_{n_a}^{n_{a0}}\frac{dn_a}{n_a} = \frac{1}{k}\ \ln\frac{1}{1-x}$$

The ratio

$$y = \frac{t}{V_r/V'_0} = \delta_a+1-\frac{\delta_a x}{\ln\frac{1}{1-x}}$$

> 1 when $\delta_a < 0$, and < 1 when $\delta_a > 0$.

P4.05.03. SPACE VELOCITY

The space velocity is the ratio of input flow rate F to the volume of the reactor,

$SV = F/V_r$

Various units are employed. Usually volumetric flow rates are measured at STP, 32 F or 0 C and 1 atm.

VHSV = volumetric hourly space velocity

WHSV = weight hourly space velocity

Part (a): A gas of molecular weight 42 is charged at 5 atm and 800 F at a rate of 12000 cfm to a reactor of volume 250 cuft. At STP,

$$V' = 12000(\frac{492}{5(1260)})(60) = 56230 \text{ SCFH}$$

$$VHSV = \frac{56230}{250} = 225 \text{ SCFH/cuft}$$

$$W' = \frac{56230(42)}{359} = 6578 \text{ lb/hr}$$

WHSV = 6578/250= 26.3 (lb/hr)/(cuft of reactor)

Part (b): A gas of molecular weight 42 is charged at 5 atm and 427 C at the rate of 425 m^3/min to a reactor of volume 9 m^3. At STP,

$$V' = 425(\frac{273}{5(700)})(60) = 1989\ m^3/hr$$

$$VHSV = 1989/9 = 221\ (m^3/hr)/(m^3\ reactor)$$

$$WHSV = \frac{1989(42)}{22.4(9)} = 414\ (kg/hr)/(m^3\ reactor)$$

Part (c): An oil charge to a reactor is metered at 10000 Bbl/day. Its specific gravity at temperature is 0.85 and at 32 F it is 0.92. The reactor volume is 2500 cuft. At 32 F,

$$W = \frac{10000(0.85)(1000)}{24(6.289)(0.92)} = 61212\ kg/hr$$

$$V_r = 250/28.3 = 88.3\ m^3$$

$$WHSV = 61212/88.3 = 693\ (kg/hr)/m^3$$

$$VHSV = \frac{10000(0.85)}{2500(0.92)} = 3.7\ (Bbl\ @\ STP/day)/(cuft\ of\ reactor)$$

Part (d): An oil vapor with molecular weight 120 is at 3 atm and 850 F. It is charged at the rate of 1500 lb/hr to a reactor with volume 250 cuft. At STP,

$$V' = \frac{1500(359)}{120} = 4488\ SCFH,\ 158.6\ m^3/hr$$

$$VHSV = 4488/250 = 17.95\ SCFH/cuft,\ 17.95\ (Std\ m^3)/(m^3\ of\ reactor)$$
$$WHSV = 1500/250 = 6\ (lb/hr)/(cuft\ of\ reactor)$$

$$\Rightarrow \frac{6(28.3)}{2.204} = 77.2\ (kg/hr)/(m^3\ of\ reactor)$$

P4.05.04. TIMES IN BATCH, PFR AND CSTR

In an isothermal batch reactor 70% of a liquid reactant is converted in 13 minutes. What times are needed to effect this conversion in a plug flow or CSTR?

At constant volumetric flow rate, the residence time in plug flow for a given conversion is the same as in batch operation.

$$-dC/dt = kC^q$$

$$kt = \frac{1}{(q-1)C_0^{q-1}}\left[(C_0/C)^{q-1} - 1\right]$$

The given data are not sufficient to determine both q and k. Assume second order. Then

$$kC_0 = \frac{1}{t}(C_0/C - 1) = \frac{1}{13}(1/0.3-1) = 0.1792$$

In a CSTR,

$$C_0 = C + k\tau C^2$$

$$\tau = \frac{1-C/C_0}{kC_0(C/C_0)^2} = \frac{1-0.3}{0.1792(0.09)} = 43.4\ min$$

P4.05.05. SPECIFIC RATES OF SERIES REACTIONS

A liquid phase reacting system has the simultaneous reactions, $A \overset{1}{\Rightarrow} B$ and $2A \overset{2}{\Rightarrow} C$. The second specific rate is known, $k_2 = 0.5$. In a plug flow reactor with an inlet concentration $C_{a0} = 1.2$, a conversion of 65% is obtained with a contact time $t = V_r/V' = 0.2$. Find the other specific rate.

$$r_a = k_1C_a + k_2C_a^2$$

$$-V'dC_a = r_a dV_r$$

$$V_r/V' = \int_{C_a}^{C_{a0}} \frac{dC_a}{C_a(k_1+k_2C_a)} = \frac{1}{k_1} \ln \frac{C_{a0}(k_1+k_2C_a)}{C_a(k_1+k_2C_{a0})}$$

Substituting data,

$$C_a = 0.35(1.2) = 0.42$$

$$0.2k_1 = \ln \frac{1.2[k_1+0.5(0.42)]}{0.42[k_1+0.5(1.2)]}$$

$$k_1 = 4.88$$

P4.05.06. SPECIFIC RATE OLEIC ACID CHLORINATION

Chlorination of oleic acid dissolved in carbon chloride was tested in a flow reactor at 12.8 C with the tabulated results(Roper, Chem Eng Sci 2 27, 1953). Chlorine (A) and oleic acid (B) were dissolved separately in CCl_4 and mixed in the liquid phase at the inlet to the reactor. Concentrations are gmol/liter and time is in seconds. Check a second order mechanism.

$$r_a = kC_aC_b = kC_a(C_{b0}-C_{a0}+C_a)$$

$$-V'dC_a = r_a dV_r$$

$$kV_r/V' = \int_{C_a}^{C_{a0}} \frac{dC_a}{C_a(C_{b0}-C_{a0}+C_a)}$$

$$= \frac{1}{C_{b0}-C_{a0}} \ln \frac{C_{a0}(C_{b0}-C_{a0}+C_a)}{C_aC_{b0}}$$

k is evaluated and tabulated for each of the five data points. The average of rather widely scattered values is k = 132.6.

V_r/V'	C_{a0}	C_{b0}	C_a	k
0.054	0.0208	0.0242	0.0181	113
0.093	0.0208	0.0242	0.0162	124
0.258	0.0186	0.0242	0.0097	133
0.350	0.0186	0.0242	0.0072	159
0.573	0.0186	0.0242	0.0056	134

P4.05.07. SPECIFIC RATE OF GAS OIL CRACKING.

Cracking of an 11.3°API gas oil was conducted experimentally in a coil 150 ft long by 0.209 in. ID, immersed in a lead bath at 850°F. The oil entered at 200°F and 475 psig at the rate of 1.6 gph. The amount converted to gas and gasoline was 12.2 wt %. The heat-transfer coefficient was computed as 31. The density of the mixture is expressed by the equation

$$\frac{1}{\rho} = 0.0229 + 0.317x$$

Hydrocarbon cracking is a first-order reaction. Neglecting pressure drop, find the specific reaction rate.

Solution. Heat-transfer calculations show that when 15 per cent of the reactor has been traversed, the oil temperature is within 5°F of the lead bath. It will be assumed that no significant conversion has occurred in the preheat section and that the reaction is substantially isothermal in the remaining 85 per cent of the reactor volume. S.G. = 0.95

$$W = \frac{8.33(1.6)(0.95)}{3{,}600} = 0.00347 \text{ lb/sec}$$

$$V_r = 0.85(150)\left(\frac{0.209}{12}\right)^2(0.785) = 0.0303 \text{ cu ft}$$

$$k = \frac{W}{V_r}\int_0^x \frac{dx}{\rho(1-x)} = \frac{W}{V_r}\int_0^x \frac{0.0229+0.317x}{1-x}\,dx$$

$$= \frac{W}{V_r}\left[0.3401\ln\frac{1}{1-x} - 0.317x\right]_0^{0.122}$$

$$= \frac{0.00347}{0.0303}\left[0.3401\ln\frac{1}{1-0.122} - 0.317(0.122)\right] = 0.00068 \text{ sec}^{-1}$$

This result may be compared with an approximate solution, taking an average reciprocal density:

$$\text{Inlet } \rho = \frac{1}{0.0229} = 43.7$$

$$\text{Outlet } \rho = \frac{1}{0.0229 + 0.317(0.122)} = 16.2$$

$$\left(\frac{1}{\rho}\right)_m = 0.5\left(\frac{1}{43.7} + \frac{1}{16.2}\right) = 0.0453$$

and $$k = \frac{W}{V_r}\left(\frac{1}{\rho}\right)_m \ln\frac{1}{1-x} = \frac{0.00347(0.0453)}{0.0303}\ln\frac{1}{1-0.122} = 0.00063 \text{ sec}^{-1}$$

P4.05.08. PFR AND CSTR IN SERIES

At present the liquid phase reaction, A + B ⇒ C + D, takes place in a plug flow reactor. A conversion of 96% is obtained with $C_{a0} = C_{b0} = 1$ mol/liter. A mixed reactor 10 times the volume of the PFR is connected in series. Find conversions with the PFR first and with the PFR second in series.

In the PFR,

$C_{a0} = 1,\ C_{a1} = 0.04$

$$k\tau_p = \frac{1}{C_{a0}}\left(\frac{C_{a0}}{C_a} - 1\right) = 24$$

With the PFR first,

$k\tau_s = 10\ k\tau_p = 240$

$C_{a1} = 0.04 = C_{a2} + 240C_{a2}^2$

$C_{a2} = 0.0152$

With the CSTR first,

$1 = C_{a1} + 240C_{a1}^2$

$C_{a1} = 0.0667$

$$k\tau_p = 24 = \frac{1}{C_{a2}} - \frac{1}{0.0667}$$

$C_{a2} = 0.0256$

Greater conversion is obtained with the PFR first.

P4.05.09. PARALLEL OR SERIES PFRs

The homogeneous gas reaction, A ⇒ 3B, follows second order kinetics. For a feed rate of 4 m^3/hr of pure A at 5 atm and 350 C, a pilot reactor consisting of a 2.5 cm ID pipe 2 m long gave 60% conversion of feed. A commercial plant is to treat 320 m^3/hr of feed consisting of 50% each of A and inerts at 25 atm and 350 C, and 80% conversion is required. Find how many 2 meter lengths of 2.5 cm ID pipe are needed. Should they be placed in series or parallel?

$$V = \frac{n_tRT}{\pi} = \frac{RT}{\pi}(3n_{a0}-2n_a)$$

$$r_a = k(n_a/V)^2$$

$$V_r = \frac{1}{k}\left(\frac{RT}{\pi}\right)^2 \int_{n_a}^{n_{a0}} \left(\frac{3n_{a0}-2n_a}{n_a}\right)^2 dn_a$$

In the pilot plant operation,

$$V_r = 0.982 \text{ liters}$$

$$n_{a0} = \frac{4000(273)}{22.4(623)}(5) = 391.3 \text{ gmol/hr}$$

$$(RT/\pi)^2 = [0.082(623)/5]^2 = 104.39$$

$$\int_{0.4}^{1} \left(\frac{3-f}{f}\right)^2 df = 4.91,\ f = n_a/n_{a0}$$

$$k = \frac{104.39(391.3)(4.91)}{0.982} = 0.2042(10^6) \text{ liter/gmol-hr}$$

Commercial plant operation,

$$n_{a0} = \frac{0.5(320)1000)(273(25)}{22.4(623)} = 78250 \text{ gmol/hr}$$

$$n_t = n_a + n_i + 3(n_{a0}-n_a) = 4n_{a0}-2n_a = 313000 - 2n_a$$

$$(RT/\pi)^2 = [0.082(623)/25]^2 = 4.176$$

$$\int_{0.2}^{1} \left(\frac{4-2f}{f}\right)^2 df = 41.47,\ f = n_a/n_{a0}$$

$$V_r = \frac{1}{0.204(10^6)}(4.176)(78250)(41.47) = 66.43 \text{ liters}$$

Heat transfer and friction are reduced by placing tubes in parallel. If neither factor is critical, either parallel or series placement is feasible. Series arrangement will be trombone type because of the great length.

P4.05.10. TWO STREAMS, TWO PFRs

Reactant A decomposes according to a second order reaction. Two streams are to be processed, the first with $C_{a0} = 1$ and $V'_1 = 1$; the other with $C_{a0} = 2$ and $V'_2 = 2$. For the first stream alone in a PFR the volume needed for 75% conversion is V_{r1}. What arrangement of streams and reactors will require the least total volume for conversion down to $C_a = 0.25$?

Original operation:

$$-V'dC_a = kC_a^2dV_{r1}$$

$$k = \frac{V'}{V_{r1}}\left(\frac{1}{0.25}-1\right) = 3/V_{r1}$$

Combined stream in a single reactor:

$$C'_{a0} = \frac{1(1)+2(2)}{3} = 1.667$$

$C_a = .25$
$V' = 3$

$$V_r = \frac{V'}{k}\left(\frac{1}{0.25} - \frac{1}{1.667}\right) = \frac{2.4(3)}{3/V_{r1}} = 2.4V_{r1}$$

Separate streams in parallel reactors:

$$V_{r2} = \frac{V_2'}{3/V_{r1}}\left(\frac{1}{0.25} - \frac{1}{2}\right) = \frac{2(3.5)}{3/V_{r1}} = 2.33V_{r1}$$

$$V_{r,total} = V_{r1} + 2.33_{r1} = 3.33V_{r1}$$

The series arrangement is better.

P4.05.11. REVERSIBLE REACTION

The reversible gas phase reaction, A ⇔ 2B, is conducted at 540 F and 3 atm in a PFR. Feed contains 30 mol% A and the balance inert materials, the total being 75 lbmols/hr. The rate equation is

$$r_a = 1.6[n_a/V - 182(n_a/V)^2], \quad \text{lbmol/cuft-min}$$

Find the reactor volume needed to produce an equimolal mixture of A and B.

Base the calculations on 1 lbmol of feed.

$n_{t0} = 1,\ n_{a0} = 0.3,\ n_a = n_b = 2(n_{a0}-n_a) = 0.2$

$n_t = n_a+n_i+2(n_{a0}-n_a) = 1.3-n_a$

$$V' = \frac{n_tRT}{\pi} = \frac{0.73(1000)(1.3-n_a)}{3} = 243(1.3-n_a)$$

$$r_a = \frac{1.6}{243(1.3-n_a)}\left[n_a - \frac{182(4)(0.3-n_a)^2}{243(1.3-n_a)}\right]$$

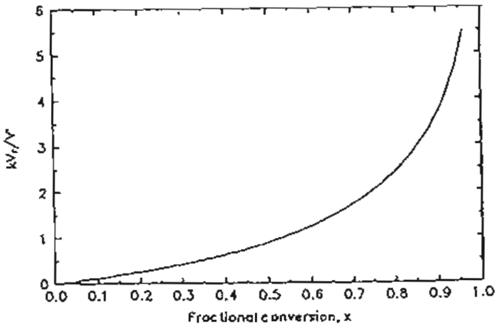
Total reactor volume is

$$V_r = \frac{75}{60}\int_{0.2}^{0.3}\frac{dn_a}{r_a} = 85.25 \text{ cuft}$$

The integration is done numerically.

P4.05.12. CONVERSION AND SIZE

For the gas phase reaction, A ⇒ 2B, in a plug flow reactor, find the relation between fractional conversion and the quantity kV_r/V_0', when starting with pure A.



$n_t = 2n_{a0}-n_a$

$$V' = \frac{n_t}{n_{t0}}V_0' = \left(\frac{2n_{a0}-n_a}{n_{a0}}\right)V_0'$$

$$r_a = k\left(\frac{n_a}{V'}\right) = \frac{kn_{a0}}{V_0'}\left(\frac{n_a}{2n_{a0}-n_a}\right) = \frac{kn_{a0}}{V_0'}\left(\frac{1-x}{1+x}\right)$$

$$V_r = \int\frac{dn_a}{r_a} = \frac{V_0'}{k}\int_x^0\left(\frac{1-x}{1+x}\right)dx$$

$$y = kV_r/V_0' = 2\ \ln\frac{1}{1-x} - x$$

When x = 0.5, y = 0.89; when x = 0.95, y = 5.08. Other values are on the graph.

P4.05.13. NEGLECTING VARIATION IN VOLUMETRIC FLOW RATE

The pair of reactions, A+B ⇒ 2C and A+C ⇒ D, are done in a PFR at 5 atm and 400 K, with $n_{a0} = 0.9$ gmols/liter and $n_{b0} = 0.3$. Find the effluent compositions as a function of reactor volume. Compare the performance when variation in volumetric flow rate is neglected.

$$n_t = 0.6+n_a-n_b, \quad \text{liters/min}$$

$$V' = \frac{0.082(400)}{5} n_t = 6.564(0.6+n_a-n_b)$$

The rate equations are

$$-\frac{dA}{dt} = 0.3AB + 0.15AC = 0.3AB + 0.15A(A-3B)$$

$$-\frac{dB}{dt} = 0.3AB$$

where the letters represent concentrations. In terms of flowing mol rates,

$$r_a = -\frac{dn_a}{dV_r} = \frac{0.3n_an_b+0.15n_a(n_a-3n_b)}{43.09(0.6+n_a-n_b)^2} \quad (1)$$

$$r_b = -\frac{dn_b}{dV_r} = \frac{0.3n_an_b}{43.09(0.6+n_a-n_b)^2} \quad (2)$$

The two equations are solved by ODE. The tabulation gives the effluent flow rates as functions of V_r.

When variation in volumetric flow rate is neglected, the denominators of both equations become $(V'_0)^2 = [6.564(1.2)]^2$. Solutions for those cases also are tabulated. The differences between the two cases are appreciably greater at higher conversions.

	Variable V'		Constant V'	
V_r	n_a	n_b	n_a	n_b
0	0.9	0.3	0.9	0.3
100	0.7785	0.1991	0.7799	0.2000
200	0.6735	0.1368	0.6810	0.1406
500	0.4396	0.0499	0.5309	0.1093
1000	0.2328	0.0125	0.3437	0.0391

P4.05.14. PFR SIZE AND SPACE VELOCITY

The reaction, A ⇒ B, is done at 1000 R and 3 atm in a tubular flow reactor. Feed rate is 50 lbmol/hr containing 30 mol% A and the rest inerts. The rate equation is $r_a = 48.6C_a$ lbmols/cuft-min. For 95% conversion, what reactor volume and what VHSV are needed?

$$V' = n_tRT/\pi = \frac{50(0.729)(1000)}{60(3)} = 202.5 \text{ cuft/min}$$

$$C_a = n_a/V'$$

$$r_a = \frac{48.6n_a}{202.5} = 0.24n_a$$

$$n_{a0} = 30/60 = 0.5 \text{ lbmol/min}$$

$$V_r = \int_{0.025}^{0.5} \frac{dn_a}{0.24n_a} = 4.167 \ln(20) = 12.48 \text{ cuft}$$

$$\text{VHSV} = \frac{\text{SCFH of feed}}{V_r \text{ cft}} = \frac{50(359)}{12.48} = 1438 \text{ /hr}$$

P4.05.15. PFR SIZE AND SPACE VELOCITY, REVERSIBLE REACTION

The reversible reaction $A \rightleftharpoons 2B$ is conducted at 540°F and 3 atma in a tubular-flow reactor. The feed contains 30 mole % A and the balance inert material, the total being at the rate of 75 lb moles/hr. The rate equation is

$$r_a = k\left[\frac{n_a}{V} - \frac{1}{K_e}\left(\frac{n_b}{V}\right)^2\right]$$

with $k = 1.6 \text{ sec}^{-1}$ and $K_e = 0.0055$. To accomplish 75 per cent of equilibrium conversion, find (*a*) the volume of the reactor, (*b*) the space velocity.

Solution. Refer all quantities to 1 lb mole of feed. Accordingly,

$$n_{t0} = 1$$

$$n_{a0} = 0.3$$

$$n_t = n_{t0} + \delta x = 1 + x$$

$$V = \frac{n_t RT}{\pi} = \frac{0.73(1{,}000)(1+x)}{3} = 243(1+x)$$

At equilibrium,

$$K_e = 0.0055 = \left(\frac{C_b^2}{C_a}\right)_e = \left(\frac{n_b^2}{Vn_a}\right)_e = \frac{(2x_e)^2}{243(1+x_e)(0.3-x_e)}$$

whence $x_e = 0.20$

$$r = 1.6\left\{\frac{0.3-x}{243(1+x)} - \frac{1}{0.0055}\left[\frac{2x}{243(1+x)}\right]^2\right\}$$

$$= 0.0066\left[\frac{0.3-x}{1+x} - 0.747\left(\frac{2x}{1+x}\right)^2\right]$$

$$\frac{V_r}{W} = \int_0^x \frac{dx}{r} = \int_0^{0.15} \frac{152\,dx}{(0.3-x)/(1+x) - 0.747[2x/(1+x)]^2}$$

$$= 134.8 \text{ cuft/(lbmol/sec)}$$

The integration was numerical. Then,

$$V_r = 134.8W = 134.8(75)/3600 = 2.81 \text{ cuft}$$

$$\text{Space velocity} = \frac{\text{Std cuft/sec of feed}}{\text{cuft of reactor}} = \frac{75(359)}{3600(2.81)}$$

$$= 2.66/\text{sec}$$

P4.05.16. PYROLYSIS OF ETHYLBENZENE

Pyrolysis of ethylbenzene was carried out at 950 F in a flow reactor (Rase & Kirk, Chem Eng Prog 30 35, 1954) with the tabulated data of fractional conversion at two pressures against W/F g catalyst/(gmol feed/hr). Find the fractional conversion at P = 1.5 and W/F = 25.

Try the rate equation

$$r = \frac{dx}{d(W/F)} = k(1-x)P^q$$

whose integral is

$$kP^q = \frac{1}{W/F} \ln \frac{1}{1-x}$$

The values of kP^q are tabulated along with the original data. In terms of the average values,

$$0.002016(0.97)^q = 0.004858(3.15)^q$$

whence

$$q = -\ 0.7467$$

and

$$k = 0.004858/3.15^{0.7467} = 0.002016/0.97^{0.7467} = 0.002063$$

The rate equation becomes

$$r = 0.002063\ P^{0.7467}(1-x)$$

When P = 1.5,

$$r = 0.002063(1.5)^{0.7467}(1-x) = 0.00279(1-x)$$

The required conversion is

$$x = 1 - \exp[-0.00279(W/F)] = 1-\exp[-0.00279(25)] = 0.067$$

	P = 0.97		P = 3.15	
W/F	x	kP^q	x	kP^q
5	0.009	0.001808	0.025	0.005064
10	0.021	0.002122	0.047	0.004814
15	0.031	0.002099	0.068	0.004695
20	0.040	0.002041		
25	0.049	0.002010		
Avg		0.002016		0.004858

P4.05.17. AUTOCATALYTIC REACTION WITH RECYCLE

Part of the effluent from a PFR is returned to the inlet. The recycle ratio is R, fresh feed rate is F_0

$$R = F_r/F_0$$

$$F_t = F_r + F_0 = F_0(R+1)$$

The concentration of the mixed feed is

$$C_{at} = \frac{C_{a0}+RC_{af}}{1+R}$$

where C_{af} is the outlet concentration. For the autocatalytic reaction, A ⇒ B, the rate equation is

$$r_a = kC_aC_b = kC_a(C_{a0}-C_a)$$

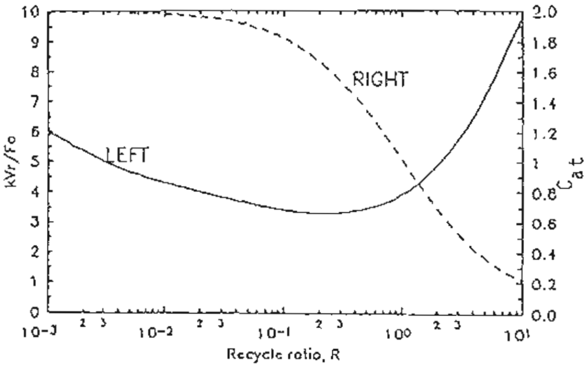
The flow reactor equation is

$$-F_t dC_a = -F_0(R+1)dC_a = r_a dV_r = kC_a(C_{a0}-C_a)dV_r$$

$$\frac{kV_r}{F_0} = (R+1)\int_{C_{af}}^{C_{at}} \frac{dC_a}{C_a(C_{a0}-C_a)}$$

The tabulation and plot are for $C_{a0} = 2$ and $C_{af} = 0.04$. A minimum reactor size is at R = 0.23.

R	C_{at}	kV_r/F_0
0	2	
0.001	1.9980	5.979
0.01	1.9806	4.316
0.1	1.8218	3.421
0.5	1.3467	3.463
1	1.0200	3.937
2	0.6933	4.810



P4.05.18. ETHANOL DECOMPOSITION

The decomposition of ethanol,

$$C_2H_5OH \Rightarrow C_2H_4 + H_2O$$

proceeds in a PFR at 423 K and 2 atm with rate equation

$$r_a = 0.52C_a^2 \text{ gmol/liter-sec}$$

Feed rate is 10 liters/sec of pure A. Find the reactor volume for 50% conversion.

$$n_{a0} = 2(10)/0.082(423) = 0.5766 \text{ gmol/sec}$$

$$n_t = 2n_{a0}-n_a$$

$$\pi/RT = 2/0.082(423) = 0.0577$$

$$C_a = n_a/V' = \frac{n_a}{2n_{a0}-n_a}(\pi/RT)$$

$$r_a = 0.52(0.0577)^2\left(\frac{n_a}{2n_{a0}-n_a}\right)^2 = \frac{1}{578.4}\left(\frac{f}{2-f}\right)^2$$

$$f = n_a/n_{a0}$$

Reactor material balance,

$$-dn_a = -n_{a0}df = r_a dV_r$$

$$V_r/n_{a0} = 578.4\int_f^1 \left(\frac{2-f}{f}\right)^2 df$$

$$= 663.8 \text{ liter sec/gmol when } f = 0.5$$

$$V_r = 0.5766(663.8 = 382.7 \text{ liters}$$

The space velocities in several kinds of units are,

$$\text{feed rate}/V_r = \frac{0.5766(3600)}{382.7} = 5.428 \text{ gmol/liter-hr}$$

$$\Rightarrow \frac{10(3600)}{382.7} = 94.1 \text{ (liters/hr)/liter of reactor}$$

P4.05.19. REACTOR LENGTH

The gas phase reaction, A ⇒ 2B, is done at 400 K in a tubular reactor 6 cm in diameter. The feed contains 50 mol% each of A and inerts, of molecular weights 40 and 20 respectively. The total feed rate is 400 kg/hr, inlet pressure is 5 atm and the specific rate is 2000/hr. Determine the reactor length for a 35% conversion of A.

$n_{t0} = 400000/30 = 13333$ gmol/hr

$$r_a = kC_a = k(\frac{\pi}{RT})(\frac{n_a}{n_t}) = 2000(\frac{5}{0.082(400)})(\frac{1-x}{1+x}) = 304.8(\frac{1-x}{1+x})$$

$x = 1-n_a/n_{a0}$

Reactor balance is

$-dn_a = n_{a0}dx = r_a dV_r$

$$V_r/n_{a0} = \frac{1}{304.8}\int_0^x (\frac{1+x}{1-x})dx$$

$\Rightarrow$ 0.001679 liters/(gmol/hr), when $x = 0.35$

$V_r = 0.7854(36)L = 0.001679(1000)(0.5)(13333)$

$L = 396$ cm reactor length

P4.05.20. ADDITION HALOGENATION ACROSS A DOUBLE BOND

A characteristic reaction of alkenes is the addition of halogens across the double bond, as

$Cl_2 + C_2H_4 \Rightarrow (CH_2Cl)_2$

Consider such a reaction carried out at 100 C in a PFR. The feed rate of each reactant is 600 gmol/hr, the specific rate is 600 liters/gmol-hr and the molal volume is 16.4 liters/gmol. What reactor volume is needed for a conversion of 60%?

$n_{a0} = n_{b0} = 600$ gmol/hr

$n_t = 0.5n_{a0}+1.5n_a$

$V' = 16.4(0.5n_{a0}+1.5n_a) = 8.2(n_{a0}+3n_a)$

$$C_a = n_a/V' = \frac{1}{8.2}(\frac{f}{1+3f})$$

$f = n_a/n_{a0}$

$$r_a = 600C_a^2 = 8.923(\frac{f}{1+3f})^2 \text{ gmol/liter-hr}$$

Flow reactor equation,

$-dn_a = -n_{a0}df = r_a dV_r$

$$V_r/n_{a0} = 0.1121\int_{0.4}^{1} (\frac{1+3f}{f})^2\,df = 0.1121(12.397)$$

$= 1.389$ liters/(gmol/hr)

$V_r = 1.389(600) = 833.5$ liters

P4.05.21. PENTANE ISOMERIZATION WITH RECYCLE.

n-Pentane isomerizes to isobutane in a first order reaction with specific rate $k = 0.00364$/min. A stream containing 95 mol/m^3 of n-pentane reacts to a content of 55 mol/m^3. Find the space-time relations for recycle processes with recycle ratio up to 10.

R = recycle ratio = $V'_{recycle}/V'_0$

Composite feed composition,

$$C_{at} = \frac{C_{a0}+RC_{af}}{1+R} = \frac{95+RC_{af}}{1+R}$$

where C_{af} is the product concentration.

$-V'_0(1+R)dC_a = kC_a dV_r$

$$V_r/V'_0 = \frac{1+R}{0.00364}\int_{C_{af}}^{C_{at}} \frac{dC_a}{C_a} = 274.7(1+R)\ \ln \frac{95+RC_{af}}{(1+R)C_{af}}$$

Two sets of results are tabulated for several values of R:

(a) Values of V_r/V'_0 are given with product $C_{af} = 55$.

(b) Values of C_{af} are given with $V_r/V'_0 = 150.1$.

R	C with $V_r/V'_0 = 150$	V_r/V'_0 with C = 55
0	55	150.1
1	58.3	170.4
5	60.4	188.6
10	60.9	193.5
∞(CSTR)	61.4	199.8

P4.05.22. BUTADIENE DIMERIZATION

A mixture of 0.5 mol of steam per mol of butadiene is dimerized in a tubular reactor at 640 C and 1 atm. The forward specific rate is k = 118 gmol/(liter)(hr)(atm)^2 and the equilibrium constant is 1.27. Find the length of 10-cm ID tube for 40% conversion when the total feed rate is 9 kmol/hr.

$2A \Leftrightarrow B$

$n_{a0} = 6$ kmol/hr

$n_t = n_s+n_a+n_b = 0.5n_{a0}+n_a+0.5(n_{a0}-n_a) = n_{a0}+0.5n_a$

$$p_a = \frac{n_a}{n_{a0}+0.5n_a} \quad (1)$$

$$p_b = \frac{0.5(n_{a0}-n_a)}{n_{a0}+0.5n_a}$$

$$r_a = k(P_a^2 - p_b/K_e) = \frac{118}{n_{a0}+0.5n_a}\left(\frac{n_a^2}{n_{a0}+0.5n_a} - \frac{n_{a0}-n_a}{2(1.27)}\right) \qquad (1)$$

Put $n_{a0} = 6$, substitute Eq (1) into the flow reactor equation and integrate numerically.

$$V_r = \int_{3.6}^{6} \frac{dn_a}{r_a} = 0.0905\ m^3$$

$$L = 0.0905(10^6)/78.5 = 1153\ cm$$

P4.05.23. ACETONE PYROLYSIS

The pyrolysis of gaseous acetone is done in a tubular flow reactor 85 cm long and 4 cm ID at 520 C and 1 atm. The specific rate is k = exp(34.34-34222/T), 1/sec. Find the flow rate for a conversion of 35%.

$CH_3COOCH_3 \Rightarrow CH_2CO + CH_4$, $A \Rightarrow B + C$

$k = 0.5342$/sec at 793 K

$V_r = 85(16)(0.7854) = 1068$ cc

$n_t = 2n_{a0}-n_a$

$V' = (2n_{a0}-n_a)(RT/\pi) = [0.082(793)](2n_{a0}-n_a)$

$$r_a = k(n_a/V') = 0.5342\ \frac{n_a}{65.03(2n_{a0}-n_a)} = \frac{1-x}{121.7(1+x)}$$

$x = 1 - n_a/n_{a0}$

$$-n_{a0}dx = r_a dV_r$$

$$V_r/n_{a0} = \int_0^{0.35} \frac{dx}{r_a} = 121.7(0.5116) = 62.26 \text{ liters/(gmol/s)}$$

$$n_{a0} = 1.068(3600)/62.26 = 61.75 \text{ gmol/hr}$$

P4.05.24. INCREASE OF FLOW RATE AND TEMPERATURE

The flow through a plug flow reactor effecting a first order reaction is increased by 20%. In order to maintain conversion at its former value, the temperature is to be raised. If the reaction has an activation energy of 4 kcal/gmol and the initial temperature is 150 C, what will be the new temperature? Would the required elevation in temperature be different if the reactor were a CSTR?

Material balance on the PFR is

$$-dn_a = n_{a0}dx = r_a dV_r = kC_{a0}(1-x)dV_r$$
$$= k_0 C_{a0}(1-x) \exp(-4000/T)$$

$$\frac{n_{a0}}{1.2n_{a0}} = \frac{\exp(-4000/423.2)}{\exp(-4000/T)}$$

$T = 431.3$ K, 158.1 C

In a CSTR the residence time is decreased by a factor 1.2.

$$C_0/C = 1 + \tau \exp(-4000/423.2) = 1 + (\tau/1.2) \exp(-4000/T)$$

This is the same relation for temperature as in the PFR.

P4.05.25. BUTENE CRACKING

Butene cracks thermally according to, $C_4H_8 \Rightarrow C_4H_6 + H_2$, and the reaction is first order,

$$r = kp_{C_4H_8} \text{ lbmols/liter-hr}$$

The feed consists of α mols of steam per mol of butene. Derive the equation for the volume of a plug flow reactor in terms of the fractional conversion, x, of butene.

$$n_t = n_s + n_a + 2(n_{a0}-n_a) = (2+\alpha)n_{a0}-n_a = (1+\alpha+x)n_{a0}$$

$$p_a = (n_a/n_t)\pi = \frac{1-x}{1+\alpha+x}\pi$$

For the flow reactor,

$$-dn_a = n_{a0}dx = r_a dV_r$$

$$V_r/n_{a0} = \int_0^x \frac{1+\alpha+x}{k\pi(1-x)}dx = \frac{1}{k\pi}[-x + (2+\alpha) \ln \frac{1}{1-x}]$$

P4.05.26 REVERSIBLE REACTION WITH HEAT TRANSFER

It is proposed to carry out to within 90% of equilibrium a gas phase reaction, $A \Leftrightarrow B$, which is first order, by passage through a plug flow reactor at 500 C and 1 atm. The pure reactant enters at 350 C and the available data are,

$$\Delta H_{r298} = -20 \text{ kcal/gmol}$$

$$\Delta G^o_{298} = -13 \text{ kcal/gmol}$$

Forward specific rate is 0.111/hr at 300 C with an activation energy of +30 kcal/gmol. The heat capacities of A and B are 8.3 and 12.4 cal/gmol-K respectively. Find the conversion, the residence time, and the amount of heat removed per mol of feed.

The heat of reaction at T,

$$\Delta H_T = \Delta H_{298} + \int_{298}^T \Delta C_p dT = -20000 + (12.4-8.3)(T-298)$$

$= -21222 + 4.1T$ (1)

$\Delta H_{773} = -18053$

Equilibrium constant,

$$K_{298} = \exp[-\Delta G^{\circ}_{298}/(1.987)(298)] = \exp(21.955)$$

$$\ln(K_{773}/K_{298}) = \int_{298}^{773} \frac{\Delta H_T}{RT^2}\,dT = -20.06$$

$$\ln K_{773} = 21.95 - 20.06 = 1.89$$

$$K_{773} = 6.62$$

Specific rate,

$$\ln \frac{k_{773}}{0.111} = \frac{30000}{1.987}\left(\frac{1}{573} - \frac{1}{773}\right) = 6.8173$$

$$k_{773} = 101.4/\text{hr}$$

Rate equation,

$$r_a = 101.4(C_a - C_b/6.62) = 101.4[C_a - (C_{a0}-C_a)/6.62] \qquad (1)$$

$$C_{ae} = C_{a0}/7.62 = 0.1312\ C_{a0}$$

At 90% of equilibrium conversion,

$$C_a/C_{a0} = 0.1 + 0.9(0.1312) = 0.2181$$

For the flow reactor,

$$f = C_a/C_{a0}$$

$$-V'\,dC_a = r_a dV_r$$

$$\tau = V_r/V' = \int_{0.2181}^{1} \frac{df}{101.4[f-(1-f)/6.62]}$$

$$= 0.0197\ \text{hr},\ 70.9\ \text{sec}$$

Heat transfer,

Q = heat of reaction - sensible heat gain

$$= 18053\ n_{a0}(1-f) - [8.3n_a + 12.4n_b](500-350)$$

$$f = 0.2181$$

$$Q/n_{a0} = 18053(1-f) - [8.3f + 12.4(1-f)](500-350)$$

$$= 12389\ \text{cal/gmol}$$

P4.05.27. REVERSIBLE REACTION. MINIMUM REACTOR SIZE

A first order reversible reaction, $A \Leftrightarrow B$, is carried out in a plug flow reactor, starting with pure A. The specific rate and equilibrium constants are functions of temperature,

$$k = A\exp(-E/T)$$

$$K_e = B\exp(-H/T)$$

(a) Find the equation of the reactor volume in terms of fractional conversion, x. (b) Find the relation between T and x that will result in a minimum reactor volume.

$$r_a = k[C_a - (C_{a0}-C_a)/K_e] = kC_{a0}[(1-1/K_e)x-1]$$

Plug flow reactor,

$$V'C_{a0}dx = r_a dV_r$$

$$V_r/V' = \int_0^x \frac{C_{a0}}{r_a}\,dx = \frac{K_e}{k(K_e-1)} \ln[1-(1-1/K_e)x] \qquad (1)$$

Substitute the temperature dependencies.

$$V_r/V' = \frac{(B/A)\exp[(E-H)/T]}{\exp(-H/T)-1} \ln\{1-[1-\exp(H/T)]x\} \qquad (2)$$

The minimum V_r is found after solving $dV_r/dT = 0$, but the task appears quite formidable algebraically.

P4.05.28. REACTOR DIMENSIONS

An organic compound undergoes pyrolysis in plug flow through a heated tube in a furnace. At the reaction temperature of 675 C, the specific rate is $k = 0.1721/\text{sec}.$. The furnace supplies $2(10^6)$ Btu/hr, its temperature is 1000 C and the heat transfer coefficient is 6 Btu/(hr)sqft)(F). The conversion is 30% and the volumetric throughput at reaction conditions is 150 cuft/sec. Find the dimensions of the reactor.

$$Q = 2(10^6) = UA\Delta T = 6(1.8)(1000-675)A$$

$$A = 569.8 \text{ sqft}$$

$$= 3.1416DL \qquad (1)$$

For the flow reactor, assuming no change in the number of mols,

$$r_a = k(n_a/V') = k\frac{n_{a0}(1-x)}{V'}$$

For the flow reactor,

$$n_{a0}dx = r_a dV_r$$

$$V_r = \frac{V'}{k}\int_0^{0.3}\frac{dx}{1-x} = \frac{V'}{0.1721}\ln(1/0.3) = 2.0725V', \text{ sec}$$

$$V_r = 2.0725(150) = 310.87 \text{ cuft}$$

$$= 0.7854D^2L \qquad (2)$$

Between Eqs (1) and (2),

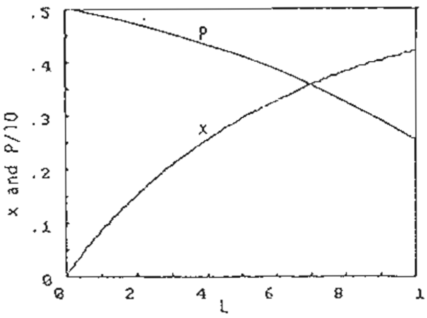
$$D = 2.182 \text{ ft}$$

$$L = 83.1 \text{ ft}$$

P4.05.29. PRESSURE DROP AND CONVERSION

A reaction, A ⇒ 3B, takes place in a tbular flow reactor at constant temperature and an inlet pressure of 5 atm. The rate equation is

$$r_a = k(n_a/V') = \frac{kP}{RT}\left(\frac{n_a}{3n_{a0}-n_a}\right) = \frac{kP}{RT}\left(\frac{1-x}{1+2x}\right)$$



When put into the plug flow equation,

$$n_{a0}dx = \frac{kP}{RT}\left(\frac{1-x}{1+2x}\right)AdL$$

or

$$\frac{dx}{dL} = 0.02\,\frac{P(1-x)}{1+2x}$$

where several factors have been combined into the numerical coefficient.

The pressure gradient due to friction is proportional to the flowing mol rate, 1+2x, and inversely to the density or the pressure. Here again several factors are incorporated in a numerical coefficient, making

$$-\frac{dP}{dL} = 0.6\,\frac{1+2x}{P}$$

The numbered equations are integrated and plotted. They show the typical fall in pressure as conversion with an increase in the number of mols proceeds.

P4.05.30. PRESSURE DROP

The gas phase reaction, A ⇒ 2B, is conducted at 600 R in a tubular flow reactor of diameter 0.2 ft. The feed contains 50 mol% A of molecular weight 40 and the balance inert of molecdular weight 20. Charge rate is 9000 lb/hr, inlet pressure is 5 atm, specific rate is 6000/hr and viscosity is 0.05 lb/ft-hr. Obtain the relation between conversion, pressure drop and volume of the reactor.

$n_{to} = 300$ mols/hr
$n_{a0} = 150$
$n_t = 3n_{a0} - n_a$

$$dL = dV_r/(0.7854)(0.15)^2 = 56.59dV_r \qquad (1)$$

$$r_a = k(n_a/V') = \frac{kP}{RT}\left(\frac{n_a}{3n_{a0}-n_a}\right) = 13.698P\left(\frac{n_a}{3n_{a0}-n_a}\right)$$

Flow reactor equation,

$$-dn_a = r_a dV_r = 13.698P\left(\frac{n_a}{3n_{a0}-n_a}\right)dV_r \qquad (2)$$

The pressure drop due to friction,

$$-dP = \frac{f\rho u^2}{2gD}\,dL = 0.046\left(\frac{\mu}{Du\rho}\right)^{0.2}\left(\frac{\rho u^2}{2gD}\right)dL$$

Applying the ideal gas law and dividing by 2118 to convert psi to atm,

$$-dP = \frac{3.228(10^{-5})(3n_{a0}-n_a)}{P}\,dL$$

$$= \frac{0.001027(3n_{a0}-n_a)}{P}\,dV_r \qquad (3)$$

Eliminate dV_r between Eqs (2) and (3).

$$\frac{dP}{dn_a} = \frac{7.497(10^{-5})}{P^2}\left(\frac{(450-n_a)^2}{n_a}\right) \qquad (4)$$

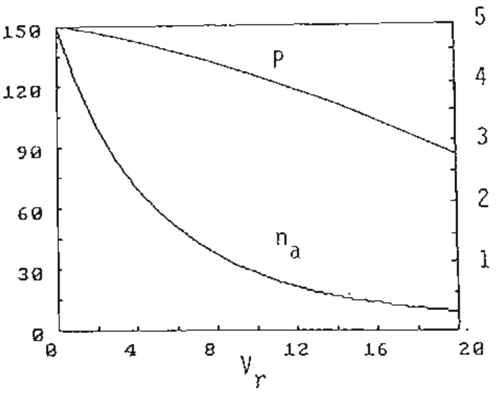
The variables in Eq (4) are separable. Some of the integrated results of P and n_a are tabulated. Then V_r is found with Eq (2), using trapezoidal integration. Some of those results also are shown.

When $n_a = 10$, $P = 3.0174$ atm, $V_r = 19.38$ cuft.

For comparison, at constant pressure, $P = 5$, the integral of Eq (2) is $V_r = 15.75$ cuft.

The graph is of the direct solution of Eqs (2) and (3) by software ODE, a much simpler procedure when the material is available.

n_a	P	V_r
150	5	0
125	4.945	0.838
100	4.866	1.960
75	4.743	3.548
50	4.529	6.030
40	4.391	7.514
30	4.189	9.553
20	3.850	12.72
10	3.017	19.38



P4.05.31. COMPLEX ADIABATIC REACTION

The gas phase reactions, $A + B \Rightarrow 2C$ and $A + C \Rightarrow D$, are run adiabatically at 5 atm with inlet temperature 350 K, $n_{a0} = 0.9$ and $n_{b0} = 0.3$. Specific rates are

$$k_1 = \exp\left(1.9152 - \frac{1091.7}{T}\right) \tag{1}$$

$$k_2 = \exp\left(1.2222 - \frac{1091.7}{T}\right) \tag{2}$$

Thermal data are

$$\Delta H_{ra} = -3000, \qquad \Delta H_{rb} = -1500, \qquad C_{pa} = C_{pb} = 10,$$
$$C_{pc} = C_{pd} = 15$$

For the mixture,

$$\begin{aligned} \sum n_i C_{pi} &= 10(n_a + n_b) + 15(n_c + n_d) \\ &= 10(n_a + n_b) + 15(0.6 + n_b - n_a) \\ &= 9 + 10n_a - 20n_b \end{aligned} \tag{3}$$

The volumetric flow rate is

$$F = \frac{zRT}{P} n_t = \frac{0.082T}{5} n_t = 0.0164T(0.6 + n_a - n_b) \tag{4}$$

The adiabatic heat balance is

$$\begin{aligned} &\Delta H_{ra}(n_{a0} - n_a) + \Delta H_{rb}(n_{b0} - n_b) = \sum n_i C_{pi}(T - T_0) \\ &-3000(0.9 - n_a) - 1500(0.3 - n_b) \\ &\quad = (9 + 10n_a - 20n_b)(T - 350) \end{aligned}$$

or

$$T = 350 + \frac{1500(2.1 - 2n_a - n_b)}{9 + 10n_a - 20n_b} \tag{5}$$

The two rate equations are

$$-\frac{dn_a}{dV_r} = n_a \frac{k_1 n_b + k_2(n_a - 3n_b)}{F^2} \tag{6}$$

$$-\frac{dn_b}{dV_r} = \frac{k_1 n_a n_b}{F^2} \tag{7}$$

Equations (1), (2), (4), and (5) are substituted into (6) and (7), and the two differential equations are solved simultaneously.

P4.05.32. ADIABATIC PFR, SPACE VELOCITY

A gas reaction, A ⇒ 2B, occurs at adiabatic flow conditions at 2 atm, starting with pure A at 600 R. Heat capacities are 20 and 15 Btu/lbmol-F, heat of reaction is $\Delta H_r = -2000$ Btu/lbmol A converted and

$$k = \exp(5.02-3000/T),\ 1/\text{sec.} \qquad (1)$$

Find the true contact time for a conversion of 80%.

$n_{a0} = n_{t0} = 1$

$n_t = n_{a0}(1+x)$

$x = 1-n_a/n_{a0}$

Sensible heat change = heat of reaction

$[20(1-x) +15(2x)](T-600) = 2000x$

$$T = 600 + \frac{200x}{2+x} \qquad (2)$$

$$V' = n_tRT/\pi = (0.73/2)(1+x)T= 0.365(1+x)T \qquad (3)$$

Flow reactor equation,

$-n_{a0}dx = r_a dV_r = k(n_a/V')dV_r$

$$V_r/n_{a0} = \int_0^{0.8} \frac{0.365T(1+x)}{k(1-x)}\,dx \qquad (4)$$

Solve Eqs (1), (2) and (4) simultaneously. The solution by ODE is

$T = 657.1$

$V_r/n_{a0} = 409$ cuft/(lbmol/sec)

$\Rightarrow 409/359 = 1.14$ cuft/(SCF/sec)

Space velocity = (SCF/sec)/(cuft of reactor)

$= 1/1.14 = 0.876$/sec

P4.05.33. SPLIT FLOW OF FEED.

The reaction is A + B ⇒ D. Feed enters at 1500 R at the rate of 20 lbmols/hr containing 40 mol% each of A and B and 20% inerts. Pressure is 5 atm. Heat input is 12000 Btu/cuft of reactor volume, heat of reaction at 500 R is +23000 Btu/lbmol of A reacted. Heat capacity of reactants, 6; of product, 10; of inerts, 5 Btu/lbmol-R. The specific rate is

$$k = \exp(32.52-29870/T),\ \text{cuft/lbmol-hr} \qquad (1)$$

Two modes of operation are to be studied: (a) All of the feed goes to the inlet. (b) Half of the feed goes to the inlet and the other half to the middle of the reactor. The reactor is of sufficient size to give 50% conversion when all of the material is charged at the inlet. What conversion is obtained by the split flow arrangement?

x = fraction of A that is converted

$n_t = n_i+n_a+n_b+n_d = 1.5n_{a0}+n_a = n_{a0}(2.5-x)$

$$V' = \frac{0.73T}{5} n_t = 0.146Tn_{a0}(2.5-x)$$

$$r_a = kn_an_b/V'^2 = k(n_a/V')^2 = k\left(\frac{1-x}{0.146T(2.5-x)}\right)^2$$

Flow reactor equation,

$$V_r = n_{a0} \int_0^x \frac{1}{k} \left[\frac{0.146T(2.5-x)}{1-x}\right]^2 dx \qquad (2)$$

Heat balance with total feed to inlet,

$$(20)(5.8)(1500-500) = [16(1-x)(6)+ 4(5)+8x(10)](T-500) + 23000(8)x-12000V_r$$

$$T = 500 + \frac{5800-9200x+600V_r}{5.8-0.8x} \qquad (3)$$

With half feed at the inlet,

$$10(5.8)(1500-500) = [8(1-x)(6) + 2(5)+4x(10)](T_2-500) + 23000(4)x -12000V_r$$

$$T = 500 + \frac{5800-9200x+1200V_r}{5.8-0.8x} \qquad (4)$$

For the second half, T_2 and x_2 and V_{r2} at midpoint,

$$10(5.8)(1500-500) + 10(5.8-0.8x_2)(T_2-500)$$
$$= [16(6)(1-x) + 4(5)+8(10)x](T-500)+23000(8)(x-0.5x_2)$$
$$-12000(V_r-V_{r2})$$

$$T = 500+ \frac{2900+(2.9-0.4x_2)(T_2-500)-9200(x-0.5x_2)+600(V_r-V_{r2})}{5.8-0.8x} \qquad (5)$$

Equations (2) and (1) together with the appropriate temperature equation, (3) or (4) or (5), are solved by POLYMATH. The full flow and the split flow operations give the same conversion in the same size reactors. At half flowrate, the values are $x_2 = 0.5$ and $T_2 = 1521$ at the midpoint, the same as the final values of the full stream.

Note: The initial conditions for integration of the second half operation are $x_0 = 0.5(0+0.5) = 0.25$ and $V_{r0} = 0.5(7.1908)$.

	Full		First Half		Second Half	
x	V	t	V	t	V	t
0.0	0.0	1500.0	3.5950	1510.1	0.0	1500.0
0.0250	0.2221	1486.7	3.7283	1505.7	0.1111	1486.7
0.0500	0.4845	1477.6	3.8712	1502.2	0.2422	1477.6
0.0750	0.7810	1471.9	4.0227	1499.7	0.3905	1471.9
0.1000	1.1040	1469.0	4.1818	1498.0	0.5520	1469.0
0.1250	1.4463	1468.0	4.3475	1497.0	0.7232	1468.0
0.1500	1.8020	1468.5	4.5188	1496.6	0.9010	1468.5
0.1750	2.1667	1470.0	4.6948	1496.7	1.0833	1470.0
0.2000	2.5375	1472.1	4.0740	1497.2	1.2687	1472.1
0.2250	2.9126	1474.7	5.0581	1498.1	1.4563	1474.7
0.2500	3.2908	1477.6	5.2441	1499.3	1.6454	1477.6
0.2750	3.6715	1480.8	5.4325	1500.8	1.8358	1480.8
0.3000	4.0543	1484.3	5.6223	1502.4	2.0271	1484.3
0.3250	4.4390	1488.0	5.8140	1504.2	2.2195	1488.0
0.3500	4.8255	1491.9	6.0073	1506.2	2.4127	1491.9
0.3750	5.2139	1496.1	6.2018	1508.4	2.6069	1496.1
0.4000	5.6043	1500.5	6.3976	1510.7	2.8021	1500.5
0.4250	5.9968	1505.1	6.5944	1513.1	2.9984	1505.1
0.4500	6.3916	1510.1	6.7923	1515.7	3.1958	1510.1
0.4750	6.7889	1515.4	6.9911	1518.4	3.3944	1515.4
0.5000	7.1889	1521.0	7.1908	1521.1	3.5945	1521.0

P4.05.34. BROMINATION OF ETHYLENE

The gas phase bromination of ethylene,

$C_2H_4 + Br_2 \Leftrightarrow C_2H_4Br_2$, $A + B \Leftrightarrow C$

has the rate equation

$$r_a = 500(n_an_b/V'^2) - 0.032(n_c/V'), \quad \text{gmols/liter-hr}$$

A tubular reactor is charged with 600 m^3/hr of gas containing 30 mol% ethylene, 60% bromine and 10% inerts at 600 K and 1.5 atm. Find the reactor volume for 60% conversion of ethylene.

$$n_{t0} = \frac{600000(273)(1.5)}{22.4(600)} = 18281 \text{ gmol/hr}$$

$n_{a0} = 5484$ gmols/hr

$n_{b0} = 10969$ gmols/hr

$n_b = n_{b0}-n_{a0}+n_a = 5485 + n_a$

$n_c = n_{a0}-n_a = 5484-n_a$

$n_t = n_a+n_b+n_I+(n_{a0}-n_a) = 12797 + n_a$

$$V' = n_tRT/\pi = \frac{0.082(600)n_t}{1.5} = 32.8(12797+n_a) \qquad (1)$$

At equilibrium,

$$\frac{500n_a(5485+n_a)}{32.8(12797+n_a)} - 0.032(5484-n_a) = 0$$

$n_{ae} = 26.65$

At 60% of equilibrium conversion,

$n_a = 0.4(5484)-0.6(26.65) = 2178$

The reactor volume is given by integration of the flow reactor equation,

$$V_r = \int_{2178}^{5484} \frac{1076(12797+n_a)^2}{500n_a(5485+n_a)-1.05(12797+n_a)(5484-n_a)}\, dn_a$$

$= 59072$ liters, 59.07 m^3

P4.05.35. ETHYLENE GLYCOL

Ethylene glycol is made by reacting chlorohydrin with sodium bicarbonate,

$C_2H_5OCl + NaHCO_3 \Rightarrow C_2H_6O_2 + NaCl + CO_2$, $A + B \Rightarrow C + \ldots$

The specific rate is k = 5.2 liter/gmol-hr at 82 C. Equal molal quantities of the reactants are to be used. They are supplied as aqueous solutions, the bicarbonate as 15 wt% and the chlorhydrin as 30 wt%. Production of glycol is to be 20 kg/hr at 95% conversion. Specific gravity of the feed mixture is 1.02. Find the required reactor volumes of a PFR and of a CSTR.

The molecular weights of A, B and C are 80.52, 84.02 and 62.07.

$n_c = 20(1000)/62.07 = 322.22$ gmol/hr

$n_{a0} = 322.22/0.95 = 339.18$ gmol/hr, 27.31 kg/hr

$n_{b0} = 339.18$ gmol/hr, 28.50 kg/hr

$$\text{Water} = \frac{27.3(0.7)}{0.3} + \frac{28.5(0.85)}{0.15} = 225.21 \text{ kg/hr}$$

Total feed = water + n_{a0} + n_{b0} = 281.02 kg/hr

$V' = 281.02/1.02 = 275.51$ liters/hr, volumetric feed rate

$C_{a0} = n_{a0}/V' = 1.231$ gmol/liter

In plug flow,

$$V_r = \int_{C_a}^{C_{a0}} \frac{V'dC_a}{kC_a^2} = \frac{V'}{kC_{a0}}(\frac{C_{a0}}{C_a} - 1) = \frac{275.51}{5.2(1.231)}(1/0.05 - 1)$$

$= 817.7$ liters

In a CSTR,

$$C_{a0} = C_a + \frac{kV_rC_a^2}{V'}$$

$$V_r = \frac{1.231(0.95)(275.51)}{5.2[0.05(1.231)]^2} = 16355 \text{ liters}$$

P4.05.36. TWO SECOND ORDER REACTIONS

The reactions, 2A ⇒ B and 2B ⇒ C, have the rate equations

$$dA/dt = -k_1A^2 \qquad (1)$$

$$dB/dt = 0.5k_1A^2 - k_2B^2 \qquad (2)$$

$$C = 0.25(A_0-A) - 0.5B \qquad (3)$$

with $A_0 = 2$, $k_1 = 1.2$ and $k_2 = 0.12$. Find the concentration profiles in a plug flow reactor.

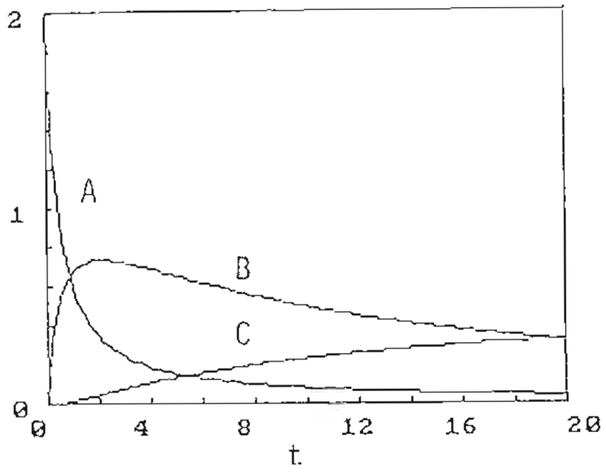
The integral of the first equation is

$$A = \frac{A_0}{1+k_1A_0t}$$

Then the second equation becomes

$$\frac{dB}{dt} = 0.5k_1\left(\frac{A_0}{1+k_1A_0t}\right)^2 - k_2B^2 \qquad (4)$$

Analytical integration cannot proceed past this stage, so the first three equations are solved numerically by ODE. B displays the characteristic peak of consecutive reactions.



P4.05.37. SEQUENCING PFR AND CSTR

The reversible reaction, 2A ⇔ B, has the rate equation,

$$r_a = 0.8[A^2 - 0.05(A_a+2B_0-A)], \quad \text{lbmol/cuft-hr}$$

A feed containing $A_0 = 1.5$ and $B_0 = 0.5$ is charged at the rate of 20 cuft/hr to a CSTR and a PFR in series. The overall conversion is to be 95% of equilibrium. One half of the conversion occurs in each reactor. Find the reactor volumes with the CSTR first in series, and with the reactors interchanged. Also compare with a single PFR for the entire conversion.

$$r_a = 0.8[A^2 -0.05(2.5-A)]$$

At equilibrium, $r_a = 0$ and $A_e = 0.329$. At 95% of equilibrium,

$$A_2 = 0.05(1.5)+0.95(0.329) = 0.3876$$

At the outlet of the first reactor,

$$A_1 = 0.3876+0.5(1.5-0.3876) = 0.9438$$

In the CSTR first,

$$1.5 = A_1+0.8\tau_s(A_1^2+0.05A_1-0.125)$$

$$\tau_s = 0.8552 \text{ hr}$$

In the PFR,

$$\tau_p = V_r/V' = \int_{0.3476}^{0.9438} \frac{dA}{0.8(A^2+0.05A-0.125)} = 3.196$$

For the two vessels,

$$V_{r,total} = V'(\tau_s+\tau_p) = 20(0.8552+3.1956) = 81.0 \text{ cuft}$$

In the PFR first,

$$\tau_p = \int_{0.9438}^{1.5} \frac{dA}{r_a} = 0.5179$$

In the CSTR with $A_1=0.9438$ and $A_2 = 0.3876$,

$$\tau_s = \frac{A_1-A_2}{0.8(A_2^2+0.05A_2-0.0125)} = 15.58$$

For the two vessels,

$$V_{r,total} = 20(0.5179+15.58) = 321.1 \text{ cuft}$$

For comparison, with a single PFR,

$$V_r = 20(0.5179+3.1956) = 74.21 \text{ cuft}$$

P4.05.38. PFR AND CSTR OF SEVERAL SIZES

A liquid phase reaction with rate equation $r = kA^2$ takes place with 50% conversion in a CSTR. (a) What will be the conversion if this reactor is replaced by one six times as large?

(b) What will be the conversion if the original reactor is replaced by a PFR of the same size?

The original material balance is

$$A_0 = A + k\tau A^2$$

$$1 = A/A_0 + k\tau A_0(A/A_0)^2$$

When $A/A_0 = 0.5$,

$$k\tau A_0 = 2$$

With a six-fold increase in the residence time

$$1 = A/A_0 + 6(2)(A/A_0)^2$$

$$A/A_0 = 0.25, \text{ or } 75\% \text{ conversion}$$

In plug flow,

$$-V'dA = kA^2dV_r$$

$$\tau = V_r/V' = \int_A^{A_0} \frac{dA}{kA^2} = \frac{1}{kA_0}(\frac{A_0}{A}-1)$$

$$A/A_0 = \frac{1}{1+k\tau A_0} = 0.333, \text{ or } 66.7\% \text{ conversion.}$$

P4.05.39. ETHANE CRACKING WITH ETHYLENE RECYCLE.

Ethane is pyrolyzed in a flow reactor at 1500 F and 2.87 atm.

$$C_2H_6 \Leftrightarrow C_2H_4 + H_2, \quad A \Leftrightarrow B + C$$

The rate equation is

$$r_a = 1.1(C_a - C_bC_c/K_e)$$

Equilibrium is represented by

$$K_p = 1.45 =(p_bp_c/p_a)_e$$

The operation is to be conducted until the relation between the partial pressures becomes

$$p_b p_c/p_a = 0.7(1.45) = 1.015$$

In order to study the repression of ethylene formation when the ethane is cracked along with other hydrocarbons, a test is proposed in which 20 mols of ethylene is to be charged along with 100 mols of ethane. If V_r/V' is to be kept the same in both cases, find how much less ethylene is formed in the recycle operation.

Without recycle:

$n_a =$ mols A/mol feed

$n_{a0} = n_{t0} = 1$

$n_b = n_c = 1-n_a$

$n_t = 2-n_a$

$$p_a = \frac{n_a}{2-n_a}\pi$$

$$p_b = p_c = \frac{1-n_a}{2-n_a}\pi$$

$$V = \frac{n_t RT}{\pi} = \frac{0.73(1960)}{2.87}(2-n_a) = 498(2-n_a)$$

The final composition is found from

$$\frac{p_a p_b}{p_c} = \frac{(1-n_a)^2}{n_a(2-n_a)(2.87)} = 0.7(1.45) = 1.015$$

$n_a = 0.485$ mols ethane/mol total feed

$\Rightarrow$ 51.5% of ethane converted (1)

Relation between equilibrium constants,

$K_p = K_c RT$

Rate equation,

$$r_a = k[\frac{n_a}{V} - \frac{n_b n_c}{V^2 K_c} = \frac{k}{V}[n_a - \frac{(1-n_a)^2}{K_p V/RT}] = \frac{k}{V}[n_a - \frac{(1-n_a)^2\pi}{K_p n_t}]$$

$$= \frac{1.1}{498(2-n_a)}[n_a - \frac{1.98(1-n_a)^2}{2-n_a}] \quad (2)$$

Flow reactor equation integrated by trapezoidal rule,

$-dn_a = r_a dV_r$

$$V_r = \int_{0.485}^{1} \frac{dn_a}{r_a} = 656 \text{ cuft/lbmol of charge} \quad (3)$$

With recycle, basis 1 mol of total feed, $V_r = 656$ cuft,

$n_{t0} = 1$

$n_{a0} = 0.833$

$n_{b0} - 0.167$

$n_t = 1.833-n_a$

$V = n_t RT/\pi = 498(1.833-n_a)$

$n_b = n_{b0}+n_{a0}-n_a = 1-n_a$

$n_c = n_{a0}-n_a = 0.833-n_a$

$$r_a = \frac{1.1}{498(1.833-n_a)}[n_a - \frac{1.98(1-n_a)(0.833-n_a)}{1.833-n_a}] \qquad (4)$$

Integrating by trapezoidal rule,

$$V_r = \int_{n_a}^{0.833} \frac{dn_a}{r_a} = 656 \text{ cuft/lbmol of feed}$$

The lower limit is established by trial as

$n_a = 0.4235$ mols ethane/mol total feed

$\Rightarrow$ 0.4235/0.833 = 0.5084 mols/mol ethane in charge

$\Rightarrow$ 49.16% conversion of ethane (5)

This is to be compared with 51.5% conversion without addition of ethylene to the feed.

P4.05.40. OPTIMUM TEMPERATURE OF REVERSIBLE REACTION

The reaction, 2A $\Leftrightarrow$ 2B, has the rate equation

$$r_a = k[(1-x)^2 - x^2/K_e]$$

with the temperature dependent constants

$k = \exp(17.2-5800/T)$

$K_e = \exp(-24.7+9000/T)$

Find the temperature at which the plug flow reactor volume is a minimum for a conversion of 90%.

The volume of a plug flow reactor is represented by the differential equation,

$$\frac{dV_r}{n_{a0}dx} = \frac{1}{r_a}$$

This is integrated by ODE for a range of temperatures. The tabulation of the results show a minimum size at T = 305.5.

T	V_r/n_{a0}	T	V_r/n_{a0}
310	132	305	77.34
309	123	304	78.5
308	85.0	303	80.2
307	79.1	302	83.0
306.5	77.9	301	86.1
306	77.31	300	89.8
305.5	77.16	295	115.5

P4.05.41. PENTANE ISOMERIZATION, PACKED BED

For the isomerization of n-pentane in a hydrogen atmosphere a proposed rate equation at 372 C is

$$r = 0.04(p_p/p_h)^{0.5} \text{ gmol converted/(gm catalyst)/(h)}$$

(Sinfelt et al, J Phys Chem 64 892, 1960). Another investigation is to be made at this temperature and 6.8 atm total pressure with a reactor 1 inch in diameter and 1 ft long. The catalyst used, Pt on alumina, has a bulk density of 187.5 lb/cuft. The volumetric feed rate is to be 12.3 Std cuft/min. What conversion can be expected with feeds composed of (a) 5% n-pentane and 95% hydrogen, (b) 20% n-pentane and 80% hydrogen?

Catalyst, W = 0.7854(187.5)/144 = 1.023 lb, 464.3 gm

n_{t0} = 12.5(60)/359 = 2.089 lbmol/hr, 948.5 gmol/h

x = fraction converted

$$p_p = \frac{n_{p0}}{n_{t0}}(1-x)\pi$$

$$p_h = \frac{n_{h0}}{n_{t0}}\pi$$

$$r = 0.04[\frac{n_{p0}(1-x)}{n_{h0}}]^{0.5}$$

Flow reactor,

$$-dn_p = n_{p0}dx = r\ dW$$

$$W = 464.3 = 25n_{p0} \int_0^x [\frac{n_{h0}}{n_{p0}(1-x)}]^{0.5}dx$$

Part (a):

$$n_{p0} = 0.05(948.5) = 47.4$$

$$464.3 = 25(47.4) \int_0^x (\frac{19}{1-x})^{0.5}\ dx$$

$$x = 0.088$$

Part (b):

$$n_{p0} = 0.2(948.5) = 189.7$$

$$464.3 = 25(189.7) \int_0^x (\frac{4}{1-x})^{0.5}dx$$

$$x = 0.0223$$

P4.05.42. PROPYLENE POLYMERIZATION IN A PACKED TOWER

Polymerization of propylene was conducted in a packed tower with gas flowing countercurrently to 98% liquid phosphoric acid (Bethea & Karchmer, Ind Eng Chem 48 370, 1956). Composition of the charge was 58% propylene, 41% propane, 0.5% butylene, 0.5% butane. On an average, 1 mol of polymer required 3.4 mols of propylene. The results at 360 F are tabulated. Check a first order rate equation.

Basis 1 mol of feed

n_i = 0.42 mols inert/mol of feed

n_{a0} = 0.52 mols propylene/mol of feed

$n_t = n_a+0.42+(n_{a0}-n_a)/3.4 = 0.5906+0.7059n_a$

R_g = 0.67 psi liters/gmol-°R, gas constant

$V = zn_tRT/\pi = 0.67(820)z(0.5906+0.7059n_a)/\pi$

$r = k(n_a/V)$

Flow reactor,

$$V_r/W = -\int \frac{V}{kn_a}\ dn_a = \frac{549.4z}{k\pi} \int_{n_a}^{0.58} \frac{0.5906+0.7059n_a}{n_a}\ dn_a$$

$$k = \frac{549.4zW/V_r}{\pi} \int$$

The values of z, W/V_r gmols/(hr)(liter) and π psia are experimental data. The calculated values of k are tabulated, and have a mean of 5.896, nearly enough constant to confirm a first order mechanism.

π	z	W/V_r	n_a	$\int$	k
415	0.83	3.25	0.0661	1.6458	5.8773
515	0.81	7.10	0.1705	1.0122	6.2100
717	0.67	7.22	0.0777	1.5420	5.7157
715	0.72	13.12	0.2291	0.7963	5.8000

P4.05.43. PROPYLENE POLYMERIZATION, TRICKLE FLOW REACTOR

Polymerization of propylene is catalyzed by phosphoric acid distributed as a thin film on quartz particles. An empirical equation is proposed (Langlois & Walkey, Petroleum Refiner, p 29, August 1942) for this conversion, namely,

$$\frac{18}{S} = \int_0^x \frac{(1-Bx)^2}{(1-x)^2+0.3x(1-x)}\,dx$$

$$B = (\text{mol fraction of monomer in feed})(1-\frac{\text{mol wt of monomer}}{\text{mol wt of polymer}})$$

S = space velocity = volume of gas feed at reactor T and P per volume of catalyst voids per hr. Voids assumed 42%.

x = fractional conversion of monomer.

A 50-50 mixture of propylene and propane is charged at 100 lbmol/hr at 300 F and 365 psia. Propylene conversion of 80% is required. A 25:75 mixture of C_6 and C_9 is made. Find the volume of catalyst needed at constant temperature.

$$S = \frac{100(379)(760)(14.7)}{(520(364.7)V_r} = \frac{2230}{V_r} \text{ (cuft/hr)/cuft of reactor}$$

Average molecular weight = 0.25(84)+0.75(126) = 115.5

$$B = 0.5(1-\frac{42}{115.5}) = 0.318$$

$$\frac{18\varepsilon V_r}{2230S} = \int_0^{0.8} \frac{(1-0.318x)^2}{(1-x)^2+0.3x(1-x)}\,dx = 2.166$$

$$V_r = \frac{2230(2.166)}{0.42(18)} = 639 \text{ cuft}$$

P4.05.44. METHANE FORMATION IN A CATALYST BED

For the kinetics of formation of methane according to

$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O$, $A + 4B \Leftrightarrow C + 2D$

an initial rate equation was developed with constants at 596 F and 30 atm as

$$r_0 = \frac{7p_ap_b^4}{(1+0.29p_a+1.73p_b)^5} \text{ lbmols methane/lbcatalyst-hr} \quad (1)$$

(Dew, White, Sliepcevich, Ind Eng Chem 47 140, 1955).This equation may be assumed to hold also over a small conversion range. Accordingly, find what amount of catalyst is needed to effect 20% conversion of CO_2 when the charge rate is 100 lbmol/hr of CO_2 and 400 lbmol/hr of H_2.

Stoichiometric balances,

$A_0-A = 0.25(B_0-B) = C = 0.5D$

$n_b = 4n_a$

$n_t = 3n_{a0}+2n_a$

$$p_a = 30n_a/n_t = \frac{30n_a}{3n_{a0}+2n_a} = \frac{30f}{3+2f}$$

$$p_b = 30n_b/n_t = \frac{120n_a}{3n_{a0}+2n_a} = \frac{120f}{3+2f}$$

$$f = n_a/n_{a0}$$

Flow reactor,

$$-dn_a = -n_{a0}df = -100df = rdW_c$$

$$W_c = 100 \int_1^{0.8} \frac{df}{r} \tag{2}$$

$$= 245.7 \text{ lb catalyst}$$

The partial pressures, the rate and the integrand are evaluated in the table. Integration is with the trapezoidal rule.

f	p_a	p_b	r	$1/r$
1	6	24	0.08204	12.189
0.95	5.816	23.265	0.08175	12.232
0.90	5.625	22.50	0.08143	12.280
0.85	2.426	21.70	0.08108	12.333
0.80	5.217	20.87	0.08066	12.398

P4.06.01 PFR WITH RECYCLE OF PRODUCT. NOTATION

The ratio of recycle stream to net product is $R = V_r'/V_p' = n_{ar}/n_{ap}$. Complete notation is on the sketch.

For the reaction $aA+bB \Rightarrow cC+dD$, $\delta_a = (c+d-a-b)/a$

Net product:

$$n_{ap} = n_{a0}(1-x_2)$$
$$n_{tp} = n_{t0}+\delta_a(n_{ao}-n_{ap})$$

Reactor inlet:

$$n_{a1} = n_{a0} + Rn_{ap} = n_{a0}[1+R(1-x_2)]$$

$$n_{t1} = n_{t0}+Rn_{tp}$$
$$V_1' = V_0'+RV_p'$$
$$C_{a1} = n_{a1}/V_1'$$

$$\Rightarrow \frac{C_{a0}+RC_{a2}}{1+R}, \quad \text{when } V_p' = V_0', \text{ or at constant density}$$

Reactor outlet:

$$C_{a2} = C_{ap}$$
$$n_{a2} = (R+1)n_{ap} = n_{a0}(R+1)(1-x_2)$$

Recycle:

$$n_{ar} = Rn_{ap}$$

In the reactor:

$$n_t = n_{t1}+\delta_a(n_{a1}-n_a)$$
$$V_t' = n_tR_gT/\pi$$

PFR, gas at constant pressure:

$$-dn_a = r_a dV_r = kC_a^q dV_r = k(n_a/V')^q dV_r$$

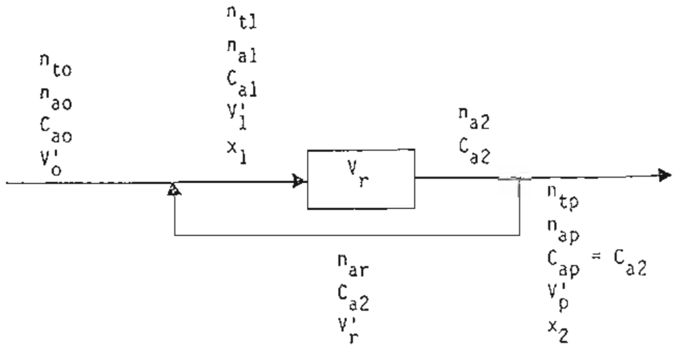
$$k(\pi/R_gT)^q V_r = \int_{n_{a2}}^{n_{a1}} (n_t/n_a)^q dn_a$$

PFR at constant density:

$$-(R+1)dC_a = kC_a^q dV_r$$

$$\frac{kV_r}{(R+1)V'_0} = \int_{C_{a2}}^{C_{a1}} \frac{dC_a}{C_a^q}$$

$$C_{a1} = \frac{C_{ao}+RC_{a2}}{1+R}$$



P4.06.02. RECYCLE REACTOR AS A DIFFERENTIAL REACTOR

For a plug flow reactor with recycle ratio R, relate the concentration change across the reactor to the overall concentration change.

At the mixing point,

$$V'_0C_0 + RV'_0 = V'_0(R+1)C_1$$

or

$$C_0+RC_2+C_2-C_2 = (R+1)C_2$$

$$C_1-C_2 = \frac{C_0-C_2}{R+1}$$

or

$$\Delta C_{reactor} = \frac{\Delta C_{overall}}{R+1}$$

Thus, across the reactor the change in concentration (or of temperature) can be made as small as desired by adjusting R, regardless of the magnitude of the overall change.

Residence time, $\Delta t = V_r/(R+1)V' = \tau/(R+1)$

$$\text{Overall rate, } r = \frac{dC}{dt} \cong \frac{\Delta C}{\Delta t} = (R+1)\frac{C_1-C_2}{\tau}$$

P4.06.03. SPECIFIC RATE FROM RECYCLE DATA

A reaction, $2A \Rightarrow B$, is conducted in the gas phase at 150 psia and 300 F in a PFR with recycle. The recycle ratio is R = 20. The reactor volume is 0.2 cuft. When the fresh feed rate is 1 lbmol/hr of pure A, 60% conversion is attained. Find the specific rate.

In the notation of problem P4.06.01,

$$n_{a0} = 1$$
$$n_{ap} = n_{a0}(1-x) = 0.4$$
$$n_{tp} = n_{t0}+\delta_a(n_{a0}-n_{ap}) = 1-0.5(1-0.4) = 0.7$$
$$n_{t1} = n_{t0}+Rn_{tp} = 1+20(0.7) = 15$$
$$n_{a2} = (R+1)n_{ap} = 8.4$$
$$n_{a1} = n_{a0}+Rn_{ap} = 1+20(0.4) = 9.0$$
$$n_t = n_{t1}+\delta_a(n_{a1}-n_a) = 15-0.5(9-n_a) = 10.5+0.5n_a$$

Substitute into the flow reactor equation,

$$k(\pi/R_gT/\pi)^2V_r = \left(\frac{150}{10.73(760)}\right)^2(0.2)k = 6.767(10^{-4})k$$

$$= \int_{n_{a2}}^{n_{a1}}(n_t/n_a)^2dn_a = \int_{8.4}^{9.0}\left(\frac{10.5+0.5n_a}{n_a}\right)^2 dn_a$$

$$= 1.7494$$

$$k = 2585 \text{ cuft/lbmol-hr}$$

P4.06.04. RECYCLE RATIO AND VESSEL SIZE

A gas phase reaction, $2A \Rightarrow B$, is conducted with recycle as on the sketch of problem P4.06.01. Feed is pure A at rate $n_{a0} = 2$. Find the following:

(a) Reactor size as a function of recycle ratio for a conversion of 80%.

(b) How the conversion varies with recycle ratio and with the reactor size fixed at the value when 80% conversion is attained without recycle.

(c) The conversion with infinite recycle ratio at the same vessel size as in part (b).

$n_{t0} = n_{a0} = 2$

$n_{ap} = n_{a0}(1-x) = 2(1-x)$

$n_{a1} = n_{a0}+Rn_{ap}$

$n_{t1} = n_{t0}+Rn_{tp} = n_{a0}+0.5R(n_{a0}+n_{ap})$

$n_t = n_{t1}+\delta_a(n_{a1}-n_a) = n_{t1}-0.5(n_{a1}-n_a) = 0.5[(R+1)n_{a0}+n_a]$

For a plug flow reactor,

$$k(\pi/RT)^2V_r = \beta V_r = \int_{n_{a2}}^{n_{a1}} (n_t/n_a)^2 dn_a$$

$$= \int_{n_{a2}}^{n_{a1}} \left(\frac{n_{a0}(R+1)+n_a}{2n_a}\right)^2 dn_a \qquad (1)$$

$\beta = k(\pi/RT)^2$

When $x = 0.8$ and $R = 0$,

$$\beta V_r = \int_{0.4}^{2.0} \left(\frac{2+n_a}{2n_a}\right)^2 dn_a = 4.010$$

Part (a): Integrate Eq (1) with these integration limits.

$x = 0.8$

$n_{a1} = n_{a0}[1+R(1-x)] = 2(1+0.2R]$

$n_{a2} = n_{a0}(R+1)(1-x) = 0.4(R+1)$

The values of βV_r are tabulated for several values of R when $x = 0.8$.

Part (b): The value of the integral is fixed at $\beta V_r = 4.010$. Estimate values of x until one is found that results in the correct value of the integral. These values of x and the corresponding integration limits also are tabulated.

Part (c): When the recycle ratio is infinite the performance is that of a CSTR. Then,

$n_t = 0.5(n_{a0}+n_a) = 0.5(2+n_a)$

$$n_{a0} = 2 = n_a+kV_r(\pi/RT)^2(n_a/n_t)^2 = n_a + 4.01\left(\frac{2n_a}{2+n_a}\right)^2$$

$n_a = 0.767,\ x = 0.617$

R	x	n_{ap}	n_{a1}	n_{a2}	βV_r
0	0.8	0.4	2	0.4	4.01
1	0.8	0.4	2.4	0.8	5.93
	0.718	0.564	2.564	1.128	3.99
2	0.8	0.4	2.8	1.2	7.23
	0.685	0.630	3.26	1.89	3.98
5	0.8	0.4	4.0	2.4	9.47
	0.652	0.696	5.48	4.176	4.01
20	0.8	0.4	10.0	8.4	12.46
	0.626	0.748	16.96	4.176	4.00
∞	0.617	0.767			4.01

P4.06.05. RECYCLE WITH STREAMS OF CONSTANT DENSITY

The liquid phase reaction, 2A ⇒ B, is conducted in a PFR with recycle. The density remains constant. Find how conversion and the reactor size depend on the recycle ratio.

In the notation of the sketch of P4.06.01,

$$C_{a2} = C_{a0}(1-x_2)$$

$$C_{a1} = \frac{n_{a0}+Rn_{a2}}{V'+RV'} = \frac{C_{a0}+RC_{a2}}{1+R}$$

For the plug flow reactor,

$$-dn_a = -(R+1)dC_a = kC_a^2\, dV_r$$

$$\beta = \frac{kC_{a0}V_r}{V'} = \frac{C_{a0}}{R+1}\int_{Ca2}^{C_{a1}} \frac{dC_a}{C_a^2} = \frac{1}{R+1}\left(\frac{C_{a0}}{C_{a2}} - \frac{C_{a0}}{C_{a1}}\right)$$

$$= \frac{1}{R+1}\left(\frac{1}{1-x_2} - \frac{R+1}{1+R(1-x_2)}\right)$$

Solutions are tabulated for several values of R: (a) The values of x at constant V_r, or $\beta = 4.0$

. (b) The values of V_r at x = 0.8.

R	x_2	β		x_2	β
0	0.8	4.0		0.8	4.0
1	0.719	4.0		0.8	6.67
2	0.685	4.0		0.8	8.57
5	0.648	4.0		0.8	12.0
10	0.631	4.0		0.8	14.67

P4.06.06. RECYCLE PFR AS R ⇒ ∞

Show that the performance of a PFR with recycle reduces to that of a CSTR when the density is constant.

At the inlet to the reactor,

$$C_{a1} = \frac{C_{a0}+RC_{a2}}{R+1}$$

$$-(R+1)V'dC_a = kC_a^q\ dV_r$$

$$\frac{kV_r}{(R+1)V'} = \frac{k\tau}{R+1} = \int_{C_{a2}}^{C_{a1}} \frac{dC_a}{C_a^q} \qquad (1)$$

For first order, q = 1,

$$\frac{k\tau}{R+1} = \ln \frac{C_{a0}+RC_{a2}}{(R+1)C_{a2}}$$

$$\frac{1}{R+1}\left(\frac{C_{a0}}{C_{a2}} + R\right) = \exp\left(\frac{k\tau}{R+1}\right)$$

$$\frac{C_{a0}}{C_{a2}} = -R + (R+1)[1 + \frac{k\tau}{R+1} + \frac{1}{2}\left(\frac{k\tau}{R+1}\right)^2 + \ldots)$$

$$\Rightarrow 1+k\tau,\ \text{as } R \Rightarrow \infty \qquad (2)$$

which is the familiar CSTR result for a first order reaction.

For second order, Eq (1) becomes

$$\frac{k\tau}{R+1} = \frac{1}{C_{a2}} - \frac{1}{C_{a1}} = \frac{1}{C_{a2}} - \frac{R+1}{C_{a0}+RC_{a2}}$$

Multiply by C_{a2}^2 and rearrange.

$$k\tau C_{a2}^2 = (R+1)[C_{a2} - \frac{(R+1)C_{a2}^2}{C_{a0}+RC_{a2}})$$

$$= \frac{R+1}{C_{a0}+RC_{a2}}[C_{a0}C_{a2} + RC_{a2}^2 - (R+1)C_{a2}^2]$$

$$\Rightarrow C_{a0} - C_{a2},\quad \text{as } R \Rightarrow \infty \qquad (3)$$

which is the correct CSTR equation of a second order reaction.

P4.06.07. RECYCLE REACTOR AND CSTR BATTERY

Find the recycle ratio that will give the same conversion as an n-stage CSTR for a first order reaction with $k\tau = 1$ and $k\tau = 5$.

The performance of an n-stage battery with total residence time τ is represented by

$$C_0/C = (1+k\tau/n)^n$$

Combine this with the equation of the recycle reactor derived in problem P4.06.06,

$$-R + (R+1)\exp\left(\frac{k\tau}{R+1}\right) = (1+k\tau/n)^n$$

Corresponding values of R and n are tabulated for the two prescribed values of $k\tau$.

n	R, $k\tau$=1	R, $k\tau$=5
1	∞	∞
1.1	13.0	22.1
1.5	2.62	4.67
22	1.32	2.45
5	0.34	0.69
10	0.15	0.32
∞	0	0

P4.06.08. HEAT AND MATERIAL BALANCES OF RECYCLE REACTOR

The changes in temperature and concentration of an adiabatic reactor are to be found in terms of the recycle ratio.

The composite feed concentration is

$$C_1 = \frac{C_0+RC_2}{R+1}$$

The change in concentration across the reactor is related to the change over the entire system by

$$C_1-C_2 = \frac{C_0+RC_2}{R+1} - C_2 = \frac{C_0-C_2}{R+1} \qquad (1)$$

At constant density and heat capacity the inlet temperature is

$$T_1 = \frac{T_0+RT_2}{R+1}$$

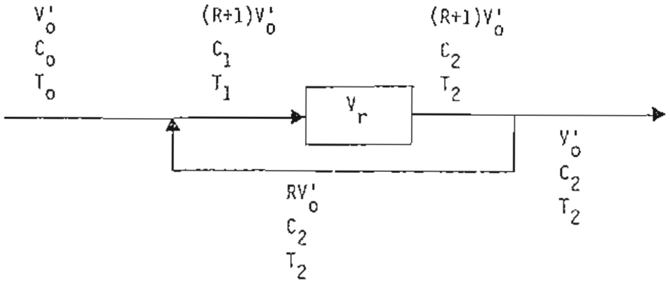
and the adiabatic heat balance is

$$-\Delta H_r V'(C_0-C_2) = \rho C_p(R+1)V'(T_1-T_2)$$

or

$$T_1-T_2 = \frac{T_0-T_2}{R+1} = \frac{-\Delta H_r}{\rho C_p(R+1)}(C_0-C_2) = \frac{-\Delta H_r}{\rho C_p}(C_1-C_2)$$

Thus, the changes in concentration and temperature across the reactor can be made as small as desired by adjusting the recycle ratio.



P4.06.09. ADIABATIC PFR WITH RECYCLE

In an adiabatic PFR the product is recycled after cooling to the 350 K temperature of the fresh feed. The reaction is 2A ⇒ B. Fresh feed concentration is $C_{a0} = 2$. The specific rate is

$$k = \exp(21-8000/T) \qquad (1)$$

and the temperature depends on the concentrations by the equation

$$T = 350 + 30(C_{a1}-C_a) \qquad (2)$$

Examine two cases for several values of R: (a) With outlet concentration $C_{a2} = 0.05$, find V_r/V'_0 and the outlet temperature. (b) With V_r/V'_0 the same as in the case with $R = 0$ and $C_{a2} = 0.05$, find the outlet temperature and the values of C_{a1} and C_{a2}.

x_2 = overall fractional conversion

$$C_{a1} = \frac{C_{a0}+RC_{a2}}{R+1} = \frac{2[1+R(1-x_2)]}{R+1} \qquad (3)$$

$$C_{a2} = C_{a0}(1-x_2) = 2(1-x_2) \qquad (4)$$

For the flow reactor,

$$-(R+1)V'_0 dC_a = kC_a^2 dV_r$$

$$V_r/V'_0 = \frac{1}{R+1}\int_{C_{a2}}^{C_{a1}} \frac{dC_a}{kC_a^2} \qquad (5)$$

Part (a):

1. Set $C_{a2} = 0.05$
2. Specify a value of R
3. Find C_{a1} from Eq (3)
4. Solve Eqs (1), (2) and (5) simulataneously for V_r/V'_0.
5. Repeat with other values of R.

Part (b):

1. Set $V_r/V'_0 = 2.0189$, the value found in part (a) when R = 0.
2. Specify R
3. Find C_{a1} from Eq (3)
4. Find the integration limit C_{a2} by trial, by simultaneous solution of Eqs (1), (2) and (5) to make the integral $V_r/V'_0 = 2.0189$.

	Part (a)			Part (b)		
R	C_{a1}	V_r/V'_0	T_2	C_{a2}	C_{a1}	T_2
0	2	2.0189	447.5	0.05	2	447.5
1	1.05	22.48	400			
2	0.7333	67.4	384.2			
5	0.4167	281	368.4	0.6007	0.8339	361.7
10	0.2727	685	361.0	0.5201	0.6546	356.7
50	0.1313	3413	354.0	0.3001	0.3334	351.7
100	0.1188	6508	353.4	0.2243	0.2419	350.9

P4.06.10. RECYCLE INTERCOOLED.

A plug flow reactor for the reversible reaction, A ⇔ B, is to be operated with recycle. Both fresh and recycle streams are at 25 C. The reactor is adiabatic. Feed concentration is $C_{a0} = 10$ and conversion is 80%. Data are,

$$r = k[(1+1/K_e)C_a - 10/K_e] \qquad (1)$$

$$k = \exp(17.2-5800/T) \qquad (2)$$

$$K_e = -24.7+9000/T) \qquad (3)$$

$$\Delta H_r/\rho C_p = -5.0$$

Reactor inlet,

$$C_{a1} = \frac{C_{a0}+RC_{a2}}{R+1} = \frac{10+2R}{R+1} \qquad (4)$$

Heat balance,

$$-\Delta H_r V'_0(R+1)(C_{a1}-C_a) = V'_0(R+1)\rho C_p(T-298)$$

$$T = 298 + 5(\frac{10+2r}{R+1} - C_a) \qquad (5)$$

Material balance,

$$-V'_0(R+1)dC_a = rdV_r$$

$$-\frac{dC_a}{d(V_r/V'_0)} = \frac{k}{R+1}[(1+1/K_e)C_a - 10/K_e] \qquad (6)$$

Results are tabulated for several values of R. They are obtained by POLYMATH solution of the numbered equations.

For comparison, in an adiabatic CSTR,

$T = 298 + 5(10-2) = 338$

$k = 1.0411$

$K_e = 6.8704$

$$\tau = V_r/V'_0 = \frac{C_{a0}-C_{a2}}{r} = \frac{10-2}{1.0411[(1+1/6.8704)(2)\ -10/6.8704]}$$

$$= 9.20$$

R	C_{a1}	C_{a2}	T_2	V_r/V'_0	
0	10	2	338.0	4.82	
1	6	2	318.0	11.1	
2	4.67	2	311.3	15.9	
4	3.60	2	306.0	22.0	
∞	10	2	338	9.2	CSTR

P4.06.11. FORMALDEHYDE IN A RECYCLE REACTOR. RATE EQUATION

Formaldehyde (F) is made by partial oxidation of methanol (M). A side reaction of formaldehyde to CO and H_2O (W) also occurs. Approximate forms of the two rate equations are

$$r_1 = \frac{k_1 p_m}{1+k_2 p_m},\ \text{oxidation of methanol}$$

$$r_2 = \frac{k_3 p_f}{1+k_4 p_w},\ \text{oxidation of formaldehyde}$$

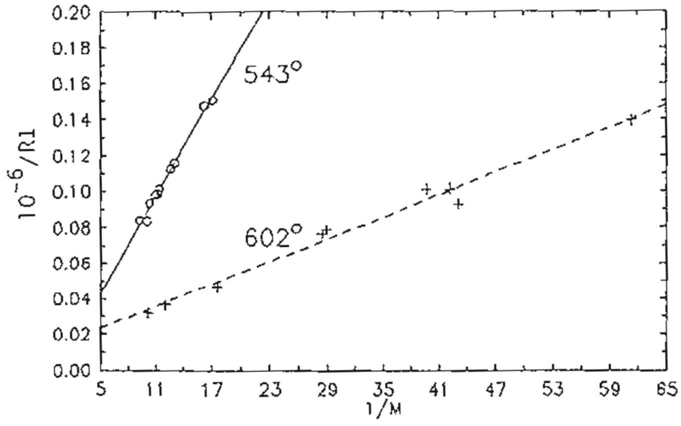
The tabulated data at two temperatures were obtained in a recycle reactor with powdered catalyst (Rase, *Fixed Bed Reactor Design and Diagnostics*, p 312, 1990). Verify that the equations are correct by checking the linearized forms,

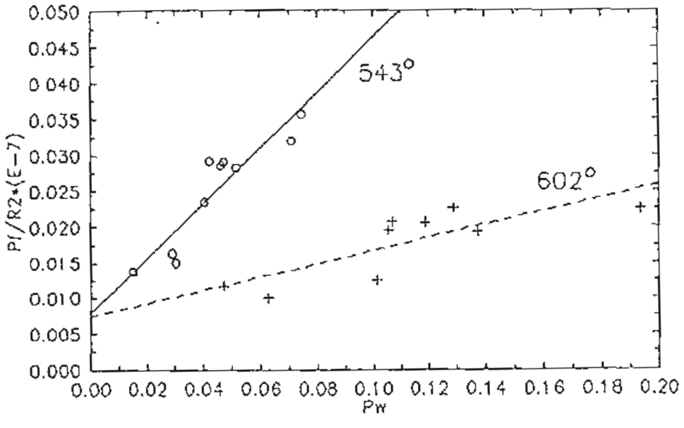
$$1/r_1 = a + b(1/p_m)$$

$$p_f/r_2 = c + dp_w$$

Both plots are roughly linear. The original constants are tabulated.

	543 K	602 K	T
$10^4 k_1$	1.1294	4.825	exp(5.76-8072.5/T)
k_2	0.1077	6.238	exp(39.2-22.55/T)
$10^5 k_3$	1.252	1.349	exp(-10.53-414.5/T)
k_4	47.85	12.43	exp(-9.92-7490.7/T)





T	p_m	p_f	p_w	$10^6 r_1$	$10^7 r_2$
543	0.0796	0.0445	0.0463	8.9062	1.5625
	0.0614	0.0704	0.0744	6.7708	1.9792
	0.0583	0.0663	0.0708	6.6146	2.0833
	0.0993	0.0289	0.0302	1.1198	1.9271
	0.0966	0.0280	0.0289	1.0677	1.7187
	0.0891	0.0392	0.0405	1.0156	1.6667
	0.0917	0.0409	0.0423	1.0208	1.4062
	0.0877	0.0499	0.0516	9.8958	1.7708
	0.1082	0.0151	0.0151	11.875	10.937
602	0.0988	0.0464	0.0474	3.1406	3.9583
	0.0163	0.1185	0.1289	7.1875	5.2604
	0.0345	0.1081	0.1185	1.2708	5.2604
	0.0350	0.1244	0.1373	1.3125	6.4583
	0.0237	0.0953	0.1052	9.8958	4.8958
	0.0251	0.0968	0.1067	9.8958	4.6875
	0.0568	0.0943	0.1012	21.406	7.6042
	0.0829	0.0597	0.0627	27.396	6.0417
	0.0232	0.1684	0.1936	10.781	7.5000

P4.06.12. INTERSTAGE REMOVAL OF PRODUCT

A process unit for the reaction, A + B ⇔ C, consists of two reactors and two separators as shown on the sketch. The separators effect complete removal of reactant A and inert I and allow only B and C to recycle. The rate equation is

$$r = p_a p_b/(1+p_a+p_b+p_c+p_i) \quad \text{lbmol/lb catalyst-hr}$$

where the pressures are in atmospheres. The charge rates A_3, B_0 and I are specified as well as the sizes of the reactors and the pressure and temperature. Explain how to find the amount of A converted in each reactor.

Material balances in reactor 1:

$A = A_3-x_2-x$ $\qquad$ $p_a = A\pi/n_{t1} = (A_3-x_2-x)\pi/n_{t1}$

$B = B_0-x$ $\qquad$ $p_b = (B_0-x)\pi/n_{t1}$

$C = x$ $\qquad$ $p_c = x\pi/n_{t1}$

$I = I$ $\qquad$ $p_i = I\pi/n_{t1}$

$n_{t1} = A_3+B_0+I-x_2-x$

$F_1 = A_3+B_0+I-x_2$

In reactor 2:

$A = A_3-x$ $\qquad p_a = (A_3-x)\pi/n_{t2}$

$B = B_0-x_1-x$ $\qquad p_b = (B_0-x_1-x)\pi/n_{t2}$

$C = x_1+x$ $\qquad p_c = (x_1+x)\pi/n_{t2}$

$I = I$ $\qquad p_i\pi/n_{t2}$

$n_{t2} = A_3+B_0+I-x$

$F_2 = A_3+B_0+I$

The rate equations become,

$$r_1 = \frac{(A_3-x_2-x)(B_0-x)\pi}{n_{t1}(n_{t1}/\pi+A_3+B_0+I-x_2-x)} = f(x_2,x)$$

$$r_2 = \frac{(A_3-x)(B_0-x_1-x)\pi}{n_{t2}(n_{t2}/\pi+A_3+B_0+I-x)} = g(x_1,x)$$

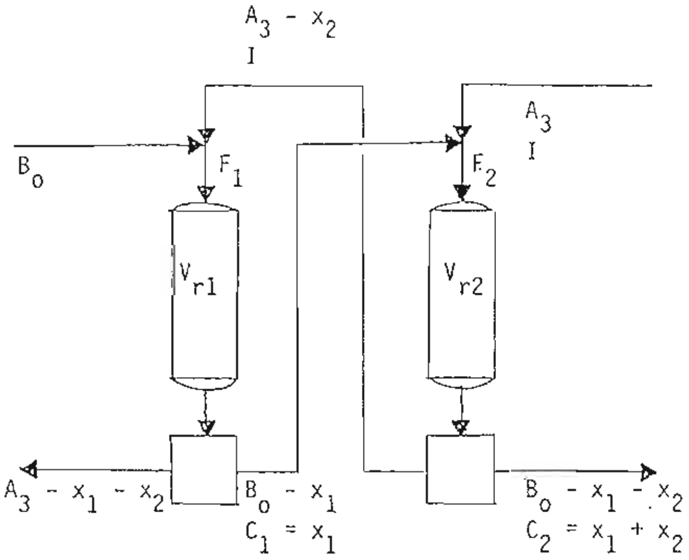
The weights of catalyst are given by the flow reactor equations

$$W_1 = \int_{x_2}^{x_1+x_2} \frac{dx}{f(x_2,\ x)} \tag{1}$$

$$W_2 = \int_0^{x_2} \frac{dx}{g(x,x_1)} \tag{2}$$

Solution procedure:

1. A_3, B_0, I, π, W_1 and W_2 are known
2. Assume a value of x_1
3. Find x_2 from Eq (2)
4. Substitute that value of x_2 into Eq (1) and integrate
5. Compare the values of x_1 from steps 2 and 4.



x_1 = mols A converted in reactor 1

x_2 = mols A converted in reactor 2

P4.06.13. REACTION WITH SIMULTANEOUS EXTRACTION

The reactions, $A \overset{1}{\Rightarrow} P \overset{2}{\Rightarrow} X$, are done in a CSTR in a liquid phase, f, that is in contact with a solvent phase, g. Product P is distributed between the phases but A and X are insoluble in the solvent phase. The distribution coefficient of P is

$$K_p = C_{pg}/C_{pf}$$

Volumetric feed rates of the two phases are V'_f and V'_g. Material balances on A and P are

$$C_{a0} = (1+k\tau_f)C_a \qquad (1)$$

$$\tau_f = V_{rf}/V'_f$$

$$0 = V'_f C_{pf} + V'_g C_{pg} - (k_1 C_a - k_2 C_{pg}) \qquad (2)$$

Make the substitutions,

$$C_{pg} = K_p C_{pf}$$

$$E_p = K_p V'_g/V'_f = C_{pg}V'_g/C_{pf}V'_f$$

Then,

$$\frac{C_{pf}}{C_{a0}} = \frac{k_1\tau_f C_a}{C_{a0}(1+E_p+k_2\tau_f)} = \frac{k_1\tau_f}{(1+k_1\tau_f)(1+E_p+k_2\tau_f)} \qquad (3)$$

The yield of P is

$$\eta_p = \frac{\text{mols P produced}}{\text{mols A charged}} = \frac{V'_f C_{pf}+V'_g C_{pg}}{V'_f C_{a0}} = (1+E_p)\frac{C_{pf}}{C_{a0}} \qquad (4)$$

For instance when

$$k_1 = k_2 = \tau_f = V'_f = V'_g = 1,$$

$$C_{pf}/C_{a0} = \frac{1}{2(2+K_p)}$$

and

$$\eta_p = \frac{1+K_p}{2(2+K_p)} = 0.25 \text{ when } K_p = 0$$

$$0.50 \text{ when } K_p \Rightarrow \infty$$

that is, the yield is appreciably greater when P is completely extracted from the reaction phase.

P4.06.14. AZEOTROPIC DISTILLATION

The synthesis of ethyl acetate according to the reaction

$$C_2H_5OH + CH_3COOH \Leftrightarrow CH_3COOC_2H_5 + H_2O, \quad A + B \Leftrightarrow C + D$$

has this rate equation at 100 C,

$$r = 7.93(10^{-6})(C_aC_b - C_cC_d/2.93) \text{ kgmol/m}^3\text{-sec}$$

The reaction is conducted under batch conditions at the boiling temperature, 100 C. The vapors enter a superimposed distillation column (of negligible holdup) where an azeotropic mixture is removed overhead. (Kramers & Westerterp, 1963). The rate of distillation is such that the mass fraction of ethyl acetate in the mixture does not exceed 0.02. The density is constant at 1.02 g/cc. Find the time needed to convert 35% of the acid. Compare this with the time required without removal of the reaction product.

Initially, kmol/m^3, A = 10.2, B = 3.91, C = 0, D = 17.56
Azeotrope, wt%, A = 8.4, B = 0, C = 82.6, D = 9.0
Molecular weights, A = 46, B = 60, C = 88, D = 18

Basis: 1 m^3 of solution originally, 1020 kg
Without distillation,

$$x = \text{kmols of acid reacted}$$

$$n_a = 10.2-x$$

$n_b = 3.91-x$
$n_c = x$
$n_d = 17.56+x$

$$w_c = \text{wt fraction of acetate formed} = \frac{88x}{1020} = 0.0862x \qquad (1)$$

Acetate removed by distillation = $1020(w_c-0.02)$ kg

$$n_a = 10.2-x-\frac{8.4(1020)(w_c-0.02)}{82.6(46)} = 10.2-x-2.26(w_c-0.02) \qquad (2)$$

$$n_b = 3.91-x \qquad (3)$$

$$n_c = \frac{0.02(1020)}{88} = 0.18 \text{ kg} \qquad (4)$$

$$n_d = 17.56+x-\frac{9(1020)(w_c-0.02)}{82.6(18)} = 17.56+x-6.17(w_c-0.02) \qquad (5)$$

$$V = (46n_a+60n_b+88n_c+18n_d)/1020 \qquad (6)$$

$$r = \frac{1}{V}\frac{dn_c}{dt} = \frac{k}{V^2}(n_an_b - n_cn_d/2.93) \qquad (7)$$

For 35% conversion of acid, $x = 0.35(3.91) = 1.37$, $n_c = 2.54$.

$$t = \int_{3.91}^{2.54} \frac{Vdn_c}{r} = \int_{3.91}^{2.54} Idn_c \qquad (8)$$

Divide the integration interval into four parts, evaluate the integrand I and apply the trapezoidal rule. The result is

$t = 0.5(0.457)(22239) = 5081$ sec

x	w_c	n_a	n_b	n_c	n_d	V	10^4r	I
0	0	10.25	3.91	0	17.683	1.02	2.973	3430.0
0.457	0.0394	9.700	3.453	0.18	17.897	0.972	2.719	3574.0x2
0.914	0.0788	9.153	2.996	0.18	18.113	0.924	2.443	3783.1x2
1.37	0.1181	8.608	2.54	0.18	18.325	0.877	2.141	4094.9
Sum								22239

P4.06.15. REVERSIBLE PRODUCT REMOVED BY DISTILLATION

Ethyl acetate (C) is to be made from ethanol (A) and acetic acid (B) in the presence of water (D). At 100 C the rate equation is

$r_a = 4.76(10^{-4})(AB-CD/2.93)$ mol/liter-min

The starting composition is

$A_0 = 10,\ B_0 = 4,\ C_0 = 0,\ D_0 = 15$ mols/liter

Two different operating modes will be examined.

Method (a). The reaction will be conducted to 90% of equilibrium conversion. Applying material balances, the rate equation becomes,

$r_a = -dA/dt = 4.76(10^{-4})[A(A-6)-(10-A)(25-A)/2.93]$

The equilibrium value is

$A_e = 7.7304$

With 90% of equilibrium conversion,

$A_{end} = 1+0.9(7.7304) = 7.957$

Integration gives the reaction time,

$$t = \int_{7.957}^{10} \frac{dA}{r_a} = 290 \text{ minutes}$$

Method (b). An alternative operation to improve the yield is described by Westerterp(p 65, 1984).The ester is removed continuously by distillation as an azeotrope. The azeotropic composition is $A_z = 0.00182$, $C_z = 0.00938$ and $D_z = 0.005$ kmol/kg.

The residual amount of ester in the reactor is specified to be 0.02 kg/kg, or

$$C_f = C_{final} = 0.02\ \rho/M = 0.02(899)/88.1) = 0.204 \text{ mols/liter}$$

The density of the solution is $\rho = 899$ g/liter, and is taken as constant over the course of the reaction.

Material balances are made for each participant, with a basis of $V_0 = 1$ liter of solution initially.

F = amount of azeotrope, gms/min

$$\frac{dV}{dt} = -F/\rho \qquad (1)$$

Ethanol balance: The rate of change of the total content , VA, equals the volume times the rate + rate of removal as azeotrope.

$$\frac{d(VA)}{dt} = V\frac{dA}{dt} + A\frac{dV}{dt} = V\frac{dA}{dt} - A\frac{F}{\rho}$$

$$= -Vr_a - FA_z$$

which is rearranged to

$$\frac{dA}{dt} = \frac{F}{V}(\frac{A}{\rho} - A_z) - r_a \qquad (2)$$

Acid balance:

$$\frac{d(VB)}{dt} = V\frac{dB}{dt} - B\frac{F}{\rho} = -\ Vr_a \text{ (since } B_z = 0) \qquad (3)$$

Ester balance:

$$\frac{d(VC_f)}{dt} = C_f\frac{dV}{dt} = -\ \frac{FC_f}{\rho} = -FC_z + Vr_a \text{ (since } C_f \text{ is constant)}$$

$$F(C_z - C_f/\rho) = Vr_a$$

$$F = \frac{1}{0.00938-0.204/899} = 109.25Vr_a \qquad (4)$$

Water balance:

$$\frac{d(VD)}{dt} = V\frac{dD}{dt} - D(F/\rho) = Vr_a - FD_z$$

$$\frac{dD}{dt} = \frac{F}{V}(\frac{D}{\rho} - D_z) + r_a = \frac{F}{V}(\frac{D}{899} - 0.005) + r_a \qquad (5)$$

At the start of the distillation, 0.204 mols of ester have been formed, and the time is found by integration of the equation in part (a),

$$t = \int_{9.796}^{10} \frac{dA}{r_a} = 11.0 \text{ min}$$

The conditions at the start of the distillation will be

$$t = 11.0,\ A = 9.80,\ B = 3.80,\ C = 0.20,\ D = 15.20$$

The numbered equations are solved simultaneously by POLYMATH. The printout shows that after 290 minutes the yield of ester is

$$4 - 0.6805(1,721) = 2.8288 \text{ mols/liter}$$

compared with

$$10 - 7.9574 = 2.0426 \text{ mols/liter in part (a)}$$

At 90% of equilibrium conversion, the amount of B remaining should be 4 - 2.043 = 1.957. This is the value of V(b) from the table. Interpolating, 90% of equilibrium is attained in 164 minutes with the distillation scheme, compared with 290 minutes without distillation.

```
The equations:
    d(v)/d(t)=-f/899
    d(a)/d(t)=f/v*(a/899-.00182)-ra
    d(b)/d(t)=f*b/v/899-ra
    d(d)/d(t)=f/v*(d/899-.005)+ra
    ra=4.76e-4*(a*b-.204*d/2.93)
    f=v*ra*109.25
```

Initial values: t_0= 11.000, v_0= 1.0000, a_0= 9.8000, b_0= 3.8000
d_0= 25.200
Final value: t_f= 290.00

```
                         Integration Results

    t            v            a            b            d        b*V
 11.000       1.0000       9.8000       3.8000       25.200
 24.950       0.9723       9.7982       3.6737       26.025
 38.900       0.9463       9.7963       3.5488       26.841
 52.850       0.9220       9.7945       3.4254       27.648
 66.800       0.8992       9.7927       3.3037       28.442
 80.750       0.8779       9.7910       3.1840       29.224
 94.700       0.8579       9.7892       3.0665       29.992
 108.65       0.8392       9.7875       2.9514       30.744
 122.60       0.8217       9.7859       2.8388       31.480
 136.55       0.8052       9.7843       2.7288       32.198
 150.50       0.7899       9.7827       2.6217       32.898     2.0709
 164.45       0.7755       9.7812       2.5175       33.579     1.9523
 178.40       0.7620       9.7797       2.4163       34.240
 192.35       0.7493       9.7783       2.3182       34.881
 206.30       0.7375       9.7769       2.2233       35.501
 220.25       0.7264       9.7755       2.1315       36.100
 234.20       0.7160       9.7742       2.0430       36.679
 248.15       0.7062       9.7730       1.9577       37.236
 262.10       0.6971       9.7718       1.8756       37.773
 276.05       0.6886       9.7706       1.7967       38.288
 290.00       0.6805       9.7695       1.7210       38.782
```

P4.07.01. VARIABLE TEMPERATURE

A first order reaction takes place in batch, starting with C_{a0} = 2 gmol/liter. The specific rate is represented by

$$k = \exp(21-7500/T)$$

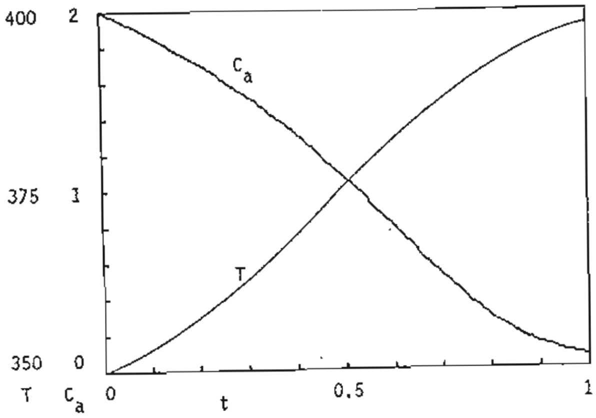
and the heat balance by

$$T = 350 + 25(2-C_a)$$

Accordingly the rate equation is

$$r = -\frac{dC_a}{dt} = kC_a = \exp[21 - \frac{7500}{350+25(2-C_a)}]\ C_a$$

The plot is of the numerical integration of this equation.



P4.07.02. ADIABATIC GAS REACTION

The gas phase reaction, A ⇒ B + C, occurs adiabatically at constant volume, starting with pure A at 600 R. Heat of reaction at this temperature is $\Delta H_r = -2500$ Btu/lbmol. Heat capacity of A is 30 and those of B and C are each 25 Btu/(lbmol)(F). The specific rate is

$$k = \exp(232.5-14000/T),\ 1/h$$

Find the time at which 50% conversion is reached.

With 600 R as the base temperature, the heat balance is

$$[30n_a + 2(25)(1-n_a)](T-600) = 2500(1-n_a)$$

$$T = 600 + \frac{250(1-n_a)}{5-2n_a}$$

The rate equation

$$-\frac{dn_a}{dt} = kn_a$$

is integrated with Simpsons rule as tabulated.

$$t = \int_{0.5}^{1} dn_a/kn_a = \frac{0.25}{3}(3.688) = 0.307 \text{ h}$$

n_a	T	k	$1/kn_a$
1	600	1.18	0.848
0.75	617.8	2.31	0.576x4
0.50	631.3	3.76	0.536
Sum			3.688

P4.07.03. ADIABATIC PFR

The reaction, A ⇒ 2B, is to be 80% converted in an adiabatic PFR. Inlet is pure A at 650 R and the pressure is $\pi = 2$ atm. Given these additional data, find V_r/n_{a0}.

$$k = 150\exp(-3000/T),\ 1/h \qquad (1)$$

$$\Delta H_r = -2000 \text{ Btu/lbmol at 600 R}$$

$$C_{pa} = 20,\ C_{pb} = 15 \text{ Btu/(lbmol)(F)}$$

The rate of reaction is

$$r_a = k\left(\frac{n_a}{V'}\right) = \frac{k\pi}{RT}\left(\frac{n_a}{2n_{a0}-n_a}\right) = \frac{k\pi}{RT}\left(\frac{f}{2-f}\right)$$

$$f = n_a/n_{a0}$$

The flow reactor equation is

$$-n_{a0}df = r_a dV_r$$

$$V_r/n_{a0} = \frac{0.73}{2}\int_{0.2}^{1} \frac{T(2-f}{kf}\,df \qquad (2)$$

The heat balance is

$$n_{a0}(20)(650-600) = [20n_a+2(15)(n_{a0}-n_a)](T-600)-2000(n_{a0}-n_a)$$

$$T = 600 + \frac{100(3-2f)}{3-f} \qquad (3)$$

Eqs (1), (2) and (3) are combined and the result integrated with Simpsons rule. The integrands are tabulated.

$$V_r/n_{a0} = 0.365(0.2/3)(13663.9) = 332 \text{ cuft/(lbmol)(h)}$$

For isothermal operation at the feed temperature of 650 R,

$$V_r/n_{a0} = \frac{0.365(650)}{1.485}\int_{0.2}^{1} \frac{2-f}{f}\,df = 159.8[2 \ln 5 - (1-0.2)]$$

$$= 386.4 \text{ cuft/(lbmol)(h)}$$

f	T	k	Integrand
1	650	1.785	437.8
0.8	663.6	1.632	609.8x4
0.6	675.0	1.762	894.1x2
0.4	684.6	1.875	1460.5x4
0.2	692.9	1.975	3157.0
Sum			13663.9

P4.07.04. ADIABATIC TWO STAGE CSTR

The reaction, $2A \underset{2}{\overset{1}{\rightleftharpoons}} C + D$, is conducted in an adiabatic two stage CSTR. Charge is a solution of pure A at the rate of 100 cuft/hr at 560 R with an inlet concentration $C_{a0} = 1.5$ lbmol/cuft. Heat of reaction is $\Delta H_r = -4000$ Btu/lbmol and independent of temperature. Heat capacity of the solution is 60 Btu/(cuft)(R). Specific rates of the forward and reverse reactions,

$$k_1 = \exp(9.26-6989/T), \text{ cuft/(lbmol)(min)} \qquad (1)$$

$$k_2 = \exp(-2.91-1851/T) \qquad (2)$$

Find the reactor sizes for 80% conversion (a) in a one stage unit; (b) in the two stage unit.

Stoichiometric balances,

$$C_{a0}-C_a = 2(C_c-C_{c0}) = 2(C_d-C_{d0})$$

Heat balances,

$$T_1 = 560 + \frac{4000(1.5-C_1)}{60} = 560 + 66.7(1.5-C_1) \qquad (3)$$

$$T_2 = 560 + 66.7(1.5-0.3) = 640$$

The rate equation,

$$r = k_1C_a^2 - 0.25k_2(1.5-C_a)^2 \qquad (4)$$

Material balances,

$$C_0 = 1.5 = C_1 + r_1\tau \qquad (5)$$

$$C_1 = C_2 + r_2\tau \qquad (6)$$

For a single stage,

$$T = 640\ ,\ k_1 = 0.180,\ k_2 = 0.0030$$

$$r = 0.18((0.3)^2 - 0.25(0.0030(1.2)^2 = 0.0152$$

$$\tau = (1.5-0.3)/0.0152 = 79 \text{ min}$$

$$V_r = 79(100)/60 = 132 \text{ cuft}$$

For two stages,

$$T_2 = 640 \text{ R},\ C_2\ 0.3,\ k_1 = 0.180,\ k_2 = 0.0030,\ r_2 = 0.0152$$

$$\tau = \frac{C_0-C_1}{r_1} = \frac{1.5-C_1}{r_1} = \frac{C_1-0.3}{0.0152} \qquad (7)$$

The solution procedure is to assume a value of C_1, find T_1 from Eq (3), r_1 from Eq (4) and finally to find C_1 from Eq (7) as a check on the assumption. The correct values are,

$C_1 = 0.617$, T_1 618.9, $\tau = 20.8$ min, $V_r = 34.7$ cuft/stage

P4.07.05. PFR SPACE VELOCITY

A tubular flow reactor is used for the gas phase reaction, A ⇒ 2B, under adiabatic conditions with a constant pressure of 2 atm. Pure A is charged at 600 R. The heat of reaction is $\Delta H_r = -2000$ Btu/lbmol of A. Heat capacities are 20 and 15 Btu/(lbmol)(R) for A and B and the specific rate is

$$k = 150\exp(-3000/T),\ 1/h \qquad (1)$$

What space velocity is needed for 90% conversion?

The heat balance,

$$2000(n_{a0}-n_a) = [20n_a+2(15)(n_{a0}-n_a)](T-600)$$

$$T = 600 + \frac{200(n_{a0}-n_a)}{3n_{a0}-n_a} = 600 + \frac{200(1-f)}{3-f} \qquad (2)$$

$$f = n_a/n_{a0}$$

$$r_a = k(n_a/V) = \frac{k\pi}{RT}\frac{f}{2-f}$$

$$V_r/n_{a0} = \frac{R}{\pi}\int_{0.1}^{1}\frac{df}{r_a} = 0.365\int_{0.1}^{1}\frac{T(2-f)}{kf}\,df \qquad (3)$$

$$= 0.365(0.3/2)(12981) = 709.7 \text{ cuft/(lbmol/h)}$$

Integration is with the trapezoidal rule, with the numbers in the table.

$$\text{Space velocity} = \frac{1}{709.7}\ \text{lbmol/(h)(cuft of reactor)}$$

$$\Rightarrow 359/709.7 = 0.506 \text{ SCFH/cuft of reactor}$$

f	T	k	Integrand
1.0	600	1.02	587
0.7	626	1.26	924x2
0.4	646.1	1.45	1783x2
0.1	685.8	1.87	6980
Sum			12981

P4.07.06. SECOND ORDER ADIABATIC REACTION

The gas phase reaction, 2A ⇒ B, occurs in a batch reactor at a constant pressure of 5 atm under adiabatic conditions. Initially the reactor contains 2 lbmol of pure A at 600 R. Heat capacity of A is 25 Btu/(lbmol)(R), that of B is 30 and enthalpy change of reange is $\Delta H_r = -1600$ Btu/lbmol. The specific rate is

$$k = \exp(24.83-14790/T),\ \text{cuft/(lbmol/h)} \qquad (1)$$

Find the time and temperature at which 75% conversion is attained.

$$n_b = 0.5(n_{a0}-n_a) = 0.5(2-n_a)$$

$$n_t = 0.5(n_{a0}+n_a)$$

$$V = n_tRT/\pi$$

Rate equation,

$$-\frac{1}{V}\frac{dn_a}{dt} = k\left(\frac{n_a}{V}\right)^2$$

$$t = \int_{n_a}^{n_{a0}} \frac{V}{kn_a^2}\, dn_a = \frac{R}{2\pi} \int_{0.5}^{2} \frac{T(2+n_a)}{kn_a^2}\, dn_a \qquad (2)$$

Heat balance,

$$[25n_a\ 30(0.5)(2-n_a)](T-600) = 1600(2-n_a)$$

$$T = 600 + \frac{160(2-n_a)}{n_a+3} \qquad (3)$$

The integrand of Eq (2) is tabulated. The trapezoidal rule gives

$$t = \frac{0.73}{2(5)}\left(\frac{0.5}{2}\right)(2673) = 48.8 \text{ min}$$

$$T = 668.5$$

n_a	T	k	Integrand
2.0	600	1.20	500
1.5	617.8	2.15	447x2
1.0	640.0	4.60	417x2
0.5	668.5	15.0	445
Sum			2673

P4.07.07. ADIABATIC CSTR

A first order gas phase reaction, A ⇒ B + C, is conducted adiabatically at a pressure of 5 atm with an inlet temperature of 600 R in a CSTR. The specific rate is

$$k = \exp(24.83-14790/T),\ 1/h \qquad (1)$$

Other data are: $n_{a0} = 2$ lbmol/hr, $n_{b0} = n_{c0} = 0$, $V_r = 50$ cuft, $\Delta H_r = -2500$ Btu/lbmol, $C_{pa} = 30$ Btu/(lbmol)(R), $C_{pb} = C_{pc} = 20$. Find the steady state conversion and temperature.

$$r_a = k(n_a/V) = \frac{k\pi}{RT}\left(\frac{n_a}{2n_{a0}-n_a}\right) = \frac{5k}{0.73T}\left(\frac{n_a}{4-n_a}\right)$$

Heat balance,

$$2500(2-n_a) = [30n_a+2(20)(2-n_a)](T-600)$$

$$T = 600 + \frac{250(2-n_a)}{8-n_a} \qquad (2)$$

Material balance,

$$n_{a0} = 2 = n_a + V_r r_a = n_a + \frac{50(5)k}{0.73T}\left(\frac{n_a}{4-n_a}\right) \qquad (3)$$

Solve Eqs (1), (2) and (3) simultaneously.

$$T = 631.9$$

$n_a = 1.122$ lbmol/hr, 43.9% conversion.

P4.07.08. ACETIC ANHYDRIDE HYDROLYSIS. ADIABATIC BATCH AND CSTR

The hydrolysis of dilute aqueous acetic anhydride is pseudo first order with specific rate

$$k = \exp(17.02-5630/T),\ 1/\text{min} \qquad (1)$$

A batch reactor of 100 liters contains 0.2 gmol of reactant at 293 R. Heat of reaction is $\Delta H_{r,298} = -50000$ cal/gmol, $C_p = 0.9$ cal/(g)(C), $\rho = 1.05$ g/cc. Find the time required for 70% conversion (a) at isothermal operation of 20 C, (b) under adiabatic conditions. (c) In a CSTR find temperature and conversion at residence times of 5, 10 and 20 min.

Part (a),

$k = 0.1128$

f = fraction reacted

$$t = \int_0^{0.7} \frac{df}{0.1128(1-f)} = 10.67 \text{ min}$$

Part (b),

$$-\Delta H_r C_0 f = \rho C_p (T-293.2)$$

$$T = 293.2 + \frac{50000(0.0002)f}{1.05(0.9)} = 293.2 + 10.582f \qquad (2)$$

$$\frac{df}{dt} = k(1-f) \qquad (3)$$

Simultaneous solution of Eqs (1), (2) and (3) is tabulated. Interpolation to f = 0.7 is

$f = 0.7$, $t = 8.106$ min, $T = 300.69$

Part (c),

Heat balance, as before, Eq (2)

Material balance,

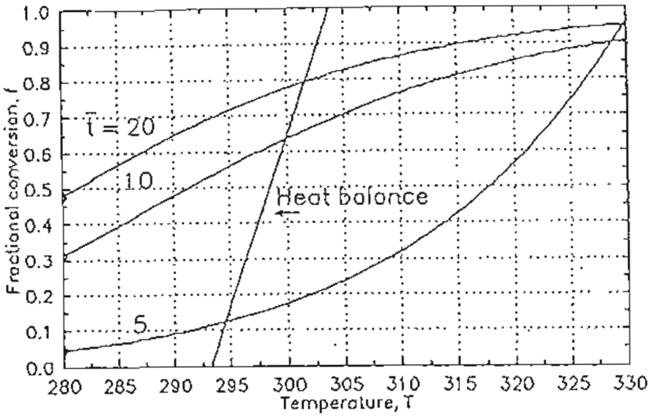
$$C_0 = C + \tau k C = C_0(1-f)(1+k\tau)$$

$$f = \frac{k\tau}{1+k\tau} \qquad (4)$$

Eqs (1), (2) and (4) are solved simultaneously at specified values of the residence time, τ. On the graph, the solutions are at intersections of the heat balance line and the material balance curves. Those intersections are:

$\tau = 5$, $f = 0.12$, $T = 294$
$\tau = 10$, $f = 0.63$. $T = 300$
$\tau = 20$, $f = 0.80$, $T = 302$

t	f	
0.0	0.0	293.20
1.0000	0.1107	294.37
2.0000	0.2162	295.49
3.0000	0.3155	296.54
4.0000	0.4077	297.51
5.0000	0.4919	298.41
6.0000	0.5678	299.21
7.0000	0.6353	299.92
8.0000	0.6945	300.55
9.0000	0.7457	301.09
10.000	0.7896	301.56



P4.07.09. ACETIC ANHYDRIDE HYDROLYSIS. ADIABATIC AND COOLED REACTORS.

A batch reactor has a 500 lb charge of a solution of acetic anhydride at a concentration of 0.0135 lbmol/cuft. The solution density is 65.5 lb/cuft and its specific heat is 0.9 Btu/(lb)(). The heat of reaction is -90,000 Btu/lbmol and the specific rate is

$$k = \exp(17.852-10576/T) \qquad (1)$$

Conversion is to be 70%. (a) Find the time under adiabatic conditions. (b) When the temperature rise is limited to 10 F, find the time and the value of the heat transfer quantity, UA, with coolant at 500 R.

Part (a).

$$dx/dt = k(1-x)$$

$$n_{a0} = \frac{500(0.0135)}{65.5} = 0.1031 \text{ lbmol anhydride}$$

Heat balance,

$$90000(0.1031)x = 5000(0.9)(T-520)$$

$$T = 520 + 20.61x$$

$$t = \int_0^{0.7} \frac{dx}{k(1-x)} \qquad (3)$$

$$= 10.49 \text{ min}$$

Eqs (1), (2) and (3) were solved simultaneously. For comparison, at constant temperature of 520 R,

$$t = \frac{1}{0.0835} \ln \frac{1}{1-0.7} = 14.42 \text{ min}$$

Part (b).

The heat transfer is

$$dQ = UA(T-500)dt \qquad (4)$$

This is combined with the rate equation into

$$dQ = UA(T-500) \frac{dx}{k(1-x)} \qquad (5)$$

The heat balance is

$$500(0.9)dT = UA(T-500) \frac{dx}{k(1-x)}$$

$$= 0.1031(90000)dx$$

or

$$\frac{dx}{dT} = \frac{450}{9275 - \frac{UA(T-500)}{k(1-x)}} \qquad (6)$$

Substitute from Eq (1) for k in terms of T and integrate Eq (6) with POLYMATH with several assumed values of UA. Some of the results are,

UA	6.5	6.74	7.0
x	0.6826	0.7000	0.7231

The interpolated value is UA = 6.74 when x = 0.7.

To find the time, rearrange the heat balance to

$$450dT + 6.74(T-500)dt = 9275k(1-x)dt$$

$$t = \int_{520}^{530} \frac{450}{9275k(1-x) - 6.74(T-500)} dT \qquad (7)$$

$$= 11.5 \text{ min.}$$

Eqs (1) and (2) were used to relate k and x to T before integrating by the trapezoidal rule. The table gives the intermediate calculations.

T	x	k	Integrand
520	0	0.0835	0.7015
525	0.3079	0.1289	0.9308
530	0.7000	0.2080	3.2249

P4.07.10. ACETYLATED CASTOR OIL HYDROLYSIS

Acetylated castor oil is hydrolyzed for the manufacture of drying oils in kettles operated batchwise. The charges are 277 kg and the initial temperature is 613 k. Complete hydrolysis yields 0.156 kg acetic acid per kg of ester. For this reaction the specific rate has been found to be

$$k = \exp(35.2-22450/T) \text{ , 1/min, T°K} \qquad (1)$$

(Grummit & Fleming, Ind Eng Chem 37 485, 1945). The specific heat of the solution is 0.6 cal/gm-K and the heat of reaction is ΔH_r = +15000 cal/gmol of acid produced. Find the relations between T and the fraction converted for several values of heat input rate, Q = kcal/min.

$$n_{a0} = \frac{227000(0.156)}{60} = 590.2 \text{ gmol acetic acid}$$

Heat balance,

$$227(0.6)dT = -590.2(15)dx + Qdt, \text{ kcal}$$

Substitute

$$dt = \frac{dx}{k(1-x)}$$

making

$$136.2dT = (-8853 + \frac{Q}{k(1-x)})dx$$

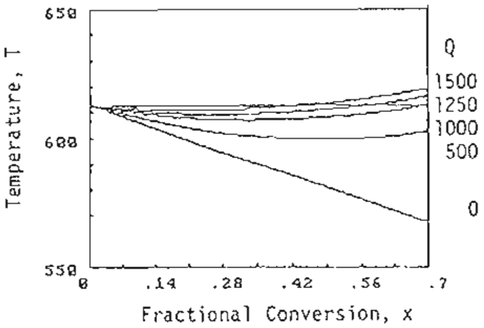
or

$$\frac{dT}{dx} = \frac{-8853 + Q/k(1-x)}{136.2} \tag{2}$$

The results of the simultaneous solutions of Eqs (1) and (2) for several values of Q are plotted. The heat input rate needed to maintain isothermicity,

$$Q = 590.2(15)\frac{dx}{dt} = 8853k(1-x) = 8852(0.241)(1-x) = 2134(1-x)$$

This ranges from 2134 when x = 0 to 640 when x = 0.7.



P4.07.11. TWO STAGE ADIABATIC CSTR. SECOND ORDER REACTION.

The feed to a two stage CSTR is at $T_0 = 325$ K and $C_0 = 5$. The reaction is second order with specific rate

$$k = \exp(1.67-500/T), \text{ liter/(gmol)(min)} \tag{1}$$

Thermal data are

$$\Delta H_r = -3000 + 5.3T$$

$$C_p = 600 \text{ cal/(liter)(K)}$$

Find the temperatures, residence time and the first stage concentration when the overall conversion is to be 90%,

Reactor 1, material and energy balances:

$$C_0 = 5 = C_1 = k_1\tau C_1^2 = C_1 + \tau C_1^2 \exp(1.67-500/T_1) \tag{2}$$

$$-\Delta H_r(C_0-C_1) = C_p(T_1-T_0)$$

$$-[-3000+5.3(325)](5-C_1) = 600(T_1-325) \tag{3}$$

Reactor 2,

$$C_1 = C_2 + k_2\tau C_2^2 = 0.5 + 0.25\tau \exp(1.67-500/T_2) \tag{4}$$

$$-(-3000+ 5.3T_2)(C_1-0.5) = 600(T_2-T_1) \tag{5}$$

The numbered equations are solved simultaneously with the results

$$C_1 = 1.184,\ \tau = 2.297,\ T_1 = 333.1,\ T_2 = 334.5.$$

P4.07.12. ADIABATIC GAS HEAT BALANCE

The reaction, $A + 2B \Leftrightarrow 2C + D$, proceeds in the gas phase under adiabatic conditions. The heat of reaction at 100 F is $\Delta H_r = -4000$ Btu/ lbmol A converted. Other data are tabulated. The temperature is in °F. Find the temperature of the mixture after 80% conversion has taken place.

Component	Initial mols	Feed °F	C_p
A	1.0	300	5+0.03T
B	3.0	200	4+0002T
C	0.10	200	5+0.06T
D	0.15	200	4+0.08T
Vessel		100	0

Initial enthalpy relative to 100 F,

$$H_1 = \int_{100}^{300}(1)(5+0.03T)dT + \int_{100}^{200} [3(4+0.02T)+0.1(5+0.06T) + 0.15(4+0.08T)]dT = 4680.$$

Final composition,

$n_a = 1-0.8 = 0.2$

$n_b = 3-2(0.8) = 1.4$

$n_c = 0.1+1.6 = 1.7$

$n_d = 0.15+0.8 = 0.95$

Final enthalpy,

$$H_2 = H_1 - (n_{a0}-n_a)\Delta H_r = 4680 - 0.8(-4000) = 7880$$

$$7880 = \int_{100}^{T} [0.2(5+0.03T) + 1.4(4+0.02T) + 1.7(5+0.06T) + 0.95(4+0.08T)]dt$$

$$= 0.133T^2 + 18.9T -3220$$

$T = 226$ F

P4.07.13. BATCH REACTOR WITH HEAT TRANSFER

A second order reaction proceeds in a batch reactor provided with heat transfer. Initial conditions are $T_0 = 350$ and $C_0 = 1$. Other data are,

$k = \exp(16-5000/T)$, cuft/(lbmol)(h) 1)

$\Delta H_r = -(5000+5T)$, Btu/lbmol (2)

$\rho C_p = 50$

The rate of heat transfer is

$Q = UA(300-T)$ 3)

The temperature and the time will be found in terms of the fractional conversion, x, when $UA/V_r = 0$ or 150.

The rate equation may be written

$$\frac{dt}{dx} = \frac{1}{kC_0(1-x)^2} \qquad (4)$$

The differential heat balance is

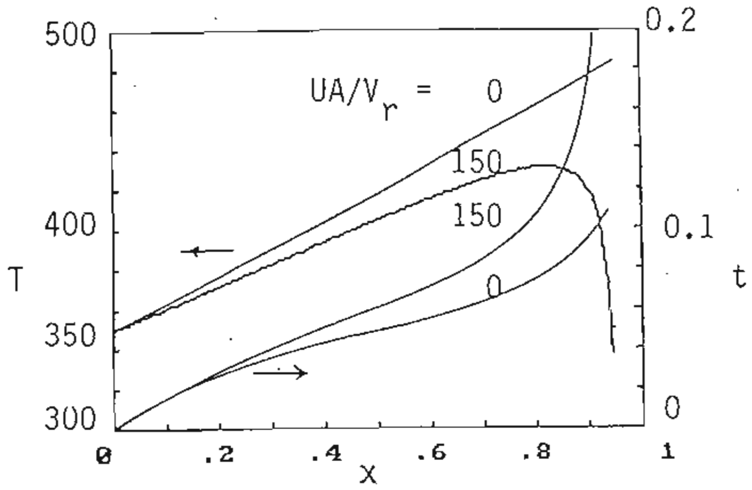
$$\rho C_p V_r dT = Qdt - \Delta H_r V_r C_0 dx$$

Substitute for dt from Eq (4) and rearrange.

$$\frac{dT}{dx} = \frac{1}{\rho C_p}\left[\frac{Q}{V_r k C_0(1-x)^2} - \Delta H_r C_0\right]$$

$$= 0.02\left[\frac{UA(300-T)}{V_r k(1-x)^2} + 5000 + 5T\right] \qquad (5)$$

Eqs (1), (4) and (5) are solved simultaneously with $UA/V_r = 0$ or 150, and the results plotted. In the adiabatic case, the temperature tends to run away.



P4.07.14. HEAT BALANCE

The reaction, 2A + 2B ⇔ C, is to be conducted adiabatically, starting at T_0. Given the following additional data, relate the temperature and n_a, the amount of A remaining.

ΔH_r = -5000 Btu/(lvbmol)(R) at 580 R
n_{a0} = 2 lbmols, n_{b0} = 3, n_{c0} = 0
C_{pa} = 15 Btu/(lbmol)(R), C_{pb} =, 20, C_{pc} = 50

Stoichiometric balances,

$$n_b = n_{b0} - n_{a0} + n_a = 1+n_a$$
$$n_c = 0.5(n_{a0}-n_a) = 0.5(2-n_a)$$

Heat balances,

$$\int_{580}^{700} \Sigma\, n_{i0}C_{pi}dT = [2(15)+3(20)](120) = 10800 \text{ Btu}$$

$$\int_{580}^{T} \Sigma\, n_iC_{pi}dT = [15n_a + 20(1+n_a)+50(2-n_a)](T-580)$$
$$= (70+10n_a)(T-580)$$

Putting it together,

$$10800 = (70+10n_a)(T-580) - 5000\ (2-n_a)$$

$$T = 580 + \frac{2080-500n_a}{7+n_a}$$

P4:07.15. ADIABATIC REACTION. SIMPSONS RULE

The gas phase reaction, 2A ⇒ B, is conducted adiabatically at 2 atm, starting with T_0 = 600 R and n_{a0} = 2 lbmol. Data are,

$$k = \exp(18.07-10018/T) \qquad (1)$$
ΔH_r = -5000 Btu/lbmol at 600 R
C_{pa} = 30 Btu/(lbmol)(R), C_{pb} = 40

Find the time and conversion when the temperature becomes 700 R.

$$n_t = n_a + 0.5(n_{a0}-n_a) = 0.5(2+na)$$

$$V = \frac{n_tRT}{\pi} = \frac{0.5(2+n_a)(0.729T}{2} = 0.1823(2+n_a)T \qquad (2)$$

Rate equation,

$$-\frac{1}{V}\frac{dn_a}{dt} = k(\frac{n_a}{V})^2$$

$$t = 0.1823\int_{n_a}^{2} \frac{T(2+n_a)}{kn_a^2}\, dn_a \qquad (3)$$

Heat balance,

$$-\Delta H_r(n_{ao}-n_a) = [30n_a+40(0.5)(2-n_a)](T-600)$$

$$T = 600 + \frac{500(2-n_a)}{n_a+4} \qquad (4)$$

When T = 700, n_a = 1. Integrate Eq (3) with Simpsons rule.

$$t = 0.1823(0.5/3)(514.8) = 15.6 \text{ min}$$

n_a	T	k	Integrand
2	600	3.948	181.98
1.5	645.5	12.80	78.46x4
1	700	42.89	48.97
Sum			514.79

P4.07.16 PFR WITH AND WITHOUT HEAT TRANSFER

A second order gas phase reaction , 2A + B ⇒ C, is done in a furnace with ambient temperature 1600 R. Inlet temperature is 1500 F, the pressure is 5 atm. The feed is 20 lbmol/hr, consisting of 40% each of A and B and 20% inerts. Given the data following, find temperature and conversion profiles when (a) the heat transfer coefficient is U = 10 Btu/(hr)(cuft)(R); (b) the process is adiabatic; (c) the process is isothermal.

$$k = \exp(32.65-30000/T), \text{ cuft/lbmol-hr} \qquad (1)$$

$$\Delta H_r = +25000 \text{ Btu/lbmol}$$

$$C_{pa} = C_{pb} = 8,\ C_{pc} = 10,\ C_{p,inert} = 5$$

Base the calculations on a feed of 1 mol/hr.

$n_{to} = 1$

$n_{ao} = n_{bo} = 0.4$

x = conversion, mols/hr

$n_a = n_b = 0.4-x$

$n_c = x$

The rate equation is

$$r_a = k(n_a/V)^2 = k(\pi/RT)^2(n_a/n_t)^2 = \frac{46.91k}{T^2}\left(\frac{0.4-x}{1-x}\right)^2 \qquad (2)$$

For the flow reactor,

$$-dn_a = dx = r_a dV_r$$

$$\frac{dx}{dV_r} = r_a \qquad (3)$$

Heat balance:

$$\Sigma n_i C_{pi} = 2(8)(0.4-x) + 10x + 5(0.2) = 7.4-6x$$

$$\Delta H_r dn_a = -\Delta H_r dx = -\Delta H_r r_a dV_r$$

$$= \Sigma n_i C_{pi} dT - dQ = (7.4-6x)dT - U(1600-T)dV_r$$

$$\frac{dT}{dv_r} = \frac{-\Delta H_r r_a + U(1600-T)}{7.4-6x} = \frac{-25000r_a+U(1600-T)}{7.4-6x} \qquad (4)$$

Differential Eqs (3) and (4) are solved simultaneously with auxiliary Eqs (1) and (2) with ODE. The plots show the cases with U = 10 and with U = 0.

For isothermal operation,

$$V_r = \int_0^x \frac{dx}{r_a} = 0.1538 \int_0^x \left(\frac{1-x}{0.4-x}\right)^2 dx \qquad (5)$$

This result also appears on the plot.

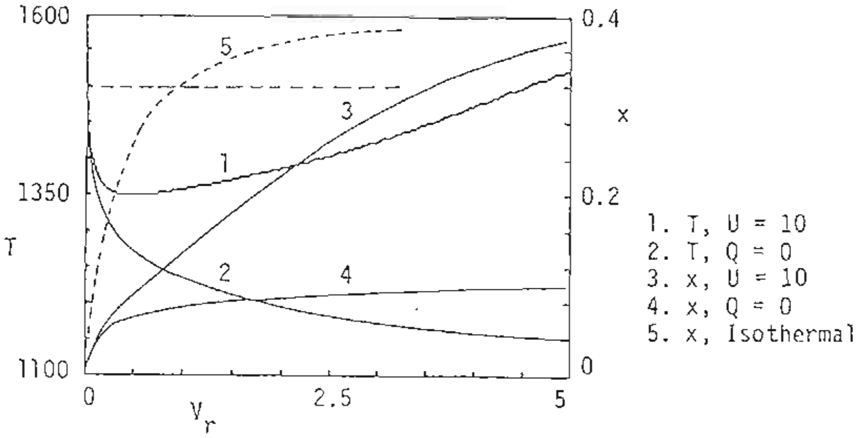
The rate of heat transfer needed to maintain the temperature at 1500 throughout the reaction is obtained by setting Eq (4) to zero.

$$Q = (1600-1500)U = 25000(6.5)\left(\frac{0.4-x}{1-x}\right)^2 \qquad (6)$$

Some values are,

x	0	0.2	0.3	0.35
Q/100	260	102	20.1	4.5

The required furnace temperature could be figured if the coefficient of heat transfer were kept at U = 10.



P4.07.17. MAINTAINING TEMPERATURE BY EVAPORATION OF SOLVENT

A second order liquid phase reaction, 2A ⇒ B, is carried out in aqueous solution. Starting at 100 F, the mixture reacts until it reaches 250 F. Thereafter water evaporates so that the temperature remains at 250. Data are:

weight of batch = 1000 lbs

C_{a0} = 0.1 lbmol/cuft

molecular weight of A = 100

density of mixture = 62 lb/cuft

latent heat of vaporization of water = 945 Btu/lb

heat capacity of mixture = 1.0 Btu/(lb)(F)

heat of reaction = 18900 Btu/lb of A reacted

$k = \exp(9.56-3675/T)$ cuft/(lbmol)(h), T in $^\circ$R

Find the following,

(a) The relation between temperature and fractional conversion during the adiabatic period.

(b) The time and the conversion when the temperature becomes 250.

(c) The time for 90% conversion, and the amount of water evaporated by that time.

Batch = 1000 lb
16.15 cuft
1.615 mols A initially = n_{a0}
161.5 lbs A initially
838.5 lbs water initially
46.6 mols water initially

Heat balance during the adiabatic period, when 100 F ⇒ 250 F,

$$1000C_p dT = -\Delta H_r M_a dn_a$$

$$1000(T-560) = 18900(100)(n_{a0}-n_a) = 1.89(10^6)(1.615-n_a)$$

$$f = \frac{n_a}{n_{a0}} = 1 - \frac{T-560}{1890(1.615)} = 1 - \frac{t-560}{3050}$$

When T = 460+250 = 710 R, f = f_1 = 0.9508.

$$-\frac{dn_a}{dt} = \frac{kn_a^2}{V} = \frac{kn_a^2}{16.15}$$

$$t = \frac{V}{n_{a0}}\int_f^{f_1}\frac{df}{kf^2} = 10\int_f^{0.9508}\frac{df}{kf^2}$$

Integrands for the trapezoidal rule are tabulated. The time for the adiabatic period becomes

$$t = 10(\frac{0.0248}{2})(0.1123) = 0.0139 \text{ h}$$

T	k	$f=n_a/n_{a0}$	integrand
560	20.0	1	0.050
635	43.5	0.9752	2(0.0242)
710	80.00	0.9508	0.0139
			0.1123 = Sum

During the isothermal period,

W = mols of water in the vessel (46.6 initially)

$18900dn_a = \lambda_w M_w dW$

$$46.6-W = \frac{18900}{945(18)}(n_{a0}-n_a) = 1.11(1.532-n_a)$$

$$V = 16.15 - \frac{(46.6-W)(18)}{62} = 16.15 - \frac{18(1.11)(1.532-n_a)}{62}$$

$$= 15.65 + 0.322n_a$$

$$t - 0.0139 = \int_{n_a}^{n_{a1}}\frac{Vdn_a}{kn_a^2} = \int_{n_a}^{1.532}\frac{(15.65+0.322n_a)}{80n_a^2}dn_a$$

$$= \frac{1}{80}[15.65(\frac{1}{n_a} - \frac{1}{1.532}) + 0.322 \ln\frac{1.532}{n_a}]$$

When n_a = 0.5(1.615) = 0.808, t = 0.1319.
When n_a = 0.1(1.615) = 0.1615, t = 1.1069.

SUMMARY

t, h	T °R	n_a	V	lbs evaporated
0	100	1.615	16.15	0
0.0015	175	1.575	16.15	0
0.0139	250	1.532	16.15	0
0.1319	250	0.808	15.91	14.9
1.1060	250	0.1615	15.70	27.8

P4.07.18. A NON-IDEAl gas

A reversible gas phae reaction, 2A ⇔ B, is conducted in an adiabatic PFR at 25 atm. Inlet conditions are T_0 = 700 K and n_{a0} = 20 gmol/hr. The equation of state is

$$P = \frac{0.08205T}{V-0.15} - \frac{15}{V^2},\ \text{atm} \qquad (1)$$

The rate equation is

$$r_a = kC_a^2,\ \text{gmol/(liter)(h)}$$

At 700 K the specific rate is 0.070 and the activation energy is 3000(1.987) °K, At the inlet temperature the enthalpy change of reaction is $\Delta H_r = +2000$ cal/gmol of A. Heat capacities are $C_{pa} = 30$ and $C_{pb} = 20$ cal/(gmol)(K). Find the volume of reactor needed for 90% conversion.

From the given data, the specific rate is

$$k = \exp(1.6265-3000/T) \qquad (2)$$

In terms of the molal volume, V, represented by the equation of state, the flow volume is

$$V_t = n_tV = 0.5(n_{a0}+n_a)V$$

$$r_a = k\left(\frac{n_a}{n_tV}\right)^2 = k\left[\frac{2n_a}{(n_a+n_{a0})V}\right]^2 \qquad (3)$$

Heat balance,

$$-\Delta H_r(n_{a0}-n_a) = \Sigma n_iC_{pi}(T-T_0)$$

$$-2000(20-n_a) = [30n_a + 20(0.5)(20-n_a)](T-700)$$

$$T = 700 - \frac{100(20-n_a)}{10+n_a} \qquad (4)$$

The PFR material balance,

$$-dn_a = r_a dV_r$$

$$V_r = \int_2^{20} \frac{1}{k}\left[\frac{(20+n_a)V}{n_a}\right]^2 dn_a$$

$$= 7811 \text{ liters.}$$

The integral is evaluated with Simpsons rule, as tabulated. The deviation from ideality is small. At 700 K for instance, V = 2.1925 from Eq (1) compared with the ideal value 2.2974.

n_a	T	k	V	$1/r_a$
20	700	0.0700	2.1925	68.72
17	688.9	0.0653	2.1515	83.95x4
14	675.0	0.0597	2.1000	108.93x2
11	652.6	0.0513	2.0165	157.34x4
8	633.3	0.0446	1.9437	259.42x2
5	600.0	0.0343	1.8161	600.99x4
2	500.0	0.0218	1.6188	3636.3
Sum				7811.0

P4.07.19. ETHANE PYROLYSIS

A reactor is made up of a series of tubes 0.102 m in diameter. It is charged with 27.13 kgmol/h of ethane at 922 K and 2.04 atm with a heat input rate through the walls of 13563 kcal/(m^2)(h). The problem is to find the profiles of temperature and conversion along the tube length. A simplified version of the reaction is

$C_2H_6 \Rightarrow C_2H_4 + H_2$, $A \Rightarrow B + C$

Data are,

$$k = \exp(38.59-41310/T) \qquad (1)$$

$$\Delta H_{r,298} = +32.73 \text{ kcal/gmol}$$

$C_{pa} = 3.75+0.0357T-10.12(10^{-6})T^2$, cal/(gmol)(K)

$C_{pb} = 5.25+0.0242T-6.88(10^{-6})T^2$

$C_{pc} = 7.00-0.000385T+0.6(10^{-6})T^2$

For the flow reactor,

$$-dn_a = k(n_a/V)dV_r = \frac{k\pi}{RT}\left(\frac{n_a}{2n_{a0}-n_a}\right)dV_r \tag{2}$$

Heat of reaction at temperature,

$$\Delta H_r = \Delta H_{r,298} + \int_{298}^{T} \Delta C_p dT = 32732 +8.50(T-298)$$

$$-5,942(10^{-3})(T^2-298^2) +1.28(10^{-6})(T^3-298^3) \tag{3}$$

Heat input rate,

$$dQ = 13563dA = 13563(4/D)dV_r = 531882dV_r = \beta dV_r \tag{4}$$

$\beta = 531882$

Differential heat balance,

$$-\Delta H_r\, dn_a + \beta dV_r = \alpha dT \tag{5}$$

$$\alpha = n_aC_{pa} + (n_{a0}-n_a)(C_{pb}+C_{pc}) \tag{6}$$

Rearranging,

$$\frac{dT}{dV_r} = \frac{\beta}{\alpha} - \frac{\Delta H_r}{\alpha}\frac{dn_a}{dV_r} = \frac{\beta}{\alpha} + \frac{\Delta H_r}{\alpha}\left(\frac{k\pi}{RT}\right)\left(\frac{n_a}{2n_{a0}-n_a}\right) \tag{7}$$

With substitutions from Eqs (1), (3) and (6), Eq (7) is numerically solvable.

P4.07.20. PHOSPHINE DECOMPOSITION

The vapor phase decomposition of phosphine is irreversible first order and is in accord with the stoichiometry,

$PH_3 \Rightarrow 0.25P_4 + 1.5H_2$, $A \Rightarrow 0.25B + 1.5C$

Pure phosphine is fed to a tubular flow reactor operating adiabatically at 1 atm with a feed temperature of 1000 K. The reaction is endothermic, with ΔH_r = 23900 J/mol at 25 C. Heat capacities in J/(mol)(K) are

$C_{pa} = 28.0+0.027T$, $C_{pb} = 25.1+0.0040T$, $C_{pc} = 30.1$

The specific rate is

$$k = T^2 \exp(27.94-43672/T) \tag{1}$$

(a) What value of V_r/V' would be needed to obtain 10% conversion adiabatically?

(b) What would be the conversion for the same V_r/V' but at 1000 K throughout?

Heat of reaction at temperature,

$$\Delta H_r = 23900 + \int_{298}^{T} \Delta C_p dT = 23900 + \int_{298}^{T} (23.425-0.026T)dT$$

$$= 18074 + 23.425T - 0.013T^2 \tag{2}$$

Compositions,

$f = n_a/n_{a0}$

$n_a = n_{a0}f$

$n_b = 0.25n_{a0}(1-f)$

$n_c = 1.5n_{a0}(1-f)$

$$\Sigma\, n_iC_{pi} = n_{a0}[51.425+0.001T+(-23.425+0.0026T)f] \tag{3}$$

Adiabatic heat balance,

$\Delta H_r dn_a = \Delta H_r n_{a0} df = \Sigma\, n_iC_{pi}dT$

$$\frac{dT}{df} = \frac{\Delta H_r n_{a0}}{\Sigma\, n_iC_{pi}} = \frac{18074+23.425T-0.013T^2}{51.425+0.001T+(-23.425+0.026T)f} \tag{4}$$

Total mols,

$$n_t = n_{a0}[f+0.25(1-f)+1.5(1-f)] = n_{a0}(1.75-0.75f) \qquad (5)$$

Flow reactor,

$$-n_{a0}df = r_a dV_r = \frac{k\pi}{RT}\left(\frac{n_a}{n_t}\right)dV_r \qquad (6)$$

$$\frac{dV_r}{df} = \frac{0.082T}{k}\left(\frac{1.75-0.75f}{f}\right) \qquad (7)$$

Equations (1), (4) and (7) are numerically solvable by ODE. Alternately, Eq (4) may be solved first to find the relation between f and T. Then the RHS of Eq (7) is evaluated and the integral is found by the trapezoidal rule. The calculations are tabulated. The result is

$$V_r = \int_{0.9}^{1}(\text{RHS})df = 96.72 \text{ liters}$$

At a constant temperature of 1000 K,

$$V_r = \frac{82.05}{0.3999}\int_{0.9}^{1}\left(\frac{1.75-0.75f}{f}\right)df = 22.43 \text{ liters}$$

f	T	k	RHS
1.00	1000.0	0.3999	205.2
0.99	994.8	0.3166	262.3
0.98	989.6	0.2501	336.2
0.97	984.4	0.1971	432.0
0.96	979.1	0.1542	559.0
0.95	973.8	0.1203	725.3
0.94	968.6	0.0941	939.1
0.93	963.3	0.0730	1225.0
0.92	958.0	0.0565	1602.3
0.91	952.7	0.0436	2101.7
0.90	947.3	0.0334	2778.2

P4.07.21. ADIABATIC AND ISOTHERMAL PFR

The reaction, $A \Rightarrow B + C$, is done at 10 atm in a PFR with a charge rate of 10 lbmols/hr consisting of 50% A and the balance inerts. Inlet temperature is 700 R and the specific rate is

$$k = \exp(7.872 - 8734/T), \text{ 1/min}$$

Heat of reaction at 600 R is $\Delta H_r = -25{,}000$ Btu/lbmol of A. Heat capacities are 30, 25, 25 and 20 for A, B, C and inerts respectively. Find the reactor volumes and space velocities for 60% conversion (a) at adiabatic conditions; (b) isothermally at 700 R.

x = mols A converted /10 mols of charge

n_{t0} = 10 mols/hr, 1/6 lbmols/min

Heat balance,

$$[30(5)+20(5)](700-600) + 25000x$$
$$= [30(5-x)+(25+25)x+20(5)](T-600)$$

$$T = 600 + \frac{1250(1+x)}{12.5+x}$$

In the flow reactor,

$$r_a = k(n_a/V) = \frac{k\pi}{RT}\left(\frac{n_{a0}-x}{n_{t0}+x}\right) = \frac{10k}{0.73T}\left(\frac{5-x}{10+x}\right)$$

$$n_{t0}dx = r dV_r$$

$$V_r/n_{t0} = 6V_r = 0.073 \int_0^3 \frac{T(10+x)}{k(5-x)} dx$$

The integrands are tabulated for the adiabatic and isothermal cases, and the integrals are evaluated with Simpsons rule.

Adiabatic, V_r = (0.073(0.5/3)(1,093,500)/6 = 2217 cuft

VHSV = 10(359)2217 = 1.62 (Std cuft/hr)/cuft

$$\text{Isothermal, } V_r = \frac{0.073 n_{t0} T}{k} \int_0^3 \frac{10+x}{5-x} dx$$

$$= \frac{0.073(700)}{6(0.01)} (0.5/3)64.44) = 9147 \text{ cuft}$$

x	T	k	$\frac{0.001T(10+x)}{k(5-x}$		$\frac{10+x}{5-x}$
0	700	0.010	140		2.0
0.5	744	0.018	96.2x4		2.33x4
1.0	785	0.0325	66.5x2		2.75x2
1.5	823	0.054	50.1x4		3.28x4
2.0	858	0.088	39.0x2		4.00x2
2.5	891	0.137	32.5x4		5.00x4
3.0	923	0.220	27.3		6.50
Sum			1093.5		64.44

P4.07.22. OPERATING MODE

A solution of density ρ = 70 lb/cuft is pumped to a reactor at 3 cuft/min with a reactant concentration C_0 = 7 lb/cuft. Inlet temperature is 104 F. Heat of reaction is ΔH_r = -500 Btu/lb reacted, and heat capacity is 0.95 Btu/lb-R. Specific rate is

$$k = \exp(16.48-11340/T), \quad \text{cuft/lb-min} \qquad (1)$$

Operation is adiabatic and conversion is to be 95%. Find the volumes of (a) a tubular flow reactor; (b) a CSTR; (c) a batch reactor when the down time is 1 hr per batch and the daily charge is 3(1440) cuft/day.

Heat balance:

$$T = T_0 - \Delta H_r(C_0-C)/\rho C_p = 564 + 500(7-C)/70(0.95)$$

$$= 564 + 7.52(7-C) \qquad (2)$$

The units of the specific rate indicate that the reaction is second order.

Part (a):

$$V_r = V' \int_C^{C_0} \frac{dC}{kC^2} = 3 \int_{0.35}^7 \frac{dC}{kC^2} = 74.58 \text{ cuft} \qquad (3)$$

The numerical value is obtained by combining Eqs (1), (2) and (3).

Part (b):

When C = 0.35, T = 614, k = 0.137

$$\frac{C_0-C}{V_r/V'} = kC^2$$

$$\frac{7-0.35}{V_r/3} = 0.137(0.35)^2$$

$$V_r = 1189 \text{ cuft}$$

Part (c): Substitute for k and T from Eqs (1) and (2). Then the reaction time is

$$\tau = -\int_{7}^{0.35} \frac{dC}{kC^2} = 24.86 \text{ min}$$

$$\text{Number of batches per day} = \frac{3(1440)}{24.86+60} = 16.97$$

$$V_r = 3(1440)/16.97 = 254 \text{ cuft.}$$

P4.07.23. ADIABATIC. VARIABLE DENSITY. CSTR AND PFR

A first order reaction, $A \Rightarrow 2B$, is carried out in a battery of two equal CSTRs followed by a tubular flow reactor with a volume $V_{r3} = 20$ cuft. The process is adiabatic. Input consists of 20 lbmols of A dissolved in 100 cuft of solvent and is at 100 F. As shown on the sketch, 25% of the fresh feed bypasses the first CSTR. Specific volumes are independent of temperature and are additive. Heat of reaction at 560 R is $\Delta H_r = -70{,}000$ Btu/lbmol and specific rate is

$$k = \exp(6.8 - 3400/T)$$

Specific volumes are 0.288, 0.91 and 1.43 cuft/lbmol of solvent, A and B ; and specific heats are 18, 36 and 24 Btu/(lbmol)(F) in the same order. It is required to find the volumes of the stirred tanks for an overall conversion of 98%.

Volumetric flow rates,

$$V_1 = 75 + 0.91n_{a1}+2(1.43)(15-n_{a1}) = 117.9 - 1.95n_{a1} \qquad (1)$$

$$V_2 = 100 + 0.91n_{a2}+2(1.43)(20-n_{a2}) = 157.2 - 1.95n_{a2} \qquad (2)$$

In the tubular reactor,

$$V_3 = 157.2-1.95n_a \qquad (3)$$

Heat balances,

$$\begin{aligned} 70000(15-n_{a1}) &= [259(18)+36n_{a1}+2(24)(15-n_{a1})](T_1-100) \\ &= (5380-12n_{a1})(T_1-100) \qquad (4) \end{aligned}$$

$$\begin{aligned} 70000(5+n_{a1}-n_{a2}) &= [346(18)+36n_{a2}+2(24)15-n_{a1})(T_2-100) \\ &\quad -36n_{a1}(T_1-100) \\ &= (7180-12n_{a1})(T_2-100) - 36n_{a1}(T_1-100) \qquad (5) \end{aligned}$$

$$\begin{aligned} 70000(n_{a2}-n_{a1}) &= (7180-12n_{a1})(T-100) \\ &\quad - (7180-12n_{a2})(T_2-100) \qquad (6) \end{aligned}$$

Material balances,

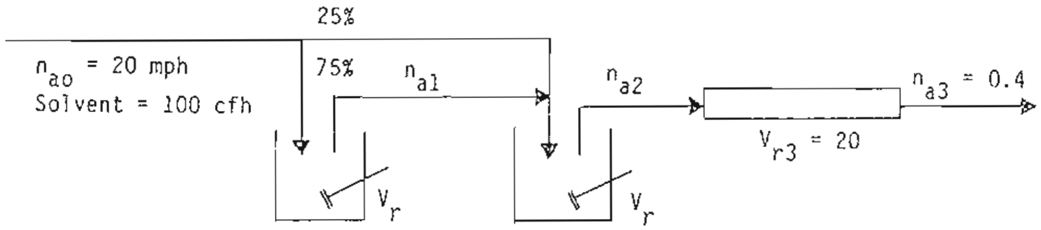
$$15 = n_{a1}(1+r_1V_r) = n_{a1}(1+\frac{k_1V_r}{V_1}) = n_{a1}(1+\frac{k_1V_r}{117.9-1.95n_{a1}}) \qquad (7)$$

$$5+n_{a1} = n_{a2}(1+\frac{k_2V_r}{V_1}) = n_{a2}(1+\frac{k_2V_r}{157.2-1.95n_{a2}}) \qquad (8)$$

$$V_{r3} = 20 = -\int_{n_{a2}}^{0.4} \frac{dn_a}{r_3} = -\int_{n_{a2}}^{0.4} \frac{157.2-1.95n_a}{kn_a}\, dn_a \qquad (9)$$

Solution procedure:

1. Assume T_1
2. Find n_{a1} from Eq (4)
3. Find V_r from Eq (7)
4. Solve Eqs (5) and (8) simultaneously to find T_2 and n_{a2}
5. Use Eq (6) as the relation between T and n_a. Substitute into Eq (9), complete the integration and note if the integral really is 20. If not, return to step 1 with another trial of T_1.



P4.07.24. ADIABATIC CSTR. MULTIPLE STEADY STATES

A second order reaction is done adiabatically in a CSTR. Data for the system are:

C_0 = 0.5 lbmol/cuft
C_p = 25 Btu/cuft-K
τ = 0.5 hr
ΔH_r = -10,000 Btu/lbmol
$k = \exp(20-6000/T)$ cuft/lbmol-hr (1)

Explore the effect of inlet temperature T_0 on the performance.

Material balance:

$$C_0 = C + k\tau C^2$$

$$x = 1-C/C_0 = \frac{-1+\sqrt{1+4k\tau C_0}}{2k\tau C_0} = 1 - \frac{-1+\sqrt{1+k}}{0.5k} \tag{2}$$

Energy balance:

$$V'C_pT_0 = V'C_pT + \Delta H_r r = V'C_pT + \frac{\Delta H_r V_r(C_0-C)}{\tau}$$

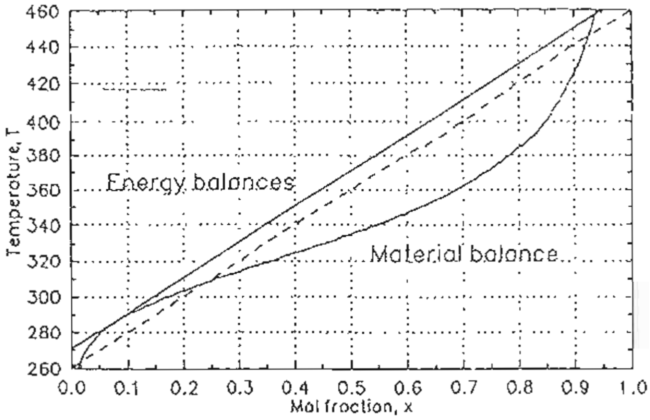
$$T = T_0 - \frac{\Delta H_r C_0}{C_p}x$$

$$= T_0 + \frac{10000(0.5)}{25}x = T_0 + 200x \tag{3}$$

(a) With T_0 = 260, the plots of Eqs (2) and (3) have three intersections or steady states,

T_0	263	309	445
x	0.015	0.245	0.928

(b) With feed slightly above 270 K, there is only the steady state, x = 0.945 at 477 K.



P4.07.25. SECOND ORDER, VARIABLE HEAT CAPACITY

The gas phase reaction, A+ B ⇒ C, occurs at constant volume with initial conditions 700 R and 10 atm. Initial charge is 4 lbmols each of A and B and 2 lbmols of inerts. The reactor weighs 300 lb. Heat of reaction at 600 R is ΔH_r -25000 Btu/lbmol and the specific rate is

$$k = \exp(6.205-7451/T) \qquad (1)$$

Heat capacities in Btu/lbmol-R are

A	30+0.005T
B	25+0.004T
C	40
Inerts	20
Reactor	0.2 Btu/lb-R

Taking adiabatic conditions, find the amount of conversion and the time when the temperature reaches 900 R. Compare with the isothermal performance at 700 R.

Heat balance:

$$\int_{600}^{700} [4(30+0.005T+25+0.004T) +2(20) + 0.2(300)]dT = 34340$$

$$= -25000x + \int_{600}^{T} [(4-x)(55+0.009T)+40x+100]dT$$

$$= -25000x + (4-x)[55(T-600) + 0.0045(T^2-600^2)] +(40x+100)(T-600)$$

Rate equation:

$$V = V_0 = n_{t0}RT/\pi = 10(0.729)(700)/10 = 510 \text{ cuft}$$

$$\frac{dx}{dt} = \frac{k}{V}(4-x)^2$$

$$t = 510 \int_0^{T=900} \frac{dx}{k(4-x)^2}$$

The integrand is tabulated as a function of x and the trapezoidal rule is applied.

$$t = 510(7.223) = 3684 \text{ sec, adiabatically}$$

$$x = 2.22, \text{ or } 2.22/4 = 0.55 \text{ fraction converted.}$$

At constant T = 700,

$$t = \frac{510}{0.0118} \int_0^{2.22} \frac{dx}{(4-x)^2} = 13477 \text{ sec}$$

x	T	k	Integrand
0	700	0.0118	5.297
0.5	740.4	0.0211	3.869
1	783.3	0.0366	3.036
1.5	829.1	0.0619	2.585
2	878	0.1022	2.446
2.1	888	0.1127	2.458
2.22	900.7	0.1265	2.495

P4.07.26. CYCLOPENTADIENE DIMERIZATION

Cyclopentadiene in a hydrocarbon mixture is to be 75% dimerized in a plug flow reactor. Feed is 15,000 kg/hr of a mixture containing 16 wt% of CPD which is equivalent to C_0 = 1.73 gmol/liter. Specific heat of the mixture is

0.55 cal/gm-C, density is 0.8 g/cc and heat of reaction is ΔH_r = -9000 cal/gmol CPD at 25 C. The rate of reaction is represented by the equation

$$r_a = C_a^2 \exp(17.363-6876/T) \text{ gmol/liter-hr} \qquad (1)$$

(a) Find the volume of reactor needed under adiabatic conditions, with the feed at 80 C. (b) Find the reactor volume for isothermal conditions of 93.3 C.

$V' = 15000/0.8 = 18750$ liters/hr

$n_{a0} = V'C_0 = 18750(1.73) = 32438$ gmol CPD/hr

Heat balance:

$$15000(1000)(0.55)(80-25) = 15000(1000)(0.55)(T-25) -9000(18750)(C_0-C)$$

$$T = 80 + 20.45(C_0-C) = 80 + 20.45C_0(1-f)$$

$$= 80+35.38(1-f) \qquad (2)$$

$$f = C/C_0$$

Flow reactor

$$V_r = \int_n^{n_0} \frac{dn_a}{r_a} = V'\int_C^{C_0} \frac{dC}{kC^2} = \frac{18750}{C_0}\int_{0.25}^{1} \frac{df}{kf^2} \qquad (3)$$

$$= 10838\ (0.125/3)(238.73) = 107808 \text{ liters}$$

$$3806 \text{ cuft}$$

The integrand of Eq (3) is tabulated and the integration is with Simpsons Rule. At constant temperature, T = 93.3 C, k = 0.2445,

$$V_r = \frac{10838}{k}(1/f - 1) = \frac{10838}{0.2445}(4-1) = 132976 \text{ liters}$$

$$4694 \text{ cuft}$$

f	T	k	Integrand
1	80	0.1205	8.299
0.875	84.42	0.1534	8.516x4
0.75	88.85	0.1941	9.159x2
0.625	93.27	0.2441	10.49x4
0.50	97.69	0.2935	13.63x2
0.375	102.11	0.3800	18.71x4
0.25	106.54	0.4706	34.00
Sum			238.73

P4.07.27. ACETALDEHYDE DECOMPOSITION

The reaction rate for the decomposition of acetaldehyde,

$CH_3CHO \Rightarrow CH_4 + CO$, $A \Rightarrow B + C$

is second order with

$$k = \exp(23.69-25080/T) \text{ cc/gmol-sec} \qquad (1)$$

The heat of reaction at 780 K is ΔH_r = -4.55 kcal/gmol. 1 kmol of pure acetaldehyde at 780 K enters a reactor which is operated at 1 atm. Find the volume of the reactor for 50% conversion under adiabatic conditions. Heat capacities are

$$C_p = a + 10^{-2}bT + 10^{-5}cT^2 + 10^{-9}dT^3, \text{ cal/gmol-K}$$

	a	b	c	d
CH_3CHO	4.19	3.164	-0.515	-3.8
CH_4	4.75	1.2	0.303	-2.63
CO	6.726	0.04	0.1283	-0.5307
Δ	7.286	-1.924	0.9463	0.6393

Flow reactor:

n_{a0} = 1 kmol/hr, 1/3600 kmol/sec

$n_t = 2n_{a0}-n_a$

$V = n_tRT/\pi = 0.082T(2n_{a0}-n_a)$

$$C_a = n_a/V = \frac{\pi}{RT}\left(\frac{n_a}{2n_{a0}-n_a}\right) = \frac{\pi}{RT}\left(\frac{1-x}{1+x}\right)$$

$$V_r/n_{a0} = \int_0^{0.5} \frac{dx}{r_a} = 0.082 \int_0^{0.5} \frac{T}{k}\left(\frac{1+x}{1-x}\right)^2 dx \qquad (2)$$

Heat balance:

$$4550(n_{a0}-n_a) = 4550n_{a0}(1-x) = \Sigma n_i \int_{780}^{T} C_{pi}dT$$

$$= n_a[4.19(T-T_0)+0.01582(T^2-T_0^2)-0.1717(10^{-5})(T^3-T_0^3)$$
$$-0.95(10^{-9})(T^4-T_0^4)] + (n_{a0}-n_a)[(4.75+6.726)(T-T_0)$$
$$+(0.6+0.02)(10^{-2})(T^2-T_0^2) + (0.101+0.0428)(10^{-5})(T^3-T_0^3)$$
$$-(0.6575+0.1327)(10^{-9})(T^4-T_0^4)] \qquad (3)$$

Corresponding values of T and fractional conversion x are found from Eq (3). The integrand of Eq (2) then is evaluated with the aid of Eq (1), and the integration is completed with the trapezoidal rule.

$V_r/n_{a0} = 0.08(0.05)(19.327)(10^6) = 79241\ m^3/(kmmol/sec)$

$V_r = 79241/3600 = 22.0\ m^3$

x	T	10^4k	Integrand (10^{-6})
0	780	2.1174	3.684
0.05	789.5	3.117	3.0993
0.10	799.1	4.565	2.6188
0.15	808.5	6.577	2.248
0.20	817.9	9.394	1.951
0.25	827.6	13.456	1.708
0.30	837.2	19.047	1.517
0.35	846.8	26.75	1.367
0.40	856.4	37.155	1.252
0.45	866.0	51.282	1.168
0.50	875.6	70.86	1.112

P4.07.28. OXIDATION OF NAPHTHALENE

The following model is proposed for the oxidation of naphthalene in a tubular flow reactor with constant wall temperature (Welsenaere & Froment, Chem Eng Science 25 1503, 1970):

$$u\frac{dp}{dz} = -\frac{M\pi\rho_b}{\rho_g}r$$

$$u\frac{dT}{dz} = -\frac{\Delta H_r\rho_b}{C_p}r - \frac{2U}{C_pR}(T - T_m)$$

$r = 0.208p\ \exp(19.837-13636/T)$

The following values of the parameters apply:

$\rho_g = 1.293\ kg/m^3$, gas density

ρ_b = 1300 kg/m^3, bulk density
M = 29.48 , molecular weight
p^o = inlet partial pressure of naphthalene, atm
p = partial pressure of naphthalene, atm
π = 1 atm
ΔH_r = -307,000 kcal/k mol, enthalpy change of reaction
C_p = 0.323 kcal/m^3-C
U = 82.7 kcal/m^3-hr-C, heat transfer coefficient
R = 0.0125 m, tube radius
T_m = 625 K, wall temperature
u = 3600 m/hr, linear velocity
z is the distance along the reactor.

Find the profiles of partial pressure and temperature along the reactor, for inlet and wall temperatures of 625 and inlet partial pressure of 0.02 atm.

The numerical equations are

$$r = 0.208p \exp(19.837-13636/T) \qquad (1)$$

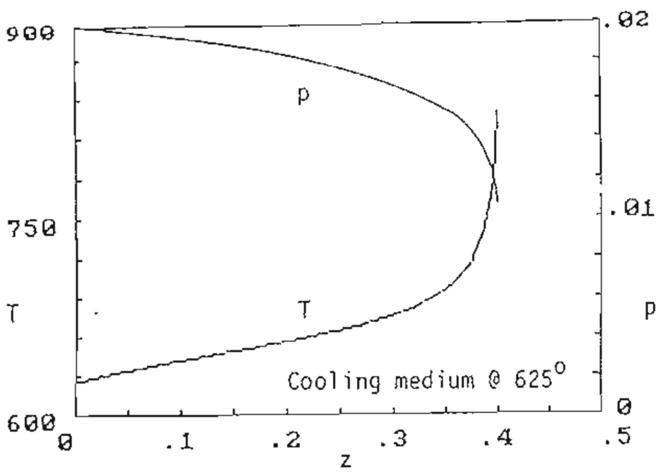
$$\frac{dp}{dz} = -\frac{29.48(1)(1300)}{1.293(3600)} r = -8.23r \qquad (2)$$

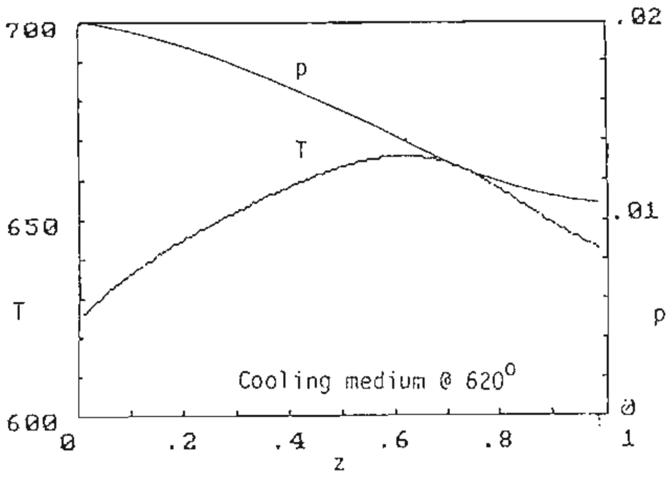
$$\frac{dT}{dz} = \frac{307000(1300)}{3600(0.323)} r - \frac{2(82.7)}{3600(0.323)(0.0125)} ($$

$$T-625)$$

$$= 343223 r - 11.38(T-625) \qquad (3)$$

Integration is done with ODE. The solution is very sensitive to the wall temperature. Plots are shown for 620 and 625 K.





P4.07.29. INSOLUBLE, FUSIBLE PRODUCT.

In the batch reaction, 2A ⇔ B, the product is insoluble; it melts at 200 F with a heat of fusion λ_b = 1000 cal/gmol. Initial conditions are: T_0 = 100 F, n_{a0} = 100 gmol, n_i(solvent) = 200 gmol, V = 50 liters. Given the additional data following, find the time for 90% conversion under (a) adiabatic conditions, (b) isothermal conditions.

$$k = \exp[5.4 - 3000/(T+460)] \text{ liters/gmol-hr} \qquad (1)$$

ΔH_r = -6500 cal/gmol A, at 60 F
C_{pa} = 15 + 0.004T, cal/gmol-F
C_{ps} = 20, solid below 200 F
C_{pl} = 35 + 0.006T, liquid above 200 F
C_{pi} = 10 + 0.002T, solvent

Heat balance:

Take a base temperature T_b = 60 F, and inlet temperature T_0 = 100.

$$\int_{T_b}^{T_0} (n_{a0}C_{pa} + n_iC_{pi})dT = \Delta H_r(n_{a0}-n_a) + n_a\int_{T_b}^{T} C_{pa}dT$$

$$+ n_i\int_{T_b}^{T} C_{pi}dT + 0.5(n_{a0}-n_a)\int_{T_0}^{T} [C_{pb}dT + \lambda_b\delta(T-200)]$$

$\delta(T-200) = 0$ when $T < 200$, $= 1$ when $T> > 200$

Substitute $f = n_a/n_{a0}$.

Below 200 F:

$$15(100-60) + 0.002(100^2-60^2) = 612.8$$

$$= -6500(1-f)+ 2[10(T-60)+0.001(T^2-60^2)]$$

$$+ f[15(T-60)+0.002(T^2-60^2)] + 0.5(1-f)[20(T-60)]$$

$$f = \frac{9732.8-0.002T^2-30T}{6192.8+0.002T^2+5T} \qquad (2)$$

When T = 200, f = 0.5023

Above 200 F:

The enthalpy of component B will be

$$H_b = 1000 + \int_{60}^{200} 20\ dT + \int_{200}^{T}(35+0.006T)dT$$

$$= 0.003T^2 + 35T -3320$$

The complete energy balance will be,

$$612.8 = -6500(1-f) +0.002T^2+20T-2020 + f(0.002T^2+15T-907.2)$$

$$+ 0.5(1-f)(0.003T^2+35T-3320)$$

$$f = \frac{10792.8-0.0035T^2-37.5T}{7252.8-0.0005T^2-2.5T} \qquad (3)$$

When T = 200, f = 0.4683. This is the fraction of substance A remaining after the hitherto generated substance B has melted.

Batch reactor:

$$-\frac{dC_a}{dt} = -\frac{C_{a0}df}{dt} = k(C_{a0}f)^2$$

$$t = \frac{1}{C_{a0}}\int_{0.1}^{1}\frac{df}{kf^2} = 0.5(3.2528) = 1.626 \text{ hrs} \qquad (a)$$

The integrand and the stepwise integrals are tabulated. The interpolation is to final temperature of T = 263.8.

At constant T = 100 F,

$$t = \frac{1}{2(1.0438)}(\frac{1}{0.1} - 1) = 4.311 \text{ hrs} \qquad (b)$$

T	f	k	$1/kf^2$	$\int_1^f$
100	1	1.0438	0.9580	0
120	0.8989	1.2556	0.9857	0.0983
140	0.7925	1.4918	1.0673	0.2075
160	0.6930	1.7529	1.1879	0.3197
180	0.5962	2.0391	1.3797	0.4439
200	0.5023	2.3503	1.6864	0.5879
200	0.4683	2.3503	1.9401	0.6495
220	0.3554	2.6865	2.9470	0.9254
240	0.2402	3.0474	5.6876	1.4228
250	0.1818	3.2370	9.3469	1.8617
260	0.1227	3.4327	19.350	2.7097
263.8	0.1000	3.5086	28.502	3.2528
270	0.0631			

P4.07.30. HEAT TRANSFER IN A CYLINDRICAL REACTOR

A reaction, A ⇒ 2B, runs in a tube provided with a cooling jacket that keeps the wall at 630 R. Inlet is pure A at 650 R and 50 atm. Other data are stated following. Find the profiles of temperature and conversion along the reactor, both with heat transfer and adiabatically.

D = 1/6 ft, tube diameter

$C_{pa} = 20$, $C_{pb} = 15$ Btu/lbmol-R

$\Delta H_r = -8000$ Btu/lbmol A

$k = \exp(7.82-3000/T)$ (1)

U = 5 Btu/hr-sqft-R, heat transfer coefficient

Heat transfer area, $dA = (4/D)dV_r = 24dV_r$

Rate equation,

$$r_a = k(n_a/V) = k(\pi/RT)(n_a/n_t) = \frac{50k}{0.729T}\left(\frac{n_a}{2n_{a0}-n_a}\right)$$

$$= \frac{68.6k}{T}\left(\frac{1-x}{1+x}\right) \qquad (2)$$

$$x = 1-n_a/n_{a0}$$

Flow reactor,

$$-dn_a = n_{a0}dx = r_a dV_r$$

$$\frac{dx}{d(V_r/n_{a0})} = r_a \qquad (3)$$

Heat balance over a differential volume dV_r,

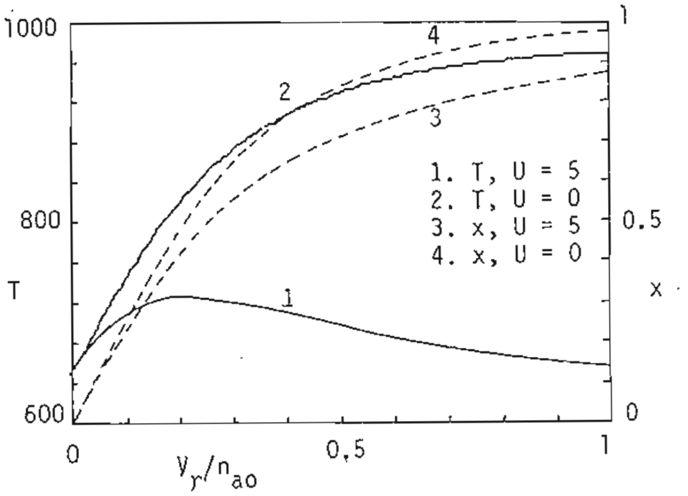
$$\Delta H_r dn_a = -\Delta H_r r_a dV_r$$

$$= \Sigma n_i C_{pi} dT + U(T-T_w)dA$$

$$= n_{a0}[20(1-x) + 15(2x]dT + 24U(T-T_w)dV_r$$

$$\frac{dT}{d(V_r/n_{a0})} = \frac{-\Delta H_r r_a - 24U(T-T_w)}{20-10x} = \frac{8000r_a - 120(T-630)}{20-10x} \qquad (4)$$

Differential Eqs (3) and (4) are solved simultaneously with auxiliary Eqs (1) and (2) by ODE. The solutions with U = 5 and with U = 0 are shown.



P4.07.31. PFR WITH AND WITHOUT HEAT TRANSFER

A second order gas phase reaction, 2A + B ⇒ C, is done in a furnace with ambient temperature 1600 R. Inlet temperature is 1500 F, the pressure is 5 atm. The feed is 20 lbmol/hr, consisting of 40% each of A and B and 20% inerts. Given the data following, find temperature and conversion profiles when (a) the heat transfer coefficient is U = 10 Btu/(hr)(cuft)(R); (b) the process is adiabatic; (c) the process is isothermal.

$$k = \exp(32.65-30000/T),\ \text{cuft/lbmol-hr} \tag{1}$$

$\Delta H_r = +25000$ Btu/lbmol

$C_{pa} = C_{pb} = 8,\ C_{pc} = 10,\ C_{p,inert} = 5$

Base the calculations on a feed of 1 mol/hr.

$n_{t0} = 1$

$n_{a0} = n_{b0} = 0.4$

x = conversion, mols/hr

$n_a = n_b = 0.4-x$

$n_c = x$

The rate equation is

$$r_a = k(n_a/V)^2 = k(\pi/RT)^2(n_a/n_t)^2 = \frac{46.91k}{T^2}\left(\frac{0.4-x}{1-x}\right)^2 \tag{2}$$

For the flow reactor,

$$-dn_a = dx = r_a dV_r$$

$$\frac{dx}{dV_r} = r_a \tag{3}$$

Heat balance:

$$\Sigma n_i C_{pi} = 2(8)(0.4-x) + 10x + 5(0.2) = 7.4-6x$$

$$\Delta H_r dn_a = -\Delta H_r dx = -\Delta H_r r_a dV_r$$

$$= \Sigma n_i C_{pi} dT - dQ = (7.4-6x)dT - U(1600-T)dV_r$$

$$\frac{dT}{dv_r} = \frac{-\Delta H_r r_a + U(1600-T)}{7.4-6x} = \frac{-25000 r_a + U(1600-T)}{7.4-6x} \tag{4}$$

Differential Eqs (3) and (4) are solved simultaneously with auxiliary Eqs (1) and (2) with ODE. The plots show the cases with U = 10 and with U = 0.

For isothermal operation,

$$V_r = \int_0^x \frac{dx}{r_a} = 0.1538 \int_0^x \left(\frac{1-x}{0.4-x}\right)^2 dx \tag{5}$$

This result also appears on the plot.

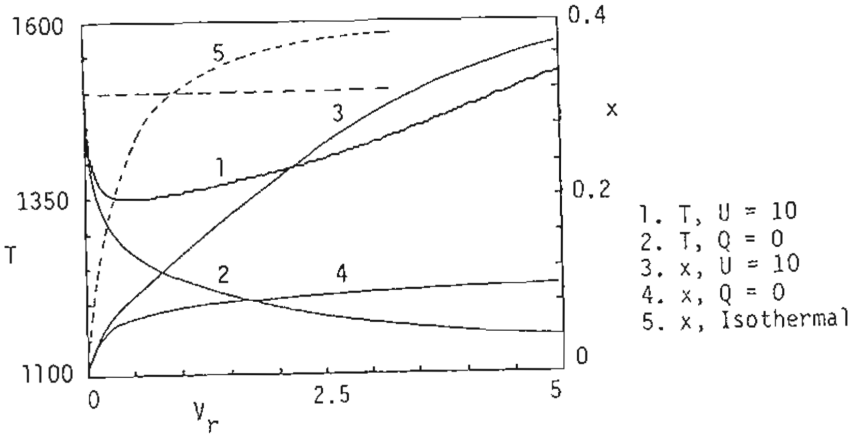
The rate of heat transfer needed to maintain the temperature at 1500 throughout the reaction is obtained by setting Eq (4) to zero.

$$Q = (1600-1500)U = 25000(6.5)\left(\frac{0.4-x}{1-x}\right)^2 \qquad (6)$$

Some values are,

x	0	0.2	0.3	0.35
Q/100	260	102	20.1	4.5

The required furnace temperature could be figured if the coefficient of heat transfer were kept at U = 10.



P4.08.01. REACTION IN LAMINAR FLOW

In laminar flow the linear velocity, u, depends on the distance $\beta = r/R$ from the center line. It is related to the average velocity $\bar{u}$ over the cross section and the velocity u_0 at the center by

$$u = 2\bar{u}(1-\beta^2) = u_0(1-\beta^2) \qquad (1)$$

The material balance for a reaction of order q in an annulus of length dL is

$$-u dC = (\text{Rate of reaction})dL = kC^q dL$$

or

$$-u_0(1-\beta^2)dC = kC^q dL$$

The concentration at position β is given by

$$C = C_0\exp(-kt) = C_0\exp[-\frac{kL}{u_0(1-\beta^2)}], \text{ when } q = 1 \qquad (2)$$

$$\frac{1}{C} - \frac{1}{C_0} = kt = \frac{kL}{u_0(1-\beta^2)}, \quad \text{when } q = 2 \qquad (3)$$

Average concentration: The average concentration over the cross section and at the outlet will be found.

The mass flow of reactant through the annulus is

$$dF_{ann} = uC(2\pi r)dr = \frac{L}{t} C(2\pi r)dr$$

and the mass flow through the entire cross section is

$$F_{total} = \bar{u}\pi R^2 = \frac{u_0}{2}\pi R^2$$

The ratio of these two flows is the mean concentration

$$\bar{C} = \frac{2}{u_0\pi R^2} \int_0^R \frac{L}{t} C(2\pi r)dr = \frac{2L}{u_0} \int_0^1 \frac{C}{t} 2\beta\, d\beta \qquad (4)$$

Either variable β or t can be eliminated in favor of the other. Here β will be eliminated.

$$t = L/u = \frac{L}{u_0(1-\beta^2)}$$

Differentiating and rearranging,

$$2\beta d\beta = \frac{L}{u_0} \frac{dt}{t^2}$$

Substituting into (4),

$$\bar{C} = \frac{2L^2}{u_0^2}\int_{t_0}^{\infty} C \frac{dt}{t^3} = 2t_0^2 \int_{t_0}^{\infty} C \frac{dt}{t^3} \qquad (5)$$

where $t_0 = \bar{t}/2$ is the residence time along the center line of the reactor.

For first order,

$$\bar{C} = 2t_0^2 C_0 \int_{t_0}^{\infty} \frac{\exp(-kt)}{t^3} dt \qquad (6)$$

For second order,

$$\bar{C} = 2t_0^2C_0 \int_{t_0}^{\infty} \frac{1}{t^3(1+kC_0t)}\, dt \qquad (7)$$

This can be integrated analytically. When X = ax+b,

$$\int\frac{dx}{x^3X} = -1/b^3[a^2 \ln(X/x) - 2aX/x + X^2/2x^2]$$

A simpler expression is obtained for the fractional conversion,

$$x = 1 - C/C_0 = kC_0t/(1+kC_0t)$$

Then the mean value is

$$\bar{x} = 1 - \bar{C}/C_0 = 2t_0^2kC_0 \int_{t_0}^{\infty} \frac{1}{t^2(1+kC_0t)}\, dt$$

$$= 2kC_0t_0^2 \left[\frac{1}{t_0} + kC_0 \ln \frac{kC_0t_0}{1+kC_0t_0}\right] \qquad (8)$$

In terms of the mean residence time, $\bar{t} = 2t_0$,

$$\bar{x} = kC_0\bar{t} \left[1 + \frac{kC_0\bar{t}}{2} \ln \frac{kC_0\bar{t}}{2+kC_0\bar{t}}\right] \qquad (9)$$

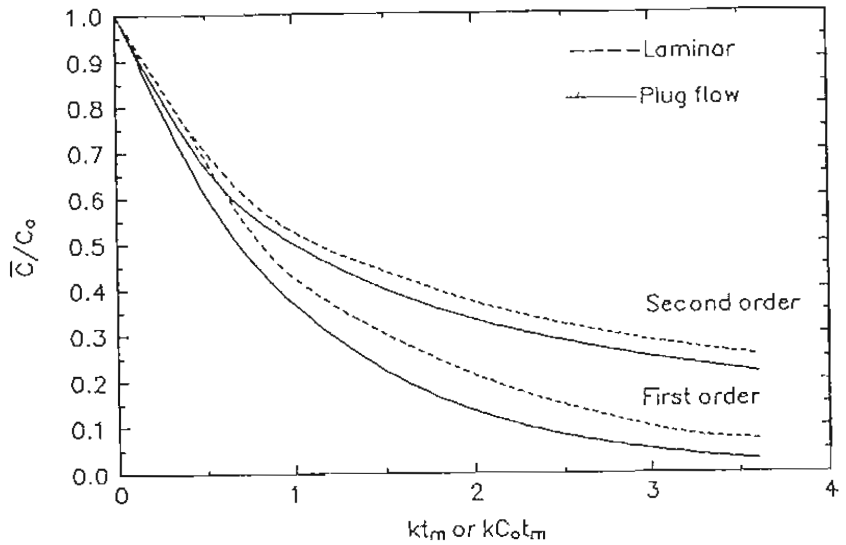
When t instead of β is eliminated from Eq (4), the result is

$$\bar{C} = 4\int_0^1 C\beta(1-\beta^2)d\beta \qquad (10)$$

and for first order reaction, Eq (6) becomes

$$\bar{C}/C_0 = 4 \int_0^1 \beta(1-\beta^2)\exp\left(- \frac{kt_0}{1-\beta^2}\right) d\beta \qquad (11)$$

The plots are of first and second order reactions.



P4.08.02. EXPERIMENTAL DATA

Data of an irreversible first order reaction under laminar conditions are available. Check them against the equations derived in problem P4.08.01.

The applicable relation is Eq (11),

$$\bar{C}/C_0 = 4\int_0^1 \beta(1-\beta^2)\exp\left(-\frac{kt_0}{1-\beta^2}\right)$$

The last column of the table records the numerical integration by the trapezoidal rule with 100 intervals and provides a good check of the experimental data.

kt_0	$\bar{C}/C_0$	Integral
0	1	
0.05	0.910	0.9098
0.10	0.835	0.8326
0.30	0.608	0.6001
0.70	0.330	0.3321
1.40	0.119	0.1291
2.00	0.060	0.0603

P4.08.03. EFFECT OF PRESSURE INCREASE

The second order reversible reaction, $2A \Rightarrow B + C$, is being carried out in the gas phase in a laminar flow reactor. When the feed rate of A is 0.1 lbmol/hr at 1 atm, conversion is 53%. (a) Find the value of $kC_0\bar{t}$. (b) In an attempt to increase conversion at the same temperature and molar flow rate it was proposed to increase the operating pressure to 10 atm; what will be the conversion under the changed conditions?

Use Eq (9) of problem P4.08.01.

$$\bar{x} = 0.53 = kC_0\bar{t}\left[1 + 0.5kC_0\bar{t}\ \ln\frac{kC_0\bar{t}}{2+kC_0\bar{t}}\right]$$

By trial, $kC_0\bar{t} = 1.40$.

The residence time is proportional to the pressure but the inlet concentration is inversely proportional to the pressure, so the quantity $kC_0\bar{t}$ is unchanged, and the conversion remains at 53%.

P4.08.04. ESTERIFICATION

A mixture of 5 mol butanol per mol acetic acid flows to a tubular reactor at the rate of 45.4 kg/h or 10 liters/h at 100 C. It also contains 0.032 wt% sulfuric acid as catalyst. Inlet concentration of the acid is 1.744 gmol/liter. The rate equation (Leyes & Othmer, *Ind Eng Chem* 37 968, 1945) is

$r_a = 0.0174C^2$, gmol acetic acid/(liter)(min).

Find the conversion in terms of V_r/V' (a) in plug flow; (b) in laminar flow.

Plug flow,

x = fraction converted

$$\frac{dx}{dt} = 0.0174C_{a0}(1-x)^2 = 0.0174(1.7444)(1-x)^2 = 0.0303(1-x)^2$$

$$V'C_{a0}dx = kC_{a0}^2(1-x)^2dV_r$$

$$\bar{t} = V_r/V' = \frac{1}{0.0303}\int_0^x \frac{dx}{(1-x)^2} = 33.0\left(\frac{1}{1-x} - 1\right)$$

Corresponding values of x and t are tabulated.

Laminar flow,

The applicable relation is Eq (9) of problem P4.08.01.

$$\bar{x} = kC_0\bar{t}[1 + 0.5kC_0\bar{t} \ln \frac{kC_0\bar{t}}{2+kC_0\bar{t}}]$$

with $kC_0 = 0.0174(1.744) = 0.03035$. Corresponding values of x and t from this equation also are tabulated. Conversion is somewhat less in laminar flow.

$\bar{t}$	x_{pf}	x_{lam}
30	0.4766	0.4288
33.1	0.5000	0.4461
35	0.5146	0.4649
40	0.5483	0.4966
40.6	0.5518	0.5000
45	0.5773	0.5243

P4.08.05. LAMINAR AND PLUG FLOWS

The ratio of residual concentrations, $f = \bar{C}/C_0$, in plug and laminar flows will be found for first and second order reactions for specific values of the parameters k and kC_0.

First order, k = 1:

$$f_{pf} = \exp(-k\bar{t}) = \exp(-0.5kt_0)$$

$$f_{lam} = 2t_0^2\int_{t_0}^{\infty} \frac{\exp(-kt)}{t^3}\,dt \qquad (1)$$

The values of the integral, f_{pf} and f_{lam} are tabulated for a range of t_0 with k = 1.

Second order, $kC_0 = 1$:

$$f_{pf} = 1/(1+kC_0\bar{t})$$

$$f_{lam} = 2t_0^2\int_{t_0}^{\infty} \frac{1}{t^3(1+kC_0t)}\,dt \qquad (2)$$

The results also are tabulated.

		First Order			Second Order		
$\bar{t}$	t_0	f_{pf}	$\int$	f_{lam}	f_{pf}	$\int$	f_{lam}
0.05	0.025	0..951	762.3	0.9528	0.9524	763.7	0.9546
0.1	0.05	0.904	182.0	0.9100	0.9091	182.8	0.9140
0.5	0.25	0.6065	5.225	0.6531	0.6069	5.606	0.7008
1	0.5	0.3678	0.8878	0.4439	0.5000	1.096	0.5480
2	1	0.1353	0.1087	0.2182	0.3333	0.1909	0.3818

P4.08.06. LAMINAR FLOW ESTERIFICATION.

Data were obtained (Hovorka & Kendall, Chem Eng Prog <u>56(8)</u> 58, 1960) for the reaction between NaOH and ethyl acetate to form sodium acetate and ethanol in a tubular reactor 3.2 cm ID at 29.8 C in which the flow rate varied between 440 and 2072 cc/min.The feed consisted of 0.1 N solutions of NaOH and ethyl acetate. Assuming physical properties of water, the corresponding Reynolds numbers vary between 370 and 1720. Thus the flow is laminar. Analyze these data and then design (a) a batch reactor and (b) a CSTR for a feed rate of 100 liters/min and a conversion of 65%.

The fractional conversion of a second order reaction in laminar flow is given by Eq (8) of problem P4.08.01.

$$\bar{x} = kC_0\bar{t}[1\ 0.5kC_0\bar{t}\ \ln \frac{kC_0\bar{t}}{2+kC_0\bar{t}}]$$

With the data given in the first two columns, values of kC_0 are calculated and tabulated there. The mean value is

$kC_0 = 0.4290$

Part (a):

$$f = C/C_0 = \frac{1}{1+kC_0t} = \frac{1}{1+0.429t} = 0.35$$

$t = 4.33$ min

This is impractical for a batch operation.

Part (b):

$$1 = f + kC_0(\frac{V_r}{V'})f^2$$

$$V_r = \frac{(1-f)V'}{kC_0f^2} = \frac{(1-0.35)100}{0.429(0.35)^2} = 1237 \text{ liters}$$

t, min	x	kC_0
0	0	
0.5	0.1675	0.4517
1	0.271	0.4326
1.5	0.351	0.4291
2	0.412	0.4233
2.5	0.462	0.4197
2.75	0.4835	0.4178

P4.08.07. LOCAL AND MEAN VALUES OF CONVERSION

A second order reaction has $kC_0 = 0.0303$. Obtain values of the ratios of fractional conversions along a stream line to the mean values over the cross section as a function of mean residence time over the range of $\beta = r/R$.

At particular values of β, Eq (3) of problem P4.08.01 can be written

$$x = \frac{0.5kC_0\bar{t}}{1-\beta^2+0.5kC_0\bar{t}} \qquad (1)$$

The mean value over the cross section is Eq (9) of P4.08.01,

$$\bar{x} = kC_0\bar{t}\ (1+\ 0.5kC_0\bar{t}\ \ln \frac{kC_0\bar{t}}{2+kC_0\bar{t}}) \qquad (2)$$

The ratio $x/\bar{x}$ is recorded in the last five columns of the table.

$\bar{t}$	$\bar{x}$	β=0	β=0.25	β=0.5	β=0.75	β=1
10	0.2102	0.6265	0.667	0.8001	1.225	4.76
50	0.5495	0.7851	0.8140	0.9152	1.154	1.82
100	0.7036	0.8567	0.8785	0.9511	1.103	1.42
∞	1					1

P4.08.08. AN L-H TYPE RATE EQUATION

A reaction with rate equation $r_c = C/(1+0.2C)$ is conducted in a laminar flow reactor. Evaluate the ratio of the mean laminar conversion to the plug flow conversion for a range of residence times.

In a plug flow reactor, or along a stream line in the laminar flow unit,

$$-V'dC = \frac{kC}{1+k_1C}\,dV_r$$

$$kt = kV_r/V' = \int_C^{C_0} \frac{1+k_1C}{kC}\,dC = \ln\frac{C_0}{C} + k_1C_0\left(1-\frac{C}{C_0}\right) \qquad (1)$$

The mean concentration in laminar flow is

$$\bar{C}/C_0 = 2t_0^2 \int_{t_0}^{\infty} (C/C_0)_{plug}\,\frac{dt}{t^3} = 2t_0^2 \int_{t_0}^{\infty} I\,dt \qquad (2)$$

Solve Eq (1) with $k = 1$ and $k_1C_0 = 0.2$ for $(C/C_0)_{plug}$. Then integrate Eq (2) numerically for $(C/C_0)_{laminar}$ at various values of t_0. The corresponding plug flow yield is the value at $\bar{t} = 2t_0$.

The last column is the ratio of fractional conversions, not of concentrations.

t_0	$\bar{t}$	C/C_0	I	$(C/C_0)_{lam}$	$(C/C_0)_{plug}$	x_{lam}/x_{plug}
0.5	1	0.650	5.204	0.500	0.4137	0.853
0.6		0.595	2.785			
0.7		0.544	1.586			
0.8		0.497	0.970			
0.9		0.454	0.622			
1	2	0.4137	0.414	0.256	0.160	0.885
1.1		0.377	0.283			
1.2		0.343	0.1988			
1.3		0.313	0.142			
1.4		0.285	0.1037			
1.5	3	0.2588	0.0767	0.138	0.0601	0.917
1.6		0.2353	0.0574			
1.7		0.2138	0.0435			
1.8		0.194	0.0333			
1.9		0.176	0.0257			
2	4	0.160	0.0200	0.0786	0.0227	0.943
2.5		0.0983	0.0063			
3		0.0601	0.00223			
3.5		0.0366	0.00085			
4		0.0227	0.00035			

P4.08.09. TRIANGULAR FLOW DISTRIBUTION

The flow distribution in a cylindrical vessel has the shape of an isosceles triangle with apex on the axis, thus $u = u_0(1-\beta)$, $\beta = r/R$. Find the mean velocity and the mean conversion of a reaction with a power law rate equation. Compare with laminar and uniform flows.

The average velocity over the cross section is

$$\bar{u} = \frac{1}{\pi R^2}\int_0^R 2\pi r u_0(1-r/R)\,dr = u_0/3 \qquad (1)$$

Reactant balance over an annulus of length dL along a stream line,

$$(2\pi r dr)uC = (2\pi r dr)u(C+dC) + (2\pi r dr)dL\,kC^q$$

or

$$\frac{dC}{dL} = -\frac{kC^q}{u} = -\frac{kC^q}{u_0(1-\beta)} \qquad (2)$$

The mean value over a cross section will be found. The mass flow of reactant through an annulus is

$$dF = uC(2\pi r dr) = \frac{L}{t}C(2\pi r dr)$$

and the total flow through the cross section is

$$F_{tot} = \pi R^2 \bar{u} = 3\pi R^2/u_0$$

The mean concentration becomes,

$$\bar{C} = \frac{3}{\pi R^2 u_0}\int_0^R C(\frac{L}{t})(2\pi r)dr = \frac{6L}{u_0}\int_0^1 \frac{C}{t}\beta\, d\beta \qquad (3)$$

The variable $\beta = r/R$ can be eliminated in favor of t, thus,

$$t = L/u = \frac{L}{u_0(1-\beta)} = \frac{t_0}{1-\beta}$$

$$\beta = 1-t_0/t$$

$$d\beta = \frac{t_0}{t^2}dt$$

Finally,

$$\bar{C} = 6t_0\int_{t_0}^{\infty}\frac{C}{t}(1-\frac{t}{t_0})(\frac{t_0}{t^2})dt = 6t_0^2\int_{t_0}^{\infty}C(1-\frac{t_0}{t})\frac{dt}{t^3} \qquad (4)$$

In terms of the mean residence time $\bar{t} = 3t_0$,

$$\bar{C} = \frac{2}{3}\bar{t}^2\int_{t_0}^{\infty}C(1-\frac{t}{t_0})\frac{dt}{t^3} \qquad (5)$$

C is replaced in terms of t by the solution of Eq (2) for the appropriate rate equation.

For comparison, in laminar flow, with $\bar{t} = 2t_0$,

$$\bar{C} = 2t_0^2\int_{t_0}^{\infty}C\frac{dt}{t^3} = 0.5\bar{t}^2\int_{t_0}^{\infty}C\frac{dt}{t^3} \qquad (6)$$

Numerical values are tabulated for a second order reaction with $kC_0 = 1$. For plug flow,

$$C/C_0 = 1/(1+kC_0\bar{t})$$

	$\bar{C}/C_0$		
$\bar{t}$	Triangular	Parabolic	Uniform
1	0.5604	0.5515	0.500
2	0.4047	0.3870	0.3333
5	0.2221	0.2058	0.1667
10	0.1272	0.1140	0.0909

P4.08.10. SPECIFIC RATE DETERMINATION

A test is made of a second order reaction in a laminar flow reactor. With a mean residence time $\bar{t} = 5$, a conversion of 85% was obtained. (a) Find the specific rate, and compare with the assumption that plug flow existed. (b) What would be the conversion in laminar flow if the plug flow value of kC_0 were valid.

(a) In plug flow,

$$C/C_0 = 0.15 = \frac{1}{1+kC_0\bar{t}} = \frac{1}{1+5kC_0}$$

$$(kC_0)_{pf} = 0.9333$$

For laminar flow, use the relation from problem P4.08.01.

$$x = kC_0t(1 + 0.5kC_0t \ln \frac{kC_0t}{2+kC_0t}) \qquad (1)$$

Substitute x = 0.85 and t = 5 and find

$$(kC_0)_{lam} = 1.481$$

(b) With the plug flow value, $kC_0 = 0.9333$, the conversion in laminar flow from Eq (1) is

$$x = 0.783$$

P4.09.01. DISSOLUTION OF SALT.

A tank contains 100 gal of brine with 50 lb of dissolved salt. The bottom of the tank is covered with a cake of salt whose surface may be assumed to remain substantially constant. The salt dissolves at a rate proportional to the difference between the conentration of the solution and the saturation value which is 3.0 lb/gal. If the water in the tank were fresh, the rate of solution would be 1.0 lb/min. Fresh water is allowed to run into the tank at the rate of 3 gpm, and brine overflows at the same rate. The solution is kept uniform by agitation. Assuming that the volume of the brine does not vary as its concentration changes, how much salt will be in solution in the tank at the end of 1 hr?

C = concentration in tank at time t

C_0 = 0.5 lb/gal, initial concentration in the tank

C_i = concentration of input

V' = 3 gal/min

The rate of solution is

$$r = k(3-C)$$

When C = 0, r = 1, k = 1/3

$$r = (3-C)/3$$

Material balance,

Input + Source = Output + Sink + Accumulation

$$0 + (3-C)/3 = V'C + 0 + V_r\frac{dC}{dt}$$

$$100\,\frac{dC}{dt} = \frac{3-C}{3} - 3C = \frac{3-10C}{3}$$

$$t = 300 \int_{0.5}^{C} \frac{dC}{3-10C} = 30 \ln \frac{2}{10C-3}$$

$$C + 0.1[3+2\exp(-t/30)]$$

When t = 60,

$$C = 0.328$$

$$V_rC = 32.8 \text{ lbs}$$

If no salt were being dissolved,

$$100\frac{dC}{dt} + 3C = 0$$

$$t = -\ 33.33 \ln (0.5/C)$$
$$C = 0.5 \exp(-0.03t)$$
$$\Rightarrow 0.083 \text{ when } t = 60$$

P4.09.02. SALT DISSOLUTION

(a) A mass of inert material containing 5 lb salt in its pores is agitated with 10 gals of water. In 5 minutes 2 lbs of salt have dissolved. A saturated solution contains 3 lb salt per gal. When will the salt be 99% dissolved?

(b) A mass of insoluble contains 30 lb of salt in its pores. The mass is agitated with 20 gal of water for one hour, when half the slat is found to be dissolved. How much would have been dissolved in the same time if twice the amount of water had been used?

Part (a):

W = weight of undissolved salt

$$-\frac{dW}{dt} = kW\left(3 - \frac{5-W}{10}\right)$$

$$0.1kt = \int_W^5 \frac{dW}{(25+W)} = 0.04 \ln \frac{5(25+W)}{30W}$$

When $t = 5$, $W = 3$, $k = 0.1767$

When $W = 0.01(5) = 0.05$,

$$t = \frac{10}{25(0.1767)} \ln \frac{5(25.05)}{30(0.05)} = 10.01 \text{ min}$$

Part (b):

W = undissolved salt

V_r = volume of water

$$-\frac{dW}{dt} = kW\left(3 - \frac{30-W}{V_r}\right)$$

$$\frac{kt}{V_r} = \int_W^{30} \frac{dW}{3V_r-30+W} = \frac{1}{3V_r-30} \ln \frac{30(3V_r-30+W)}{3V_rW}$$

When $V_r = 20$, $t = 1$, $W = 15$, RHS $= 0.01352$

$$k = 0.01352(20) = 0.2703$$

When $V_r = 20$, $t = 1$,

$$\frac{0.2703}{40} = \frac{1}{90} \text{LN} \frac{30(120-30+W)}{120W}$$

W = 14.18 lbs undissolved salt, 15.82 lbs dissolved salt.

P4.09.03. TWO BRINE TANKS

Brine containing C_0 lb/gal of dissolved salt flows at the rate V' into a tank of volume V_{r1} which is initially full and contains x_0 lb dissolved salt. Overflow at V' gpm runs into a second tank of volume V_{r2} which also is initially full and contains y_0 lb dissolved salt. Overflow from this tank also is at the rate V'. Both tanks are well stirred. Express the instantaneous amounts x and y as functions of time.

$$C_{10} = x_0/V_{r1},\ C_{20} = y_0/V_{r2}$$

$$x = V_{r1}C_1,\ y = V_{r2}C_2$$

Material balance on the first tank,

$$V'C_0 = V'C_1 + V_r\frac{dC_1}{dt}$$

$$C_0 = C_1 + \tau_1\frac{dC_1}{dt} \quad (1)$$

$$t/\tau_1 = -\ln\frac{C_0-C_1}{C_0-C_{01}}$$

$$C_1 = C_0 -(C_0-C_{01})\exp(-t/\tau_1) \quad (2)$$

For the second tank,

$$C_2 + \tau_2\frac{dC_2}{dt} = C_1 = C_0 -(C_0-C_{01})\exp(-t/\tau_1) \quad (3)$$

Solve by Laplace Transform.

$$\bar{C}_2 + \tau_2(s\bar{C}_2 - C_{02}) = \frac{C_0}{s} - \frac{C_0-C_{01}}{s+t/\tau_1}$$

$$\bar{C}_2 = \frac{1}{\tau_2 s+1}\left(\tau_2 C_{02} + \frac{C_0}{s} - \frac{C_0-C_{01}}{s+t/\tau_1}\right) \quad (4)$$

This is inverted term by term.

$$C_2 = C_{02}\exp(-t/\tau_2) + C_0[1 - \exp{-t/\tau_2})]$$

$$- \frac{C_0-C_{01}}{1-\tau_2/\tau_1}[\exp(-t/\tau_1) - \exp(-t/\tau_2)] \quad (5)$$

When the tanks are the same size, $\tau_1 = \tau_2 = \tau$, and the third term on the right of Eq (5) is replaced by

$$(C_0-C_{01})\left(\frac{t}{\tau}\right)\exp(-t/\tau) \quad (6)$$

P4.09.04. GASEOUS REACTANT OF LIMITED SOLUBILITY

A reaction has the rate equation, $r_a = kC_aC_b$. The reactor initially contains only reactant A. B is a gas of limited solubility. It is charged at a rate sufficient to keep the solution saturated at a concentration C_{b0}. Find the relation between the time and the variable feed rate of B, V'_b, sufficient to keep the solution saturated as the reaction goes on.

The material balances on the two participants:

Input = Sink + Accumulation

$$0 = kV_rC_aC_{b0}dt + V_rdC_a$$

$$C_a = C_{a0}\exp(-kC_{b0}t)$$

The rate of input of B equals the rate of reaction.

$$V'_b = kV_rC_aC_{b0}$$

$$= kV_rC_{a0}C_{b0}\exp(-kC_{b0}t)$$

P4.09.05. ELUTRIATION OF AIR.

Oxygen flows through one tube into a liter flask filled with air and escapes through another tube after thorough mixing. What percentage of oxygen will the gas contain after 3 liters have passed through the vessel? How much after 10 liters?

Material balance:

$$V'C_f = V'C + V_r\frac{dC}{dt}$$

$$C_f = 1,\ C_0 = 0.21,\ V_r = 1$$

$$\frac{V'}{V_r}t = \int_{C_0}^{C} \frac{dC}{C_f-C} = \ln \frac{C_f-C}{C_f-C_0} = \ln \frac{1-C}{1-0.21}$$

$$C = 1 - 0.79 \exp(-V't/V_r)$$

Some numerical values are:

$V't/V_r$	0	1	3	10
C	0.21	0.7094	0.9607	0.99995

P4.09.06. SULFUR DISSOLUTION

In a laboratory experiment (Hitchcock & Robinson, 1936), spent iron oxide from a gas works, containing 52 wt% of sulfur, was extracted with boiling benzol. The following data were obtained with 25 gm of oxide and 100 gm of benzol:

t	0	10	20	30	40	50	60	70	80	90
W	0	2.15	3.4	4.32	5.10	5.73	6.32	6.78	7.04	7.42

The time is in minutes and W is in gms of sullfur dissolved per 100 gms benzol. The solubility of sulfur in benzol at the boiling point is 11.7 gm/100 gm benzol. Fit an equation to the data which should represent the data within the precision of the experiment, about 5%.

Assume the rate of solution to be proportional to the amount of undissolved sulfur and to the displacement from saturation.

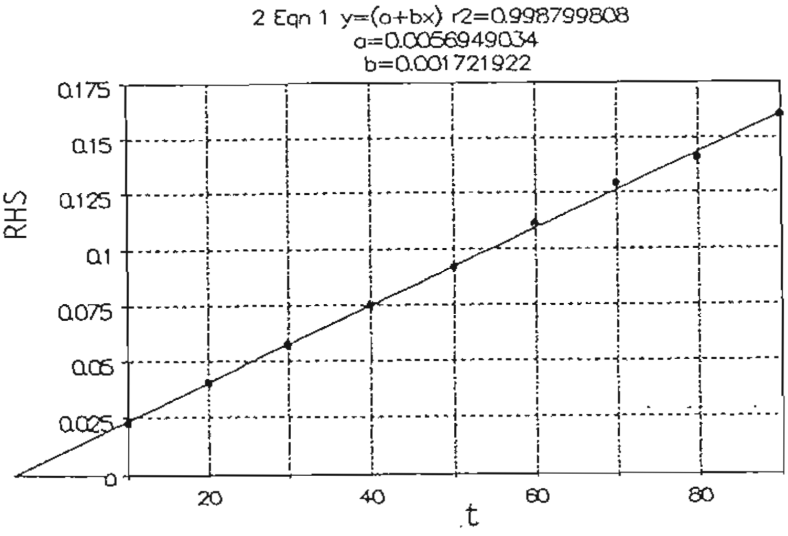
W = dissolved sulfur

$W_0 = 0.52(25) = 13$, initial sulfur content

$$-\frac{dW}{dt} = k(13-W)(11.7-W)$$

$$kt = \int_{W}^{0} \frac{dW}{(13-W)(11.7-W)} = \ln \frac{11.7(13-W)}{13(11.7-W)}$$

The plot of the RHS of this equation against t is straight, possibly confirming the assumed relation. The fact that the time data do not pass through the origin indicates that the actual start of the dissolution process was about 3 minutes before the first record, obtained by extrapolation of the plot to zero ordinate.



P4.09.07. CO_2 SEPARATION FROM HELIUM

A current consisting of equal contents of CO_2 and Helium is passed through a tube packed with small lumps of CaO. If after passing through 2 ft of the packing the $\%CO_2$ declines by half, what will be the decline after 4 ft?

Assume that CaO is in excess. Also, assume that the rate of reaction is proportional to the concentration of the CO_2.

n_a = molal flow rate of CO_2

$n_t = n_{He} + n_a = 0.5 + n_a$

$V' = (0.5+n_a)RT/\pi$

$$C_a = n_a/V' = \frac{\pi}{RT}\left(\frac{0.5+n_a}{n_a}\right)$$

Flow reactor,

$V_r = A_{\text{cross section}}L$

$$\frac{k\pi}{RT}V_r = \int_{n_a}^{0.5}\frac{0.5+n_a}{n_a} = 0.5\ln(0.5/n_a) + 0.5 - n_a$$

When $L = 2$, $n_a = 0.5n_{a0} = 0.25$, $k\pi A/RT = 0.4716$

In general,

$$0.4716\,L = \ln(0.5/n_a) + 0.5 - n_a$$

from which

$n_a = 0.1118$, or 77.64% removed when L = 4 ft.

P4.09.08. REMOVAL OF CO_2 FROM AIR

A current of air containing 0.0004% CO_2 is passed through a tube of uniform cross section packed with small lumps of freshly prepared CaO. If after passing through 2 ft of packing the concentration has fallen to 0.0002%, what will it be after 4 ft?

The rate of removal is

$$-\frac{dP}{dt} = kA(P - P_s)$$

where A is the interfacial area and P_s is the backpressure at the surface of the CaO, but is assumed zero with fresh material. The integral is

$$kAt = \frac{kAL}{u} = \ln(P_0/P)$$

When $L = 2$, $P_0/P = 2$ and $kA/u = 0.3466$

When $L = 4$,

$P/P_0 = \exp[-0.3466(4)] = 0.25$

$C = 0.25(0.0004) = 0.0001\%$

P4.09.09. SEMIBATCH REACTION. EQUATIONS

The reaction, $A + B \Rightarrow$ Products, is carried out by first charging B to the vessel to a concentration C_{b0} and a volume V_{r0}, then feeding a solution of concentration C_{a0} at volumetric rate V' for a time t.

Volume of solution in the tank,

$$V_r = V_{r0} + V't \tag{1}$$

Stoichiometric balance,

$$V'tC_{a0} - V_rC_a = V_{r0}C_{b0} - V_rC_b$$

$$C_b = C_a + \frac{V_{r0}C_{b0} - V'tC_{a0}}{V_{r0} + V't} \tag{2}$$

Material balance on A,

Input = Output + Sink + Accumulation

$$V'C_{a0} = 0 + kV_rC_aC_b + \frac{d(C_aV_r)}{dt}$$

$$= kV_rC_aC_b + V_r\frac{dC_a}{dt} + C_aV'$$

$$\frac{dC_a}{dt} + kC_aC_b + \frac{V'C_a}{V_r} = \frac{V'C_{a0}}{V_r} \qquad (3)$$

Eqs (1), (2) and (3) are combined into

$$\frac{dC_a}{dt} = \frac{V'}{V_{r0}+V't}(C_{a0}-C_a) - kC_a\left(C_a+ \frac{V_{r0}C_{b0}-V'tC_{a0}}{V_{r0}+V't}\right) \qquad (4)$$

A numerical solution is required.

P4.09.10. A SEMI-BATCH PROCESS

A tank is charged initially with v_{r0} = 100 liters of a solution of concentration C_{b0} = 2 gmol/liter. Another solution then is pumped in at V' = 5 liters/min with concentration C_{a0} = 0.8 until a stoichiometric amount has been added. The rate equation is

$r = 0.015C_aC_b$ gmol/liter-min

Find the concentration during the filling period and for 50 minutes afterward.

Apply the equations of problem P4.09.09.

$$V_r = 100 + 5t \qquad (1)$$

$$C_b = C_a + \frac{100(2)-5(0.8)t}{100+5t} = C_a + \frac{40-0.8t}{20+t} \qquad (2)$$

$$\frac{dC_a}{dt} = \frac{0.8-C_a}{20+t} - 0.015C_a\left(C_a + \frac{40-0.8t}{20+t}\right) \qquad (3)$$

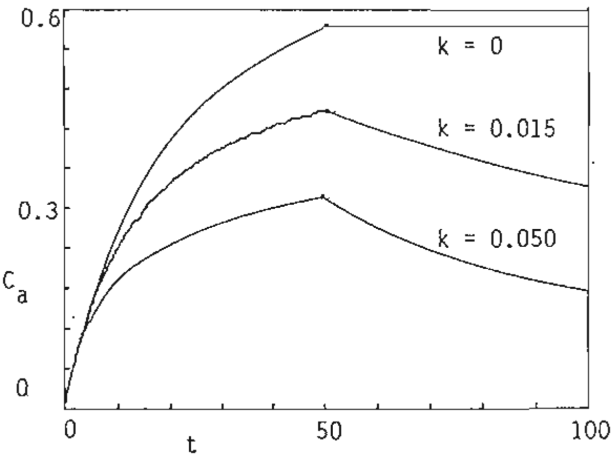
The input is continued until 200 lbmols of A have been added, which is for 50 minutes. Eq (3) is integrated for this time interval. After input is discontinued the rate equation is

$$-\frac{dC_a}{dt} = kC_a^2 \qquad (4)$$

At t = 50, $C_a = C_{a1} = 0.4467$.

$$C_a = \frac{1}{1/C_{a1}+k(t-50)} = \frac{1}{2.2386+0.015(t-50)} \qquad (5)$$

Plots are shown for several specific rates, including k = 0 when no reaction takes place.



P4.09.11. CONTROL OF TEMPERATURE BY LIMITING FEED RATE

The reaction, A + B ⇒ C, involves a high rate of heat generation and the rate of heat removal is limited. Accordingly, B is charged to the vessel at reaction temperature, and A is added gradually also at reaction temperature.The initial charge is 1.0 lbmol of B. The specific volumes of both A and B are 1 cuft/lbmol. The reaction is first order with respect to B with k = 3/hr, assumed independent of temperature (!!). Heat of reaction is 150,000 Btu/lbmol A reacted and the maximum rate of heat removal is 50,000 Btu/hr. What is the maximum possible rate of addition of A?

F = mols B/hr = cuft/hr, rate of addition of A

$V_r = 1 + Ft$

$C_{af} = 1$ lbmol/cuft

$(Ft)_{final} = 1$ lbmol

Stoichiometric balance,

$$C_b = C_a + \frac{V_{r0}C_{b0}-FtC_{a0}}{V_{r0}+Ft} = C_a + \frac{1-Ft}{1+Ft} \qquad (1)$$

The rate of heat generation,

$$\frac{dQ}{dt} = 150000r_a = 150000(3)C_aC_b = 450000C_a(C_a + \frac{1-Ft}{1+Ft}) \qquad (2)$$

The material balance is represented by Eq (4) of problem P4.09.09.

$$\frac{dC_a}{dt} = \frac{F}{1+Ft}(1-C_a) - 3C_a(C_a + \frac{1-Ft}{1+Ft}) \qquad (3)$$

When t_f is the time for input of A, $Ft_f = 1$ lbmol. Equations (2) and (3) are integrated by ODE for various combinations of F and t_f, with the tabulated results. When $t_f = 0.73$ and $F = 1.37$ mols/hr, the average heat evolution over the period is close to 50,000 Btu/hr.

t_f	F	Q	Q/t_f	C_a	
0.5	2.0	28797	57594	0.3519	
0.7	1.429	35600	50857	0.3184	
0.73	1.370	36487	49983	0.3141	Check
0.8	1.25	38448	48060	0.3046	
0.9	1.111	41007	45563	0.2922	
1	1	43322	43322	0.2812	

P4.09.12. NONISOTHERMAL BATCH FILLING PROCESS

A batch filling process involves a reaction, A + B ⇒ C. Initial charge of A is V_{r0} liters at T_0. B then is charged at the rate V'_b liters/hr at C_{b0} and T_0. The enthalpy change of reaction, the density and the heat capacity are related by $\Delta H_r/\rho C_p$ = constant. The reaction is first order with respect to B. Obtain expressions for the behavior of T and n_b with time.

$$k = \exp(a-b/T) \qquad (1)$$

$$V_r = V_{r0} + V'_b t \qquad (2)$$

Heat balance,

$V'_bC_{b0}t$ = total input of B

V_rC_b = amount of unreacted B

$-\Delta H_r(V'_bC_{b0}t - V_rC_b) = \rho C_p(T-T_0)$

$$T = T_0 - \frac{\Delta H_r}{\rho C_p}(V_b' C_{b0} t - V_r C_b) \qquad (3)$$

Material balance on B,

$$r_b = kC_b = k(n_b/V_r)$$

$$F_b C_{b0} = V_r k C_b + \frac{d(V_r C_b)}{dt} = V_r k C_b + V_b' C_b + V_r \frac{dC_b}{dt}$$

$$\frac{dC_b}{dt} = -(k + \frac{V_b'}{V_r})C_b + \frac{F_b C_{b0}}{V_r} \qquad (4)$$

The differential equation, Eq (4), and the auxiliary numbered equations can be solved simultaneously for the variables C_b, T, k and V_r in terms of the time t.

P4.09.13. SEMIBATCH OPERATION OF A SECOND ORDER REACTION

The reaction, A + B ⇒ Products, occurs isothermally in a stirred vessel. Reactant A of concentration C_{a0} is charged to the reactor to a volume V_{r0}; then reactant B is pumped in at a rate V_b' of concentration C_{b0}. Find the relation between the time and the amount of unreacted A in the vessel, and apply it to the numerical case following.

$$V_r = V_{r0} + V_b' t \qquad (1)$$

$$C_a = n_a/V_r$$

Stoichiometric balance,

$$V_b' C_{b0} t - V_r C_b = V_{r0} C_{a0} - V_r C_a$$

$$C_b = C_a + \frac{V_b' C_{b0} t - V_{r0} C_{a0}}{V_r} \qquad (2)$$

Balance on A,

$$-\frac{dn_a}{dt} = kV_r C_a C_b = \frac{kn_a(n_a + V_b' C_{b0} t - V_{r0} C_{a0})}{V_r}$$

Example: Integrate the equation for these numerical values,

$V_{r0} = 100$

$C_{a0} = 2$

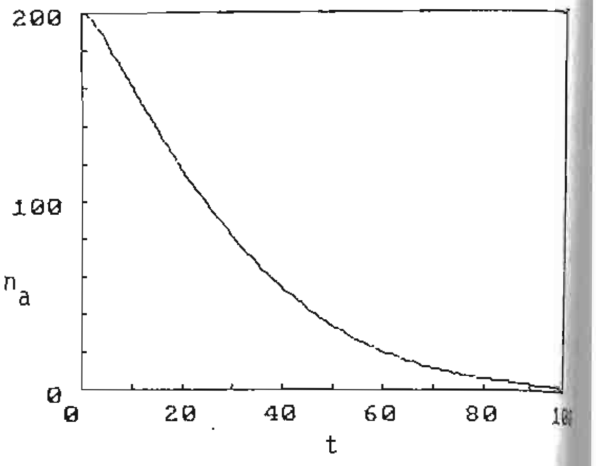
$V_b' = 15$

$C_{b0} = 0.5$

$k = 0.2$

$$-\frac{dn_a}{dt} = \frac{0.2n_a[n_a + 15(0.5)t - 100(2)]}{100 + 15t}$$

The solution is plotted.



P4.09.14. CONTROLLED INPUT RATE OF A REACTANT

Initially a reactor contains 2 m^3 of a solvent. A solution containing 2 kmol/m^3 of reactant A is pumped in at the rate of 0.06 m^3/min until the volume becomes 4 m^3. The rate equation is $r_a = 0.25C_a$, 1/min. Compare the time-composition profile of this operation with charging all of the feed instantaneously.

During the filling period,

$$V_r = 2 + 0.06t$$

$$V'C_{ao} = kV_rC_a + \frac{d(V_rC_a)}{dt} = kV_rC_a + V_r\frac{dC_a}{dt} + C_a\frac{dV_r}{dt}$$

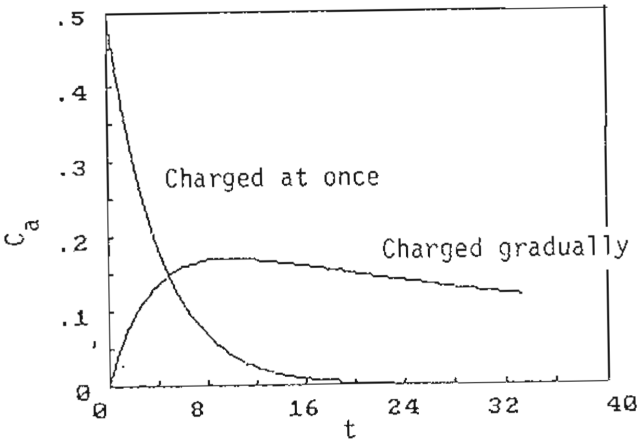
$$0.06(2) = 0.25(2+0.06t)C_a + (2+0.06t)\frac{dC_a}{dt} + 0.06C_a$$

$$\frac{dC_a}{dt} = \frac{0.12 - (0.56+0.015t)C_a}{2+0.06t},\quad C_{a0} = 0 \qquad (1)$$

When all of A is charged at the beginning,

$$\frac{dC_a}{dt} = -0.25C_a,\quad C_{a0} = 0.5 \qquad (2)$$

The integrals of these two equations are plotted. A peak value, $C_{a0} = 0.1695$, is reached in the first operation at t = 10.



P4.09.15. HYDROCHLORINATION OF LAURYL ALCOHOL

A rate equation for the hydrochlorination of lauryl alcohol is

$$-\frac{dC_a}{dt} = 0.68\left(\frac{G}{V_r}\right)^{0.55} C_a^{0.5} \quad \text{gmol LA/liter-hr}$$

where G/V_r has the units (gmol HCl/hr)/(liter of liquid phase). Initial concentration in the liquid phase is 3.66 gmol LA/liter. A semibatch operation is required, in which the feed rate of HCl is varied so as to maintain 90.9% utilization of the HCl at all times, that is

$$G = -1.1\, V_r\frac{dC_a}{dt}$$

Find how C_a and G/V_r vary with time up to 5 hrs.

$$-\frac{dC_a}{dt} = 0.68\left(1.1\frac{dC_a}{dt}\right)^{0.55} C_a^{0.5}$$

$$= 0.4769C_a^{1.111} \qquad (1)$$

Integrating,

$$0.4769t = -\int_{3.66}^{C_a} = 9(C_a^{-0.111} - 0.8657)$$

$$C_a = (0.8657+0.05298t)^{-9} \qquad (2)$$

$$\frac{dC_a}{dt} = -9(0.05298(0.8657+0.05298t)^{-10}$$

$$G/V_r = -1.1(\frac{dC_a}{dt}) = 0.5245C_a^{1.111} \qquad (3)$$

The values are tabulated.

t	C_a	G/V_r
0	3.660	2.2186
1	2.145	1.2249
2	1.295	0.6992
3	0.8033	0.4111
4	0.5103	0.2484
5	0.3313	0.1537

P4.09.16. ABRUPT CHANGE IN FEED CONCENTRATION

A CSTR operation of a second order reaction has a steady state equation

$$C_0 = C + 0.3\tau C^2$$

with C_0= 1.5 and τ = 4. After steady state has been achieved, the concentration of the feed is changed abruptly to C_0 = 1.8. How long does it take to attain 95% of the new steady state value?

The original steady concentration is obtained from

$$1.5 = C + 1.2C^2,$$
$$C = 0.7765$$

The new steady state concentration is obtained from

$$1.8 = C + 0.3(4)C^2$$
$$C_s = 0.8770$$

The time is to be found when

$$C = 0.05(0.7765) + 0.95(0.8770) = 0.8720$$

The unsteady material balance is

$$1.8V' = V'C + kV_rC^2 + V_r\frac{dC}{dt}$$

$$1.8 = C + k\tau C^2 + \tau\frac{dC}{dt}$$

$$= C + 1.2C^2 + 4\frac{dC}{dt} \qquad (1)$$

This equation is integrated from the initial condition C = 0.7765 to the final condition C = 0.8720. The tabulation shows the numerical solution. Interpolating, t = 6.38 at 95% approach to steady state.

```
     t          c          t          c
0.0         0.3367     6.0000     0.8705
0.6000      0.5093     6.6000     0.8729
1.2000      0.6333     7.2000     0.8745
1.8000      0.7184     7.8000     0.8754
2.4000      0.7751     8.4000     0.8761
3.0000      0.8121     9.0000     0.8765
3.6000      0.8359     9.6000     0.8767
4.2000      0.8510     10.200     0.8768
4.8000      0.8606     10.800     0.8769
5.4000      0.8667     11.400     0.8770
6.0000      0.8705     12.000     0.8770
```

P4.09.17. FILLING AND UNSTEADY STATE PERIODS.

A stirred reactor is being charged at 5 cuft/min with a solution of reactant at 2 mol/cuft. The reactor has a cpacity of 150 cuft but is initially empty. The rate of reaction is

$$r = 0.02C^2 \text{ lbmol/cuft-min.}$$

After the tank is filled, pumping is continued and overflow is permitted at the same flow rate. Find the concentration in the tank when it first becomes full, and find how long it takes for the effluent concentration to get within 95%of the steady state value.

Filling period:

$$V_r = V't$$

$$V'C_0 = kV_rC^2 + \frac{dV_r}{dt} = kV_rC^2 + C + t\frac{dC}{dt}$$

$$\frac{dC}{dt} = \frac{C_0-ktC^2-C}{t} = \frac{2-0.02tC^2-C}{t}, \quad C = 2 \text{ when } t = 0$$

The numerical solution is C = 1.3269 when t = 30.

Unsteady period:

$$V'C_0 = V'C + kV_rC^2 + V_r\frac{dC}{dt}$$

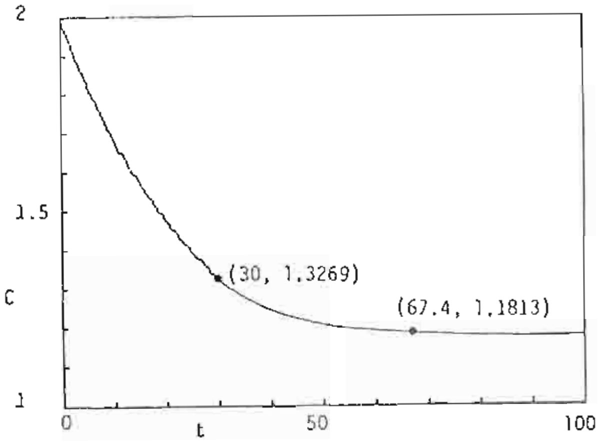
$$\frac{dC}{dt} = \frac{C_0-C-k\tau C^2}{\tau} = \frac{2-C-0.02(30)C^2}{30}, \quad C = 1.3269 \text{ when } t = 30.$$

The variables are separable, but the plot is of a numerical solution. The steady state concentration is 1.1736.

At 95% approach to steady state from the condition at t = 30,

$$C = 0.05(1.3269)+0.95(1.1736) = 1.1813$$

From a printout of the solution, t = 67.4 min at this value.



P4.09.18. FILL, REACT AND DISCHARGE

A solution with A_0 = 1 lbmol/cuft and another with B_0 = 1.2 lbmol/cuft are pumped at 2.5 cuft/min each into a 100 cuft tank where they react according to the rate equation,

$$r_a = -\frac{dA}{dt} = 0.03[A(0.2+A) - 0.04(1-A)^2] \quad \text{lbmol/cuft-min}$$

After 95% of equilibrium conversion is reached, the tank is emptied to storage at the rate of 5 cuft/min. Find the times and concentrations (a) when the filling is complete. (b) when the required 95% of equilibrium is reached in the reactor. (c) the concentration in the tank when the discharge is complete and no reaction occurs there.

$A_0 = 0.5,\ B_0 = 0.6$

At equilibrium,

$$A(0.2+A) - 0.04(1-A)^2 = 0$$

$$A_e = 0.1050$$

At 95% approach to equilibrium,

$$A = 0.05(1)+0.95(0.1050) = 0.1498$$

During the filling period,

$$V_r = Ft = 5t$$

Material balance on A,

$$FA_0 = 0 + Ftr_a + \frac{d(FtA)}{dt} = Ftr + Ft\frac{dA}{dt} + FA$$

$$\frac{dA}{dt} = \frac{1-A}{t} - 0.03[A(0.2+A) - 0.04(1-A)^2],\quad A = 1 \text{ when } t = 0.$$

The integral is plotted.

When $t = 20,\ A = 0.7494$ (a)

During the reaction period after filling,

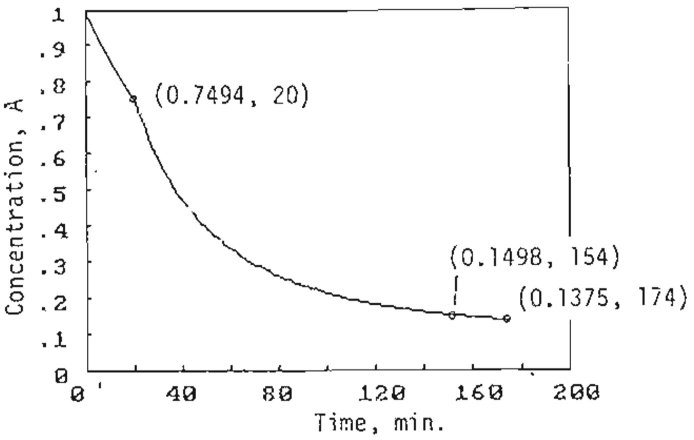
$$-\frac{dA}{dt} = 0.03[(0.2+A)-0.04(1-A)^2],\ \text{with } A = 0.7494 \text{ when } t = 20.$$

Integration shows that

when $A = 0.1498,\ t = 154$ min

During the discharge period, reaction continues in the tank in accordance with the same rate equation, for the 20 minutes of the discharge time. The concentrations during this period are tabulated. The mean value to storage is obtained by trapezoidal integration,

$$\bar{A} = 0.01\int_{154}^{174} A\,dt = 0.05\int_{154}^{174} A\,dt = 0.1447 \qquad \text{(c)}$$



t	A
154	0.1493
156	0.1479
158	0.1466
160	0.1453
162	0.1441
164	0.1429
166	0.1417
168	0.1406
170	0.1395
172	0.1385
174	0.1375

P4.09.19. UNSTEADY TWO STAGES

A CSTR battery consists of a 5 liter vessel and a 10 liter one. Originally they contain acetic anhydride solution of concentrations $C_{10} = C_{20} = 0.5(10^{-4})$ gmol/cc. Solution of concentration $C_0 = 3(10^{-4})$ is charged to the battery at 2 liters/min. The reaction is pseudo first order with k = 0.38/min. Find the concentrations of both vessels as functions of time.

First stage:

$$FC_0 = FC_1 + kV_{r1}C_1 + V_{r1}\frac{dC_1}{dt}$$

$$\frac{dC_1}{dt} + (k+\frac{1}{\tau_1})C_1 = \frac{C_0}{\tau_1}$$

$$C_1 = \frac{C_0}{1+k\tau_1}\ \exp[(k+1/\tau_1)t] + I$$

When $t = 0$, $C_1 = C_{10}$, $I = C_{10} - \frac{C_0}{1+k\tau_1}$

$$C_1 = \frac{C_0}{1+k\tau_1} + (C_{10} - \frac{C_0}{1+k\tau_1})\exp[(k+1/\tau_1)t] \qquad (1)$$

Second stage:

$$\frac{dC_2}{dt} + (k+\frac{1}{\tau_2})C_2 = \frac{C_1}{\tau_2} \qquad (2)$$

Conditions are $C_2 = C_{20}$ when $t = 0$. Substitute for C_1 from Eq (1) and solve as a first order linear equation, or solve both equations numerically.

With $\tau_1 = 2.5$, $\tau_2 = 5$ and the given values for the fixed concentrations, the equations become

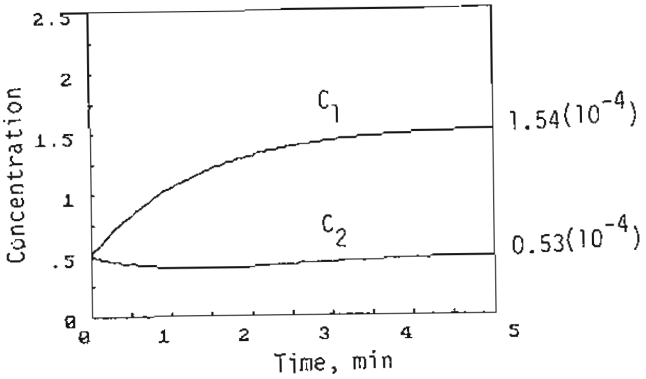
$$\frac{dC_1}{dt} + 0.78C_1 = 1.2(10^{-4}) \qquad (3)$$

$$\frac{dC_2}{dt} + 0.58C_2 = 0.2C_1 \qquad (4)$$

The limiting concentrations are

$$C_1 = 1.2(10^{-4})/0.78 = 1.54(10^{-4})$$

$$C_2 = 0.2C_1 = 0.53(10^{-4})$$



P4.09.20. CONSECUTIVE REACTIONS IN TWO STAGES

The reactions, A ⇒ B ⇒ 2C, are conducted in a continuous battery of two stages. The specific rates are 4/hr and 2/hr. Initially both reactors are charged with solution containing 1.5 lbmol/cuft of substance A and none of B or C. The ultimate condition is to be 90% conversion of A. The reactors are left undisturbed until the conversion of A in the second stage has become 80% of the steady state value. Pumping of fresh solution to the first stage is resumed at 120 cuft/hr, and overflow is at the same rate.

(a) Find the reactor sizes needed for 90% conversion of A.

(b) What is the length of the incubation period?

(c) How long after pumping restarts does it take to attain 98% of the steady state value in the first reactor? In the second reactor?

$$C_{a2}/C_{a0} = 0.1 = \frac{1}{(1+k_1\tau)^2} = \frac{1}{(1+4\tau)^2}$$

$\tau = 0.5406$

$V_r = F\tau = 120(0.5406) = 64.8$ cuft, each (a)

Incubation period,

$C_{a0} = 1.5, \quad C_a = 1.5 - 0.8(1.35) = 0.42$

$$t_{inc} = \frac{1}{k_1}\ln(C_0/C) = 0.25\ln(1.5/0.42) = 0.32 \text{ hr} \qquad \text{(b)}$$

Steady states,

$$C_{a1} = \frac{1.5}{1+4(0.5406)} = 0.4743$$

$$C_{a2} = \frac{1.5}{[1+4(0.5406)]^2} = 0.1500$$

At 98% of steady state, starting with both concentrations 0.42,

$C_{a1} = 0.42 - 0.98(0.4743-0.42) = 0.4732$

$C_{a2} = 0.42 - 0.98(0.42-0.15) = 0.1554$

Unsteady material balance, first stage,

$$FC_{a0} = FC_{a1} + kV_rC_{a1} + V_r\frac{dC_{a1}}{dt}$$

$$\frac{dC_{a1}}{dt} = C_{a0}/\tau - (k+1/\tau)C_{a1} = 1.5/0.5406 - (4+1/0.5406)C_{a1}$$

$$= 2.7747 - 5.85C_{a1} \qquad (1)$$

The time for the first stage to get within 98% of steady state,

$$t_1 = \int_{0.42}^{0.4732}\frac{dC_{a1}}{2.7747-5.85C_{a1}} = 0.667$$

Second stage unsteady balance,

$$\frac{dC_{a2}}{dt} + 5.85C_{a2} = C_{a1}/0.5406 = 1.85C_{a1} \qquad (2)$$

Eqs (1) and (2) are solved simultaneously with 0.42 as both initial concentrations. Interpolating in the printout, the times are 0.667 hr for 0.4732 in the first stage and 0.626 hr for 0.1554 in the second stage.

t	C_{a1}	C_{a2}
0	0.4200	0.4200
0.05	0.4338	0.3478
0.10	0.4441	0.2948
0.15	0.4517	0.2560
0.20	0.4575	0.2276
0.25	0.4617	0.2067
0.30	0.4649	0.1915
0.35	0.4673	0.1803
0.40	0.4691	0.1721
0.45	0.4704	0.1662
0.50	0.4714	0.1618
0.55	0.4721	0.1586
0.60	0.4727	0.1563
0.65	0.4731	0.1546
0.70	0.4734	0.1533
0.75	0.4736	0.1524
0.80	0.4738	0.1518
0.85	0.4739	0.1513
0.90	0.4740	0.1509
0.95	0.4741	0.1507
1.00	0.4742	0.1505

P4.09.21. ESTERIFICATION

Ethyl acetate is to be made in a 10 cuft CSTR by the reaction,

$$\text{Ethanol} + \text{Acid} \underset{2}{\overset{1}{\Leftrightarrow}} \text{Ester} + \text{Water}, \quad A + B \Leftrightarrow C + D$$

Initial concentrations in the tank are $A_0 = 0.28$ lbmol/cuft, $B_0 = 0.38$ and $D_0 = 1.63$. Pure ethanol, $A_i = 1.07$ lbmol/cuft, is charged at the rate of 0.2 cuft/min and overflow is at the same volumetric rate, making $\tau = 50$ min. The specific rates are $k_1 = 76(10^{-4})$ cuft/lbmol-min and $k_2 = 26(10^{-4})$. Analyze the performance during the first hour.

The rate equation is

$$r_a = r_b = -r_c = -r_d = k_1AB - k_2CD \tag{1}$$

The unsteady material balances are,

$$1.07 = A + \tau r_a + \tau\frac{dA}{dt} = A + \tau(k_1AB - k_2CD) + \tau\frac{dA}{dt} \tag{2}$$

$$0 = B + \tau r_a + \tau\frac{dB}{dt} \tag{3}$$

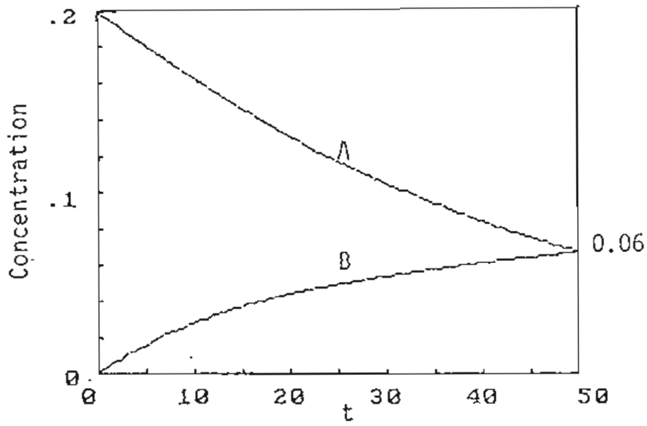
$$0 = C - \tau r_a + \tau\frac{dC}{dt} \tag{4}$$

$$0 = D - \tau r_a + \tau\frac{dD}{dt} \tag{5}$$

The POLYMATH solution of the five numbered equations are tabulated. Production of ester is made up of the amount remaining in the tank after one hour and the amount in the overflow. The latter is found with the trapezoidal rule.

$$\text{Ester} = V_rC_{final} + F\int_0^{60} C\,dt = 10(0.0259) + 0.2(1.058)$$

$$= 0.4706 \text{ lbmols}$$



```
The equations:
    d(a)/d(t)=(1.07-a-50*r)/50
    d(b)/d(t)=-b/50-r
    d(c)/d(t)=-c/50+r
    d(d)/d(t)=-d/50+r
    r=76e-4*a*b-26e-4*c*d
Initial values: t0= 0.0, a0= 0.2800, b0= 0.3800, c0= 0.0
 d0= 1.6300
Final value:  tf= 60.000
```

Integration Results

t	a	b	c	d
0.0	0.2800	0.3800	0.0	1.6300
3.0000	0.3236	0.3554	0.244×10^{-2}	1.5375
6.0000	0.3645	0.3322	0.488×10^{-2}	1.4506
9.0000	0.4029	0.3102	0.725×10^{-2}	1.3667
12.000	0.4390	0.2894	0.954×10^{-2}	1.2917
15.000	0.4731	0.2698	0.0117	1.2192
18.000	0.5051	0.2514	0.0137	1.1509
21.000	0.5353	0.2341	0.0156	1.0866
24.000	0.5639	0.2178	0.0173	1.0259
27.000	0.5906	0.2026	0.0188	0.9687
30.000	0.6162	0.1883	0.0202	0.9148
33.000	0.6403	0.1750	0.0214	0.8639
36.000	0.6630	0.1625	0.0225	0.8159
39.000	0.6845	0.1508	0.0234	0.7706
42.000	0.7049	0.1400	0.0241	0.7278
45.000	0.7241	0.1298	0.0247	0.6874
48.000	0.7424	0.1204	0.0252	0.6493
51.000	0.7596	0.1115	0.0255	0.6133
54.000	0.7760	0.1033	0.0257	0.5793
57.000	0.7915	0.0957	0.0258	0.5471
60.000	0.8062	0.0886	0.0259	0.5168

P4.09.22. SAPONIFICATION OF ETHYL ACETATE

Ethyl acetate is saponified by adding 0.2 N NaOH at the rate of 2 liters/min to a tank containing 100 liters of ethyl acetate in concentration C_{bo} = 0.2 mol/liter. Input continues until a stoichiometric amount has been added. The rate of reaction of NaOH is given by

$$r_a = -\frac{dC_a}{dt} = 0.18C_aC_b$$

Find concentrations as functions of time.

Unsteady material balances,

Loading time = 50 minutes

$V_r = 100 + 2t$

$$FC_{af} = 2(0.2) = 0 + V_r r_a + \frac{d(V_rC_a)}{dt} = kV_rC_aC_b + 2C_a + V_r\frac{dC_a}{dt}$$

$$\frac{dC_a}{dt} = \frac{0.4-2C_a}{100+2t} - 0.15C_aC_b \qquad (1)$$

$$0 = V_rC_b + \frac{d(V_rC_b)}{dt} = kV_rC_aC_b + 2C_b + V_r\frac{dC_b}{dt}$$

$$\frac{dC_b}{dt} = -\frac{0.2C_b}{100+2t} - 0.18C_aC_b \qquad (2)$$

The plot of the numerical integration of these two equations shows that the concentration at the end of the pumping period is $C_a = C_b = 0.0668$, and

Conversion = 100(0.2)-200(0.0668) = 6.64 lbmols ethyl acetate.

P4.09.23. CORROSION

A continuous stirred tank reactor is being used to accomplish a second order reaction that is catalyzed by hydrogen ions. Residence time is 0.2 hrs. Under normal conditions the inlet acid concentration is 0.002 N. The tank is made partly of ferrous alloy that corrodes slowly in the acid environment. In contact with 0.001 N acid, laboratory results show that the corrosion rate is

0.005 inches per year or 0.006 gm equivalents of iron/liter-hr. In the plant, the amount of exposed ferrous surface does not change appreciably as corrosion goes on.

Because of an operator error, the concentration of the incoming acid changes suddenly to 0.01 N and stays at this value.

(a) What is the corrosion rate at the original steady state conditions?
(b) What is the corrosion rate at the new steady state?
(c) What is the corrosion 0.1 hrs after the upset?
(d) How long does it take to get within 5% of the new steady condition?

C = gm equivalents of acid/liter

The reaction will be first order.

$$r = kC = \frac{0.006}{0.001}C = 6C$$

Original steady condition,

$$C_1 = \frac{C_f}{1+k\tau} = \frac{0.002}{1+6(0.2)} = 0.00091$$

$$r_1 = 6(0.00091) = 0.00546 \text{ gm equiv/liter-hr}$$

Steady condition after upset,

$$C_2 = \frac{C_{f2}}{1+k\tau} = 0.01/2.2 = 0.00455$$

$$r_2 = 6(0.00455) = 0.0273$$

Unsteady state,

$$C_{f2} = C + \tau(kC + \frac{dC}{dt})$$

$$\frac{dC}{dt} = \frac{C_{f2}}{\tau} - (k+\frac{1}{\tau})C = 0.05 - 11C$$

$$t = \int_{0.00091}^{C} \frac{dC}{0.05-11C} = 0.0919 \ln \frac{0.0399}{0.05-11C}$$

When t = 0.1, C = 0.00303.

At 95% of steady concentration,

$$t = \frac{1}{11} \ln \frac{0.0399}{0.05-11(0.95)(0.00455)} = 0.252 \text{ hrs}$$

P4.09.24. RISING TEMPERATURE

A liquid phase reaction with rate equation $r = kC^2$ is to be carried out to 90% conversion, starting with a concentration of 2 lbmol/cuft. The starting temperature is 550 R. It is to be raised 2°F/min for 60 minutes, then kept at 670 R until the desired conversion is reached. The specific rate is given by

$$k = \exp(3.322-5000/T)$$

Find (a) the concentration when 670 R is reached. (b) the time for 90% conversion.

$$T = 530 + 2t$$

$$-\frac{dC}{dt} = C^2 \exp(3.322-\frac{5000}{530+2t})$$

$$\frac{1}{C_{60}} - \frac{1}{2} = \int_0^{60} \exp(3.322-\frac{5000}{530+2t})dt = 0.4959$$

$$C_{60} = 1.0041$$

For 90% conversion at 670 R, C = 0.2, k = 0.0159 = 1/62.84

$$t = 60 + \frac{1}{k}(\frac{1}{C} - \frac{1}{C_{60}}) = 60 + 62.84(5 - \frac{1}{1.0041}) = 311.5 \text{ min}$$

P4.09.25. UNSTEADY DISCHARGE THROUGH A PFR

At a certain time the concentration in a batch reactor is 0.2 lbmol/cuft. The content of the reactor is 100 cuft. The rate equation is

$$r = 0.01591\ C^2 \text{ lbmol/cuft-min}$$

The mixture is discharged to storage at the rate of 2 cuft/min through a pipeline that has a holdup of 30 minutes. Reaction does not continue in storage. Find the average concentration in storage.

In the reactor, for the second order reaction,

$$C^* = \frac{C_0^*}{1+kC_0^*t} = \frac{0.2}{1+0.003182t} \quad (1)$$

In the transfer line,

$$\tau = 15 \text{ minutes}$$

$$-V'dC = rdV_r = kC^2dV_r$$

$$\tau = V_r/V' = \frac{1}{k}\int_C^{C^*}\frac{dC}{C^2} = \frac{1}{k}(\frac{1}{C} - \frac{1}{C^*})$$

Substitute from Eq (1) and rearrange,

$$C = \frac{1}{k\tau + 1/C^*} = \frac{1}{k\tau+5+0.0159t} = \frac{1}{0.001591(15)+5+0.0159t}$$

$$= \frac{1}{5.024+0.0159t}$$

$$C_{storage} = \frac{1}{15}\int_0^{15}\frac{dt}{5.024+0.0159t} = 0.1945$$

The last concentration leaving the batch tank is

$$C^* = \frac{0.2}{1+0.003182(15)} = 0.1909$$

P4.09.26. SECOND ORDER IN TWO STAGES

A second order reaction is conducted in a two equal CSTR stages. The residence time per stage is $\tau = 1$ and the specific rate is $kC_0 = 0.5$. Feed concentration is C_0. Two cases are to be examined: (a) with pure solvent initially in the tanks. (b) with concentrations C_0 initially in both tanks, that is, with $C_{10} = C_{20} = C_0$.

The unsteady balances on the two reactors are

$$f_i = C_i/C_0$$

$$FC_0 = FC_1 + V_rkC_1^2 + V_r\frac{dC_1}{dt}$$

$$1 = f_1 + 0.5f_1^2 + \frac{df_1}{dt} \quad (1)$$

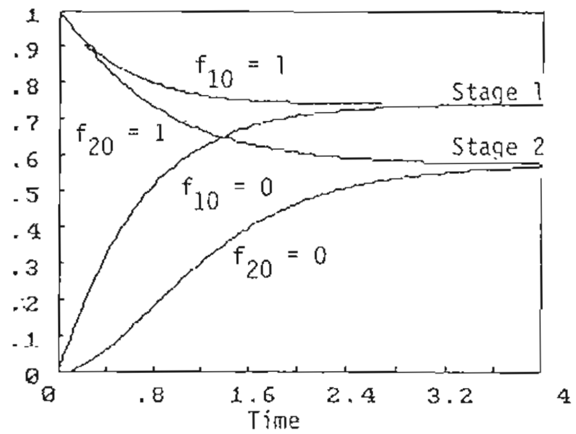
$$FC_1 = FC_2 + V_rkC_2^2 + V_r\frac{dC_2}{dt}$$

$$f_1 = f_2 + 0.5f_2^2 + \frac{df_2}{dt} \quad (2)$$

The steady state values are the same for both starting conditions, obtained by zeroing the derivatives in (1) and (2). Then

$$f_1 = 0.5702, \; f_2 = 0.7321$$

The plots are of numerical solutions.



P4.09.27. FOUR STAGE UNSTEADY OPERATION

A first order reaction with $k = 0.097$/min is conducted in a battery of four CSTRs, each of which has a residence time of $\tau = 8$ min. Initially the tanks are full of pure solvent, $C_0 = 0$. Inlet stream has concentration C_f. Find how long it takes to reach 90% of steady state in the fourth stage.

For the steady state,

$$C_4/C_f = \frac{1}{(1+k\tau)^4} = \frac{1}{[1+0.097(8)]^4} = 0.1005$$

For the first stage, the transient material balance is

$$FC_f = FC_1 + kV_rC_1 + V_r\frac{dC_1}{dt}$$

$$\frac{dC_1}{dt} + aC_1 = C_f/\tau$$

where $a = k+1/\tau = 0.097 + 0.125 = 0.222$.

Transforming,

$$s\bar{C}_1 + a\bar{C}_1 = \frac{C_f}{\tau s}$$

$$\bar{C}_1 = \frac{C_f}{\tau s(s+a)}$$

For subsequent stages,

$$\bar{C}_m = \frac{\bar{C}_{m-1}}{\tau(s+a)} = \frac{C_f}{\tau^m s(s+a)^m} \tag{1}$$

The partial fraction expansion of the four stage transform is

$$\frac{1}{s(s+a)^4} = -\frac{1}{a^4}\left(\frac{a^3}{(s+a)^4} + \frac{a^2}{(s+a)^3} + \frac{a}{(s+a)^2} + \frac{1}{s+a} - \frac{1}{s}\right)$$

The inverse of Eq (1) is

$$\frac{C_4}{C_f} = \frac{1}{a^4}\{1-\exp(-at)[\frac{(at)^3}{6} + \frac{(at)^2}{2} + at + 1]\} \qquad (2)$$

At 90% approach to steady state,

$C_4/C_f = 0.9(0.1005) = 0.0905$

The times for various approaches to steady state are figured from Eq (2) and tabulated.

%	C_4/C_f	t
0	0	0
10		7.86
30		12.45
50	0.0503	16.54
70		21.45
90	0.0905	30.09
95		34.9
99		45.2
100	0.1005	∞

P4.09.28. FILLING, REACTING, DISCHARGING

A second order reaction with rate equation, $r_a = 0.1125C_aC_b$, is carried out in three steps:

(a) 100 lbmols of B in 50 cuft of solution is charged to the vessel. Then 100 lbmols of A are charged over a period of 10 minutes, also with 2 lbmols/cuft. Find the concentration C_a at the conclusion of the filling period.

(b) The reaction continues until 90% conversion is obtained. At what time is this accomplished?

(c) The reacting solution is discharged to storage in 10 minutes through a transfer line in which the residence time is 5 minutes. What is the average concentration in the storage tank if no reaction occurs there?

Part (a):

$V_r = 50 + 5t$, cuft

$\Delta n_b = \Delta n_a$

$100-n_b = 10t-n_a$

$n_b = n_a+100-10t$

$$r_a = -\frac{1}{V_r}\frac{dn_a}{dt} = k\frac{n_an_b}{V_r^2}$$

$$-\frac{dn_a}{dt} = \frac{n_a(n_a+100-10t)}{50+5t} \qquad (1)$$

Unsteady material balance on A,

$10\,dt = V_rr_adt + dn_a$

$$\frac{dn_a}{dt} = 10 - \frac{kn_an_b}{V_r} = 10 - \frac{0.1125n_a(n_a+100-10t)}{50+5t} \qquad (2)$$

Integration of this equation by ODE results in,

$n_a = 62.26$ when $t = 10$ (a)

Part (b):

During the batch reaction, $V_r = 100$

$$-\frac{dn_a}{dt} = \frac{kn_a^2}{V_r} = \frac{0.1125n_a^2}{100}$$

The integral is

$$0.001125(t-10) = \frac{1}{n_a} - \frac{1}{62.26} \qquad (3)$$

When $n_a = 10$, $t = 84.62$ (b)

Part (c):

The concentration in the vessel continues to fall according to Eq (3) during the discharge period. Those concentrations are labelled C_a^* in the table. In the transfer line,

$$-V'dC_a = r_a dV_r$$

$$V_r/V' = \tau_p = 5 = \frac{1}{k}\int_{C_a}^{C_a^*} \frac{dC_a}{C_a^2} = \frac{1}{k}\left(\frac{1}{C_a} - \frac{1}{C_a^*}\right)$$

$$C_a = \frac{1}{5(0.1125)+1/C_a^*} \qquad (4)$$

These values are tabulated. The concentration in storage is the average of these values, or

$C_{avg} = 0.0904$ (c)

compared with $C_2^* = 0.100$ in the reactor at the beginning of the discharge period.

t	C_a	$100C_a^*$	$100C_{TL}$
0	0		
10	0.6226		
84.62	0.1000	10	9.47
+1		9.89	9.37
+2		9.78	9.27
+3		9.67	9.17
+4		9.57	9.08
+5		9.47	8.99
+6		9.37	8.90
+7		9.27	8.81
+8		9.17	8.72
+9		9.08	8.64
+10		8.99	8.56

P4.09.29. A PAIR OF SECOND ORDER REACTIONS IN A CSTR

For the pair of reactions, A + B ⇒ 2C and A+C ⇒ D, the rate equations are

$$r_a = -\frac{dA}{dt} = k_1AB - k_2AC = 0.3AB - 0.15A(A-3B) \qquad (1)$$

$$r_b = -\frac{dB}{dt} = 0.3AB \qquad (2)$$

Feed concentrations are $A_0 = 0.9$ and $B_0 = 0.3$. The material balances over the unsteady period ,

$$V'A_0 = V'A + V_r r_a + V_r\frac{dA}{dt}$$

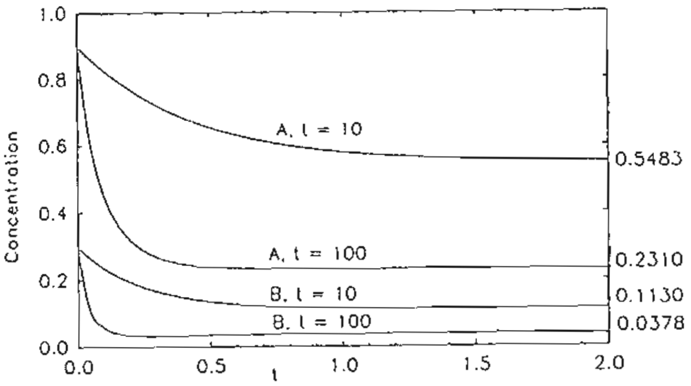
$$\frac{dA}{dt} = \frac{A_0-A}{\tau} - -0.3AB + 0.15A(A-3b) \qquad (3)$$

$$V'B_0 = V'B + V_r r_b + V_r\frac{dB}{dt}$$

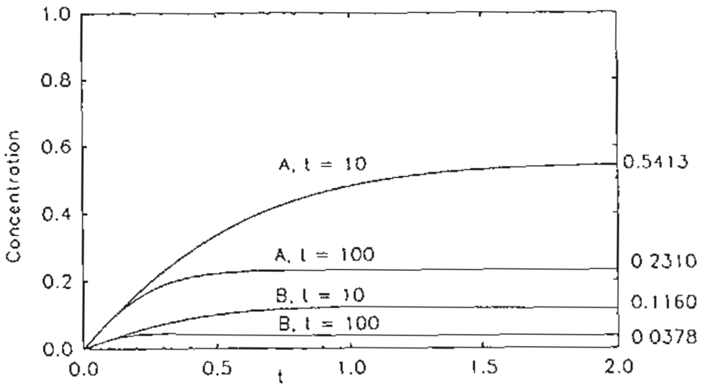
$$\frac{dB}{dt} = \frac{B_0-B}{\tau} - 0.3AB \qquad (4)$$

Eqs (3) and (4) are solved by ODE with τ = 10 or 100; and with initial composition in the tank the same as that of the feed, or with the initial composition in the tank free of reactants.

The steady state compositions are practically attained before t = 2.0.



(a)



(b)

P4.09.30. SECOND ORDER IN MULTISTAGE CSTR

The unsteady material balance on the m-th stage is

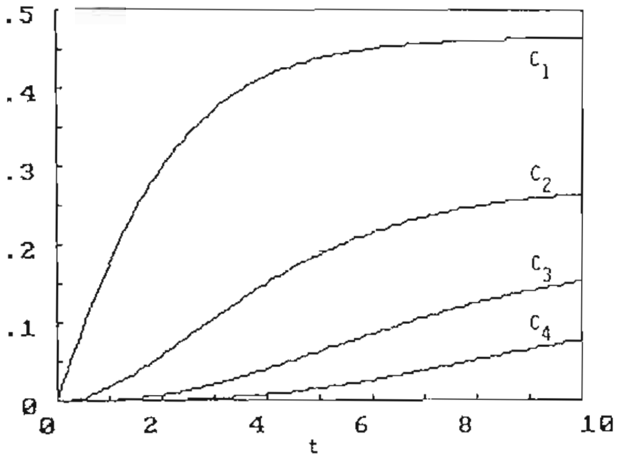
$$F_{m-1}C_{m-1} = F_mC_m + r_mV_m + \frac{d(C_mV_m)}{dt}$$

When the volumetric flow rate is uniform throughout and the vessel is always full,

$$\frac{dC_m}{dt} = \frac{C_{m-1} - C_m}{\tau} - kC_m^2$$

Analytical solution is possible only for the first stage. The plotted and tabulated results for four stages are obtained with ODE, with the constants C_0 = 1, k = 0.5 and τ = 5, and with solvent only in the tank at the start. The later stages approach steady state more slowly .

t/τ	C_1	C_2	C_3	C_4
0	0	0	0	0
1	0.4380	0.1877	0.0626	0.0159
2	0.4624	0.2642	0.1527	0.0776
3	0.4633	0.2736	0.1807	0.1198
4	0.4633	0.2746	0.1861	0.1342
5	0.4633	0.2747	0.1870	0.1379
6	0.4633	0.2747	0.1871	0.1387



P4.09.31. RATIO OF CONCENTRATIONS

A stirred tank conducts the second order reaction, A+ B ⇒ Products, initial concentrations C_{a0} and C_{b0}. A solution of substance B of concentration C_{bf} is pumped in at a volumetric rate F and the solution overflows the well stirred tank at the same rate. Determine the progress of the reaction with these numerical values:

$V_r = 100$
$F = 15$
$k = 0.05$
$C_{ao} = 20$
$C_{bo} = 10$
$C_{bf} = 5$ or 10

The unsteady material balances for the two reactants,

$$0 = FC_a dt + rV_r dt + V_r dC_a$$

$$FC_{bf} dt = FC_b dt + rV_r dt + V_r dC_b$$

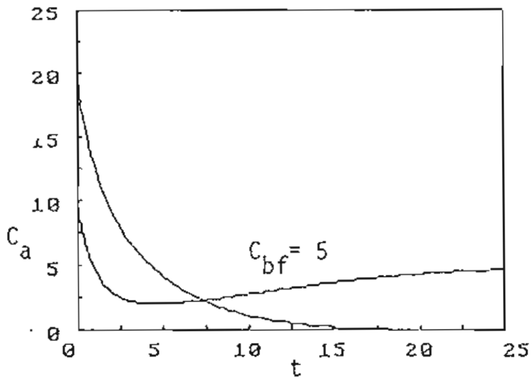
These are rearranged into

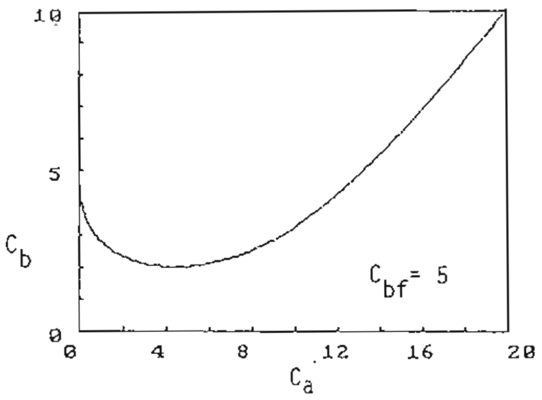
$$\frac{dC_a}{dt} = -\frac{C_a}{\tau} - kC_aC_b = -0.15C_a - 0.05C_aC_b \qquad (1)$$

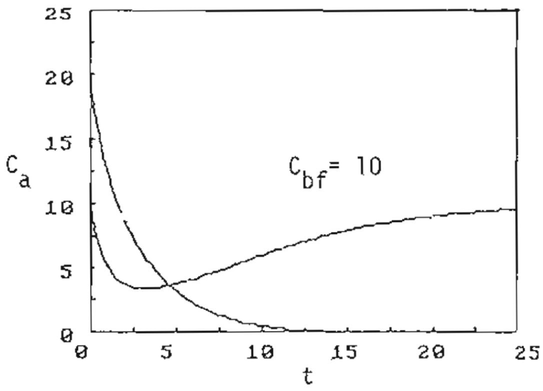
$$\frac{dC_b}{dt} = \frac{C_{bf}-C_b}{\tau} - kC_aC_b = 0.15(C_{bf}-C_b) - 0.05C_aC_b \qquad (2)$$

$$\frac{dC_a}{dC_b} = \frac{-3C_a-C_aC_b}{3(C_{bf}-C_b)-C_aC_b} \qquad (3)$$

The first two equations are solved simultaneously by ODE. The other equation is solved separately, but also by ODE since an analytical solution is not obvious. The plots are for the two feed concentrations.







P4.09.32. HYDROLYSIS OF ACETIC ANHYDRIDE

Acetic anhydride is hydrolyzed in a battery of two stirred tanks each 1800 liters. Feed rate is 600 liters/hr containing 0.6 gmol/liter. The specific rate is 0.38/hr. After steady state is reached, the concentration of the feed is reduced to 0.3 gmol/liter. How long does it take to reach 90% of the new steady state?

For the original conditions, the steady values are

$$C_1 = \frac{0.6}{1+0.38(3)} = 0.2804$$

$$C_2 = 0.6/(2.14)^2 = 0.1310$$

For the new conditions the unsteady material balances are,

$$0.3 = C_1 + 0.38(3)C_1 + 3\frac{dC}{dt} \tag{1}$$

$$C_1 = C_2 + 0.38(3)C_2 + 3\frac{dC_2}{dt} \tag{2}$$

The Laplace transforms are

$$\bar{C}_1 = \frac{0.1 + 0.2804s}{s(s+0.713)} \tag{3}$$

$$\bar{C}_2 = \frac{0.333(0.1+0.2804s)}{s(s+0.713)^2} + \frac{0.1310}{s+0.713} \tag{4}$$

The inverses can be found with a table of transforms and the results evaluated numerically.

The direct numerical solutions are obtained with ODE. The steady state values appear to be 0.1403 and 0.0656. The 90% values are

$C_1 \Rightarrow 0.1(0.2884)+0.9(0.1483) = 0.1551$, which is reached by t = 3.2.

$C_2 \Rightarrow 0.1(0.1310)+0.9(0.0656) = 0.0721$, which is reached by t = 5.5.

```
      t           c1         c2
    0.0         0.2804     0.1310
    1.0000      0.2091     0.1201
    2.0000      0.1741     0.1034
    3.0000      0.1569     0.0896
    4.0000      0.1484     0.0800
    5.0000      0.1443     0.0739
    6.0000      0.1422     0.0703
    7.0000      0.1412     0.0682
    8.0000      0.1407     0.0670
    9.0000      0.1405     0.0663
    10.000      0.1404     0.0659
    11.000      0.1403     0.0657
    12.000      0.1403     0.0656
    13.000      0.1403     0.0656
```

P4.09.33. REVERSIBLE REACTION

A reversible first order reaction, A ⇔ B, is conducted in a CSTR. Initial concentration in the tank is $C_{a0} = 0$, feed concentration is $C_{af} = 1$, residence time is $\tau = 5$, specific rate is $k = 3$ and several values of equilibrium constant K_e are to be examined.

Stoichiometric balance,

$$\Delta n_b = \Delta n_a$$

$$V_rC_b + FtC_b = V_rC_{a0} + FtC_{af} - FtC_a - V_rC_a$$

$$C_b = C_a - \frac{\tau C_{a0}+tC_{af}}{\tau+t} = C_a - \frac{t}{5+t} \tag{1}$$

Rate equation,

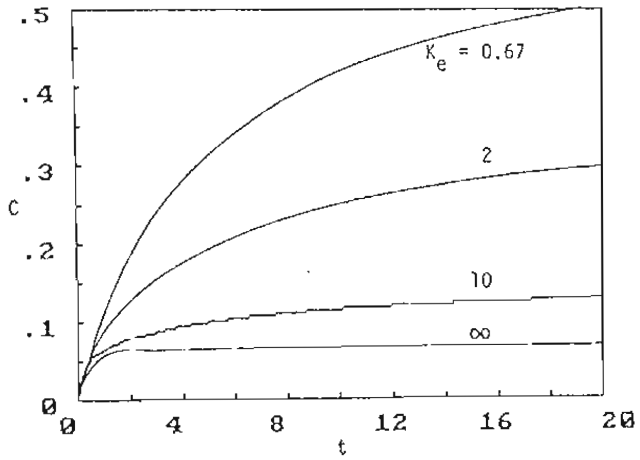
$$r_a = k(C_a - C_b/K_e) = 3[C_a - \frac{1}{K_e}(C_a - \frac{t}{5+t})] \tag{2}$$

Unsteady material balance,

$$fC_{af} = FC_a + V_rr_a + V_r\frac{dC_a}{dt}$$

$$\frac{dC_a}{dt} = \frac{C_{af}-C_a}{\tau} - r_a = \frac{1-C_a}{5} - r_a \tag{3}$$

Substitute Eq (2) and (3) and integrate by ODE for the values of K_e shown in the plots. The case with $K_e = 10$ almost reaches steady state in this time range.



P4.09.34. SINSOIDAL INPUT OF CONCENTRATION, TEMPERATURE, OR FEED RATE.

Automatic controllers can produce small oscillations of the controlled variable. The effect of sinsoidal variations in concentration, temperature or feed rate on the effluent concentration of a second order reaction in a CSTR will be examined. The unsteady material balance is

$$C_f = C + k\tau C^2 + \tau\frac{dC}{dt} \tag{1}$$

Part (a):

The concentration of the feed varies with time according to $C_f[1+ \sin(t)]$. With $C_f = \tau = 1$, the material balance becomes

$$\frac{dC}{dt} = 1 + \sin(t) - C -kC^2,\ C_0 = 0 \tag{2}$$

The plot shows the input and the responses with k = 1 or 10. The response at the higher reaction rate still is cyclic but with a smaller amplitude.

Part (b):

The temperature of the feed varies with time according to

$$T_f = 350 + 20\sin(5t) \qquad (3)$$

The heat balance is

$$-\Delta H_r C_f(1-C) = \rho C_p(T-T_f)$$

In numerical terms, in this case,

$$T = T_f + 10(1-C) \qquad (4)$$

The specific rate is

$$k = \exp(24.6-8490/T) \qquad (5)$$

Put Eqs (3), (4) and (5) into the material balance which is

$$\frac{dC}{dt} = \frac{1-C}{\tau} - kC^2, \quad C_0 = 0 \qquad (6)$$

This set of equations is solved by ODE with $\tau = 5$. For comparison, the case with constant input temperature also is done. The steady state effluent concentration is 0.255 at constant temperature, but falls to 0.22 on the average with fluctuating temperature. The difference between these values of course can be reduced by reducing the temperature fluctuations which are high, $\pm 20^\circ$ in this case.

Part (c):

The inlet flow rate depends on time according to

$$F = 1 + 0.2\sin(t)$$

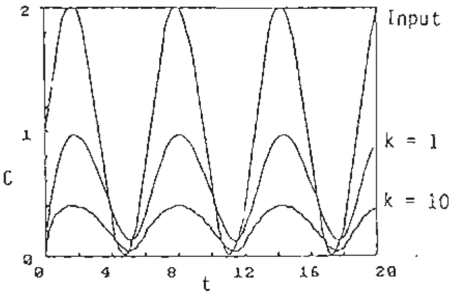
The unsteady material balance is

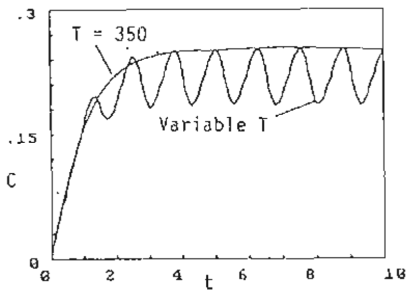
$$FC_f = FC + kV_rC^2 + V_r\frac{dC}{dt}$$

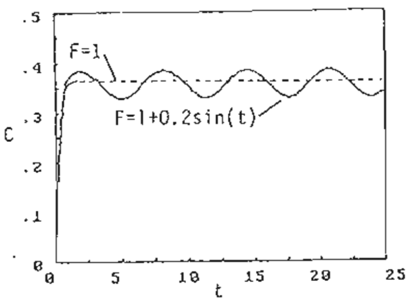
Make $C_f = 1$, $V_r = 1$ and $k = 5$.

$$\frac{dC}{dt} = (1-C)[1 + 0.2\sin(t)] - 5C^2, \quad C_0 = 0 \qquad (7)$$

The plot of the concentration against time from this equation is compared with that at the average value of the feed rate.







P4.10.01. ADIABATIC CSTR, PROFILES OF CONCENTRATION AND TEMPERATURE.

For a first order adiabatic reaction in a CSTR, the variation of concentration and temperature with time and in the steady state will be analyzed. Heat and material balances are based on the relation,

Inputs + Sources = Outputs + Sinks + Accumulation

The material balance,

$$FC_f = FC + V_r kC + V_r \frac{dC}{dt}$$

$$\tau\frac{dC}{dt} = C_f - (1+k\tau)C \qquad (1)$$

The energy balance with a heat transfer rate $Q = UA(T-T_m)$,

$$F\rho C_p T_f = F\rho C_p T - \Delta H_r V_r kC + UA(T-T_m) + V_r \rho C_p \frac{dT}{dt}$$

After dropping the heat transfer term,

$$\tau\frac{dT}{dt} = T_f - T + -\frac{\Delta H_r k\tau C}{\rho C_p} \qquad (2)$$

The specific rate is

$k = \exp(20-7550/T) \qquad (3)$

The numbered equations will be solved simultaneously with these numerical values:

T_f = 250, 275, 300, 325, feed temperature
C_f = 3, feed concentration
C_0 = 0, initial vessel concentration
T_0 = 300, initial vessel temperature
τ = 300, residence time
$\Delta H_r/\rho C_p = -50$

Accordingly the differential equations become,

$$300\frac{dC}{dt} = 3-(1+300k)C,\ C_0 = 0 \qquad (4)$$

$$300\frac{dT}{dt} = T_f - T + 15000\ kC,\ T_0 = 300 \qquad (5)$$

For the steady state, the material and energy balances become,

$C = C_f/(1+k\tau) = 3/(1+300k) \qquad (6)$

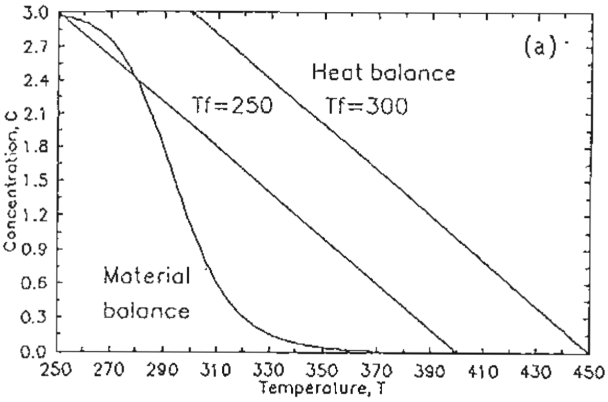
$$C = C_f + \frac{\rho C_p}{\Delta H_r}(T-T_f) = 3 - 0.02(T-T_f) \qquad (7)$$

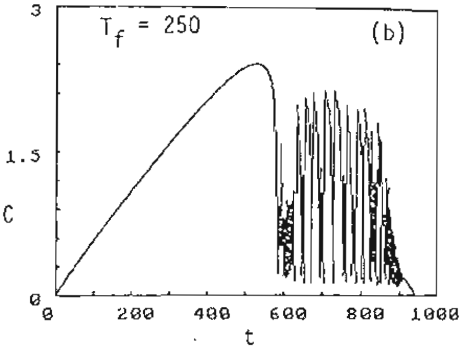
Figure (a) plots the steady state Eqs (6) and (7). Only one steady condition appears when $T_f = 300$, with $C \cong 0$. With a feed temperature of 250 there are three steady states, of which the middle point is unstable,

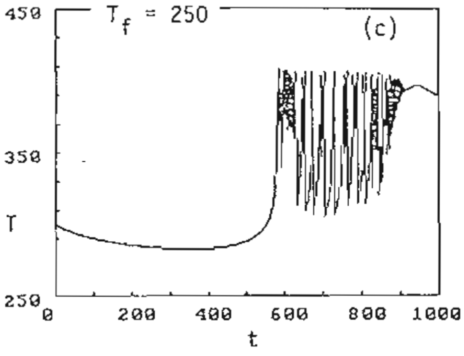
$(T,C) = (\cong 250, \cong 3), (280, 2.4), (400, \cong 0)$

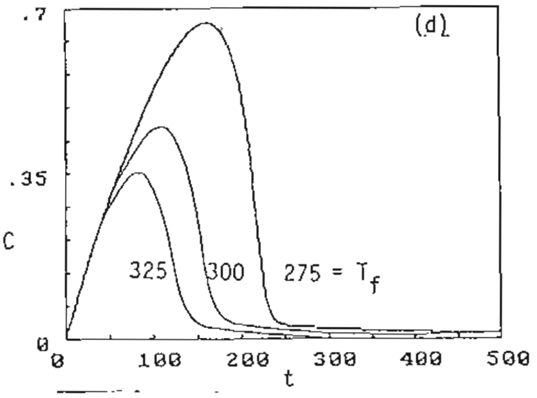
Figures (b) and (c) are of the unsteady equations when T_f = 250. C and T begin to behave erratically in the vicinity of the middle point, but eventually reach the rightmost point, (400, 0).

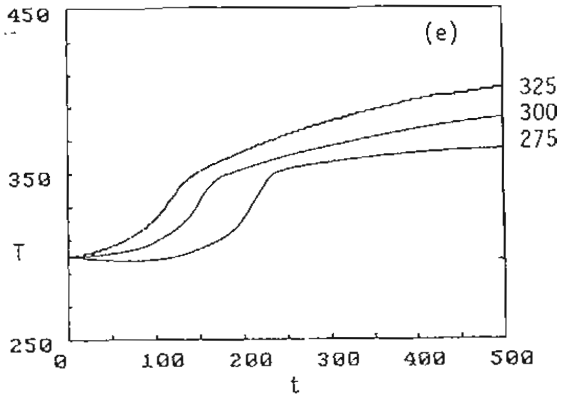
Figures (d) and (e) show transients of C and T with different inlet temperatures. Figure (f) is a plot of T against C and is called a phase portrait.

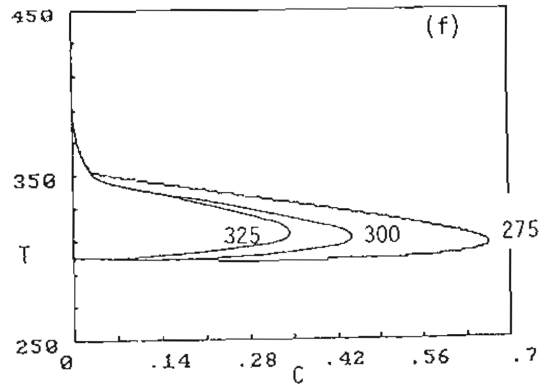












P4.10.02. SEVERAL DIFFERENT RATE EQUATIONS

Material balances relating concentration and temperature of adiabatic reaction in a CSTR are obtained for several different rate equations or conditions. The curves are drawn with feed concentration C_{af} = 1 and residence time τ = 1 in the equation,

$$C_{af} = C_a + \tau r_a$$

In every case the curve is S-shaped in certain ranges, and may have as many as three steady states with particular heat balances, as Figure (d) indicates..

(a) For a second order reaction,

$$r = kC^2$$

$$C = \frac{-1+\sqrt{1+4k\tau C_f}}{2k\tau}$$

$$k = \exp(20-7550/T)$$

(b) Reversible first order,

$$r = k\left(C - \frac{C_f - C}{K_e}\right)$$

$$C_f = C + k\tau\left[\left(1+\frac{1}{K_e}\right)C - \frac{C_f}{K_e}\right]$$

$$C = \frac{(1+k\tau/K_e)C_f}{1+k\tau+k\tau/K_e}$$

$$k = \exp(20-5800/T)$$

$$K_e = \exp(-25+9000/T)$$

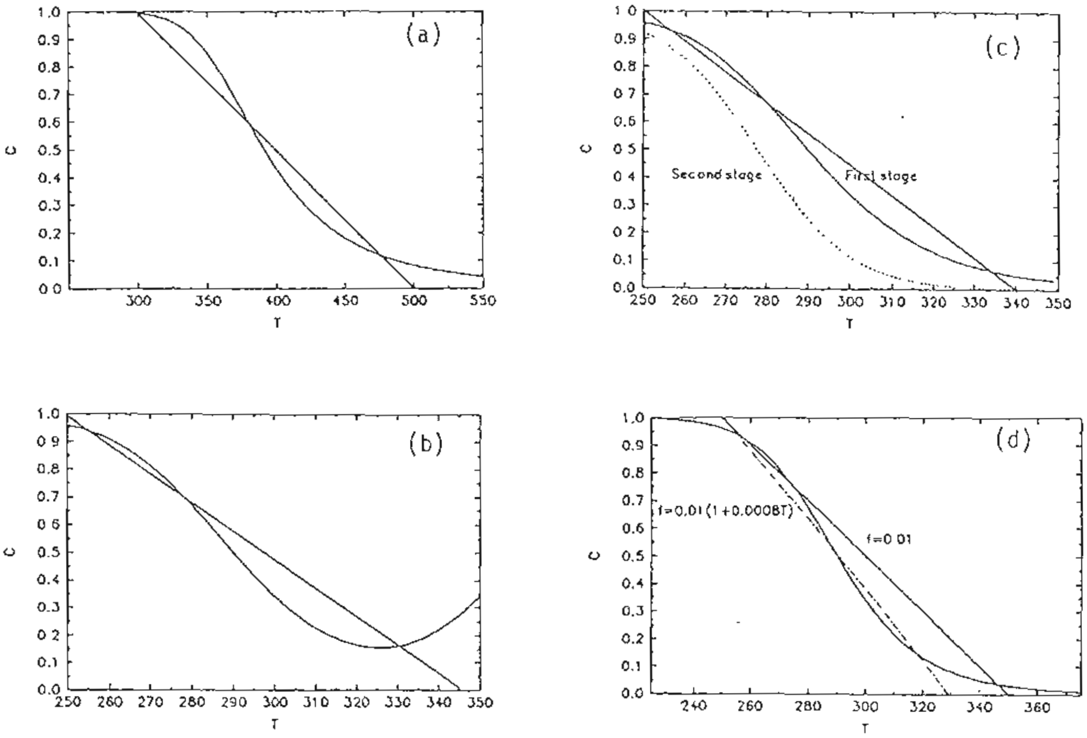
(c) First order in two stages,

$$C_1 = C/(1+k\tau)$$

$$C_2 = C_f/(1+k\tau)^2$$

$$k = \exp(20-5800/T)$$

(d) First order reaction with temperature dependent physical properties. The quantity $f = \rho C_p/\Delta H_r$ occurs in the heat balances. The effect of taking into account its dependence on temperature is shown in this figure. Then the heat balance line is not quite straight, and is capable of shifting the natures of the steady states in comparison with assuming temperature independence.



P4.10.03. MULTIPLE STEADY STATES

Data for a first order reaction in an adiabatic CSTR are

$C_f = 3$, $T_f = 283$, $\tau = 1000$, $\rho C_p = 3.5$, $\Delta H_r = -168$

$$k = \exp(17.67-8000/T) \qquad (1)$$

The material and energy balances will be written in terms of fractional conversion, x.

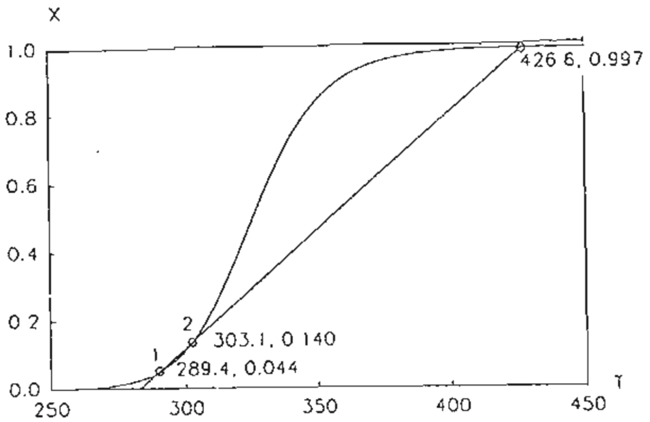
$$\frac{C}{C_f} = \frac{1}{1+k\tau}$$

$$x = 1-C/C_f = \frac{k\tau}{1+k\tau} \qquad (2)$$

$$\rho C_p(T-T_f) = \Delta H_r(C_f-C) = -\Delta H_r C_f x$$

$$x = \frac{\rho C_p}{-\Delta H_r C_f}(T-T_f) = 0.006944(T-283) \qquad (3)$$

Replace k from (1) into (2) and plot Eqs (2) and (3). The number and locations of intersections which define steady state conditions can be varied by adjusting T_f or C_f.



P4.10.04. MULTIPLE STEADY STATES

A first order adiabatic reaction in a CSTR has these characteristics:

$T_f = 298$

$C_f = 3$ gmol/liter

$F = 0.06$ liters/sec

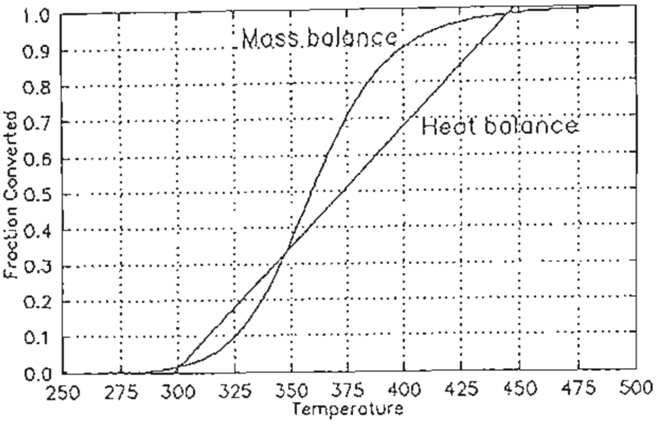
$V_r = 18$ liters

$C_p = 1$ cal/gm-K

$\rho = 1000$ g/liter

$\Delta H_r = 50000$ cal/gmol

$k = \exp(15.32-7550/T)$



Material balance,

$$C_f = C + \tau k C_f(1-x)$$

$$x = \frac{k\tau}{1+k\tau} = \frac{300k}{1+300k}$$

Heat balance,

$$-\Delta H_r C_f x = \rho C_p(T-T_f)$$

$$x = \frac{\rho C_p}{-\Delta H_r C_f}(T-T_f) = \frac{T-298}{150}$$

The plot shows the steady values to be

$(x,T) = (0.02,\ 300),\ (0.33,\ 345)$ and $(0.98,\ 445)$

with the middle point unstable and the last point most desirable because of the high conversion.

P4.10.05. SECOND ORDER REACTION

A second order reaction is conducted adiabatically in a CSTR. The material and energy balances are,

$$C_f = C + k\tau C^2$$

$$C/C_f = \frac{-1+\sqrt{1+4k\tau C_f}}{2k\tau C_f} = \frac{-1+\sqrt{1+4k}}{2k}$$

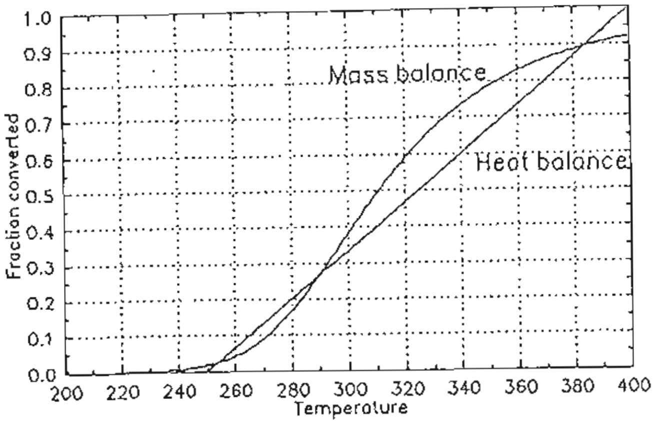
$$x = 1 - C/C_f = \frac{2k-1+\sqrt{1+4k}}{2k} \qquad (1)$$

$$-\Delta H_r C_f x = \rho C_p(T-T_f)$$

$$x = \frac{T-T_f}{150} \qquad (2)$$

$$k = \exp(20-6000/T) \qquad (3)$$

Numerical values have been put into Eqs (1) and (2). The plot is similar to those for first order reactions.



P4.10.06. SOLVING SIMULTANEOUS EQUATIONS

These data apply to a first order adiabatic reaction in a CSTR:

$$k = \exp(33.2-14570/T) \qquad (1)$$

$C_f = 0.9,\ T_f = 293,\ \tau = 25,\ \rho = 0.9,\ C_p = 0.5,\ \Delta H_r = -83$

The material balance in terms of fraction converted is,

$$x = \frac{k\tau}{1+k\tau} = \frac{25k}{1+25k} = \frac{\exp(33.2-14570/T)}{0.04+\exp(33.2-14570/T)} \qquad (2)$$

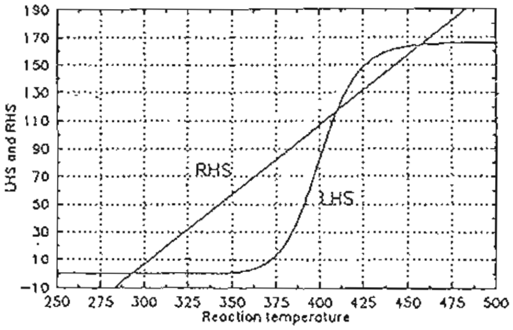
The energy balance,

$$-\Delta H_r C_f x = \rho C_p(T-T_f)$$

$$x = 0.00602(T-293) = \frac{\exp(33.2-14570/T)}{0.04+\exp(33.2-14570/T)} \qquad (3)$$

Eq (3) is solved for T by ROOT SOLVER or SEQS or POLYMATH. Then x is found from Eq (2) or (3). The roots are tabulated. They also are found graphically.

T	k	x
293	0.0000	0
409.79	0.0949	0.704
527.29	3.813	0.990



P4.10.07. WITH HEAT TRANSFER

A well stirred reactor is effecting a first order exothermic reaction with heat transfer under the following conditions:

$\tau = 1$ min

$C_f = 1$ mol/liter

$T_f = 350$, feed temperature

$T_m = 350$, coolant temperature

$k = \exp(25-10000/T)$, 1/min (1)

$UA/\rho V_r C_p = 1$/min

$\Delta H_r/\rho C_p = -200$ °K liter/mol

Find the steady operating conditions.

$x = 1-C/C_f$, fractional conversion

$x = k\tau/(1+k\tau)$, material balance

$$= \frac{\tau \exp(25-10000/T)}{1+\tau \exp(25-10000/T)} \qquad (2)$$

$r = C_f x/\tau$

Heat of reaction + heat input = sensible heat gain

$$-\Delta H_r V_r r + UA(T_m-T) = \rho C_p V_r (T-T_f) \qquad (3)$$

$$\frac{-\Delta H_r}{\rho C_p}\frac{C_f x}{\tau} + \frac{UA}{\rho C_p V_r}(T_m-T) = T - T_f$$

Sustituting numbers,

$$200x + T_m - T = T - T_f$$

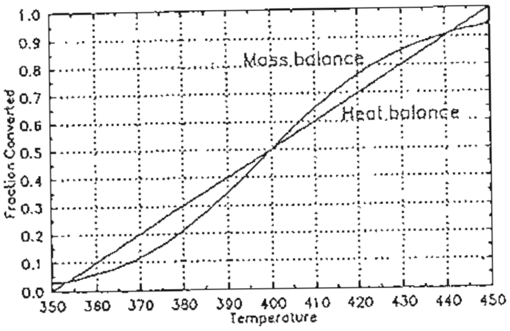
$$x = 0.005(2T-T_f-T_m) = 0.005(2T-700) \qquad (4)$$

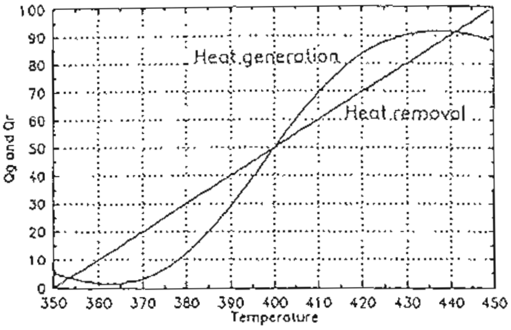
Plot Eqs (2) and (4). The steady states are defined by the intersections

(T,x) = (354, 0.036), (400, 0.500), (441, 0.9115)

Points of tangency are (421, 0.78) with $T_f = 341$ and (374,0.15) with $T_f = 359$.

Another interpretation is to plot the left and right sides of Eq (3) against T. The LHS is interpreted as the heat generated, Q_g, and the RHS as the heat removed, Q_r. The steady temperatures are established this way. The corresponding values of x then are found from one of the other equations. The steady states are the same by the two methods.





P4.10.08. TWO CASES

Operating conditions are to be found for two cases for which the data are:

	Case I	Case II
C_f	0.27 lbmol/cuft	1 gmol/liter
T_f	530 R	350 K
T_m	530 R	350 K
τ	0.5 hr	1 min
V_r	100 cuft	
F	200 cuft/hr	
UA	500 Btu/hr-R	
$-\Delta H_r/\rho C_p$		200°K/gmol-liter
$UA/\rho C_p F$		1/min
k	exp(18.42-10000/T), 1/hr	exp(25-10000/T), 1/min

The rate equation is

$$r = kC = kC_f/(1+k\tau) \tag{1}$$

$$x = 1-C/C_f = \frac{k\tau}{1+k\tau} \tag{2}$$

The energy balance is

Heat generated = Heat removed

$$-\Delta H_r V_r r = F\rho C_p(T-T_f) + UA(T-T_m) \tag{3}$$

Case I:

$$\frac{10000(100)(.27)k}{1+0.5k} = 200(50)(T-530) + 500(T-530) \tag{4}$$

$$T = 530 + \frac{25.71k}{1+0.5k} \tag{5}$$

The left and right sides of Eq (34) are plotted against T. Only one intersection occurs, that at T = 550. The corresponding x = 0.118 from Eq (2).

Case II:

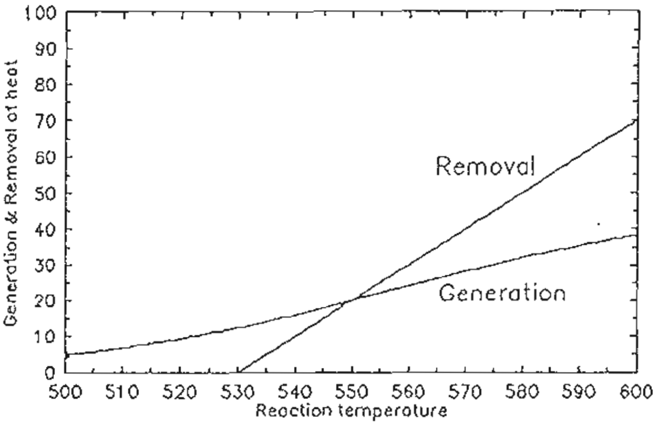
Substitute numbers into Eq (3) and rearrange.

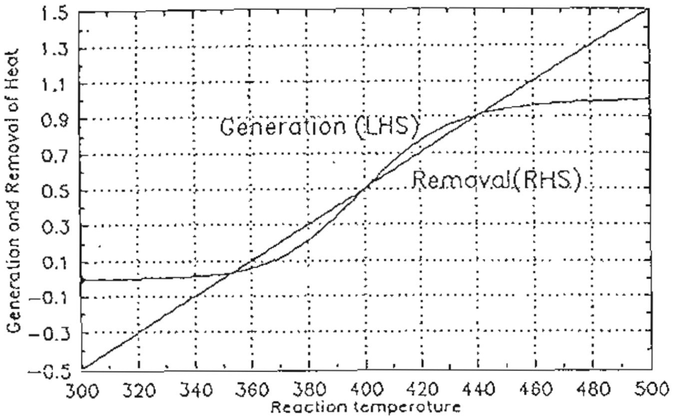
$$\frac{-\Delta H_r\tau}{\rho C_p}\,\frac{kC_f}{1+k\tau} = (T-T_f) + \frac{UA}{\rho C_p F}(T-T_m)$$

$$200(1)\frac{k}{1+k} = 2(T-350) \tag{6}$$

The LHS and RHS of Eq (6) are plotted against T. Values of x corresponding to the intersections are found from Eq (2). The steady conditions are tabulated.

T	k	x
352	0.03	0.03
400	1.00	0.50
441	10.22	0.911





P4.10.09. OLEFINS HYDROGENATION. ISOTHERMAL.

A mixed reactor is to be used for the hydrogenation of olefins at isothermal conditions. The reactor is 10 m^3 and the feed rate is 0.2 m^3/sec with an inlet concentration C_{a0} = 13 $kmol/m^3$. For these conditions the rate equation is

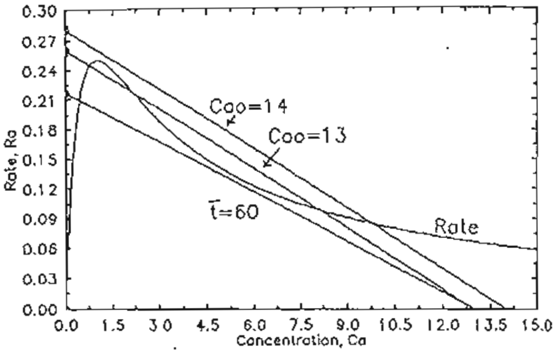
$$r_a = \frac{C_a}{(1+C_a)^2} \qquad (1)$$

$$= \frac{C_{a0}-C_a}{\tau}\ ,\ kmol/m^3\text{-sec} \qquad (2)$$

The second expression derives from the material balance on a CSTR.

It is suspected that this nonlinear rate form, which has a maximum value, may cause certain regions of unstable operation with multiple steady states. How should the operation be conducted to ensure unique steady conditions?

The plot of Eqs (1) and (2) against C_a does show three intersections with C_{a0} = 13. Making C_{a0}= 14 results in one steady state, but the conversion is poor, with C_a = 9.75 or 30% conversion. Keeping C_{a0} = 13 but making the residence time τ = 60 instead of 50 changes the steady operation to C_a = 0.6 or x = 0.95. (This problem has been investigated by Matsuura & Kato, Chem Eng Sci 26 17, 1967).



P4.10.10. FIVE STEADY OPERATING CONDITIONS

For the reaction, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, with inlet conditions A_f and T_f the material balances in a CSTR are,

$$A = \frac{A_f}{1+k_1\tau} \qquad (1)$$

$$B = \frac{k_1\tau A_f}{(1+k_1\tau)(1+k_2\tau)} \qquad (2)$$

The heat balance is

$$-\Delta H_a(A_f-A) - \Delta H_b(B-B_f) = \rho C_p(T-T_f)$$

$$\beta = \Delta H_b/\Delta H_a$$

$$\frac{-A_f\Delta H_a}{\rho C_p}\left(\frac{k_1\tau}{1+k_1\tau}\right)\left(1+\frac{\beta k_2\tau}{1+k_2\tau}\right) = T-T_f \qquad (3)$$

The plots of the RHS and LHS of Eq (3) against T show that five steady states can exist, of which 1, 3 and 5 are stable. Compositions at these points are found from Eqs (1) and (2) as soon as the temperatures are known. Numerical data for which the plots are made are:

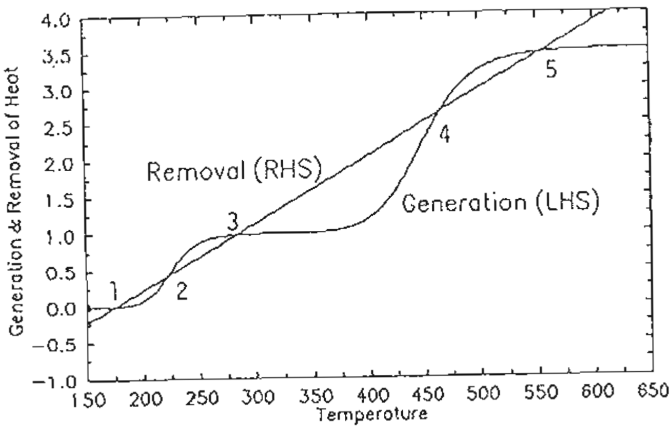
$k_1\tau = \exp(20-4500/T)$

$k_2\tau = \exp(20-9000/T)$

$\beta = 2.5$

$T_f = 175$

$-A_f\Delta H_a/\rho C_p = 110$



P4.10.11. ADJUSTING INLET CONDITIONS TO A CSTR

A first order reaction has specific rate

$$k = \exp(12.1-6050/T) \qquad (1)$$

The material balance in a CSTR gives for the fractional conversion,

$$f = \frac{k\tau}{1+k\tau} = \frac{50k}{1+50k} \qquad (2)$$

For adiabatic operation the heat balance is

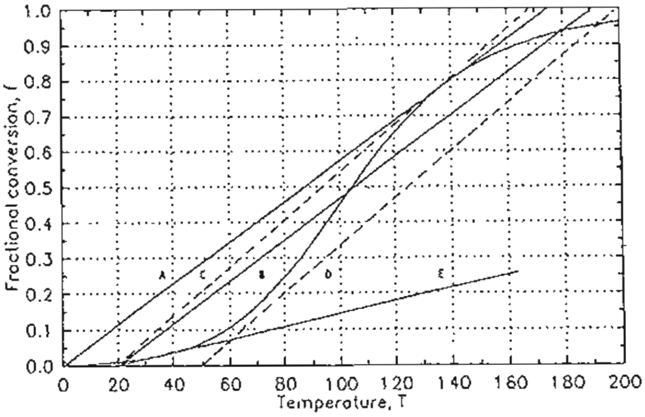
$$-\Delta H_r C_f f = \rho C_p(T-T_f)$$

Substitute numerical values and rearrange to

$$f = \frac{\rho C_p(T-T_f)}{-\Delta H_r C_f} = \frac{1.2(0.9)(T-T_f)}{46000C_f} \qquad (3)$$

Eqs (2) and (3) are plotted as f against T. The table and plots show operating points with several combinations of inlet concentration and temperature, C_f and T_f. The number of steady states can be one, two or three, if zero or complete conversion are considered possibilities.

Line	T_f	$1000C_f$	(f,T)
A	0	4.0	(0,0), (0.8,140)
B	20	4.0	(0.94,180), (0.49,103), 0.01,21)
C	20	3.5	(0.01,21), (0.8,140)
D	50	3.5	(0.96,192)
E	50	13	(0.04,40), (≅ 1.0, >200)



P4.10.12. A TUBULAR FLOW REACTOR

A first order reaction is to be conducted in a choice of tubular reactors of diameters 25, 50 or 75 mm that are heated through the wall with a heat transfer medium at T_m. Data are

$F = 0.835\ m^3/hr$

$C_0 = 3.2\ kmol/m^3$

$T_0 = 100$

$\Delta H_r = +13000\ kcal/gmol$

In order to avoid unwanted byproducts the temperature must kept between 110 and 120 C. The heat generated is $Q_r = -\Delta H_r r$; the values at different temperatures are tabulated. The heat fluxes through the different diameters are $Q_m = UA(T-T_m)$; values of UA are tabulated.

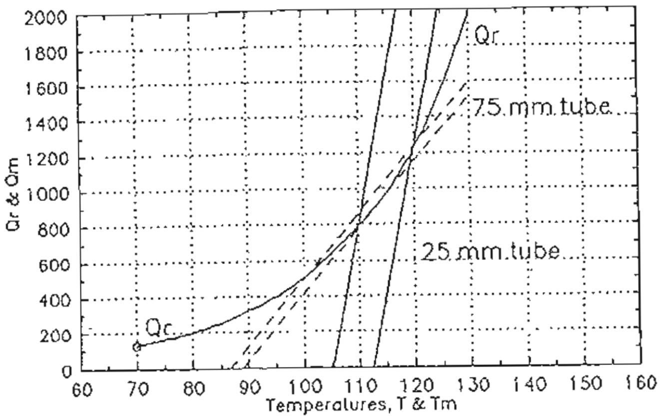
T	100	110	120	130	//	Dia	25	50	75
Q_r	500	795	1220	1970	//	UA	165	69	37

For convenience, a curve fit of the data is

$Q_r = \exp(1.671 + 0.0454T)$

The temperatures T_m of the heat transfer medium required at the operating limits 110 and 120 of the reaction are found by making $Q_r = Q_m$. The results are tabulated. Plots are shown for 25 mm and 75 mm. In the largest pipe T_m must be controlled in the narrow range 86.6-88.8°. The spreads of 7.3° and 3.5° of the other two sizes may be practicable.

Dia	T	T_m
25	110	105.2
25	120	112.5
50	110	98.6
50	120	102.1
75	110	88.8
75	120	86.6



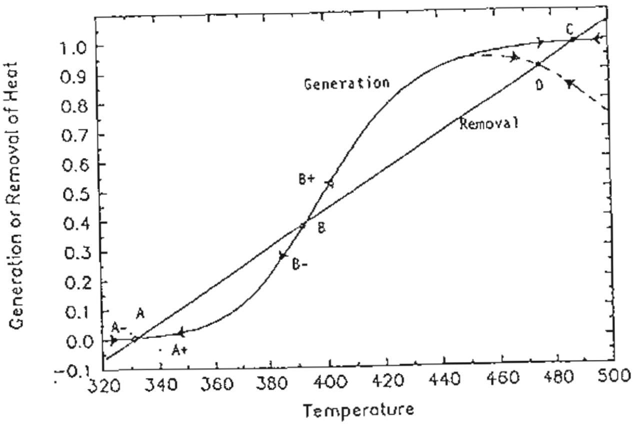
P4.10.13. STABLE OR UNSTABLE OPERATING CONDITION?

Whether or not a steady condition in a CSTR is stable depends on the relative magnitudes of the generation and removal of heat. When generation is greater than removal, the temperature will rise, and when it is smaller the temperature will fall.

At point B+ on the plot, generation is greater than removal so the temperature will rise away from point B; at point B-, generation is less than removal so the temperature will fall away from point B. Thus point B is unstable.

At point A+, generation is less than removal so the temperature will fall towards A; at point A-, generation is greater than removal so the temperature will rise towards A. Thus point A is stable. Similarly it appears that points C and D likewise are stable. The dashed curve is for a reversible reaction.

The shapes of curves of T against fractional conversion derived from material and heat balances are similar to this plot (see for instance problem P4.10.07) so the same identification is made of stable and unstable steady conditions.



P4.11.01. OPTIMUM TEMPERATURE PROFILE OF REVERSIBLE FIRST AND SECOND ORDER REACTIONS.

Minimum reaction time and maximum conversion of reversible reactions occcur when the rate of reaction is made a maximum at each concentration. The relations between temperature T and fractional conversion x will be derived for three cases.

Part (a), first order:

$$r = k_1(1-x)-k_2x = k_1(1-x-\frac{x}{K_e}) \qquad (1)$$

with

$k_1 = A_1\exp(-B_1/T)$
$k_2 = A_2\exp(-B_2/T)$
$K_e = A_3\exp(-B_3/T)$

The condition

$$(\frac{dr}{dT})_x = 0$$

leads to

$$-(1-x)A_1B_1\exp(-B_1/T) + xA_2B_2\exp(-B_2/T) = 0$$

This is solved explicitly as

$$T = \frac{B_1-B_2}{\ln \dfrac{A_1B_1(1-x)}{A_2B_2x}} \qquad (2)$$

or

$$\frac{1}{x} = 1 + \frac{A_2B_2}{A_1B_1}\exp(-\frac{B_1-B_2}{T} \qquad (4)$$

Part (b), second order:

The reaction is
$A + B \Leftrightarrow C + D$
$A = A_0(1-x)$
$M = B_0/A_0$
$B = B_0-A_0+A = A_0(M-1)+A = A_0(M-x)$
$C = D = A_0x$

$$r = k_1AB - k_2CD = A_0^2[k_1(M-x)(1-x)-k_2x^2] \qquad (5)$$

Upon setting dr/dT = 0,

$$T = \frac{B_1-B_2}{\ln \dfrac{A_1B_1(1-x)(M-x)}{A_2B_2x^2}} \qquad (6)$$

Part (c), flow reactor at constant pressure:

$$n_{a0}dx = (k_1n_a-k_2n_b)\frac{dV_r}{V'}$$

$$V' = n_{a0}RT/\pi$$

$$r = \frac{n_{a0}R}{\pi}\frac{dx}{dV_r} = \frac{1}{T}[k_1(1-x)-k_2x] \qquad (7)$$

with $n_{b0} = 0$.

On setting dr/dT = 0,

$$\frac{1}{T}[\frac{A_1B_1(1-x)}{T^2}\exp(-B_1/T) - \frac{A_2B_2x}{T^2}\exp(-B_2/T)]$$

$$+ \frac{1}{T^2} [A_1(1-x)\exp(-B_1/T) - \frac{A_2x}{T^2}\exp(-B_2/T)] = 0$$

Whence,

$$\frac{1-x}{x} = \frac{A_2(B_2-T)}{A(B_1-T)} \exp(\frac{B_1-B_2}{T}) \qquad (8)$$

P4.11.02. BEST TEMPERATURE PROFILE OF BATCH REACTION

A batch first order reaction is limited to a maximum of 600 K. Find the temperature profile that will give the maximum conversion. The rate equation is

$$r = \frac{dx}{dt} = k_1(1-x)-k_2x \qquad (1)$$

$$k_1 = 100 \exp(-1000/T) = A_1\exp(-B_1/T)$$

$$k_2 = 2000 \exp(-2500/T) = A_2\exp(-B_2/T)$$

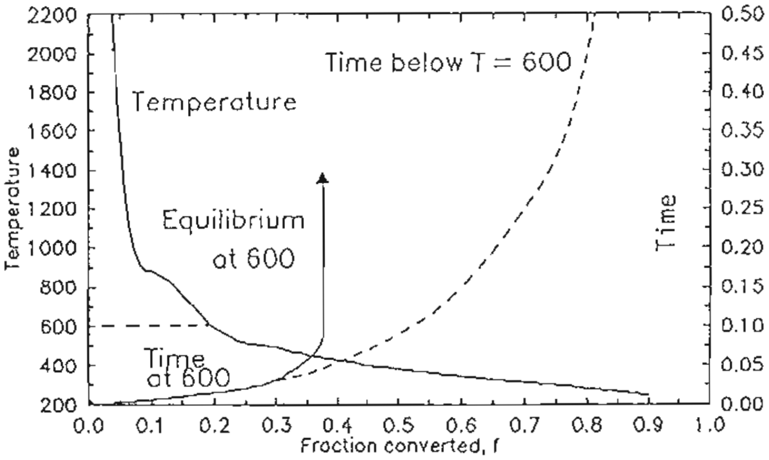
Use Eq (2) of problem P4.11.01 for the optimum temperature..

$$T = \frac{2500-1000}{\ln\frac{2500(2000)x}{1000(100)(1-x)}} = \frac{1500}{\ln\frac{50x}{1-x}} \qquad (2)$$

The equilibrium compositions at several temperatures and the reaction times for 95% of equilibrium comversions are found from Eq (1).

T	k_1	k_2	x_e	t
600	18.89	31.01	0.378	0.059
500	13.53	13.48	0.501	0.111
400	8.21	3.86	0.680	0.248

The next table presents the results with Eq (2), and shows conversion of x = 0.9 with a final temperature of 245.5. The listed times are the shortest possible ones at each particular conversion.



		--- 1/r ---		--- t ---	
x	T	@T	@600	T<600	T=600
0	-197	.0001	.0529	0	0
.01	-2195	.0107	.0544		
.02	74257	.0172	.0559		
.03	3441	.0230	.0575		
.04	2044	.0283	.0592		
.05	1550	.0334	.0610	.0028	.0028
.1	875	.0581	.0719	.0062	.0062
.15	689	.0837	.0877		
.196	600	.1098	.1098		
.2	594	.1122	.1122	.0147	.0147
.25	533	.1450	.1559	.0211	.0217
.30	489	.1837	.2551	.0298	.0321
.35	456	.2303	.7018		.056
.378			∞		∞
.4	428	.2877		.0531	
.45	404	.3598			
.5	383	.4524		.0896	
.55	365	.5746			
.6	347	.7410		.1481	
.65	331	.9765			
.7	315	1.3265		.2486	
.75	299	1.8821			
.80	283	2.8500		.4472	
.85	266	4.7932			
.90	246	9.2872		1.003	

P4.11.03. OPTIMUM TEMPERATURE IN A TUBULAR FLOW REACTOR

Determine the operating temperature at which volume of a tubular reactor is a minimum for a conversion of 70% at the outlet. Equimolar amounts of A and B at 1 atm undergo the reaction, $A + B \underset{2}{\overset{1}{\Leftrightarrow}} C + D$.

$$k_1 = \exp(31.4-12582/T) \qquad (1)$$

$$k_2 = \exp(34.2-15098/T) \qquad (2)$$

$$n_t = 2n_{a0}$$

$$V = 2n_{a0}RT/\pi$$

$$(n_{a0}/V)^2 = (\pi/2RT)^2 = (\frac{1}{0.104T})^2 = 37.18/T^2$$

$$r_a = k_1(\frac{n_a}{V})^2 - k_2(\frac{n_{a0}-n_a}{V})^2 = (\frac{n_{a0}}{V})^2[k_1(1-x)^2 - k_2x^2]$$

$$= \frac{37.18}{T^2}[k_1(1-x^2 - k_2x^2] \qquad (3)$$

Flow reactor equation,

$$-dn_a = n_{a0}dx = r_a dV_r$$

$$\frac{V_r}{n_{a0}} = \frac{T^2}{37.18}\int_{0.7}^{0} \frac{dx}{k_1(1-x)^2-k_2x^2} \qquad (4)$$

As the temperature is raised, the residence time decreases but the rate of reaction goes up. Accordingly it is possible for an optimum temperature to exist. Eq (4) could be integrated analytically and then differentiated with respect to temperature to find an optimum. Here, however, the integrations were done numerically at specific temperatures. The tabulation shows a minimum value of $V_r/n_{a0} = 7.76$ at 552 K.

T	V_r/n_{a0}	T	V_r/n_{a0}
530	13.04	553	7.77
540	9.66	554	7.85
545	8.55	555	8.04
549	7.95	556	8.41
550	7.86	557	9.14
551	7.79	558	10.85
552	7.76	559	17.23

P4.11.04. PFR WITH OPTIMUM TEMPERATURE PROFILE

For a reversible reaction, the minimum reactor size obtains when the temperature is adjusted to make the rate a maximum at each position or conversion. Take the reaction, 2A ⇔ 2B.

$$r_a = -\frac{dC_a}{dt} = kC_{a0}^2((1-x)^2 - x^2/K_e) \tag{1}$$

$$k = k_0\exp(-E/RT) = 2.68(10^5)\exp(-10000/RT)$$
$$K_e = K_{e0}\exp(-\Delta H_r/RT) = 0.0309\exp(5000/RT)$$

$$\frac{dk}{dt} = \frac{k_0E}{RT^2}\exp(-E/RT) = \frac{kE}{RT^2} \tag{2}$$

$$\frac{dK_e}{dT} = \frac{K_e\Delta H_r}{RT^2} \tag{3}$$

Apply $dr_a/dT = 0$ to Eq (1).

$$-kx^2\left(\frac{-\Delta H_r}{K_eRT^2}\right) + \frac{kE}{RT^2}[(1-x)^2 - x^2/K_e] = 0$$

$$K_e = -\left(\frac{x}{1-x}\right)^2\left(\frac{\Delta H_r}{E} - 1\right) = -\left(\frac{x}{1-x}\right)^2\left(-\frac{5000}{10000} - 1\right) = 1.5\left(\frac{x}{1-x}\right)^2$$
$$= 0.0309\exp(5000/RT)$$

Solve for T in terms of x,

$$T = \frac{2500}{\ln[48.54(\frac{x}{1-x})^2]} \tag{4}$$

Restrict the temperature to a maximum of 1000.

The PFR equation is

$$-dn_a = F_0C_{a0}dx = r_adV_r$$

$$\frac{V_rC_{a0}}{F_0} = \int_0^x \frac{dx}{k[(1-x)^2 - x^2/K_e]} \tag{5}$$

At the upper limit of temperature, 1000 K,

$$k = 2.68(10^5)\exp(-5) = 1806$$

$K_e = 0.0309\exp(2.5) = 0.376$

The integrand is evaluated as a function of x and the trapezoidal rule is applied in the last column. Thus,

When $x = 0.75$, $C_{a0}V_r/F_0 = 1.608$

When $x = 0.80$, $C_{a0}V_r/F_0 = 5.982$

The preceding are the smallest possible values. In comparison, for 75% conversion at isothermal $T = 411.2$, $k = 1.40$, $K_e = 13.5$,

$$C_{a0}V_r/F_0 = \frac{1}{1.4}\int_0^{0.75} = 3.01$$

For 80% conversion at isothermal $T = 375.6$, $k = 0.443$, $K_e = 24.0$,

$$C_{a0}V_r/F_0 = \frac{1}{0.443}\int_0^{0.8} = 12.64$$

x	K_e	T	k	$1/r_a$	$C_{a0}V_r/F_0$
0			1806	0.00055	0
0.1	0.0185*	-4882**	1806	0.00071	0.00006
0.2	0.0938*	2252**	1806	0.00104	0.00015
0.3	0.2755*	1143**	1806	0.0021	0.00031
0.4	0.6667	814	576	0.0145	0.00115
0.5	1.5	644	114	0.1054	0.00714
0.6	3.38	533	22.6	0.827	0.0538
0.7	8.07	448	3.81	8.748	0.5325
0.75	13.5	411.2	1.40	34.29	1.608
0.775	17.8	393.3	0.808	73.3	2.953
0.8	24.0	375.6	0.443	169.0	5.982

* Use $K_e = 0.376$

** Use $T = 1000$

P4.11.05. MINIMUM TIME IN A PFR

A reversible reaction, $A \Leftrightarrow B$, is conducted in a plug flow reactor. The rate equation is

$r = kC_{a0}(1-x-x/K_e)$

with $C_{a0} = 4$ and

$k = \exp(17.2-5800/T)$

$K_e = \exp(-24.7+9000/T)$

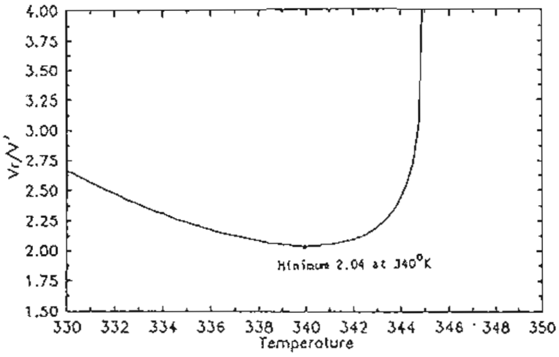
Find the conditions for minimum V_r/V' when conversion is 80%

The flow reactor equation is

$-dn_a = V'C_{a0}dx = kC_{a0}(1-x-x/K_e)dV_r$

$$\frac{V_r}{V'} = \frac{1}{k}\int_0^{0.8}\frac{dx}{1-x-x/K_e} = \frac{1}{k(1+1/K_e)}\ln\frac{1}{0.2-0.8/K_e} \qquad (1)$$

The plot of this equation shows the minimum to be $V_r/V' = 2.04$ at $T = 340$ K.



P4.11.06. MINIMUM PFR SIZE

The operating temperature is to be found for which the reactor volume is a minimum for 80% conversion. The rate equation is

$$\frac{dx}{dt} = k_1(1-x) - k_2x$$

$$k_1 = 20\exp(-600/T)$$

$$k_2 = 40\exp(-1500/T)$$

The integral of the flow reactor equation is

$$V_r/F = \int_0^x \frac{dx}{1-(k_1+k_2)x} = \frac{1}{k_1+k_2}\ln\frac{k_1}{k_1-(k_1+k_2)x} \qquad (1)$$

The tabulation is made for x = 0.8 and shows a minimum to exist of V_r/F = 0.6074 when T = 368.

T	V_r/F	T	V_r/F
350	0.6152	371	0.6076
360	0.6091	372	0.6077
361	0.6087	373	0.6080
362	0.6084	374	0.6082
363	0.6081	375	0.6086
364	0.6079	380	0.6111
365	0.6075	390	0.6213
366	0.6074	400	0.6408
367	0.6074	430	0.9576
368	0.6074	432	1.1495
369	0.6074		
370	0.6075		

P4.11.07. OPTIMUM TEMPERATURE OF BATCH REACTION

A liquid phase reaction, $2A \underset{2}{\overset{1}{\Leftrightarrow}} B + C$, has the rate equation

$$r_a = k(C_a^2 - C_bC_c/K_e) = kC_{a0}^2[(1-f)^2 - f^2/K_e],\ \text{kmol/m}^3\text{-hr}$$

f = fractional conversion

$$C_{a0} = 1$$

$$k = \exp(4.5-2500/T)$$

$$K_e = \exp(28.8-0.037t-\frac{5178}{T})$$

The downtime is 1 hr per batch. Find the temperature at which the daily production is a maximum.

The reaction time of one batch is

$$t_b = \frac{1}{k}\int_0^f \frac{df}{(1-f)^2 - f^2/K_e} \qquad (1)$$

$$\text{Batches/day} = \frac{24}{t_b+1}$$

maximum

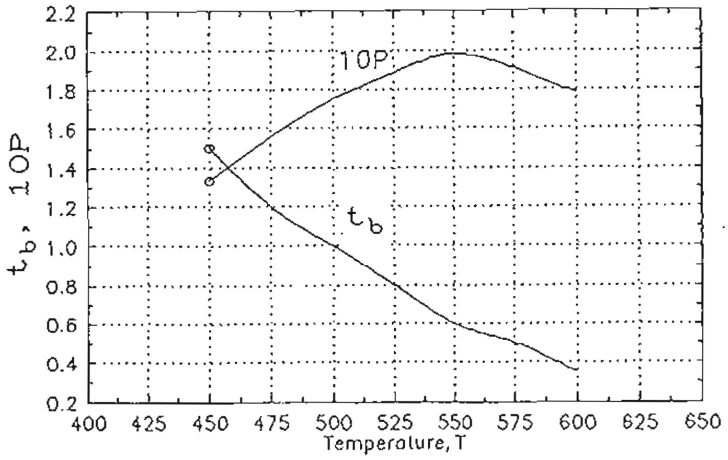
$$\text{Daily production} = \frac{24}{t_b+1} V_r C_{a0} f$$

Maximize $P = f/(t_b+1)$ as a function of temperature. Eq (1) is integrated with POLYMATH for several temperatures and the results plotted. The tabulation gives the integration at 550 K. The peak value of $P = f/(t_b+1) = 0.1941$ at 550 K, $t_b = 0.6$ and $f = 0.3105$.

$$\text{Maximum daily production} = 0.1941(24)V_rC_{a0}$$
$$= 4.66V_r \text{ kmol/day}$$

```
The equations:
    d(f)/d(t)=k*((1-f)**2-f**2/ke)
    x = 550
    k=exp(4.5-2500/x)
    ke=exp(28.6-5178/x-.037*x)
    p=f/(t+1)
Initial values: t0= 0.0,  f0= 0.0
Final value:  tf= 2.0000

     t            f            p
  0.0          0.0          0.0
  0.2000       0.1562       0.1302
  0.4000       0.2535       0.1811
  0.6000       0.3105       0.1941
  0.8000       0.3427       0.1904
  1.0000       0.3605       0.1802
  1.2000       0.3702       0.1683
  1.4000       0.3755       0.1565
  1.6000       0.3784       0.1455
  1.8000       0.3799       0.1357
  2.0000       0.3807       0.1269
```



P4.11.08. OPTIMUM TEMPERATURE

For a reverible first order reaction the specific rate and equilibrium constant are

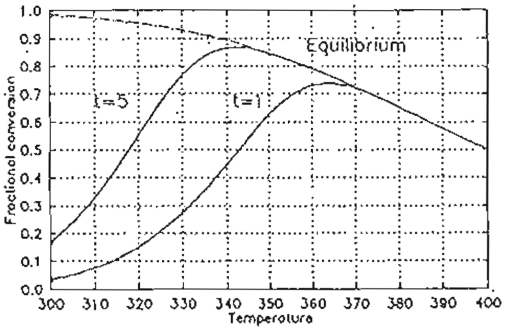
$$k = \exp(20.7-7200/T)$$
$$K_e = \exp(-12+4800/T)$$

and the rate equation is

$$r = \frac{dx}{dt} = k(1-x-x/K_e)$$

The equilibrium composition is given by

$$x_e = \frac{K_e}{K_e+1}$$



In a plug flow reactor,

$$-dn_a = V'C_{a0}dx = rdV_r$$

$$t = V_r/C_{a0}V' = \int_0^x \frac{dx}{k(1-x-x/K_e)} = \frac{K_e}{k(K_e+1)}\ln\frac{K_e}{K_e-(K_e+1)x}$$

$$x = \frac{K_e}{K_e+1}\left[1-\exp\left(-\frac{K_e+1}{K_e}kt\right)\right] \qquad (4)$$

Eq (4) is plotted as x against T at t = 1 or t = 5. At t = 5, for instance, the maximum conversion is x = 0.86 at T = 346; if higher temperatures are used the conversion will fall along the equilibrium line which is a plot of Eq (3). Similarly at t = 1, the peak conversion is x = 0.7 at about 373 K.

P4.11.09. MAXIMUM AND ECONOMIC OPTIMUM YIELD OF BATCH REACTION

The batch esterification

ethanol + acetic acid ⇔ ester + water, $A + B \Leftrightarrow C + D$

has initial concentrations $A_0 = 6$, $B_0 = 4$, $C_0 = 0$, $D_0 = 15$. At 100 C the rate equation is

$$r_a = -\frac{dA}{dt} = 0.0286[A(A-2)-(6-A)(21-A)/2.93] \qquad (1)$$

Downtime is 1.5 hr/batch.

Part (a): Find the maximum daily production of ester.

Eq (1) is integrated to obtain the relation between the reaction time t_b and the yield, C = 6-A. The results are tabulated. The number of batches per day is

$$N = \frac{24}{t_b+1.5}$$

$$y = \text{yield/day} = \frac{24(6-A)}{t_b+1.5}\ \text{kmol/m}^3\text{-day} \qquad (2)$$

The tabulation shows the maximum to be 6.406 kmol/m^3-day when t_b = 2.25.

Part (b): The operating cost during reaction is 20 monetary units (MU) per hour and during downtime it is 10 MU/hr. The operating cost per kmol/m^3 of product is

$$k = \frac{20t_b+1.5(10)}{6-A} \qquad (3)$$

This is tabulated and has a minimum at t_b = 1.75 hr of

$$k_{min} = 58.73\ \text{MU/(kmol of ester/m}^3)$$

```
The equations:
    d(a)/d(t)=-.0286*(a*(a-2)-(6-a)*(21-a)/2.93)
    k=(20*t+15)/(6.001-a)
    y=24*(6-a)/(t+1.5)
Initial values: t0= 0.0, a0= 6.0000
Final value:   tf= 5.0000
```

```
      t            a            y           k
 0.0          6.0000       0.0          15000
 0.2500       5.8373       2.2312       122.18
 0.5000       5.6911       3.7072       80.663
 0.7500       5.5594       4.6994       67.940
 1.0000       5.4408       5.3684       62.477
 1.2500       5.3338       5.8145       59.948
 1.5000       5.2371       6.1034       58.907
 1.7500       5.1497       6.2793       58.733*
 2.0000       5.0706       6.3729       59.115
 2.2500       4.9990       6.4063 *-    59.882
 2.5000       4.9342       6.3951       60.928
 2.7500       4.8754       6.3509       62.187
 3.0000       4.8220       6.2826       63.614
```

P4.11.10. MAXIMUM REACTION RATE

The reaction, $A \Leftrightarrow 2B$, takes place in a TFR with $C_{a0} = 3$ kmol/m^3. Find the temperature at which the reaction rate is a maximum for 50% conversion, given these data:

$k = \exp(20.7233-10000/T)$, 1/sec (1)

$K_e = 100$ at 300 K

$\Delta H_r = -3000$ cal/gmol, independent of temperature

$$\ln (K_e/K_{e300}) = \int_{300}^{T} \frac{\Delta H_r}{RT^2}\, dT$$

$$K_e = 100 \exp[-3000(\frac{1}{300} - \frac{1}{T})] \qquad (2)$$

Rate of reaction,

$$r_a = k[C_a - (C_{a0}-C_a)^2/K_e] = k[3(1-x)-9x^2/K_e]$$

When $x = 0.5$,

$$r_a = 3k(0.5-0.75/K_e) \qquad (3)$$

The tabulation shows the rate to be a maximum, $r_a = 0.5788$, at $T = 495$. Equation (3) could be differentiated analytically and the maximum found from the condition, $dr_a/dT = 0$.

T	r_a	T	r_a	
450	.1941	495	.5788	Maximum
460	.2791	496	.5780	
470	.3808	497	.5757	
480	.4865	498	.5720	
490	.5660	499	.5666	
491	.5705	500	.5595	
492	.5741	505	.4932	
493	.5768	510	.3604	
494	.5784	515	.1364	

P4.11.11. TEMPRATURE FOR MAXIMUM YIELD OF CONSECUTIVE REACTIONS

The reactions, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, are carried out in a CSTR, starting with pure A. The residence time is $\tau = 0.5$ hr and the minimum operating temperature is 50 C. The specific rates are

$k_1 = \exp(31.32-12581/T)$ (1)

$k_2 = \exp(34.14-14595/T)$ (2)

At what temperature is the maximum yield of B obtained?

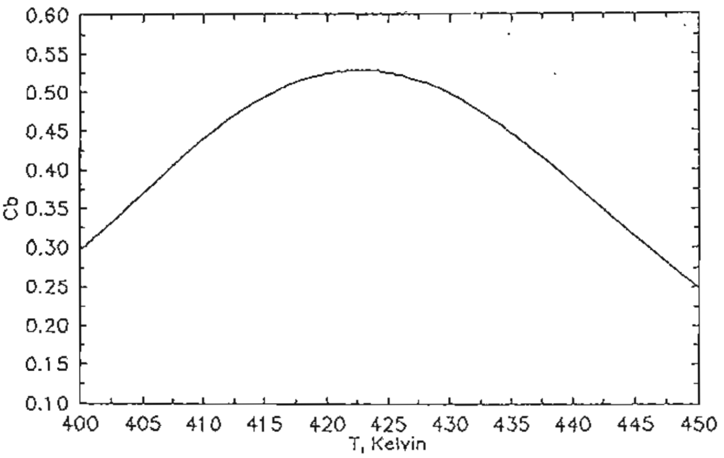
The material balances are

$$C_a = C_{a0}/(1+k_1\tau)$$

$$C_b = \frac{k_1\tau C_a}{1+k_2\tau}$$

$$\frac{C_b}{C_{a0}} = \frac{k_1\tau}{(1+k_1\tau)(1+k_2\tau)} = \frac{0.5k_1}{(1+0.5k_1)(1+0.5k_2)} \tag{3}$$

Substitute for k_1 and k_2 and plot yield against T. The plot shows a maximum, $C_b/C_{a0} = 0.53$, at $T = 423$. Eq (3) could have been differentiated analytically and the maximum found from the condition that the derivative is zero.



P4.11.12. CONSECUTIVE REACTIONS IN BATCH AND CSTR

For the consecutive reactions, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, numerical values are $k_1 = 0.35$, $k_2 = 0.13$, $C_{a0} = 4$ and $C_{b0} = C_{c0} = 0$. Find the maximum concentrations attained by B when operating as (a) a batch reactor, (b) single CSTR, (c) two stage CSTR.

Part (a): The rate equations are

$$r_a = -dC_a/dt = k_1C_a$$

$$r_b = -dC_b/dt = k_2C_b - k_1C_a$$

Integration gives C_b as a function of t,

$$C_b = \frac{k_1C_{a0}}{k_2-k_1}[\exp(-k_1t) - \exp(-k_2t)]$$

After equating the derivative to zero, the result is

$$-k_1\exp(-k_1t) + k_2\exp(-k_2t) = 0$$

$$t = \frac{\ln(k_1/k_2)}{k_1-k_2} = \frac{\ln(0.35/0.13)}{0.35-0.13} = 4.55$$

$$(C_b)_{max} = \frac{0.35(4)}{0.35-0.13}\{\exp[-0.13(4.55)]-\exp(-0.35(4.55)]\}$$

$$= 2.23 \tag{a}$$

Part (b): In a CSTR,

$$C_{a1}/C_{a0} = \frac{1}{1+k_1t}$$

$$C_{b1}/C_{a0} = \frac{k_1t}{(1+k_1t)(1+k_2t)} \tag{1}$$

After equating the derivative to zero,

$$(1+k_1t)(1+k_2t)-t[k_1(1+k_2t) +k_2(1+k_1t)] = 0$$

$$t = \sqrt{1/k_1k_2} = \sqrt{1/(0.35)(0.13)} = 4.70$$

$$(C_{b1})_{max} = \frac{0.35(4)(4.7)}{[1+0.35(4.7)][1+0.13(4.7)]} = 1.54 \qquad (b)$$

Part (c): Two stage CSTR,

$$C_{b1} = C_{b2} + t(k_2C_{b2} - k_1C_{a2})$$

$$C_{b2}(1+k_2t)/C_{a0} = \frac{k_1t}{(1+k_1t)(1+k_2t)} + \frac{k_1}{(1+k_1t)^2} \qquad (2)$$

The maximum is found in the tabulation, where it appears that

$$(C_{b2})_{max} = 1.82 \qquad (c)$$

t	0	0.5	1	1.5	2	2.5	3	5	10
C_{b2}	0	1.003	1.500	1.725	1.815	1.820	1.782	1.505	0.892

P4.11.13. SERIES-PARALLEL REACTIONS

For the series-parallel reactions, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$ and $A \overset{3}{\Rightarrow} D$, find the conditions for maximum yield of B in (a) in plug flow, (b) in mixed flow.

Part (a):

$$-\frac{dA}{dt} = (k_1+k_3)A$$

$$A = A_0\exp[(-k_1-k_3)t]$$

$$\frac{dB}{dt} = k_1A-k_2B = k_1A_0\exp[(-k_1-k_2)t] - k_2B$$

The solution of this first order linear differential equation with B = 0 when t = 0 is

$$B = \frac{k_1A_0}{k_2-k_1-k_3}\{\exp[(-k_1-k_3)t]-\exp(-k_2t)\} \qquad (1)$$

For a maximum, dB/dt = 0.

$$-(k_1+k_3)\exp[-k_1-k_3)t] + k_2\exp(-k_2t) = 0$$

$$t = \frac{1}{k_2-k_1-k_3}\ln\frac{k_2}{k_1+k_3} \qquad (2)$$

On substitution of (2) into (1),

$$(C_b)_{max}/C_{a0} = \frac{k_1}{k_1+k_3}\left(\frac{k_2}{k_1+k_3}\right)^{k_2/(k_1-k_2+k_3)} \qquad (a)$$

Part (b): Material balances in a CSTR,

$$A_0 = A + t(k_1+k_3)t$$

$$A = \frac{A_0}{1+k_1t+k_2t}$$

$$0 = B + t[-(k_1+k_3)A + k_2B]$$

$$B = \frac{(k_1+k_3)tA_0}{(1+k_1t+k_3t)(1+k_2t)} \qquad (3)$$

For a maximum, dB/dt = 0.

$$(1+k_2t)(1+k_1t+k_3t)(k_1+k_2)A_0$$
$$= (k_1+k_3)tA_0[(1+k_1t+k_3t)k_2+(1+k_2t)(k_1+k_3)] \qquad (4)$$

Solve for t from (4) and substitute into (3). The result is,

$$t = \frac{1}{\sqrt{k_2(k_1+k_3)}}$$

$$(C_b)_{max}/C_{a0} = \frac{k_1}{(\sqrt{k_1+k_3} + \sqrt{k_2})^2} \qquad (b)$$

P4.11.14. OPTIMUM TEMPERATURES IN BATCH AND CSTR

Find the temperatures at which yields are maximized in the following cases.

Case (a): A reversible first order reaction.

$$\frac{dx}{dt} = k_1(1-x)-k_2x$$

$$t = \int_0^x \frac{dx}{k_1-(k_1+k_2)x} = \frac{1}{k_1+k_2} \ln \frac{k_1}{k_1-(k_1+k_2)x}$$

$$x = \frac{k_1\{1- \exp[-(k_1+k_2)t]}{k_1+k_2} \qquad (1)$$

Take the specific rates,

$k_1 = \exp(18.42-5000/T)$

$k_2 = \exp(36.84-10000/T)$

The plots show that when $t = 1$, $x_{max} = 0.43$ at $T = 271$; and when $t = 5$, $x_{max} = 0.67$ at $T = 258$.

Case (b): The reaction, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, is conducted in a two stage CSTR. The specific rates are

$k_1 = \exp(32.24-12000/T)$

$k_2 = \exp(34.54-15000/T)$

The temperatures will be found at which the concentration is a maximum when $\tau = 1$ or 5. The material balances are

$$A_2 = A_0/(1+k_1\tau)^2$$

$$0 = B_1+ \tau(-k_1A_1+k_2B)$$

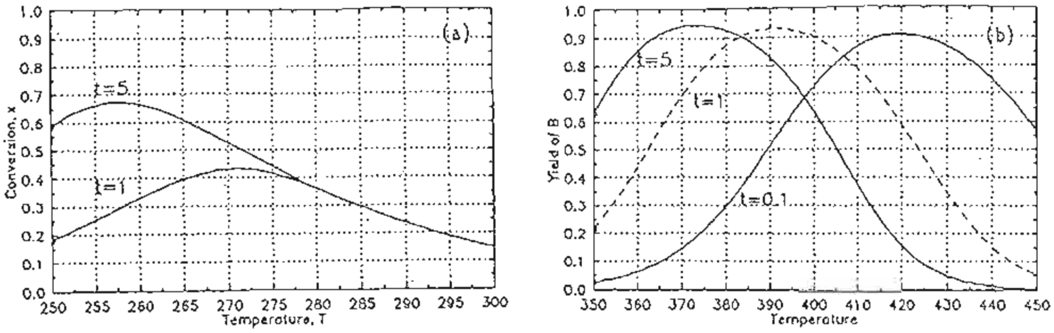
$$B_1 = \frac{k_1\tau A_1}{1+k_2\tau} = \frac{k_1\tau A_0}{(1+k_1\tau)(1+k_2\tau)}$$

$$= B_2 +\tau(-k_1A_2+k_2B_2)$$

$$B_2 = \frac{k_1\tau A_0}{(1+k_1\tau)(1+k_2\tau)}\left(\frac{1}{1+k_1\tau} + \frac{1}{1+k_2\tau}\right) \qquad (2)$$

The plots show that B reaches maxima at these times and temperatures:

τ	T	B_{max}/A_0
0.1	420	0.90
1	390	0.93
5	372	0.94



P4.11.15. OPTIMUM SIZES OF THREE STAGE CSTR.

Benzoquinone (A) and cyclopentadiene (B) are reacted in a three stage CSTR at a flow rate of 0.3 m^3/ksec with $C_{a0} = C_{b0} = 0.1$. At 25 C the specific rate is k = 9.92 m^3/(knol)(ksec). Conversion is to be 95%. Compare the total residence time for an optimum distribution of reactor sizes with the case when all sizes are the same.

$$r_a = kC_a^2 = 9.92C_{a0}^2f^2$$

$$f = C_a/C_{a0}$$

For the several stages,

$$0.992\tau_1 = \frac{1-f_1}{f_1^2} \tag{1}$$

$$0.992\tau_2 = \frac{f_1-f_2}{f_2^2} \tag{2}$$

$$0.992\tau_3 = \frac{f_2-f_3}{f_3^2} = \frac{f_2-0.05}{0.0025} \tag{3}$$

The minimum value of $\tau = \tau_1+\tau_2+\tau_3$ is to be found. Take the derivatives with respect to f_1 and f_2.

$$-\frac{2}{f_1^3}+\frac{1}{f_1^2}+\frac{1}{f_2^2} = 0 \tag{4}$$

$$-\frac{2f_1}{f_2^3}+\frac{1}{f_2^2}+\frac{1}{f_3^2} = 0 \tag{5}$$

Solve for f_1 and f_2. Reactor volumes are

$$V_i = F\tau_i = 0.3\tau_i$$

where the τ_i are obtained from Eqs (1), (2) and (3).

$f_1 = 0.2622$, $0.992\tau_1 = 10.73$, $V_1 = 3.25$

$f_2 = 0.1018$, $0.992\tau_2 = 15.48$, $V_2 = 4.68$

$f_3 = 0.05$, $0.992\tau_3 = 20.72$, $V_3 = 6.27$

$$V_{total} = 14.2\ m^3$$

With equal stages,

$$\frac{1-f_1}{f_1^2} = \frac{f_1-f_2}{f_2^2} = \frac{f_2-0.05}{0.0025}$$

$$f_1 = 0.2204,\ f_2 = 0.0901,\ f_3 = 0.05$$

$$1 = f_1+\frac{0.992f_1^2V_r}{F}$$

Substitute F = 0.3 and f_1 = 0.2204 and find

$V_r = 4.854 \text{ m}^3$ per stage

$(V_r)_{total} = 14.56 \text{ m}^3$

The optimum total volume is only slightly less than with equal stages.

P4.11.16. OPTIMUM SIZE RATIO, SECOND ORDER IN TWO STAGES

For a second order reaction in a two stage CSTR, find the size ratio for a minimum total residence time.

The material balances are,

$$A_0 = A + k\tau_1 A_1^2$$

$$kA_0\tau_1 = \frac{1-f_1}{f_1^2}$$

$$kA_0\tau_2 = \frac{f_1-f_2}{f_2^2}$$

$$f = A/A_0$$

For the total residence time, $\tau = \tau_1+\tau_2$,

$$kA_0\tau = \frac{1}{f_1^2} - \frac{1}{f_1} + \frac{f_1}{f_2^2} - \frac{1}{f_2} \tag{1}$$

Find the minimum τ as a funtion of overall conversion function f_2. Equating the derivative of (1) to zero,

$$-\frac{2}{f_1^3} + \frac{1}{f_1^2} + \frac{1}{f_2^2} = 0$$

or

$$f_1^3 + f_2^2 f_1 - 2f_2^2 = 0 \tag{2}$$

The size ratio is

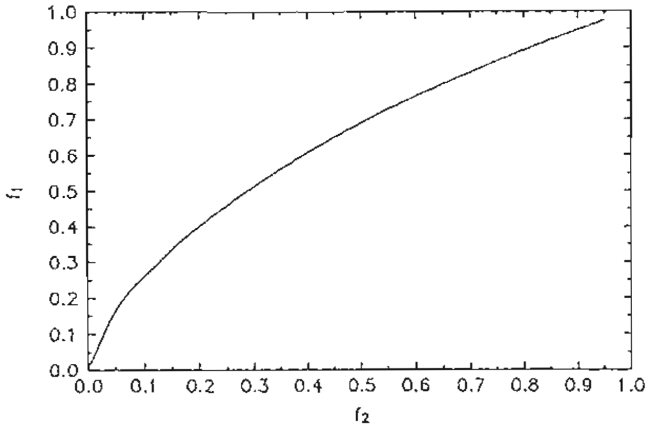
$$R = \tau_2/\tau_1 = \frac{f_1-f_2}{1-f_1}\left(\frac{f_1}{f_2}\right)^2 \tag{3}$$

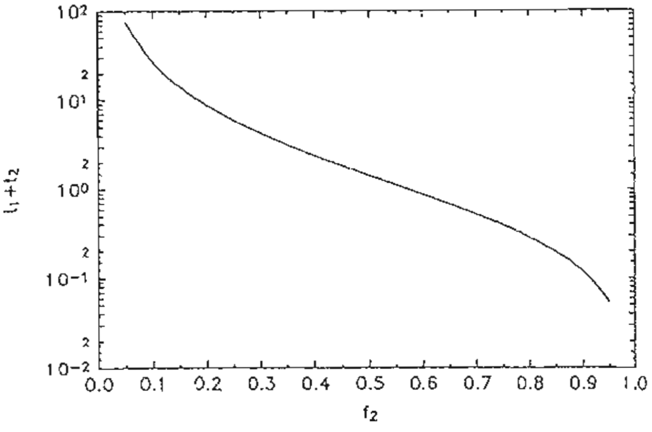
The three plots are of Eqs (1), (2) and (3) with $kA_0 = 1$, all with the abscissa f_2, the overall conversion function.

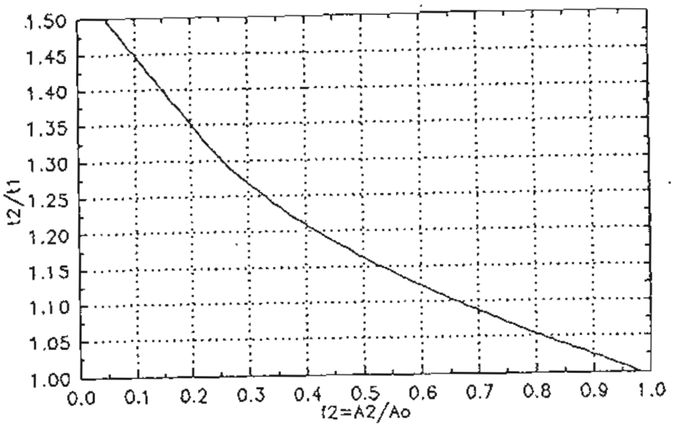
Figure 1. Minimum total time against f_2.

Figure 2. First stage, f_1, against f_2.

Figure 3. Size ratio, $V_2/V_1 = \tau_2/\tau_1$, against f_2.







P4.11.17. SECOND ORDER REVERSIBLE IN TWO STAGES

A reaction has the rate equation

$$\frac{dC}{dt} = 0.5[C^2 - 0.04(1.2 - C^2)]$$

Current operation achieves 90% of equilibrium conversion in a single CSTR. The single unit is to be replaced by two units with the same total residence time. Find the proportions of the two stages that will give the highest conversion.

At equilibrium,

$$(1.2 - C_e)/C_e = \sqrt{25},\quad C_e = 0.2$$

In the single stage,

$$C_1 = 1.2 - 0.9(1.2 - 0.2) = 0.3$$

$$1.2 = 0.3 + 0.5\tau[0.3^2 - 0.04(1.2 - 0.3)^2]$$

$$\tau = 31.25$$

In the two stages, with total residence time 31.25,

$$1.2 = C_1 + 0.5\tau_1[(C_1^2 - 0.04(1.2 - C_1)^2] \qquad (1)$$

$$C_1 = C_2 + 0.5(31.25 - \tau_1)(C_2^2 - 0.04(1.2 - C_2)^2] \qquad (2)$$

Eqs (1) and (2) are solved for specific values of residence time ratio, $\tau_1/(\tau_1+\tau_2)$. The tabulation shows the highest conversion to be when the two vessels are the same size.

$\tau_1/31.25$	C_1	C_2	
1	0.3	0.3	
0.9	0.3085	0.2590	
0.8	0.3187	0.2450	
0.7	0.3311	0.2383	
0.6	0.3466	0.2348	
0.5	0.3667	0.2333	Minimum
0.4	0.3937	0.2334	
0.3	0.4327	0.2352	
0.2	0.4953	0.2395	
0.1	0.6207	0.2499	
0	1.2	0.3000	

P4.11.18. DIFFERENT SPECIFIC RATES IN THE TWO STAGES.

Specific rates can be different in the two stages by reason of temperature differences. Some cases will be considered of the effect of differences of k and rate equation on the relative sizes of the two stages.

Part (a): First order reaction, $r = kC$.

τ is the time in the first stage and ϑ is the time in both stages.

$C_1 = C_0/(1+k_1\tau)$

$C_2 = C_1/[1+k_2(\vartheta-\tau)]$

$y = C_0/C_2 = (1+k_1\tau)[1+k_2(\vartheta-\tau)]$

To find the minimax, put $d y/d\tau = 0$.

$(1+k_1\tau)(-k_2) + k_1[1+k_2(\vartheta-\tau)] = 0$

$$\tau = \frac{k_1-k_2+k_1k_2\vartheta}{2k_1k_2}$$

When $k_1 = k_2$, the residence times of the two stages are the same, otherwise not.

Part (b): Second order, $r = kC^2 = kC_o f^2$, $f = C/C_0$.

$$C_0\tau_1 = \frac{1-f_1}{k_1f_1^2}$$

$$C_0\tau_2 = \frac{f_1-f_2}{k_2f_2^2}$$

$$y = C_0(\tau_1+\tau_2) = \frac{1}{k_1f_1^2} - \frac{1}{k_1f_1} + \frac{f_1}{k_2f_2^2} - \frac{1}{k_2f_2}$$

For the minimax, put $dy/df_1 = 0$ at constant f_2.

$$-\frac{2}{k_1f_1^3} + \frac{1}{k_1f_1^2} + \frac{1}{k_2f_2^2} = 0 \qquad (1)$$

Find f_1 at specified values of f_2, k_1 and k_2 from Eq (1). The ratio of volumes is

$$\frac{V_1}{V_2} = \frac{\tau_1}{\tau_2} = \frac{(1-f_1)k_2}{(f_1-f_2)k_1}\left(\frac{f_2}{f_1}\right)^2$$

Some numerical values are tabulated for (a) $k_1 = k_2$; (b) $k_1 = 1$, $k_2 = 2$.

	$k_1 = k_2$		$k_1 = 1,\ k_2 = 2$	
f_2	f_1	V_1/V_2	f_1	V_1/V_2
0.1	0.2592	0.6926	0.3225	6.541/11.125 = 0.588
0.3	0.5117	0.7928	0.627	0.9488/1.8167 = 0.5223
0.5	0.6894	0.8626	0.835	0.2367/0.6700 = 0.3533

Part (c): Reversible first order, $r = k[C-(C_0-C)/K_e]$

$C_0 = C_1 + k_1\tau_1[(1+1/K_{e1})C_1 - C_0/K_{e1})$

$$C_1/C_0 = \frac{1+k_1\tau_1/K_{e1}}{1+k_1\tau_1(1+1/K_{e1})} \qquad (1)$$

$$C_1 = C_2 + k_2\tau_2[(1+1/K_{e2})C_2-C_0/K_{e2}] \qquad (2)$$

$$C_2/C_0 = \frac{C_1/C_0 + k_2\tau_2/K_{e2}}{1+k_2\tau_2(1+1/K_{e2})} \qquad (3)$$

Substitute (1) into (3), put $\tau_2 = \vartheta - \tau_1$, and find minimax by

$$\frac{d(C_2/C_0)}{d\tau_1} = 0 \text{ at constant } \vartheta$$

This procedure will result in the best conversion for an overall specified residence time and the proportions of the residence time in each stage. The required algebra, however, is discouraging.

P4.11.19. LAGRANGE MULTIPLIERS FOR CONSTRAINED OPTIMUM

The reaction, A ⇒ B, takes place in two CSTR stages at different temperatures and residence times. Find a relation for the minimum overall residence time at a specified overall conversion.

The method of Lagrange Multipliers finds an extremum subject to some constraint on the variables. (Franklin, Methods of Advanced Calculus, 67, 1944; Wylie & Barrett, Advanced Engineering Mathematics, 841, 1982).

The material balance on the two stages is

$$y = C_0/C_2 = (1+k_1\tau_1)(1+k_2\tau_2) \quad (1)$$

or

$$g(\tau_1, \tau_2) = (1+k_1\tau_1)(1k_2\tau_2) - y = 0 \quad (2)$$

The minimum of $(\tau_1+\tau_2)$ is sought. By Lagranges method,

$$\tau_1+\tau_2 - \lambda[(1+k_1\tau_1)(1+k_2\tau_2) - y] \Rightarrow \text{Minimum} \quad (3)$$

Equate the derivatives with respect to τ_1 and τ_2 to zero.

$$1 - \lambda k_1(1+k_2\tau_2) = 0 \quad (4)$$

$$1 - \lambda k_1(1+k_1\tau_1) = 0 \quad (5)$$

Between Eqs (1), (4) and (5),

$$1+k_1\tau_1 = (1+k_2\tau_2)(\frac{k_1}{k_2}) = \frac{y}{1+k_2\tau_2}$$

$$\tau_2 = \frac{1}{k_2}(\sqrt{k_2y/k_1} - 1) \quad (6)$$

$$z = \sqrt{k_2C_0/k_1C_2} - 1$$

$$\tau_1 = \frac{1}{k_1}(\frac{y}{1+k_2\tau_2} - 1) = \frac{1}{k_1}(\frac{y}{1+z} - 1) = \frac{y-1-z}{k_1(1+z)} \quad (7)$$

For instance, if $k_2 = \alpha k_1$ and $y = C_0/C_2 = 2$,

$$z = \sqrt{2\alpha} - 1$$

$$\tau_1 = \frac{2-\sqrt{2\alpha}}{k_1\sqrt{2\alpha}}, \quad \tau_2 = \frac{\sqrt{2\alpha}-1}{\alpha k_1}$$

Also, when $k_1 = k_2$,

$$\tau_1 = \tau_2 = \frac{1}{k_1}(\sqrt{C_0/C_2} - 1)$$

which is evident from Eq (1). (See also problem P4.11.18).

P4.12.01. ECONOMICS OF RECYCLING

A liquid phase reaction, 2A ⇒ B, is conducted in a plug flow reactor. When a solution containing 10 kgmol/m^3 of reactant is charged at the rate of 100 m^3/hr, 50% conversion is obtained.

The same process is to be operated with recycle of 95% of the unconverted material in a concentration of 9 kgmol/m^3. These cost data apply, in monetary units (MU) per kgmol

Cost of fresh A	3.5
Value of product B	12.0
Cost or recovering unconverted A	$0.15 + 0.2/\sqrt{1-x_a}$

Find the feed rate, n_{a0}, and fraction conversion, x_a, that will result in the maximum hourly profit.

From the original operation,

$$kV_r = \int_{0.5C_{a0}}^{C_{a0}} \frac{V'dC}{C^2} = \frac{100}{10}(2-1) = 10.$$

Various flow rates are identified on the sketch.

$$x_a = 1-n_{a3}/n_{a0}$$

$$n_{a3} = n_{a0}(1-x_a0$$

$$n_{b3} = 0.5n_{a0}x_a$$

$$n_{ar} = 19n_{a3} = 19n_{a0}(1-x_a)$$

$$V'_r = \frac{19}{9}n_{a0}(1-x_a) = 2.11n_{a0}(1-x_a)$$

$$n_{a1} = n_{a0}+n_{ar} = 20n_{a0}(1-0.95x_a)$$

$$V'_1 = V_0+V'_r = n_{a0}[0.1+2.11(1-x_a)] = 2.211n_{a0}(1-0.9548x_a)$$

$$n_{a2} = 20n_{a3} = 20n_{a0}(1-x_a)$$

Flow reactor equation,

$$kV_r = \int_{n_{a2}}^{n_{a1}} \frac{dn_a}{C_a^2} = \int(\frac{V'_1}{n_a})^2 dn_a = \frac{(V')^2}{n_{a1}}(\frac{n_{a1}}{n_{a2}} -1)$$

$$= \frac{[2.211n_{a0}(1-0.9548x_a)]^2}{20n_{a0}(1-0.95x_a)}(\frac{1-0.95x_a}{1-x_a} -1)$$

$$= \frac{0.2444n_{a0}(1-0.9548x_a)^2(0.05x_a)}{(1-0.95x_a)(1-x_a)} = 10$$

$$n_{a0} = \frac{818.33(1-0.95x_a)(1-x_a)}{x_a(1-0.9548x_a)^2} \qquad (1)$$

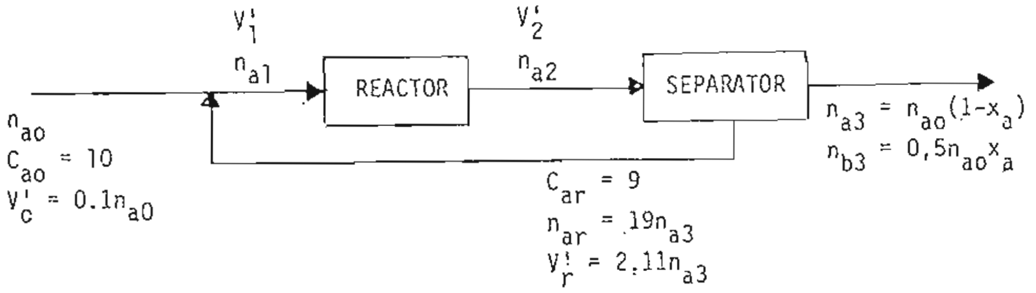
The hourly profit is

$$P = 12n_{b3} -3.5n_{a0} -n_{ar}(0.15 + \frac{0.2}{\sqrt{1-x_a}})$$

$$= 12(0.5)n_{a0}x_a - 3.5n_{a0} -19n_{a0}(1-x_a)(0.15+ \frac{0.2}{\sqrt{1-x_a}}) \qquad (2)$$

The table is constructed with Eqs (1) and (2). The maximum profit is 598 MU/hr.

x_a	n_a	P	
0.8	880.4	-853.1	
0.9	666.2	+275.4	
0.95	486.2	+587.2	
0.96	431.5	+598.0	Maximum
0.97	364.4	+574.3	
0.98	278.8	+497.7	



P4.12.02. OPTIMUM CONVERSION IN RECYCLING

A plug flow reactor is operated with partial recycle of unconverted material. The reaction is second order liquid phase, 2A ⇒ B. Concentration of the fresh feed is $C_{a0} = 10$ kmol/m^3 and that of recycle is $C_{ar} = 9$ kmol/m^3. Recovery of A is 90%. The function $kV_r = 10$, with time in hrs. Other data are indicated on the sketch. Cost data are:

Cost of A	\$30/kmol
Value of B	\$90/kmol
Cost of recovery	$2.2 + 1.8/\sqrt{1-x_a}$, \$/kmol of A

The problem is to find the feed rate n_{a0} and the fractional conversion x_a for the maximum profit rate.

$x_a = 1-n_{a3}/n_{a0}$, overall fractional conversion
$n_{b3} = 0.5n_{a0}x_a$, product rate
$n_{a3} = n_{a0}(1-x_a)$, wasted A
$n_{ar} = 9n_{a3} = 9n_{a0}(1-x_a)$, recycled A
$n_{a1} = n_{a0}+n_{ar}\ 10n_{a0}(1-x_a)$, feed to reactor
$n_{a2} = 10n_{a3} = 10n_{a0}(1-x_a)$, reactor effluent
$F_0 = n_{a0}/C_{a0} = 0.1n_{a0}$, fresh volumetric rate
$F_r = n_{ar}/C_{ar} = n_{a0}(1-x_a)$, recycle volumetric rate
$F = F_0+F_r = n_{a0}(1.1-x_a)$, reactor volumetric rate

The PFR equation is

$$-dn_a = k(\frac{n_a}{F})^2 dV_r$$

$$kV_r = 10 = \int_{n_{a2}}^{n_{a1}} (\frac{F}{n_a})^2 dn_a = F^2(\frac{1}{n_{a1}} - \frac{1}{n_{a2}})$$

$$= n_{a0}^2(1.1-x_a)^2[\frac{1}{10n_{a0}(1-x_a)} - \frac{1}{10n_{a0}(1-0.9x_a)}]$$

$$\frac{100}{n_{a0}} = (1.1-x_a)^2(\frac{1}{1-x_a} - \frac{1}{1-0.9x_a}) \qquad (1)$$

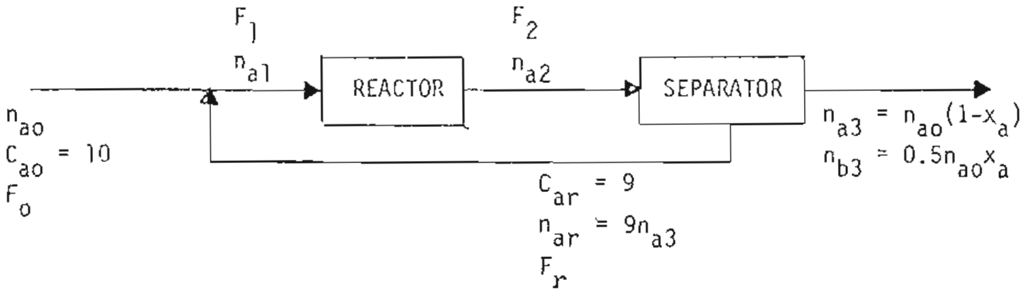
The operating profit is

$$P = 90n_{b3} - 30n_{a0} - (2.2+1.8/\sqrt{1-x_a})n_{ar}$$
$$= n_{a0}[45x_a - 30 - 9(2.2+1.8/\sqrt{1-x_a})(1-x_a)] \qquad (2)$$

The table is prepared with Eqs (1) and (2) and shows the optimum condition to be

$x_a = 0.9465$, $n_{a0} = 355$ kmol/hr, $P = \$2767$/hr

x_a	n_{a0}	P	
0.900	528	1793	
0.940	384	2743	
0.941	380	2750	
0.942	375	2755	
0.943	371	2760	
0.944	367	2763	
0.945	362	2766	
0.946	358	2767	Maximum
0.947	353	2767	
0.948	349	2766	
0.949	344	2764	
0.950	339	2760	
0.960	289	2651	
0.990	91	1159	



P4.12.03. BATCH OPERATION.

The aqueous second order reaction, $2A \Rightarrow 2B$, has the specific rate $k = 1.0$ liter/mol-hr and the initial concentration $C_{a0} = 1$ mol/liter. Downtime is 1 hr/batch. Cost of fresh reactant is \$100/batch and the value of the product is $\$200x_a$/batch, where x_a is the fractional conversion of A. What is the daily profit for each of these modes of operation?

(a) Maximum production of B
(b) Unreacted A is discarded
(c) Unreacted A is recycled at no cost
(d) Unreacted A is recycled at one-half the cost of fresh A.

Total time per batch,

$$\tau_t = 1 + \int_x^0 \frac{dx}{kC_{a0}(1-x_a)^2} = 1 + \left(\frac{1}{1-x_a} - 1\right) = \frac{1}{1-x_a} \qquad (1)$$

$N = 24(1-x_a)$, number of batches /day

$n_b = NV_rC_{a0}x_a = 24V_rx_a(1-x_a)$, daily product

Part (a): For maximum daily product,

$$\frac{dn_b}{dx_a} = 24V_r(1-2x_a) = 0$$

$x_a = 0.5$

The profit is

$p = 200x_a - 100 = 0$ per batch (a)

Part (b):

$P = N(200x_a - 100) = 24(1-x_a)(100)(2x_a-1)$

$$\frac{dP}{dx_a} = 2400[2(1-x_a)-(2x_a-1)] = 0$$

$x_a = 0.75$

$P = 2400(1-0.75)(1.5-1) = \$300/\text{day}$ (b)

Part (c):

Net cost of feed = $100x_a$/batch

$P = 24(1-x_a)(200x_a-100x_a)$

$$\frac{dP}{dx_a} = 0,\ x_a = 0.5$$

$P = 2400(0.5)(0.5) = \$600/\text{day}$ (c)

Part (d):

Cost of consumed reactant = $100x_a$, per batch

Reclaiming cost = $0.5(100)(1-x_a)$, per batch

$P = 24(1-x_a)[200x_a-100x_a-50(1-x_a)] = 1200(1-x_a)(3x_a-1)$

$dP/dx_a = 0,\ x_a = 0.667$

$P = 1200(1-0.667)(2-1) = \$400/\text{day}$ (d)

<u>P4.12.04. THREE REACTORS IN SERIES.</u>

A reactor system consists of two CSTRs and one PFR, all of the same volume. The reaction is $2A \Rightarrow B$, specific rate is 40 cuft/lbmol-hr, F = 1000 cuft/hr, C_{a0} = 1.5 lbmol/cuft, and 90% conversion is required.

Find the reactor volumes with the three possible series arrangements.

$C_{a3} = 0.05(1.5) = 0.075$

$k\tau = 40V_r/1000 = 0.04V_r$

PFR first:

$$C_{a1} = \frac{1.5}{1+kC_{a0}\tau} = \frac{1.5}{1+0.06V_r}$$

$C_{a1} = C_{a2} + k\tau C_{a2}^2 = C_{a2} + 0.04V_rC_{a2}^2$

$C_{a2} = 0.075+0.04V_r(0.075)^2$

PFR second:

$1.5 = C_{a1} + k\tau C_{a1}^2$

$$C_{a2} = \frac{C_{a1}}{1+k\tau C_{a1}}$$

$C_{a2} = 0.075 + k\tau(0.075)^2$

PFR third in line:

$1.5 = C_{a1} + k\tau C_{a1}^2$

$C_{a1} = C_{a2} + k\tau C_{a2}^2$

$$0.075 = \frac{C_{a2}}{1+k\tau C_{a2}}$$

Substitute for $k\tau = 0.04V_r$ and solve the three sets of three equations each. The results are tabulated. PFR first is the best arrangement.

PFR	C_{a1}	C_{a2}	$k\tau$	V_r
First	0.2629	0.171	3.137	78.4
Second	0.4092	0.1116	6.514	162.9
Third	0.386	0.170	7.459	186.5

P4.12.05. CONSECUTIVE REACTIONS.

The reaction, $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$, is to be conducted in an n-stage CSTR under the most economical conversion conditions. Inlet concentation is $C_{a0} = 1.5$ lbmol/cuft. The specific rates are $k_1 = 0.3$/hr, $k_2 = 0.15$/hr. Unconverted A will be recovered, at a price, and returned to storage. Required production of B is to be 50 lbmol/hr. The annual operating cost, exclusive of the cost of fresh and recycled material, depends on the number n of vessels and the size of each vessel, V_r cuft, according to the equation,

$$K = 200n(100+V_r^{0.7}),\ \text{MU (money units)}$$

Other cost data are:

Cost of fresh charge A	5.00 MU/lbmol
Cost of recovering A	0.6 MU/lbmol
Value of product B	10.00 MU/lbmol
Value of product C	1.50 MU/lbmol

Find the optimum operating conditions.

τ = total residence time in n stages

$$\alpha = 1/(1+k_1\tau/n) \qquad (1)$$

$$\beta = 1/(1+k_2\tau/n) \qquad (2)$$

In problem P4.04.52 it is shown that the concentrations of the n-th stage products are

$$A_n = A_a\alpha^n = 1.5\alpha^n \qquad (3)$$

$$B_n = \frac{k_1\tau A_0\alpha\beta}{\beta-\alpha}(\beta^n-\alpha^n) \qquad (4)$$

$$C_n = A_0-A_n-B_n \qquad (5)$$

Production of B = FB_n = 50 lbmol/hr

F = volumetric feed rate

= $50/B_n$

Basis 1 hr:

Value of product B = 50(10) = 500

Value of product C = $1.5(1.5-A_n-B_n)(50/B_n)$

Cost of converted A = $(1.5-A_n)(50/B_n)$

Cost of recovered A = $0.6A_n(50/B_n)$

Net cost, product - material,

$$K_c = 365(24)[425 + 145(\frac{A_n}{B_n})- \frac{262.5}{B_n}] \qquad (6)$$

Profit $K_{total} = K_c$ - annual operating cost

$$K_t = K_c - 200n[100+ (\frac{50\tau}{B_n})^{0.7}] \qquad (7)$$

where the substitution $V_r = F\tau = 50\tau/B_n$ has been made.

The solutions of Eqs (1) - (7) are tabulated. The main numbers are of $10^{-6}K_t$. The conditions making the maximum annual profit are:

$K_t = 1.9112\ (10^6)$ MU/yr
$n = 3$ stages
$\tau = 2.1$ hrs
$V_r = 50\tau = 105$ cuft
$A_n = 0.8467$ lbmol/cuft
$B_n = 0.7068$ lbmol/cuft
$C_n = 0.0535$ lbmol/cuft

τ	n=1	n=2	n=3	n=4	n=5
1.5	1.7514	1.8524	1.8704	1.8668	1.8546
1.6	1.7614	1.8651	1.8840	1.8809	1.8689
1.7	1.7681	1.8744	1.8943	1.8917	1.8799
1.8	1.7722	1.8810	1.9018	1.8996	1.8881
1.9	1.7740	1.8852	1.9069	1.9052	1.9839
2.0	1.7739	1.8874	1.9100	1.9086	1.8976
2.1	1.7721	1.8879	$\underline{1.9112}$	1.9103	1.8995
2.2	1.7689	1.8868	1.9110	1.9105	1.8998
2.3	1.7645	1.8845	1.9094	1.9092	1.8988
2.4	1.7590	1.8809	1.9065	1.9067	1.8965
2.5	1.7526	1.8763	1.9026	1.9031	1.8931

P4.12.06. REVERSIBLE REACTION

The reversible liquid phase reaction, $2A \Leftrightarrow B$, has the rate equation

$$r_a = 2.7(C_a^2 - 6.67C_b) \quad \text{lbmol/cuft-hr} \qquad (1)$$

It is carried out in a CSTR . The feed is pure A, the product is 99 mols/hr of B and 1 mol/hr of A. Unconverted A is recycled as a mixture with 95% A and 5% B. The operating cost is made up of vessel and material costs as

$$K = 200V_r^{0.7} + 1.2n_{tf} + 8(n_{t1})^{0.9} + 3.5n_{t1},\ \text{MU/hr} \qquad (2)$$

Subscript notations are identified on the sketch. The n_i are lbmols/hr. Find the flow rates that will result in the minimum operating cost.

Stoichiometric balances:

$$0.5(n_{af}-n_{a1}) = n_{b1}-n_{bf} = n_{b1}-n_{ar}/19$$

$$n_{af} = n_{ar}/19 + 0.5(n_{a0}+n_{ar}-n_{a1}) = 0.5n_{a0}+0.5526n_{ar}-0.5n_{a1}$$

Volumetric flow rate out of the reactor,

$$V_1' = (n_{a1}+n_{b1})/5 = 0.1n_{a1}+0.1n_{a0}+0.11052n_{ar}$$

Since

$$n_{ar} = n_{a1} - 1$$

and

$$n_{a0} = 2n_{bp} + n_{ap} = 2(99) + 1 = 199$$

then

$$n_{b1} = 0.5(199)+0.5526(n_{a1}-1) - 0.5n_{a1}$$
$$= 0.0526n_{a1} + 98.9474 \qquad (3)$$

$$V_1' = 0.1n_{a1}+0.1(199) + 0.11052(n_{a1}-1)$$
$$= 0.21052n_{a1} + 19.78948 \qquad (4)$$

$$C_{a1} = \frac{n_{a1}}{V_1'} = \frac{n_{a1}}{0.21052n_{a1}+19.78948} \qquad (5)$$

$$C_{b1} = \frac{n_{b1}}{V_1'} = \frac{0.0526n_{a1}+98.9474}{0.21052n_{a1}+19.78948} \qquad (6)$$

The material balance on the CSTR is

$$n_{af} = n_{ao} + n_{ar} = 199 + n_{a1} - 1 = 198 + n_{a1}$$

$$= n_{a1} + V_r r_a$$

$$V_r = \frac{198}{r_a} = \frac{198}{2.7(C_a^2-6.67C_{b1}^2)} \qquad (7)$$

Total feed rate to the reactor ,

$$n_{tf} = n_{af} + n_{bf} = n_{ao}+n_{ar}+n_{br} = 199+1.0526(n_{a1}-1)$$

$$= 197.95 + 1.0526n_{a1} \qquad (8)$$

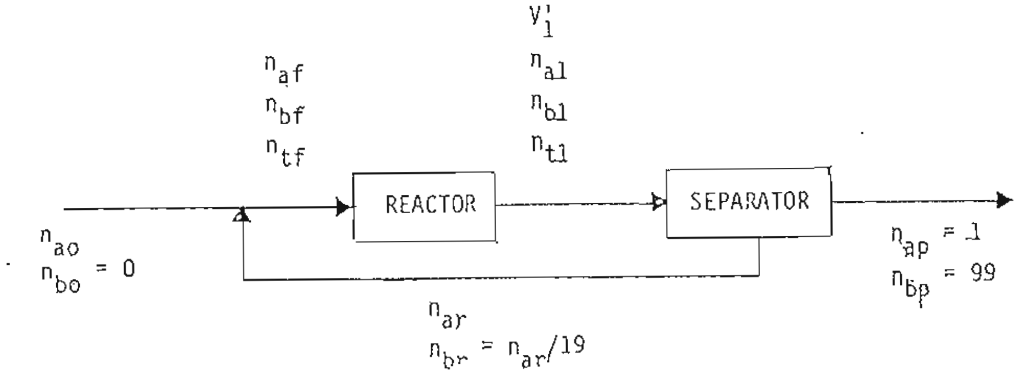
Total effluent from the reactor,

$$n_{t1} = n_{a1} + n_{b1} = 98.95 + 1.0526n_{a1} \qquad (9)$$

All terms in the cost Eq (2) now are expressed in terms of n_{a1}. The minimum cost is found by trial. From the tabulation, the minimum hourly cost occurs when $n_{a1} = 320$. Then

$K = 5014$ MU/hr, $V_r = 15.86$ cuft.

n_{a1}	C_{a1}	C_{b1}	V_r	K	
300	3.617	1.383	19.00	5040	
310	3.645	1.355	17.25	5018	
320	3.672	1.328	15.86	5014	Minimum
325	3.684	1.316	15.26	5018	
330	3.697	1.303	14.72	5024	
340	3.721	1.279	13.78	5044	



P4.12.07. VERY FAST REACTION

The very fast reaction, A + B ⇔ 2C, takes place in a plug flow reactor. It has the equilibrium constant $K_e = 4$. Find the ratio of A to B in the charge that would minimize the total reactant cost to produce a given amount of C. Unconverted products are discarded. Cost of A is \$α/lbmol, that of B is \$β/lbmol.

Since the reaction is very fast, equilibrium may be assumed attained in any size of reactor.

$$n_a = n_{ao} - 0.5n_c$$

$$n_b = n_{bo} - 0.5n_c$$

$$K_e = 4 = \frac{n_c^2}{(n_{ao}-0.5n_c)(n_{bo}-0.5n_c)}$$

$$n_c = \frac{2n_{a0}n_{b0}}{n_{a0}+n_{b0}} \qquad (1)$$

The reactant cost per unit of product,

$$K = \frac{\alpha n_{a0}+\beta n_{b0}}{n_c} = \frac{(\alpha n_{a0}+\beta n_{b0})(n_{a0}+n_{b0})}{2n_{a0}n_{b0}}$$

$$= 0.5(\alpha\phi + \alpha + \beta + \beta/\phi) \qquad (2)$$

$$\phi = n_{a0}/n_{b0}$$

For a minimum cost,

$$\frac{dC}{d\phi} = 0$$

$$\alpha - \beta/\phi^2 = 0$$

$$\phi = \sqrt{\beta/\alpha}$$

P4.12.08 FIRST ORDER IN A PFR

One hundred gmols of B are to be made hourly from a feed of $C_{a0} = 0.1$ mol/liter in a plug flow reactor. The reaction is $2A \Rightarrow 2B$ and the rate equation is

$r_a = 2C_a^2$ liter/mol-hr

Cost of A = \$0.5/gmol

Other costs = \$0.01/(hr)(liter of reactor volume)

(a) Find the reactor size, feed rate and conversion for optimum operation. (b) What is the unit cost of B if unreacted A is discarded?

$$n_b = n_{a0} - n_a = V'(C_{a0}-C_{ap}) = V'(0.1-C_{ap}) = 100 \text{ mols/hr}$$

$$V' = \frac{100}{0.1-C_{a_p}}$$

C_{ap} = concentration in the effluent

In the flow reactor,

$$-V'dC_a = r_a dV_r = 2C_a^2 dV_r$$

$$V_r = \int_{C_{ap}}^{0.1} \frac{V'dC_a}{2C_a^2} = \frac{50}{0.1-C_{ap}} \int_{C_{ap}}^{0.1} \frac{dC_a}{C_a^2} = \frac{50}{0.1-C_{ap}}\left(\frac{1}{C_{ap}} - 10\right)$$

$$= \frac{500}{C_{ap}} \qquad (1)$$

Total cost,

$$K = 0.01V_r + 0.5V'C_{a0} = \frac{5}{C_{ap}} + \frac{0.5(100)(0.1)}{0.1-C_{ap}} \qquad (2)$$

For a minimum cost, $dK/dC_{ap} = 0$,

$$-\frac{5}{C_{ap}^2} + \frac{5}{(0.1-C_{ap})^2} = 0$$

$C_{ap} = 0.05$

K = \$200/hr

Unit cost of B = 200/100 = \$2/gmol

P4.12.09. OPTIMUM CONVERSION IN A CSTR

A plant makes 40 kmol of B in a mixed reactor from a feed stream of 1 kmol/m^3 of reactant A. The reaction is pseudo first order. Two percent of the incoming A goes through unreacted and is discarded. Fixed and operating costs for this process are \$20/hr, reactant cost is \$1//kmol and product can be sold for \$1.32/kmol. It is suspected that the plant is not being operated at optimum conditions. (a) What are the present profits/hr? (b) How should conditions be changed to maximize profits?

Material balance on the CSTR,

$$n_{a0} = n_a + kV_rC_a = (1+kV_r/V')n_a = (1+kV_r/V')n_{a0}(1-x_a)$$

$$kV_r = \frac{V'x_a}{1-x_a}$$

Originally,

$$x_a = 0.98$$

$$n_b = n_{a0}x_a = 40$$

$$n_{a0} = 40.82 \text{ kmol/hr}$$

$$V' = n_{a0}/C_{a0} = 40.82 \text{ m}^3\text{/hr}$$

$$kV_r = \frac{40.82(0.98)}{0.02} = 2000.18$$

Current profit,

$$K = 1.32(40)-40.82-20 = -\$8.02/\text{hr}$$

Part (b):

$$x_a = 1-\frac{1}{1+kV_r/V'} = \frac{kV_r}{n_{a0}+kV_r}$$

$$n_b = n_{a0}x_a = \frac{n_{a0}kV_r}{n_{a0}+kV_r}$$

The profit now is expressed in terms of n_{a0},

$$K = \frac{1.32n_{a0}kV_r}{n_{a0}+kV_r} -1.00n_a - 20 \Rightarrow \text{Maximum}$$

On making $dK/dn_{a0} = 0$,

$$(n_{a0}+kV_r)^2 = 1.32(kV_r)^2$$

$$n_{a0} = 0.1489kV_r = 0.1489(2000.18) = 297.8 \text{ kmol/hr}$$

$$x_a = 1-\frac{1}{1+kV_r/V'} = 1-\frac{1}{1+kV_r/n_{a0}} = 1-\frac{1}{1+2000.18/297.8}$$

$$= 0.8704$$

$$n_b = n_{a0}x_a = 297.8(0.8704) = 259.2 \text{ kmol/hr}$$

$$K = 1.32(259.2)-297.8-20 = \$24.34/\text{hr}$$

P4.12.10. WASTE STREAM RECOVERY

A waste stream of 20,000 liters/day contains chemical A in concentration 0.01 kg/liter which can be hydrolyzed in aqueous solution to give chemical B which has a value of \$1.00/kg. The reaction is pseudo first order with k = 6/day. A CSTR is contemplated. Cost data are

Annual fixed charges, \$225$V_r^{0.5}$, with V_r in liters

Labor and operating costs, \$20/day for 300 days/yr

Find the conditions that will give the maximum profit.

CSTR balance,

$$V'(C_{a0}-C_a) = kV_rC_a$$

$$V_r = \frac{V'(C_{a0}-C_a)}{kC_a} = \frac{20000}{6}\left(\frac{n_{a0}}{n_a}-1\right) = 3333\left(\frac{200}{n_a}-1\right) \quad (1)$$

The profit is

$$K = (n_{a0}-n_a)(1.00)-20-\frac{225}{300}V_r^{0.5}$$

$$= 200-n_a-20-43.30\left(\frac{200}{n_a}-1\right)^{0.5}$$

For a maximum profit, $dK/dn_a = 0$,

$$-1+21.65\left(\frac{200}{n_a}-1\right)^{-0.5}\left(\frac{200}{n_a^2}\right) = 0$$

$$n_a = 49.995 \text{ kg/hr}$$

$$V_r = 3333\left(\frac{200}{49.995}-1\right) = 10{,}000 \text{ liters}$$

$$K = 200-49.995-20-0.75(10000)^{0.5} = \$30/\text{day}, \quad \$9000/\text{yr}$$

P4.12.11. SIMULTANEOUS REACTIONS

Chemicals A and B react as follows:

$A + B \Rightarrow R$, $r_r = 68.8C_aC_b$, liter/mol-hr

$2B \Rightarrow S$, $r_s = 34.4C_b^2$, liter/mol-hr

Reactants are available in separate streams at $C_{a0} = C_{b0} = 0.1$ mol/liter and both cost \$0.50/mol. Fixed costs are \$0.01/(hr)(liter of reactor volume). Find the optimum conditions for making 100 mol/hr of product R.

Stoichiometric balance,

$$n_{a0}-n_a = n_r = 100 \text{ mols/hr} \quad (1)$$

Volumetric flow rate,

$$V' = V'_a + V'_b = n_{a0}/C_{a0} + n_{b0}/C_{b0} = 10(n_{a0}+n_{b0}) \quad (2)$$

Material balance,

$$n_{a0} = n_a + k_1V_r(n_an_b/V')^2 \quad (3)$$

$$n_{b0} = n_b + (V_r/V'^2)(k_1n_an_b+2k_2n_b^2) \quad (4)$$

Combining Eqs (2) and (3),

$$\frac{k_1V_r}{V'^2} = \frac{100}{n_an_b} = \frac{n_{b0}-n_b-(n_{a0}-n_a)}{n_b^2} \quad (5)$$

From which

$$n_a = \frac{100n_b}{n_{b0}-n_b-100} \quad (6)$$

$$V_r = \frac{100V'^2}{k_1n_an_b} = \frac{100[10(100+n_a+n_{b0})]^2}{68.8n_an_b}$$

$$= \frac{145(100+n_a+n_{b0})}{n_an_b} \quad (7)$$

The operating cost,

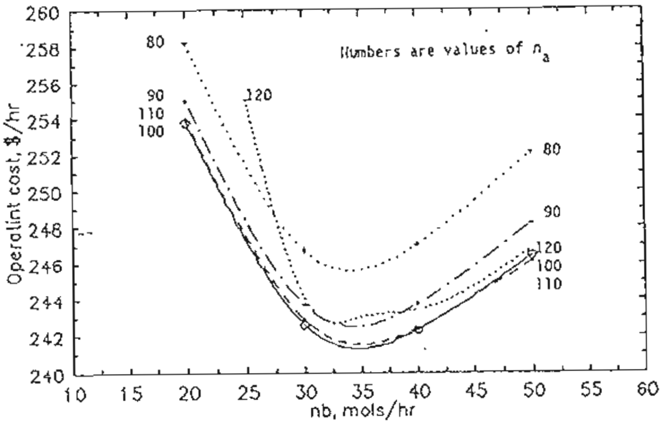
$$K = 0.5(n_{a0}+n_{b0}) + 0.01V_r = \phi(n_a, n_b) \quad (8)$$

For a minimum operating cost,

$$\frac{\partial K}{\partial n_a} = \frac{\partial K}{\partial n_b} = 0$$

Instead of carrying out the differentiation analytically, the minimum is found by plotting several constant values of n_a over a range of n_b and noting the smallest value of K. The conclusion is,

n_r = 100 mols/hr
n_a = 100 mols/hr
n_b = 35 mols/hr
K = \$242/day
V_r = 5672 liters
n_{a0} = 200 mols/hr
n_{b0} = 170 mols/hr



P4.12.12. BATCH REACTION WITH RECYCLE.

A batch reaction is conducted with partial recovery of unconverted reactants. The reaction is A + B ⇒ C with rate equation

$$-\frac{dC_a}{dt} = 0.4C_a(0.2+C_a) \quad \text{cuft/lbmol-hr}$$

and C_{a0} = 1.2 and C_{b0} = 1.4 lbmol/cuft. The reactor volume is 150 cuft. Downtime is 1.25 hrs/batch. Costs of A and B are \$5/lbmol, value of C is \$30/lbmol or \$25/lbmol and recovery cost is \$1.5/lbmol. Recovery of unconverted A is 95%, and the same recovered proportion of B as exists in the charge to the reactor. Find the conditions for the maximum daily profit.

n_{a0} = charge of A to the reactor = 1.2(150) = 180 lbmols/batch

$n_{b0} = (1.4/1.2)n_{a0}$ = 210 mols/batch

Reaction time,

$$\tau_r = \int_{1.2}^{C_a} \frac{dC_a}{0.4C_a(0.2+C_a)} = 2 \ln \frac{0.8571(0.2+C_a)}{C_a} \qquad (1)$$

Batch time,

$$\tau = \tau_r + 1.25 \qquad (2)$$

Number of daily batches,

$$N = \frac{24}{\tau_r+1.25} \qquad (3)$$

Cost of A = cost of charge - value of recovered A + cost of recovering A

$= 5(n_{a0} - 0.95n_a)+1.5(0.95)n_a$

$$\text{Cost of B} = \frac{1.4}{1.2}[5(n_{a0} -0.95n_a)+1.5(0.95)n_a]$$

Value of C = $30(n_{a0}-n_a)$ or $25(n_{a0}-n_a)$

Profit K = $30(180-n_a) - 2.167[5(180) -3.5(0.95)n_a]$, per batch

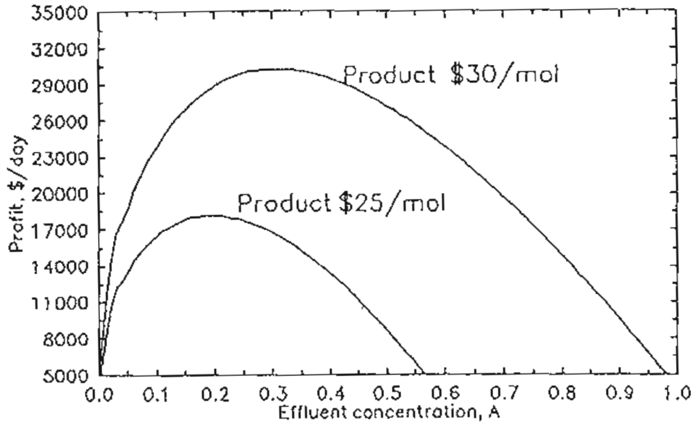
Daily profit,

$$K_{tot} = (3449.7-22.795n_a)\left(\frac{24}{\tau_r+1.25}\right), \text{ Product at \$30} \qquad (4)$$

$$(2549.7-22.795n_a)\left(\frac{24}{\tau_r+1.25}\right),\ \text{Product at \$25} \qquad (5)$$

$$n_a = V_rC_a = 150C_a \qquad (6)$$

Combine Eqs (1), (6) and either (4) or (5). The plots show the maximum profit
= \$29400/day at $C_a = 0.3$ with product at \$30/lbmol
\$17400/day at $C_a = 0.19$ with product at \$25/lbmol



P4.12.13. HOW MANY STAGES?

It is required to find the cheapest CSTR battery for converting 2000 lbmols/24 hr of a reactant for which the rate equation is

$$r = -\frac{dC}{dt} = 0.1C^2 \text{ lbmol/cuft-min}$$

Inlet concentration is 1.25 and outlet is to be 0.15 lbmol/cuft. Cost data are:

Reactors: Assembled cost is \$5/lb. Dished bottoms, open tops, height equal to diameter, bottom surface equals 1.5 times the surface of a flat plate of the same diameter. Tanks of over 1500 gal capacity are of 1/4" plate, smaller ones of 3/16" plate. Freeboard equals volume of the dished head.

Agitators: The cost = $190V_r^{0.3}$, in dollars, where V_r is the volume of the straight side of the tank, in cuft.

$$F = \text{flow rate} = \frac{2000}{1440(C_0-C_n)} = \frac{2000}{1440(1.25-0.15)} = 1.25 \text{ cuft/min}$$

Since the the volumes of freeboard and dished head are equal, the volume of the vessel equals that of the straight side.
Vessel cost = 5(Volume of walls)(Density)

$$= 5[\pi HD+1.5(0.7854)D^2](\frac{485}{48}) = 218.8D^2$$

$$\Rightarrow 218.8(\frac{V_r}{0.7854})^{2/3} = 255.9V_r^{2/3}\text{, for 1/4" plate}$$

$$191.7V_r^{2/3}\text{, for 3/16" plate}$$

Material balance for the n-th stage,

$$C_{n-1} = C_n + (V_r/F)\, C_n^2 = C_n + 0.8V_rC_n^2$$

$$C_0 = 1.25,\ C_{last} = 0.15$$

The calculations are summarized in the table. They show the cheapest battery to be three stage.

n	V_r, each	$V_r^{2/3}$	$V_r^{0.3}$	-----------Cost--------- Vessels	 Agitators	 Total	
1	611.1	72.03	6.85	13808	1302	15110	
2	102.4	21.89	4.01	8393	1524	9917	
3	48.3	13.26	3.20	7626	1881	9507	Minimum
4	30.6	9.78	2.79	7499	2120	9619	
5	22.1	7.88	2.53	7553	2404	9957	
6	17.2	6.66	2.35	7660	2679	10339	
7	14.1	5.84	2.21	7837			

P4.12.14. PRODUCTION COST

Optimum conditions are to be found for conducting the reaction, 2A ⇒ B, in a CSTR, with a rate equation

$$r_a = 0.4C_a^2 \quad \text{kmol/m}^3\text{-min}$$

Inlet concentration is 1 kmol/m^3 and the production rate of B is to be 100 kmol/min. Cost of A is \$1.2/kmol and operating cost is \$0.2/(m^3 reactor)(min). Unconverted A is discarded.

Material balance,

$$C_a = \frac{-1+\sqrt{1+4k\tau C_{a0}}}{2k\tau} = \frac{-1+\sqrt{1+1.6\tau}}{0.8\tau} \qquad (1)$$

Feed rate,

$$F_a = \frac{200}{C_{a0}-C_a} = \frac{200}{1-C_a} \qquad \text{m}^3\text{/min}$$

Production cost,

$$K = 1.2F_a + 0.2V_r = (1.2 + 0.2\tau)F_a \quad \$/\text{min}$$

Per unit of B, cost is

$$K_b = \frac{2(1.2+0.2\tau)}{1-C_a} \qquad (2)$$

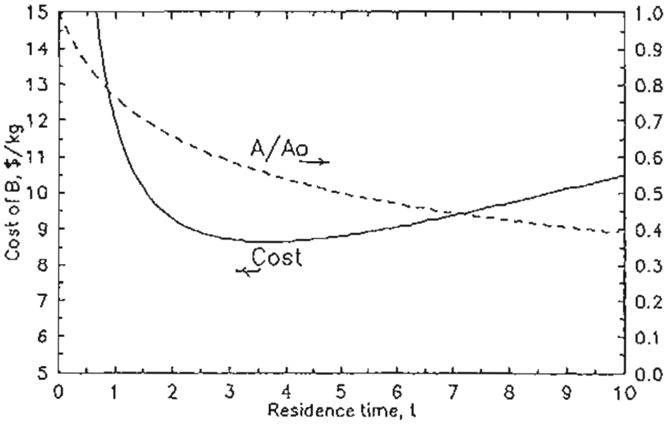
The plot of K_b against τ reveals the optimum condition to be

K_b = \$8.64/kmol

τ = 3.7 min

$C_a = 0.55$ kmol/m^3

$F_a = 200/(1-0.55) = 444.4$ kmol A/min



P4.12.15. CSTR WITH HEAT INPUT

The endothermic liquid phase reaction, $2A \Rightarrow B + C$, is to be conducted in a heated CSTR. Feed rate is F = 20 cuft/min at 310 F. The reaction temperature is maintained at 400 F by heat transfer. Inlet concentration is $C_{a0} = 1$ lbmol/cuft. The rate equation is

$$r_a = 1.5C_a^2 - 2.2(C_{a0}-C_a)^2 = 1.5(1-x)^2 - 2.2x^2 \qquad (1)$$

Thermal data: $\Delta H_r = +15000$ Btu/lbmol A, $\rho C_p = 45$ Btu/cuft-°F.

Cost data: Q = \$20/million Btu
A = \$3 /lbmol
$A_{unreacted}$ = \$2/lbmol
B = \$30/lbmol
C = \$6/lbmol
Reactor, $(25/60)V_r$ \$/min, V_r in cuft

Material balance,

F = volumetric feed rate of A

$$C_{a0} = C_a + (V_r/F)r_a$$

$$V_r = \frac{F(C_{a0}-C_a)}{r_a} = \frac{Fx}{1.5(1-x)^2-2.2x^2} \qquad (2)$$

Heat balance,

$$Q = \Delta H_r V_r r_a - F\rho C_p(400-310)$$
$$= F[15000x - 45(90)], \text{ Btu/min}$$

Costs:

$$\text{Heat, } K_Q = 20(10^{-6}Q = (0.3x-0.081)F, \text{ \$/min}$$

$$\text{Reactor, } K_r = (25/60)V_r = \frac{0.4167Fx}{r_a}, \text{ \$/min}$$

$$\text{Feed, } K_f = 3F$$

$$\text{Products, } K_p = 0.5(30+6)Fx + F(1-x)(2.00) = F(16x+2)$$

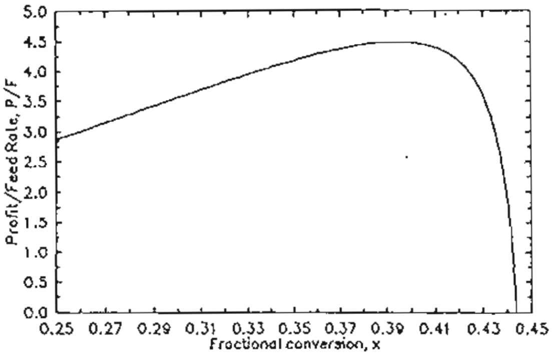
Profit,

$$P/F = 16x + 2 - 3 - (0.3x-0.081) - \frac{0.4167x}{r_a}$$

$$= 15.7x - 0.919 - \frac{0.4167x}{1.5(1-x)^2-2.2x^2} \qquad (3)$$

The plot of Eq (3) shows the optimum conditions to be

$P/F = 4.48$ \$/(lbmol A/min)
$x = 0.39$, fractional conversion of A
$V_r = 20(1-x) = 12.2\ m^3$



P4.12.16. TUBULAR FLOW REACTOR

Substance A with a concentration $C_{a0} = 2.5\ kmol/m^3$ at a flow rate of 12 m^3/hr is converted to B in a tubular reactor. The value of the product is \$1.5/kgmol of B. The cost of operation is \$2.50/(m^3 of reactor volume)(hr). The specific rate is 30/hr. Find the maximum profit.
Flow reactor balance,

$$-FdC_a = r_a dV_r = kC_a dV_r$$

$$V_r = \frac{F}{k}\int_{C_a}^{2.5} \frac{dC_a}{C_a} = \frac{12}{30}\ln\frac{2.5}{C_a} \qquad (1)$$

Profit,

$$P = 1.5F(C_{a0}-C_a) - 2.5V_r = 1.5(12)(2.5-C_a) - \ln\frac{22.5}{C_a} \qquad (2)$$

For a maximum, $dP/dC_a = 0$,
$-18 + 1/C_a = 0$
$C_a = 1/18$ lbmol/cuft
$V_r = 1.52$ cuft
$P = \$40.19/hr$

P4.12.17. TUBULAR FLOW REACTOR

Substance B is produced at the rate of 100 kmol/hr from an aqueous feed with $C_{a0} = 1\ kmol/m^3$. The first order reaction has a specific rate k = 2/hr. Unused A is discarded. Cost of the feed stream = \$0.40/kmol of A, fixed costs = \$0.20/(m^3 of reactor)(hr). Find the optimum operating conditions.
Material balance,

$$-dn_a = n_{a0}dx = kC_a dV_r = k\left[\frac{n_{a0}(1-x)}{V'}\right]dV_r$$

$$V_r/V' = V_r/n_{a0} = \int_x^0 \frac{dx}{2(1-x)} = 0.5\ln\frac{1}{1-x} \qquad (1)$$

Production of B $= 100 = n_{a0}x$
$n_{a0} = 100/x$
Production cost,

$$K = 0.4n_{a0} + 0.2V_r = n_{a0}(0.4 + 0.1\ln\frac{1}{1-x})$$

$$= \frac{100}{x}(0.4-0.1 \ln \frac{1}{1-x}) \Rightarrow \text{Minimum}$$

Differentiating,

$$-\frac{40}{x^2} + \frac{10}{x^2}\ln\frac{1}{1-x} - \frac{10}{x(1-x)} = 0$$

$x = 0.8364$

$n_{a0} = 100/0.8364 = 119.6$ kmol/hr

$P = \$0.6947$/kmol of B, production cost

$V_r = 108.25\ m^3$

P4.12.18. THIRD ORDER REACTION IN A PFR

A reaction, 3A ⇔ B, has the rate equation

$r_a = 3(C_a^3 - C_b/14)$ mols/liter-hr

Feed concentration is 1.4 mol/liter. Production rate of B is 10 mol/hr. Product B is valued at \$5/mol, fresh A at \$1.2/mol. 80% of unconverted A is recovered; its value is \$1.00/mol. The fixed cost of the reactor is \$0.35/(liter of reactor)(hr). Find the maximum hourly profit.

Write the rate equation in terms of fractional conversion.

$$r_a = 3[C_{a0}^3(1-x)^3 - \frac{C_{a0}x}{3(14)}) = 3C_{a0}[1.96(1-x)^3 - 0.0238x) \quad (1)$$

Equilibrium value is found from $r_a = 0$.

$x_e = 0.788$

Stoichiometric relations,

$$n_{b1} = 10 = \frac{n_{a0}x_1}{3}, \text{ product rate}$$

$n_{a0} = 30/x_1$, feed rate (2)

Flow reactor,

$$-dn_a = n_{a0}dx = \frac{30}{x_1}dx = r_a dV_r$$

$$V_r = \frac{30}{3C_{a0}x_1}\int_0^{x_1}\frac{dx}{1.96(1-x)^3 - 0.0238x} = \frac{7.1428}{x_1}\int_0^{x_1} \quad (3)$$

Values of the integral are tabulated. The hourly cost is

K = Value of product + value of recovered A - cost of fresh A - fixed costs

$$K = 5(10)+0.8(1.00)n_{a0}(1-x_1)-1.2n_{a0} -0.35V_r$$

$$= 50-\frac{30}{x_1}(0.4+0.8x_1)-0.35V_r \quad (4)$$

Values of K are tabulated. The optimum performance is

$K = \$5.32$/hr

$x_1 = 0.70$

$n_{a0} = 42.86$ mol/hr

x_1	$\int_0^{x_1}$	$0.35V_r$	K	
0.3	0.0889	0.74	-14.74	
0.4	0.1526	0.95	-4.95	
0.5	0.2603	1.30	0.73	
0.6	0.4683	1.95	4.05	
0.62	0.5339	2.16	4.49	
0.64	0.6132	2.39	4.86	
0.66	0.7107	2.69	5.13	
0.68	0.8336	3.07	5.28	
0.70	0.9933	3.54	5.32	Maximum
0.72	1.2107	4.2	5.10	
0.74	1.5293	5.17	4.61	
0.76	2.0669	6.80	3.41	
0.78	3.4797	11.16	-0.54	
0.788	∞			

CHAPTER 5
REACTOR EFFICIENCY

THEORY

PROBLEMS

5.1. INTRODUCTION

Vessels in which chemical reactions are conducted in the plant or laboratory are of various shapes and internal arrangements. The distribution of residence times in them of various reacting molecules or aggregates, the RTD, is a key datum for determining the performance of a reactor, either the expected conversion or the range in which the conversion must fall. How the RTD is measured or calculated and applied is the subject of this chapter. The main application of interest here is to find how nearly a particular vessel approaches some standard ideal behavior, or what its efficiency is.

A number of special terms are defined in the Glossary, Table 5.1. Equations for tracer response functions are summarized in Table 5.2.

5.2. TRACERS

Primarily non-reactive substances that can be easily analyzed for concentration are used as tracers. When making a test, tracer is injected to the inlet of the vessel along with the normal charge of process or carrier fluid, according to some definite time sequence. The progress of both the inlet and outlet concentrations with time is noted. Those data are converted to a residence time distribution, RTD, that tells how much time each fraction of the charge spends in the vessel.

Although it is of great help in analyzing the dynamics of a reactor, the RTD does not define the mixing behavior in a vessel completely. It is not unique, in that several arrangements of the internals of a vessel may give the same tracer response, for example any series arrangements of reactor elements such as plug flow or completely mixed elements.This is a consequence of the fact that tracer behavior is described by linear differential equations. The lack of uniqueness limits direct application of tracer studies to first order reactions with constant specific rates (isothermal systems). For other reactions, the tracer curve may determine the upper and lower limits of reactor performance. When this range is not too broad, the result can be useful. Tracer data also may be taken at several representative positions within the vessel in order to develop a realistic model for the reactor.

5.3. REACTOR EFFICIENCY

Quantitatively, the efficiency at a specified conversion level, x, is defined as the ratio of the mean residence time or reactor volume in a plug flow reactor (PFR) to that of the reactor in question,

$$\eta_x = (\bar{t}_{pf}/\bar{t})_x = (V_{pf}/V)_x$$

The conversion level often is taken at 95% of equilibrium.

Other measures of efficiency are derived from the experimental RTD. Such a curve is characterized at least approximately by the variance, $\sigma^2(t_r)$. This quantity is zero for plug flow and unity for complete mixing, so there are natural bounds to the variance and thus to the efficiency. The quantity,

$$\eta = 1-\sigma^2(t_r)$$

approaches unity as plug flow is approached. It is possible for the variance to fall outside this range when stagnancy or bypass occurs.

A related measure of efficiency is the equivalent number of stages, n_{Erlang}, in a CSTR battery with the same variance as the measured RTD. The dispersion coefficient, D_e, also is a measure of deviation from plug flow and has the merit that limited correlations in terms of operating conditions have been made.

At present, the chief value of RTD studies is for the diagnosis of the performance of existing equipment, for instance maldistribution of catalyst in a packed reactor, or the presence of bypassing or stagnant zones in stirred tanks. No correlations have been achieved for $\sigma^2(t_r)$ or n_{Erlang} in terms of operating conditions, and only limited correlations for D_e.

5.4. TRACER RESPONSE

Tracer response is formulated as an unsteady material balance in terms of linear differential equations with constant coefficients that relate an input function, $C_f(t)$, to a response function, $C(t)$. Such equations of ordinary type have the form

$$\Sigma_0^n\ a_n \frac{d^nC}{dt^n} = C_f$$

The general form of the material balance is the familiar one,

Inputs + Sources = Outputs + Sinks + Accumulation

Formulation of differential equations in general is described in Chapter 1. Usually the ODE is of the first or second order and is readily solvable directly or by aid of the Laplace Transform. For example, for the special case of initial equilibrium or dead state (All derivatives zero at time zero), the preceding equation has the transform

$$\bar{C} = \bar{C}_f \ / \sum a_n s^n$$

where the individual transform is

$$\bar{C} = C(s) = \int_0^\infty e^{-st} C(t)\, dt$$

and similarly for C_f. The value of C(t) then is found by inversion of the transform by standard procedures. Although transforms may not be always invertable, important characteristics such as the various moments of the RTD can be obtained from them without the need for inversion.

The ratio of transforms,

$G(s) = C(s)/C_f(s)$

is called a <u>transfer function.</u> It is useful in the representation of systems consisting of several elements in series and parallel.

A particularly useful property of linear differential equations may be explained by comparing an equation and its derivative in operator form,

$$f(D)y = g(t) \quad \text{and} \quad f(D)z = \frac{dg(t)}{dt}$$

where the RHS of the second equation is the derivative of the RHS of the first equation. The property in question is that z = dy/dt. That is, if the RHS's of the two equations are related as function and derivative, the solutions likewise are related as function and derivative. The chief use of this property in this text is with the step and impulse functions, the impulse being the derivative of the step. Often problems are easier to visualize and formulate in terms of the step input, but the solution usually desired is for an impulse input which gives the RTD directly. For example,

$df/dt + f = t^2, \quad f = 2(1-t+t^2/2-e^{-t})$

$dg/dt + g = d(t^2)/dt = 2t, \quad g = df/dt = 2(-1+t+e^{-t})$

Numerical solution of higher order differential equations is accomplished most conveniently by first converting them into an equivalent set of first order equations. Thus the second order equation

$$\frac{d^2C}{dz^2} = f\left(\frac{dC}{dz}, C\right)$$

becomes the pair,

$dC/dz = p, \ dp/dz = f(p, C)$

with the dependent variables C and p.

5.4.1. KINDS OF INPUTS

Since a tracer material balance is represented by a linear differential equation, the response to any one kind of input is derivable from the response to some other known input either analytically or numerically. This is evident from a comparison of transformed equations. Take for instance,

$$f(s)\bar{C}_1 = g(s), \quad f(s)\bar{C}_2 = h(s), \quad \bar{C}_2 = [h(s)/g(s)]\bar{C}_1$$

Because of this relation, the function $C_2(t)$ is derivable by inversion of the known transform.

Although in practice some arbitrary variation of input concentration with time may be needed, five mathematically simple input signals supply most needs. They are illustrated in Figure 5.1, and responses to some of them in Figure 5.2.

a. Impulse. A fixed amount of tracer, m, is injected over an infinitesimal period then discontinued. The resulting mean concentration in the vessel of volume V_r at the time of injection then is designated $\bar{C}_0 = m/V_r$.

b. Step. The concentration of tracer is changed at time t = a and maintained at a constant value during the period of interest.

c. Square pulse. The concentration is changed suddenly at time t = a, maintained constant for an interval, then reduced to its original value.

d. Ramp. The concentration is increased at a constant rate for the period of interest.

e. Sinusoid. A signal that varies sinusoidally with time. Sinusoidal concentrations are not easy to achieve, but such variations of flow rate and temperature are widely used in studies of automatic control. A vast literature exists on that topic that may have potential for tracer studies.

5.4.2. RESPONSE FUNCTIONS

A number of quantities based on tracer tests are used for the representation and utilization of residence time distribution behavior. Table 5.2 summarizes the chief ones and some of their relationships.

Effluent concentrations resulting from impulse and step inputs are designated by C_δ and C_u respectively. The initial mean concentration resulting from an impulse input of magnitude m into a vessel of volume V_r is $C^0 = m/V_r$. The mean residence time is the ratio of the volume to the volumetric flow rate, $\bar{t}=V_r/V'$ or $\bar{t} = \int_0^\infty tC_\delta\,dt/\int_0^\infty C_\delta\,dt$. The reduced time is $t_r = t/\bar{t}$.

Residence time distributions are expressed in two forms: normalized, $E(t_r) = C_\delta/C^0$; or plain, $E(t) = C_\delta/\int_0^\infty C_\delta\,dt$. The relation between them is $E(t_r) = \bar{t}E(t)$. On a time plot, the area under either RTD curve is unity: $\int_0^\infty E(t_r)dt_r = \int_0^\infty E(t)dt = 1$. Moreover, the area between the ordinates at t_1 and t_2 is the fraction of the total effluent that has spent the period between those times in the vessel. This fraction also is given directly by the difference of the ordinates on the response to a step input, $F(t_2)-F(t_1)$. The age distribution is defined in terms of step input as $F(t) = C_u/C_f = \int_0^t E(t)dt$

From the graphs of these functions on Figure 5.1, it is apparent that the impulse is the derivative of the step. Then these relations follow:

$$E(t_r) = dF(t_r)/dt_r$$

$$E(t) = dF(t)/dt = [dF(t)/dt_r]/\bar{t}$$

Conversely,

$$F(t) = F(t_r) = \int_0^t E(t)dt = \int_0^{t_r} E(t_r)dt_r$$

The intensity function, $\Lambda(t) = E(t)/[1-F(t)]$, occurs in the maximum mixing concept and is of value in detecting maldistributions in a vessel.

The variance, $\sigma^2(t)$ or $\sigma^2(t_r)$, the skewness, $\gamma^3(t)$, and higher moments are characterizations of RTD curves.

5.4.3. ELEMENTARY MODELS

Reactors sometimes conform to some sort of ideal mixing behavior, or their performance may be simulated by appropriate combinations of ideal models. The commonest ideal elements are stated following, together with their tracer material balances. Initial values, boundary conditions and solutions of the equations depend on the kinds of inputs and are stated with individual solved problems.

a. Plug flow model, in which all portions of the charge have the same residence time. The concentration varies with time and position,

$$\frac{\partial C}{\partial t} + V'\frac{\partial C}{\partial V_r} = 0$$

b. CSTR model, with the effluent concentration the same as the uniform vessel concentration. With the mean residence time, $\bar{t} = V_r/V'$, the material balance is

$$\bar{t}\frac{dC}{dt} + C = \text{Input}$$

c. Dispersion model is based on Fick's diffusion law with an empirical dispersion coefficient substituted for the diffusion coefficient. The material balance is like that of the plug flow model but with the addition of a dispersion flow term.

$$\frac{\partial C}{\partial t} + V'\frac{\partial C}{\partial V_r} - D_e\frac{\partial^2 C}{\partial V_r^2} = 0$$

d. Laminar flow or power law model in which the linear velocity varies with the radial position in a cylindrical vessel. Plug flow exists along any streamline and the mean concentration is found by integration over the cross section.

e. Distribution models are curve fits of empirical RTDs. The Gaussian distribution is a one parameter model based on the statistical rule with that name. The Erlang and Gamma models are based on the concept of the multistage CSTR. Many concentration profiles also can be well curve fitted by ratios of polynomials, for instance,

$$C(t) = (a+bt+ct^2+\ldots)/(1+dt+\ldots)$$

5.4.4. REAL BEHAVIOR

Empty tubular reactors often are simulated by the simple plug flow model or by a dispersion model with a small value of the dispersion coefficient.

Stirred tank performance often is nearly ideal CSTR or the model may need to take into account bypassing, stagnant zones or other parameters associated with the geometry and operation of the vessel and the agitator. Sometimes the vessel can be visualized as a zone of complete mixing in the vicinity of the impellers followed by a plug flow zone elsewhere, thus a CSTR followed by a PFR.

Packed beds usually deviate substantially from plug flow behavior. The dispersion model and some combinations of PFRs and CSTRs or of multiple CSTRs in series may approximate their behavior.

Fluidized bed behavior is especially complex. Small beds approximate CSTR behavior, but large ones exhibit bypassing, stagnancy, nonhomogeneous regions and several varieties of contact between catalyst particles and fluid.

The concept of transfer functions facilitates the combination of linear elements. The rule is

Output Transform = (Transfer Function)(Input Transform)

or

$$C(s)_{out} = G(s)C(s)_{in}$$

Figure 5.3 develops the overall transform of a process with a PFR in parallel with two CSTRs in series. Overall transforms often are complex enough to require numerical inversion for finding $C(t)_{out}$.

5.5. TRACER EQUATIONS

Differential equations and solutions for some response functions will be stated for the elementary models with the main kinds of inputs. Since the DEs are linear, solutions by Laplace Transform are feasible. Details are to be provided by the solved problems which include derivations and applications.

5.5.1. THE IDEAL CSTR

With a step input of magnitude C_f, the unsteady material balance is

$$V_r dC/dt + V'C = V'C_f$$

or

$$dC/dt_r + C = C_f$$

so that

$$C/C_f = F(t_r) = 1-\exp(-t_r)$$

With an impulse input of magnitude m or initial mean concentration $C^0 = m/V_r$, the equation is

$$dC/dt_r + C = 0, \quad \text{with } C= C^0 \text{ when } t=0$$

and

$$C/C^0 = E(t_r) = \exp(-t_r)$$

The material balance and condition also can be written

$$V_r dC/dt + V'C = m\delta(t) = C^0\bar{t}\delta(t)$$

whose transform and inverse are

$$(\bar{t}s+1)\bar{C} = C^0\bar{t}, \quad C/C^0 = \exp(-t_r)$$

From these results it is clear that

$$E(t_r) = dF(t_r)/dt_r$$

Further details of the CSTR model are in problem P5.01.01.

5.5.2. THE PLUG FLOW REACTOR, PFR

The material balance over a differential volume dV_r is

$$V'C = V'(C+dC) + \frac{\partial C}{\partial t} dV_r$$

or

$$V'\frac{\partial C}{\partial V_r} + \frac{\partial C}{\partial t} = 0$$

With step input the boundary conditions are

$$C(0,t) = C_f u(t), \quad C(V_r,0) = 0$$

By Laplace Transform the solution is

$$F(t) = C/C_f = u(t-\bar{t}) = 0 \text{ when } t \le \bar{t} \;; \; = 1 \text{ when } t \ge \bar{t}.$$

that is, the effluent step is delayed by $\bar{t}$. For impulse input the conditions are

$$C(0,t) = C^0\bar{t}\delta(t), \quad C(V_r,0) = 0$$

so the solution is

$$E(t_r) = C/C^0 = \bar{t}\delta(t-\bar{t}) = \bar{t}\delta[\bar{t}(t_r-1)] = \delta(t_r-1)$$

that is, the effluent impulse from an input impulse is delayed by $t_r = 1$.

The PFR is studied in more detail in problem P5.01.03.

5.5.3. THE MULTISTAGE CSTR

This model has a particular interest because it has a bell shaped RTD curve, somewhat resembling experimental RTDs of packed beds and some empty tubes.

For any series arrangement of CSTRs the overall transfer function is the product of the individual transfer functions. With an impulse input, $m\delta(t) = C^0\bar{t}\delta(t)$, the transform of the response is

$$\bar{C}_n = \frac{1}{(t_1s+1)(t_2s+1)\ldots(t_ns+1)}\,C^0\bar{t}$$

For two stages the inverse is

$$C_2/C^0 = [\exp(-t/\bar{t}_1)-\exp(-t/\bar{t}_2)]/(\bar{t}_2-\bar{t}_1)$$

When the stages are equal,

$$C_2/C^0 = 4t_r\exp(-2t_r)$$

For more than two stages the case of primary interest is that of n equal sized vessels. Then $\bar{t}_i = \bar{t}/n$ and $C_1^0 = nC^0$, where C^0 is the mean initial concentration in the entire battery and $\bar{t}$ is the residence time in the entire battery. Accordingly the overall transform becomes

$$\bar{C}_n = C^0\bar{t}/[(\bar{t}/n)^n(s+n/\bar{t})^n]$$

The inverse is obtained by induction after trying n = 2, 3, ..., with the result

$$E(t_r) = C_n/C^0 = \frac{n^n}{(n-1)!}\,t_r^{n-1}\exp(-nt_r)$$

Step response is obtained by integration, thus,

$$F(t_r) = \int_0^{t_r}E(t_r)dt_r = 1-\exp(-nt_r)\sum_{j=0}^{n-1}(nt_r)^j/j!$$

The peak of the E-curve is reached at $t_r = (n-1)/n$ and has a magnitude

$$E(t_r)_{max} = \frac{n(n-1)^{n-1}}{(n-1)!}\exp(1-n)$$

Another significant characteristic of the E-curve is the variance or the second moment which is

$$\sigma^2(t_r) = \int_0^\infty(t_r-1)^2E(t_r)dt_r = -1 + \int_0^\infty t_r^2E(t_r)dt_r$$

$$= -1 + \frac{n^n}{(n-1)!}\int_0^\infty t_0^{n+1}E(t_r)dt_r = 1/n$$

The E-equation can be rearranged to a linear form:

$$t_rE(t_r) = \frac{n^n}{(n-1)!}[t_r\exp(-nt_r)]^n$$

Taking logarithms,

$$\ln[t_rE(t_r)] = \ln[\frac{n^n}{(n-1)!}] + n\ln[t_r\exp(-t_r)]$$

With appropriate coordinates the slope of a loglog plot is n.

When n is integral, this model goes by the name Erlang; when it is non integral it is called Gamma. Further details of the derivation are in problem P5.01.02.

5.5.4 COMBINED MODELS. TRANSFER FUNCTIONS.

A particular vessel behavior sometimes can be modelled as a series or parallel arrangement of simpler elements, for example, some combination of a PFR and a CSTR. Such elements can be combined mathematically through their transfer functions which relate the Laplace transforms of input and output signals. In the simplest case the transfer function is obtained by transforming the linear differential equation of the process. The transfer function relation is

$$\bar{C}_{output} = (\text{Transfer Function})\ \bar{C}_{input}$$

Some common transfer functions are,

Element	Transfer Function
Ideal CSTR	$1/(1 + \bar{t}s)$
PFR	$\exp(-\bar{t}s)$
n-stage CSTR (Erlang)	$1/(1 + \bar{t}s/n)^n$
Erlang with time delay	$\exp(-\bar{t}_1 s)/(1 + \bar{t}_2 s/n)^n$

The last item is of a PFR and an n-stage CSTR in series. More complex combinations are the subject of problems P5.01.33, P5.03.10, P5.03.02 and others.

A transfer function may not be always analytically invertable, but it has nevertheless value in that the moments of an RTD may be derived from it, notably the variance.. One or two of the moments often are adequate characterizations of an RTD curve and enable useful deductions about the behavior of a vessel as a chemical reactor. Problem P5.02.01 covers the basic theory and P5.02.07 is another application. Figure 5.3 is of a simple process flow diagram, individual transfer functions, and the overall transfer function.

5.6. CHARACTERIZATION OF CURVES.

An RTD curve, for instance, can be represented in algebraic form in more than one way and for different purposes. The characteristic bell shape of many RTDs is evident in the real examples of Figure 5.4. Such shapes invite comparison with some well-known statistical distributions and representation of the RTD by their equations. Or a realistic mechanism may be postulated, such as a network of reactor elements and a type of flow pattern, and the parameters of that mechanism evaluated from a measured RTD.

Several of the standard statistical distributions are described by Hahn & Shapiro (Statistical Models in Engineering, 1967) with mention of their applicability. The most useful models are the Gamma (or Erlang) and the Gaussian and some of their minor modifications. As an illustration of something different the Weibull distribution is touched on in problem P5.02.18. These distributions usually are representable by only a few parameters that define the asymmetry, the peak and the shape in the vicinity of the peak. The moments are such parameters.

5.6.1. MOMENTS OF RTD CURVES

Quantities called moments are derivable from any set of data, typically (C,t) data. The four that are most commonly used are numbered first, second, etc, and are also named. In terms of impulse response data, they and their formulas are,

Number	Name	Equation

First mean $\mu(t) = \int_0^\infty tC_\delta(t)dt/\int_0^\infty C_\delta(t)dt$

Second variance $\sigma^2(t) = \int_0^\infty (t-\bar{t})^2 E(t)dt$

Third skewness $\gamma^3(t) = \int_0^\infty (t-\bar{t})^3 E(t)dt$

Fourth kurtosis $\delta^4(t) = \int_0^\infty (t-\bar{t})^4 E(t)dt$

How the various moments can be calculated from the transfer function of a process without data is described in problem P5.02.01.

5.6.2. THE GAMMA OR ERLANG DISTRIBUTION

In the general field of statistics, the RTD of an n-stage CSTR battery is called an Erlang distribution, or a Gamma distribution when n is not integral. Then (n-1)! is replaced by Γ(n) in the equation given in Section 5.5.3. The value of n is the only parameter in the equation. Four main methods can be used to find its value when the RTD is known experimentally or by calculation.

1. From the variance, as $n = 1/\sigma^2(t_r) = 1/\bar{t}^2\sigma^2(t)$. This relation is derived in problem P5.01.02.

2. From a suitable loglog plot of the data as utilized in problems P5.02.04, P5.02.05 and P5.02.06.

3. From the peak of the curve, for which the formula is derived in problem P5.01.02.

4. From the Peclet number of dispersion when the Peclet number can be found from other correlations. The relationships are brought out in problems P5.08.04 and P5.08.14.

Many RTD curves of quite different shapes may have the same variance and may result in quite different performances as chemical reactors. Several such cases are in the problem section.

When such situations are encountered, a model based on some realistic mechanism may be mandatory.

5.6.3. THE GAUSSIAN DISTRIBUTION

The best known statistical distribution is the Normal or Gaussian distribution whose equation may be written

$$C(t_r) = \frac{1}{\sigma\sqrt{2\pi}} \exp[-\frac{(t_r-1)^2}{2\sigma^2}], \qquad -\infty \le t_r \le +\infty$$

Since only positive values of t_r are of concern in RTD work, this function is normalized by dividing by the integral from 0 to ∞ with the result,

$$E(t_r) = f(\sigma) \exp[-\frac{(t_r-1)^2}{2\sigma^2}]$$

where theoretically

$$f(\sigma) = \frac{2}{\sigma\sqrt{2\pi}[1+\mathrm{erf}(1/\sigma\sqrt{2})]}$$

Other more convenient equations for $f(\sigma)$ that do not require access to values of the error function are in problem P5.02.08.

The Gaussian is a one parameter model, the variance. The RTD curves are bell shaped. At smaller values of the variance (or the larger values of n of the Erlang), the Erlang and Gaussian RTD curves approach each other, and the peaks also approach each other. The peak values are studied by problem P5.02.12. In some cases the Gaussian may provide a better fit to RTD data than the Gamma, but in general the Gamma is more often superior, particularly at larger variances or smaller values of n. Several comparisons appear in the problem section.

5.6.4. THE GRAM-CHARLIER SERIES

Some modifications of the Gaussian distribution have been made. The log normal applies when the logarithm follows a normal distribution, but it does not seem to be useful for RTD representation. The Gram-Charlier series (Kendall, Advanced Theory of Statistics, vol. 1, 1958) is an infinite series whose coefficients involve the Gaussian distribution and its derivatives. The derivatives in turn are expressed in terms of the moments. The series truncated at the coefficient involving the fourth moment is

$$E(t_r)_{GC} = E(t_r)_{Gauss}[1 - m_3(3z-z^3)/6 + (m_4-3)(z^4-6z^2+3)/24]$$

where

$$z = (t_r-1)/\sigma$$

$$m_3 = (\gamma/\sigma)^3 = \int_0^\infty \left(\frac{t_r-1}{\sigma}\right)^3 E(t_r)dt_r$$

$$m_4 = (\delta/\sigma)^4 = \int_0^\infty \left(\frac{t_r-1}{\sigma}\right)^4 E(t_r)dt_r$$

Comparisons of Gram-Charlier with data and other distributions are in problems P5.02.15 and P5.02.16. In one of these, the third order GC fits better than the fourth order. More experience is needed, however, before a judgement can be made regarding the relative merits of GC and other distributions. At large variances the finite value of the ordinate at $t_r = 0$ appears to be a fatal objection to both the Gaussian and GC distributions.

Accurate values of the higher moments are not easy to obtain. The substantial sensitivity of an RTD curve to small differences in a third moment is brought out in problem P5.02.07A.

5.6.5. EMPIRICAL EQUATIONS

Tabular (C,t) data usually are easier to manipulate when put in the form of an algebraic equation. Then necessary integrals and derivatives can be formed readily and most accurately. The calculation of chemical conversions by such mechanisms as segregation, maximum mixing or dispersion also is easier with data in the form of equations.

Procedures for curve fitting by polynomials are widely available. Bell shaped curves usually are fitted better and with fewer constants by ratios of polynomials. Problem P5.02.02 compares a Gamma fit with those of other equations, of which a log normal plot is the best. In figuring chemical conversion, fit of the data at low values of E(t) need not be highly accurate since those regions do not affect the overall result very much.

5.7. CHEMICAL CONVERSION

A distinction is to be drawn between situations in which (a) the flow pattern is known in detail; (b) only the residence time distribution is known or can be calculated from tracer response data. Different networks of reactor elements can have similar RTDs, but fixing the network also fixes the RTD. Accordingly reaction conversions in a known network will be unique for any type of rate equation, whereas conversions figured when only the RTD is known proceed uniquely only for linear kinetics, although they can be bracketed in the general case.

5.7.1. WHEN THE FLOW PATTERN IS KNOWN

Conversion in a known network and flow pattern is evaluated from appropriate material and energy balances. For first order irreversible isothermal reactions, the conversion equation can be obtained from the transfer function if that is known by replacing the parameter s by the specific rate k. Thus if $G(s) = \bar{C}/\bar{C}_0 = 1/(1+\bar{t}s)$, then $C/C_0 = 1/(1+k\bar{t})$. Complete knowledge of a network enables incorporation of energy balances into the solution, whereas the RTD approach cannot do that.

5.7.2. SEGREGATED FLOW

In segregated flow, the molecules travel as distinct groups, in which all molecules that enter the vessel together leave together. The groups are small enough so that the RTD of the whole system is represented by a smooth curve. For reaction orders above one, with a given RTD the conversion is a maximum in segregated flow and a minimum under "maximmum mixing"conditions. This point is discussed in detail in Section 5.8.

Each group of molecules reacts independently of any other group, that is, as a batch reactor. Batch conversion equations for power law rate equations are

$$(C/C_0)_{batch} = \exp(-kt) = \exp(-k\bar{t}t_r) \qquad \text{first order}$$

$$\left[\frac{1}{1+(n-1)kC_0^{n-1}t}\right]^{1/(n-1)} \qquad \text{order n}$$

For other types of rate equations a numerical solution may be needed.

Referring to an RTD like that of Figure 5.2, the flow of a group of molecules having a mean residence time $\bar{t}_i$ is $V'E(t_i)\Delta t$, where Δt represents the range of which $\bar{t}_i$ is the mean. When each of these fractional flows is multiplied the the batch conversion for its particular residence time and the results are summed up, the sum will represent the mean conversion of all the segregated groups. Thus

$$(C/C_0)_{segregated} = \int_0^\infty (C/C_0)_{batch}E(t)dt$$

$$\int_0^\infty (C/C_0)_{batch}E(t_r)dt_r$$

In the second formula, replace $t = \bar{t}t_r$ in the equation for batch conversion.

Conversion in segregated flow is less than in plug flow and somewhat greater than in a CSTR battery with the same variance or RTD. Thus the variance does not guarantee the segregated conversion, but it often gives an acceptable estimate.

When a conversion and an RTD are known, the specific rate can be found by trial: a value of k is assumed, the segregated integral is evaluated and compared with the known value. Moreover, if a series of conversions at several residence times are known, the order of reaction can be found by trying different orders and noting which gave a constant series of specific rates. A catch here, however, is that the RTD depends on the hydrodynamics of the process and may change somewhat with the residence time.

5.7.3. MAXIMUM MIXEDNESS.

Maximum mixedness is represented on Figure 5.5 and in problem P5.07.01 by a plug flow vessel with multiple side inlets whose flow pattern is given by the RTD. The main flow in the vessel is plug flow, but at each inlet the incoming material is completely mixed over the cross section with the axial flow. This means that each portion of fresh material is mixed with all the material that has the same life expectation, regardless of the actual residence time in the vessel up to the time of mixing. The life expectation under plug flow conditions is measured by the remaining distance to be travelled before leaving the vessel.

In contrast to segregated flow in which mixing occurs only after each sidestream leaves the vessel, under maximum mixedness mixing of all molecules having a certain period remaining in the vessel (the life expectation) occurs at the time of introduction of fresh material, that is, as soon as possible consistent with the RTD. These two extremes, as late as possible and as soon as possible - both consistent with a particular RTD - represent the extreme performances of the vessel as a chemical reactor.

Distribution of life expectances is the same as that of residence times, the usual RTD.

The maximum mixedness equation is derived in problem P5.07.01. The equation is

$$\frac{dC}{dt} = r_c - \frac{E(t)}{1-F(t)}(C_0-C) \qquad \text{(a)}$$

where r_c is a rate equatioon. If the reaction has an order q, $r_c = kC^q$. In the units $f = C/C_0$ and $t_r = t/\bar{t}$, accordingly,

$$\frac{df}{dt} = k\bar{t}C_0^{q-1}f^q - \Lambda(t_r)(1-f) \qquad \text{(b)}$$

The boundary condition is

$$\frac{dt}{dt_r} = 0 \text{ for } t_r \Rightarrow \infty$$

which makes

$$k\bar{t}C_0^{q-1}f_\infty^q - \Lambda(\infty)(1-f_\infty) = 0 \qquad \text{(c)}$$

The conversion achieved in the vessel is the solution of Equation (a) or (b) at the exit of the vessel where t = 0. The starting point for an integration is $(f_\infty,\ t_\infty)$. In practice, however, the RTD becomes essentially zero by the time t_r becomes 3 or 4, and the value of the integral beyond that point is nil. Accordingly the integration interval is from $(f_\infty,\ t_r = 3 \text{ or } 4)$ to $(f_{effluent},\ t_r = 0)$, where f_∞ is found by solving Equation (c).

Equation (c) breaks down when $\Lambda(\infty) \Rightarrow \infty$ which is the case for instance with the Gaussian distribution. Then values of time over a range can be tried until the results of integration of Equation (b) assume a constant value. This technique is applied in problems P5.07.04, P5.07.14 and P5.07.15.

Relative sizes of vessels with segregated and maximum mixed flows of the same variance are derived over a range of parameters in some of the problems, particularly P5.07.06.

5.8. THE DISPERSION MODEL

An impulse input to a stream flowing through a vessel may spread axially because of a combination of molecular diffusion and eddy currents that together are called dispersion. Mathematically the process can be described by Fick's equation with a dispersion coefficient instead of a diffusion coefficient. The dispersion coefficient D is associated with a linear dimension L and a linear velocity u in the Peclet number, Pe = uL/D.

In plug flow, D = 0 and Pe ⇒ ∞; in a CSTR, D ⇒ ∞ and Pe = 0.

The dispersion coefficient is orders of magnitude larger than the molecular diffusion coefficient. Some correlations of the Peclet number that have been achieved are cited in problem P5.08.14. It is related to the variance of an RTD, as discussed in problem P5.08.04. Consequently the dispersion model and the Gamma or Gaussian are interrelated.

A significant merit of the dispersion model is some experimental correlations for the Peclet number. There are no such direct correlations for the parameters of the Gamma or Gaussian or other similar models.

In a vessel with dispersion in the axial direction, the steady state equation for a reaction of order n is

$$\frac{d^2f}{dz^2} = Pe(\frac{df}{dz} - R_c) = Pe(\frac{df}{dz} - k\bar{t}C_0^{n-1}f^n) \qquad (a)$$

where the normalized variables are $f = C/C_0$ and $z = x/L$. For tracer flow, $R_c = 0$, and the time derivative appears,

$$\frac{\partial f}{\partial t_r} = \frac{1}{Pe}\frac{\partial^2 f}{\partial z^2} - \frac{\partial f}{\partial z} \qquad (b)$$

The derivation and other forms of the dispersion-reaction equation are in problem P5.08.01. The solution of the partial differential Equation (b) for tracer operation is recorded in the Literature and is quoted in problem P5.08.04.

5.8.1. BOUNDARY CONDITIONS

Two different sets of boundary conditions are applicable to these differential equations. The corresponding operating conditions are shown on the figure with problem 5.08.01 In normal operation with "closed ends", reactant is brought in by bulk flow and carried away by both bulk and dispersion flow, so at the inlet where L = 0 or z = 0,

$$uC_0 = (uC - D\frac{\partial C}{\partial L})_{L=0} \qquad (c)$$

or

$$f_0 = (f - \frac{1}{Pe}\frac{\partial f}{\partial z})_{z=0} \qquad (d)$$

At the exit where z = 1,

$$(\frac{\partial f}{\partial z})_{z=1} = 0 \qquad (e)$$

The discontinuity at the inlet is examined in problems P5.08.02 and P5.08.12.

In "open ends" operation dispersion exists before and after the measuring point. This mode may be used with tracer studies when tracer is injected and sampled some distances from the ends of the vessel for the purpose of making accurate measurements of dispersion behavior. The boundary conditions are

$$C(\pm\infty, t) = 0,\ C(z, 0) = 0,\ C(0, t) = C(t) \qquad (f)$$

5.8.2. INTEGRATION OF THE EQUATION

For other than first or zero order reactions, the differential equation is nonlinear and most usually it is to be solved numerically. Then the second order Equation (a) is converted into a pair of first order equations

$$df/dz = f' \text{ and } df'/dz = Pe(f' - kC_0^{n-1}f^n) \qquad (g)$$

with the "closed ends" boundary conditions,

$$\text{at } z = 1,\ f' = df/dz = 0 \qquad (h)$$

at $z = 0$, $f_0 = (f - f'/Pe)_{z=0}$ (i)

This two-point boundary condition problem is solved by the shooting method with this procedure:

1. Assume a value f_{exit} at $z = 1$ where $f' = 0$.
2. Integrate backward to $z = 0$ to find f_0 and f_0' individually and in the combination of Equation (i).
3. If condition (i) is not satisfied, repeat with other trial values of f_{exit}.

Initial trial values may be selected by comparison of conversion with a CSTR if Pe is small, or with a PFR if Pe is large.

Sometimes it is desirable to have a solution of Equation (b) in even approximate analytical form rather than in the tabular or graphical form that a numerical solution provides. Suitable methods are described in such books as Bender & Orszag (Advanced Mathematical Methods for Scientists and Engineers, 1978)

5.8.3. COMPARISON OF MODELS

Only scattered and inconclusive results have been obtained on the relative performances of the different models as converters. In problems P5.08.13 and 22, dispersion gives higher conversion than segregation; in problems P5.08.17 and 21 they are about the same; in problem P5.08.20, dispersion falls in between segregation and maximum mixedness.

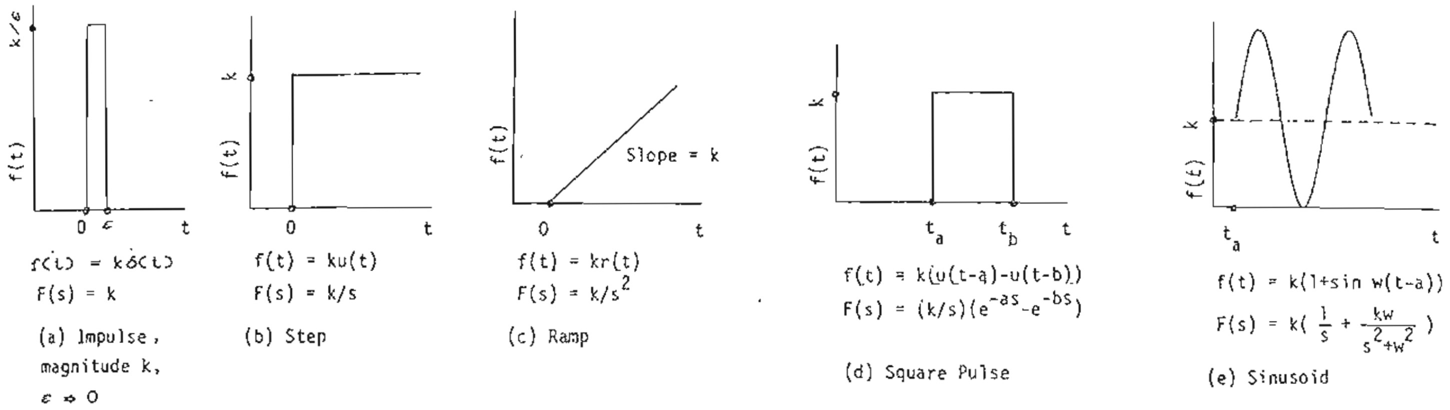


Figure 5.1. Input signals and their Laplace transforms.

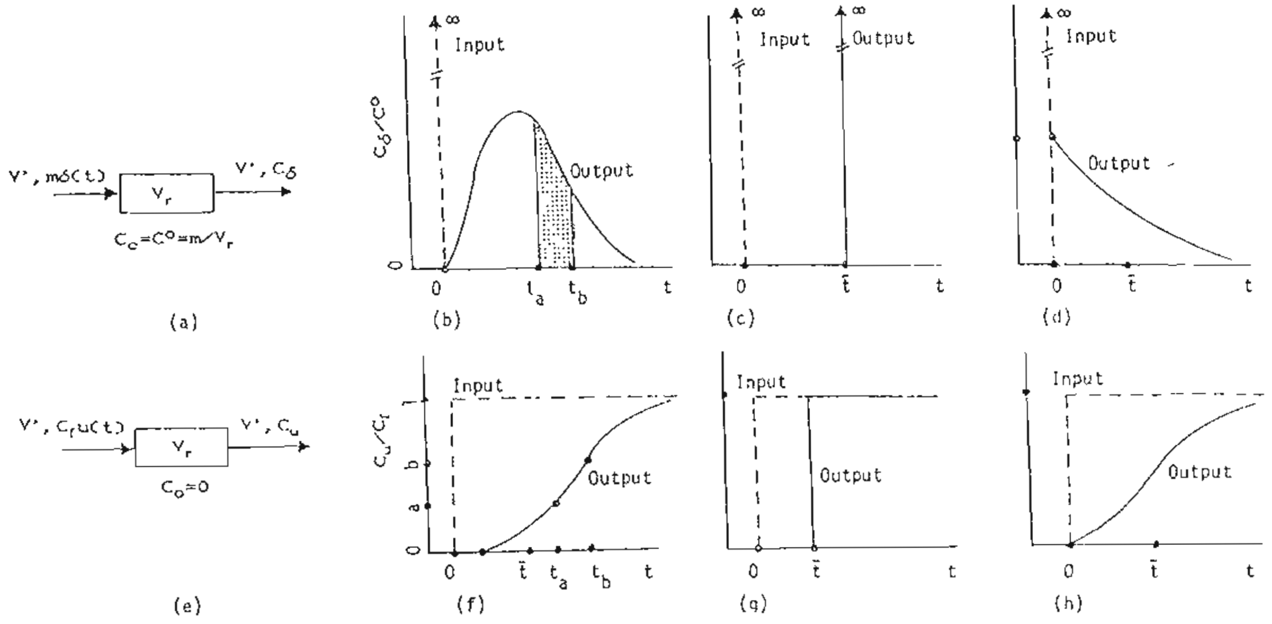
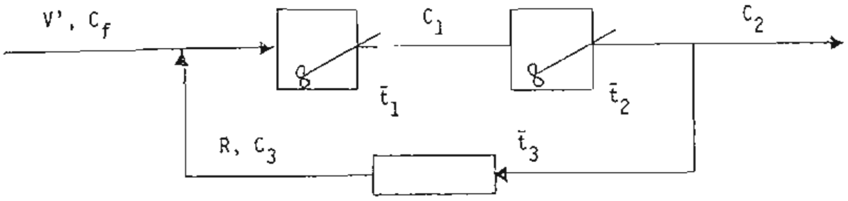
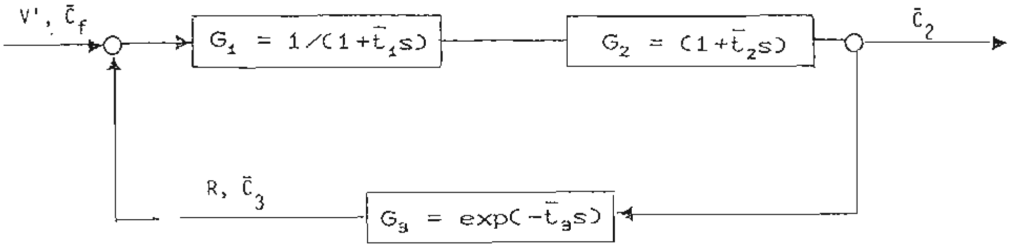


Figure 5.2. Impulse and step inputs and responses. Typical, PFR and CSTR. (a) Experiment with impulse input of tracer. (b) Typical behavior; area between ordinates at t_a and t_b equals the fraction of the tracer with residence time in that range. (c) Plug flow behavior; all molecules have the same residence time. (d) Completely mixed vessel; residence times range between zero and infinity. (e) Experiment with step input of tracer; initial concentration zero. (f) Typical behavior; fraction with ages between t_a and t_b equals the difference, b-a, between the ordinates. (g) Plug flow behavior; zero response until $t = \bar{t}$ has elapsed, then constant concentration C_f. (h) Completely mixed behavior; response begins at once, and ultimately reaches feed concentration.

Process flow diagram



Transfer function diagram



Combination of transfer functions

$$(V'\bar{C}_f+R\bar{C}_3)G_1G_2 = (V'+R)\bar{C}_2$$

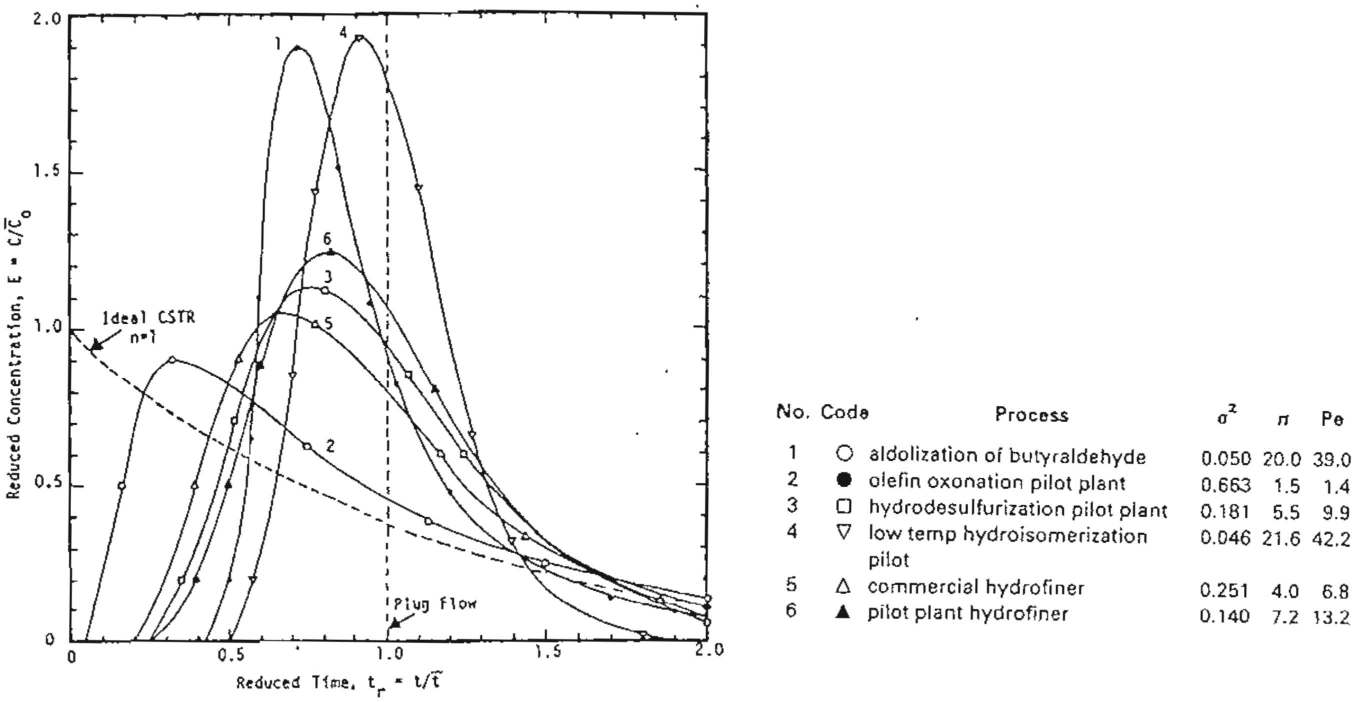
$$(V'\bar{C}_f+RG_3\bar{C}_2)G_1G_2 = (V'+R)\bar{C}_2$$

$$\bar{C}_2 = \frac{V'G_1G_2}{V'+R-RG_1G_2G_3}\,\bar{C}_f$$

Overall transfer function

$$\bar{C}_2/\bar{C}_f = \frac{1}{(1+R/V')(1+t_1s)(1+t_2s)-(R/V')\exp(-t_3s)}$$

Figure 5.3. Process and transfer function diagrams of complex process.



No.	Code	Process	σ^2	n	Pe
1	○	aldolization of butyraldehyde	0.050	20.0	39.0
2	●	olefin oxonation pilot plant	0.663	1.5	1.4
3	□	hydrodesulfurization pilot plant	0.181	5.5	9.9
4	▽	low temp hydroisomerization pilot	0.046	21.6	42.2
5	△	commercial hydrofiner	0.251	4.0	6.8
6	▲	pilot plant hydrofiner	0.140	7.2	13.2

Figure 5.4. Residence time distributions of pilot and commercial catalyst packed reactors (Walas, *Chemical Process Equipment Selection and Design*, 1990).

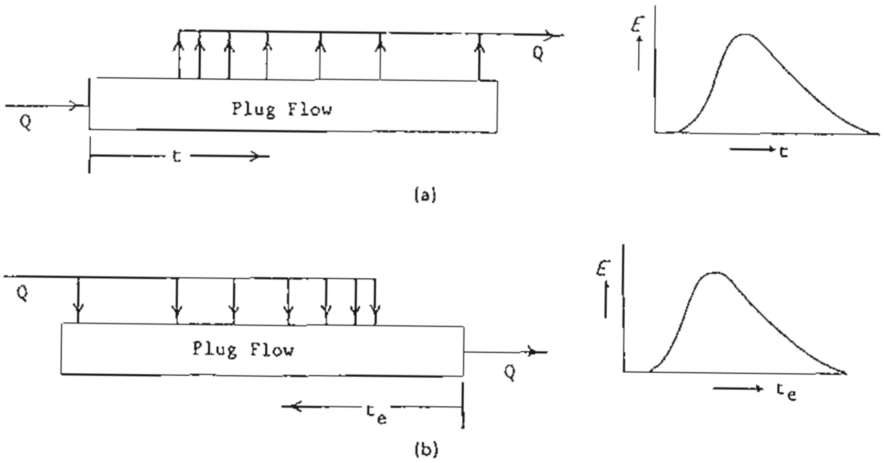


Figure 5.5. The two limiting flow patterns with the same RTD. (a) Segregated flow, in which all molecules of any exit stream have the same residence time. (b) Maximum-mixed flow, in which all molecules of an external stream with a certain life expectation are mixed with all molecules of the internal stream that have the same life expectation.

Table 5.1. GLOSSARY OF RTD TERMS

Age, $F(t)=C_u/C_f$, the ratio of an effluent concentration to the magnitude of a constant input concentration. On a plot against t, the ordinate at t_1 is the fraction of the material that has a residence time less than t_1.

Closed end vessel. One in which the inlet and outlet streams are completely mixed and dispersion occurs only between the terminals. At the inlet where z=0, $uC_0 = [uC-D_e(\partial C/\partial z)]_{z=0}$; at the outlet where z = L, $(\partial C/\partial z)_{z=L} = 0$. This is the normal condition for reactors.

Concentration. The main special kinds are: C_δ, that of the effluent from a vessel with impulse input; $C^0 = m/V_r$, the initial mean concentration resulting from impulse input; C_u, that of the effluent from a vessel with a step input of magnitude C_f.

Danckwerts' boundary condition. See closed end vessel.

Dispersion. The movement of aggregates of molecules under the influence of a gradient such as concentration, temperature, density, etc. The effect is represented by Fick's diffusion equation with a dispersion coefficient substituted for molecular diffusivity. Thus, Rate of Transfer = $-D_e(\partial C/\partial z)$.

Impulse. An amount of tracer injected instantaneously into a vessel. The symbol $m\delta(t-a)$ represents an impulse of magnitude m injected at time t = a. The effluent concentration resulting from an impulse input is designated C_δ.

Internal age of a molecule or aggregate in a vessel at a particular time is the time that it has thus far remained in the vessel. The distribution of internal ages is represented by $I(t)=1-F(t)$.

Life expectation, λ, of a molecule or aggregate in a vessel at a particular time is the period that it will remain in the vessel before ultimately leaving. The distribution of life expectancies is identical with that of residence times, $E(\lambda) = E(t)$.

Macromixing is a state in which aggregates of molecules remain as aggregates during a period of interest. The aggregates are considered to be large enough (10^{12} to 10^{18} molecules or 10^{-6} to 10^{-12} gmols) for a concentration expression to be meaningful yet small enough to have their time distribution represented closely by a continuous function.

Maximum mixedness exists when any molecule that enters a vessel immediately becomes associated with those molecules with which it will eventually leave the vessel, that is, with those molecules that have the same life expectation. All molecules with the same life expectation are completely mixed regardless of their internal ages. A state of MM is associated with every RTD. MM is not the same as ideal mixing; the latter is associated with an exponential RTD.

Micromixing occurs on a molecular level, and individual molecules are free to move throughout the volume of the system.

Mixing, ideal, is a state of complete uniformity of composition and temperature in a vessel. The residence time distribution is exponential, ranging from zero to infinity.

Open end vessel is one in which there are no discontinuities (abrupt changes) in concentration at the inlet and outlet where both bulk and dispersion flow occur. The boundary condition are : $C = C_0$ when z=0 and $\partial C/\partial z = 0$ when $z=\infty$.

Peclet number for dispersion, $Pe = uL/D_e$, where u is a linear velocity, L is a linear dimension and D_e is the dispersion coefficient. In packed beds, u is the interstitial velocity and the linear dimension is the particle diameter; then $Pe = ud_p/D_e$.

Plug flow is a condition in which all effluent molecules have had the same residence time.

Pulse is a kind of input in which the concentration of tracer in the input stream is changed suddenly, maintained at a non-zero value for a definite period, then changed to the original value and maintained that way for the period of interest. When the pulse is of constant magnitude it is called a square pulse.

Residence time distribution (RTD). In the case of elutriation of tracer from a vessel that contained an initial average concentration C^0 the area under the plot of $E(t) = C_{effluent}/C^0$ between ordinates at t_1 and t_2 is the fraction of molecules that have residence times in this range. In the case of constant input concentration, C_f, to a vessel in which the initial concentration is zero, the ratio $F(t) = C_{effluent}/C_f$ at time t_1 is the fraction of molecules with residence times less than t_1. These concepts are illustrated in Figure 5.2.

Residence time, mean, is the average time spent by all molecules in the vessel. Mathematically, it is the first moment of the effluent concentration from a vessel with impulse input, or $\bar{t} = \int_0^\infty tC_\delta\, dt \,/\, \int_0^\infty C_\delta\, dt$

Segregated flow occurs when the fluid is macromixed and all molecules that enter together leave together. A State of segregation is associated with every RTD. Each aggregate of molecules reacts independently of every other aggregate, thus as an individual batch reactor.

Skewness is the third moment of a residence time distribution, $\gamma^3(t) = \int_0^\infty (t-\bar{t})^3 E(t)\, dt$. It is a measure of symmetry.

Step is a kind of input in which the concentration of tracer is changed instantaneously to some constant value C_f and maintained at this level indefinitely. The symbol $C_f u(t-a)$ represents a step of magnitude C_f beginning at $t = a$. The resulting effluent concentration is designated C_u. The symbol $C_f H(t-a)$ also is used.

Tracer is a substance that is used for measuring the residence time distribution in a vessel. Usually it is inert, useable in small concentrations so as not to change the physical properties of the process fluid appreciably, and analyzable for accurately.

Variance is the second moment of the RTD. There are two forms, one in terms of the absolute time and the other in terms of a reduced time, $t_r = t/\bar{t}$. The relations between the two kinds are,

$$\sigma^2(t) = \int_0^\infty (t-\bar{t})^2 C_\delta\, dt \,/\, \int_0^\infty C_\delta\, dt = \int_0^\infty (t-\bar{t})^2 E(t)\, dt$$

$$\sigma^2(t_r) = \int_0^\infty (t_r-1)^2 E(t_r)\, dt_r = \sigma^2(t)/\,\bar{t}^2$$

Table 5.2. TRACER RESPONSE FUNCTIONS

Name	Relation
Mean residence time	$\bar{t} = \int_0^\infty tC_\delta \, dt / \int_0^\infty C_\delta \, dt$
	$= \int_0^{C_{u\infty}} t\,dC_u \; / \; C_{u\infty}$
Initial mean concentration	$C^0 = V'\int_0^\infty C_\delta \, dt/V_r = \int_0^\infty C_\delta \, dt/\bar{t} = m/V_r$
Reduced time	$t_r = t/\bar{t}$
Residence time distribution (normalized)	$E(t_r) = C_\delta/C^0 = dF(t_r)/dt_r$
	$= \bar{t}C_\delta / \int_0^\infty C_\delta . dt = \bar{t}E(t)$
	= Impulse output/Initial mean concn
Residence time distribution	$E(t) = C_\delta \; / \int_0^\infty C_\delta dt = E(t_r)/ \; \bar{t} = dF(t)/dt$
Age	$F(t) = C_u/C_f = F(t_r)$ = Step Output/Input
	$= \int_0^t C_\delta dt \; / \; \int_0^\infty C_\delta dt$
Internal age	$I(t) = 1-F(t)$
Intensity	$\Lambda(t) = E(t)/[1-F(t)] = E(t)/I(t)$
Variance (plain)	$\sigma^2(t) = \int_0^\infty (t-\bar{t})^2 \, E(t)dt$
	$= -\bar{t}^2 + \int_0^\infty t^2 C_\delta \, dt \; / \int_0^\infty C_\delta dt$
Variance (normalized)	$\sigma^2(t_r) = \int_0^\infty (t_r-1)^2 E(t_r) \, dt_r = \sigma^2(t)/ \; \bar{t}^2$
	$= -1 + \int_0^\infty t^2 C dt \; / \; \bar{t}^2 \int_0^\infty C dt$
	$= \int_0^1 (t_r-1)^2 \, dF(t_r)$
Skewness	$\gamma^3(t_r) = \int_0^\infty (t_r-1)^3 E(t_r) \, dt_r$

PROBLEMS, CHAPTER 5

P5.01.01. CSTR TRACER PROFILES

Effluent concentrations from a CSTR will be found for several kinds of input by several methods, seven cases in all. The differential equations represent the material balances in the form: Input = Output + Accumulation.

(1) Step input, direct solution of the differential equation.

$$\bar{t}\frac{dC}{dt} + C = C_f, \text{ with } C = 0 \text{ when } t = 0.$$

$$\ln(C_f-C) + t/\bar{t} = I = \ln(C_f)$$

$$F(t_r) = C/C_f = 1-\exp(-t/\bar{t}) = 1-\exp(-t_r)$$

(2) Step input, transform solution.

$$\bar{t}\frac{dC}{dt} + C = C_f u(t), \text{ with } C = 0 \text{ when } t = 0.$$

$$\bar{t}s\bar{C} + \bar{C} = C_f/s$$

$$\bar{C} = \frac{C_f}{s(\bar{t}s+1)}$$

$C/C_f = 1-\exp(-t/\bar{t})$, as before.

(3) Impulse input, direct solution.

$$\bar{t}\frac{dC}{dt} + C = 0, \text{ with } C = C^o = m/V_r \text{ when } t = 0$$

$$\ln(C) + t/\bar{t} = \text{Integration Constant} = \ln(C^o)$$

$$E(t_r) = C/C^o = \exp(-t_r)$$

(4) Impulse input with $\delta(t)$, transform solution.

$$V_r\frac{dC}{dt} + V'C = m\,\delta(t) = C^oV_r\delta(t), \text{ with } C = 0 \text{ and } \bar{C} = 0 \text{ when } t = 0.$$

$$V_rs\bar{C} + V'\bar{C} = C^oV_r$$

$$\bar{C} = \frac{C^oV_r}{V'(\bar{t}s+1)}$$

$$E(t_r) = C/C^o) = \exp(-t_r)$$

(5) Impulse response derived from the step response. The equations for step and impulse inputs may be written in operator form, with $f(D) = d/dt + V'$:

$$f(D)C_u = V'C_f u(t)$$

$$f(D)C_\delta = C^oV_r\delta(t)$$

Since $\delta(t) = du(t)/dt$,

$$C_\delta/C^o = (V_r/V')\frac{d(C_u/C_f)}{dt} = \frac{d[1-\exp(-t_r)]}{dt_r} = \exp(-t_r)$$

(6) Square pulse, transform solution.

$$\bar{t}\frac{dC}{dt} + C = C_f[u(t)-u(t-a)], \text{ with } C = 0 \text{ when } t = 0$$

The transform is rearranged to

$$\bar{C} = \frac{C_f}{s(\bar{t}s+1)}[1-\exp(-as)]$$

Inverting,

$$C/C_f = [1-\exp(-t/\bar{t})] - \{1-\exp[-(t-a)/\bar{t}]\}u(t-a)$$

The plot of this function is shown in problem P5.01.11.

(7) Sinusoidal input, transform solution.

$$\bar{t}\frac{dC}{dt} + C = C_f \sin(\omega t)$$

$$\bar{C} = \frac{C_f\omega}{(\bar{t}s+1)(s^2+\omega^2)}$$

$$C/C_f = \frac{1}{\sqrt{(\omega\bar{t})^2+1}}\sin[\omega t-\arctan(\omega\bar{t})] + \frac{\omega\bar{t}\exp(-t/t)}{(w\bar{t})^2+1}$$

The exponential term is a "transient" that disappears after a few multiples of $\bar{t}$. The remaining sine term is called the steady state response. Plots of input and output are shown in problem P5.01.28.

P50102. CSTR BATTERY OF n EQUAL SIZED VESSELS

C^0 = hypothetical uniform initial concentration in the whole battery after impulse input. First stage material balance is

$0 = V'C_1 + V_{r1}dC_1/dt$, with $C_1^0 = nC^0$ when $t = 0$

The transform is,

$$\bar{C}_1 = \frac{nC^0}{s+n/\bar{t}}$$

For any subsequent stage,

$$\frac{V_r}{n}\frac{dC_n}{dt} + V'C_n = V'C_{n-1}$$

The transform is,

$$\bar{C}_n = \frac{\bar{C}_{n-1}}{\bar{t}s/n+1} = \frac{nC^0}{(\bar{t}/n)^{n-1}(s+n/\bar{t})^n}$$

The inverse is found by induction after trying n = 1, 2, ...

$$E(t_r) = \frac{C_n}{C^0} = \frac{n}{(n-1)!}t_r^{n-1}\exp(-nt_r), \qquad t_r = t/\bar{t}$$

The peak of the curve is a significant characteristic. Thus,

$$\frac{dE(t_r)}{dt_r} = 0$$

$$= -nt_r^{n-1}\exp(-nt_r) = (n-1)t_r^{n-2}\exp(-nt_r)$$

from which $t_r = (n-1)/n$ and

$$E(t_r)_{max} = \frac{n(n-1)^{n-1}\exp(1-n)}{(n-1)!}$$

For step input,

$$F(t_r) = \int_0^{t_r} E(t_r)dt_r = \frac{n^n}{(n-1)!}\int_0^{t_r} t_r^{n-1}\exp(-nt_r)dt_r$$

$$= 1 - \exp(-nt_r)[1 + nt_r + (nt_r)^2/2! + \ldots + (nt_r)^{n-1}/(n-1)!]$$

The variance is a major characteristic of this RTD.

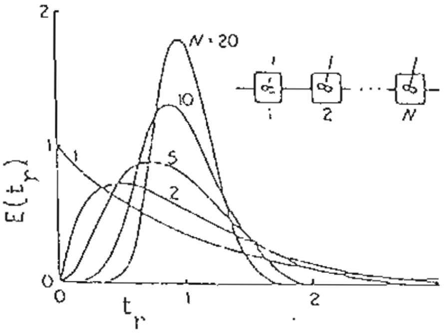
$$\sigma^2(t_r) = -1 + \int_0^\infty t_r^2 E(t_r)dt_r$$

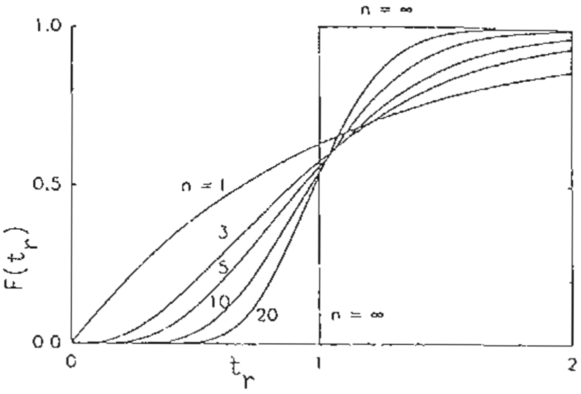
$$= -1 + \frac{n^n}{(n-1)!}\{\exp(-nt_r)[- t_r^{n+1}/n$$

$$+ \sum_{k=1}^{n+1} \frac{(-1)^k(n+1)(n)(n-1)\ldots(n-k+2)}{(-n)^{k+1}} t_r^{n-k+1}])\}_0^\infty$$

At the upper limit the integral is zero, and at the lower limit only the last term of the sum remains. Therefore, the variance is

$\sigma^2(t_r) = 1/n$.





<u>P5.01.03. PLUG FLOW. STEP OR IMPULSE INPUT</u>

Since there is no axial mixing, clearly any input is delayed at the outlet by the period of the residence time. This result also can demonstrated formally by solving the pertinent differential equations.

The material balance on a differential volume dV is

$$V'C = V'(C+dC) + \frac{dC}{dt}dV$$

which is rearranged to the first order partial DEqn,

$$V'\frac{\partial C}{\partial V} + \frac{\partial C}{\partial t} = 0$$

For step input the boundary conditions are

$C(0, t) = C_f u(t)$ and $C(V,0) = 0$

which transform into

$\bar{C}(0,s) = C_f/s$ and $\bar{C}(V,0) = 0$

Transforming the differential equation with respect to t,

$$V'\frac{d\bar{C}}{dV} + s\bar{C} = 0$$

The solution of this linear equation is

$$\bar{C} = (C_f/s)\exp(-sV/V')$$

and the inverse is

$$F(t) = C/C_f = u(t-V/V')$$

$$= \begin{vmatrix} 0 \text{ when } t \le V/V' \\ 1 \text{ when } t \le V/V' \end{vmatrix}$$

Thus the step is delayed at the outlet, when $V = V_r$, by the residence time $\bar{t} = V_r/V'$.

For impulse input, replace C_f with $C^o\bar{t}\delta(t)$ and $\bar{C}_f$ with $C^o\bar{t}$. Then

$$\bar{C} = C^o\bar{t}\ \exp(-sV/V')$$

Inverting,

$$C = C^o\bar{t}\ \delta(t-V/V')$$

At the outlet, $V = V_r$ and $V_r/V' = \bar{t}$. Then

$$E(t_r) = \begin{vmatrix} C/C^o = \bar{t}\delta(t-\bar{t}) = \bar{t}\delta[\bar{t}((t_r-1)] = \delta(t_r-1) \\ 0 \text{ when } t_r \ne 1, \text{ and } \ne 0 \text{ when } t_r = 1. \end{vmatrix}$$

Known properties of the delta function were used in this reduction. Clearly, the impulse input is delayed at the outlet by the period of the residence time.

5.01.04. TRACER DATA ON A n-BUTYRALDEHYDE REACTOR

Results of tracer impulse input data for aldolization of n-butyraldehyde are in the first two columns of the table. The tracer was carbon-14 tagged octadecane. Find the variance and the skewness.

The integrals are evaluated trapezoidally.

$$\int_0^\infty C dt = 0.9880, \quad \int_0^\infty tC dt = 0.9417, \quad \bar{t} = 0.9417/0.9880 = 0.9531,$$

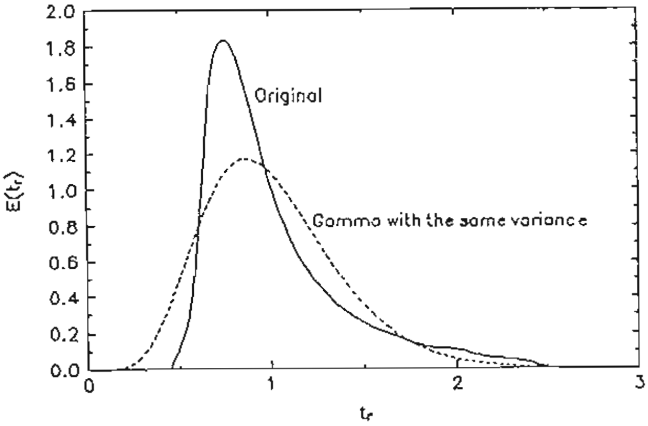
$$C^0 = 0.9880/0.9531 = 1.0366, \quad t_r = t/0.9531, \quad E(t_r) = C/1.0366,$$

$$\sigma^2(t_r) = \int_0^\infty (t_r-1)^2 E(t_r) dt_r = 0.1309,$$

$$\gamma^3(t_r) = \int_0^\infty (t_r-1)^3 E(t_r) dt_r = 0.0683.$$

Note that the vessel appears to have dead space corresponding to a residence time t = 0.425 in series with the active portion. The $E(t_r)$ plot is compared with that of a Gamma distribution with $n = 1/\sigma^2(t_r) = 7.64$ and $\Gamma(7.64) = 2460.9$.

$$E(t_r)_{\text{Gamma}} = \frac{7.64^{7.64}}{\Gamma(7.64)}\ t_r^{6.64}\exp(-7.64t_r)$$



t	C	t_r	$E(t_r)$	$t_rE(t_r)$	$(t_r-1)^2E(t_r)$	$(t_r-1)^3E(t_r)$
0.4250	0.0000	0.4459	0.0000	0.0000	0.0000	0.0000
0.5000	0.2000	0.5246	0.1929	0.1012	0.0436	-0.0207
0.5500	0.4800	0.5771	0.4631	0.2672	0.0828	-0.0350
0.6000	1.1200	0.6295	1.0805	0.6802	0.1483	-0.0549
0.6500	1.7200	0.6820	1.6593	1.1316	0.1678	-0.0534
0.7000	1.8900	0.7344	1.8233	1.3391	0.1286	-0.0341
0.7500	1.8800	0.7869	1.8136	1.4271	0.0824	-0.0175
0.8000	1.7200	0.8394	1.6593	1.3927	0.0428	-0.0069
0.8500	1.5200	0.8918	1.4663	1.3077	0.0172	-0.0019
0.9000	1.2800	0.9443	1.2348	1.1660	0.0038	-0.0002
0.9500	1.0600	0.9967	1.0226	1.0192	0.0000	-0.0000
1.0000	0.9000	1.0492	0.8682	0.9109	0.0021	0.0001
1.1000	0.6400	1.1541	0.6174	0.7126	0.0147	0.0023
1.2000	0.4800	1.2590	0.4631	0.5830	0.0311	0.0080
1.3000	0.3600	1.3640	0.3473	0.4737	0.0460	0.0167
1.4000	0.2800	1.4689	0.2701	0.3968	0.0594	0.0278
1.5000	0.2220	1.5738	0.2142	0.3371	0.0705	0.0405
1.6000	0.1800	1.6787	0.1736	0.2915	0.0800	0.0543
1.7000	0.1400	1.7837	0.1351	0.2409	0.0829	0.0650
1.8000	0.1200	1.8886	0.1158	0.2186	0.0914	0.0812
1.9000	0.1100	1.9935	0.1061	0.2115	0.1047	0.1041
2.0000	0.0800	2.0984	0.0772	0.1619	0.0931	0.1023
2.1000	0.0600	2.2033	0.0579	0.1275	0.0838	0.1009
2.2000	0.0500	2.3083	0.0482	0.1113	0.0826	0.1080
2.4000	0.0000	2.5181	0.0000	0.0000	0.0000	0.0000

P5.01.05. PACKED BED HYDRODESULFURIZER

Normalized tracer response data for a packed bed hydrodesulfurizer are tabulated. The time will be found at which 75% of the tracer has left the vessel. The fraction of the tracer that has exited the vessel is represented by the integral of the last column. Interpolating, $E(t_r) = 0.75$ when $t_r = 1.05$.

t_r	$E(t_r)$	$\int_0^{t_r}$
0	0	
0.4	0	
0.5	0.05	0.003
0.6	0.30	
0.7	0.92	
0.8	1.52	
0.9	1.81	
1.0	1.70	0.544
1.1	1.38	0.698
1.2	0.96	0.815
1.3	0.60	
1.4	0.29	
1.5	0.20	

P5.01.06. MEAN RESIDENCE TIME, NUMERICAL INTEGRATION

Response to an impulse of tracer was measured with the tabulated results. The mean residence time is found by trapezoidal integration.

$$\bar{t} =, \int_0^2 tCdt/\int_0^2 Cdt = 7.60/7.60 = 1.00$$

t	C	tC
0	0	0
0.2	0.60	0.120
0.4	0.80	0.320
0.6	0.92	0.552
0.8	0.98	0.784
1.0	1.00	1.000
1.2	0.98	1.176
1.4	0.92	1.288
1.6	0.80	1.280
1.8	0.80	1.080
2.0	0	0

P5.01.07. RTD FUNCTIONS

Response to impulse input of tracer is shown in the first two columns. Find the principal RTD functions and prepare plots of $E(t_r)$ and $F(t_r)$. Identify the times between which a specified fraction of the tracer has left the vessel.

Various integrations are performed trapezoidally.

$$\int_0^\infty Cdt = 50.0, \quad \int_0^\infty tCdt = 257.5, \quad \int_0^\infty t^2Cdt = 1630,$$

$$\bar{t} = 257.5/50 = 5.15,$$

$$\sigma^2(t) = -\bar{t}^2 + \int_0^\infty t^2Cdt/\int_0^\infty Cdt = -(5.15)^2 + 1630/50 = 6.08$$

$$\sigma^2(t_r) = \sigma^2(t)/\bar{t}^2 = 0.229$$

$$E(t_r) = \bar{t}C/\int_0^\infty Cdt = 0.103\ C$$

$$F(t_r) = \int_0^{t_r} E(t_r)dt_r$$

The shaded area under the $E(t_r)$ curve and the difference between the ordinates on the F-curve at $t_r = 1.2$ and $t_r = 1.5$, $0.83 - 0.7 = 0.12$, represent the fraction of the tracer that had residence times between these two times.

t	C	$E(t_r)$	$F(t_r)$
0	0	0	0
1	1	0.103	0.01
2	5	0.515	0.07
3	8	0.824	0.20
4	10	1.030	0.38
5	8	0.824	0.56
6	6	0.618	0.70
7	4	0.412	0.80
8	3	0.309	0.87
9	2.2	0.227	0.922
10	1.5	0.155	0.959
12	0.6	0.062	1.001
14	0	0	1.013

P5.01.08. COMMERCIAL HYDRODESULFURIZER RESPONSE FUNCTIONS

Tracer impulse response data of a commercial hydrodesulfurizer are given by Sherwood (Course in Process Design, 1963) and are given in the first two columns. Various response functions will be found.

$\int_0^\infty C dt = 539.3, \quad \int_0^\infty tC dt = 12306.3, \quad \int_0^\infty t^2 C dt = 302612,$

$\bar{t} = 12306.3/539.3 = 22.82, \quad C^0 = 539.3/22.82 = 23.63, \quad t_r = t/22.82$

$$\sigma^2(t_r) = -1 + \frac{302612}{(22.82)^2(539.3)} = 0.0775$$

$n = 1/\sigma^2(t_r) = 12.9$

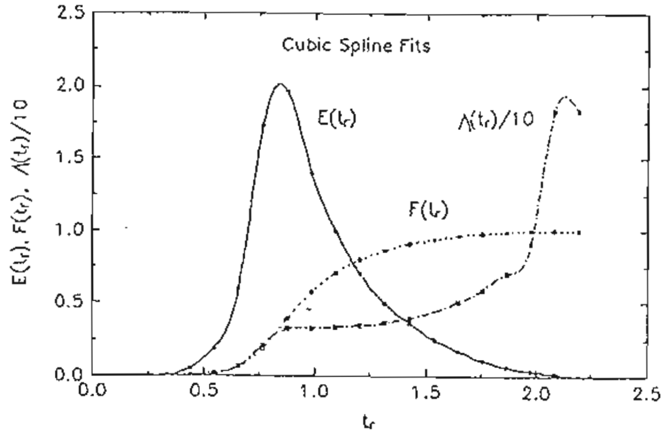
$E(t_r) = C/23.63$

$F(t_r) = \int_0^t C dt / \int_0^\infty C dt$

$\Lambda(t_r) = E(t_r)/[1-F(t_r)]$

If this were a true Gamma distribution the limiting value of the intensity function would be $\Lambda(\infty) = n = 12.9$, instead of the approximately 18 found here. That last number, however, may not be valid because data at the high end are uncertain.

t	C	tC	t^2C	$\int Cdt$
7.500	0.000	0.000	0.000	0.00
10.000	1.200	12.000	120.000	1.50
12.500	4.500	56.250	703.125	8.63
15.000	14.200	213.000	3195.000	32.00
17.500	40.700	712.250	12464.375	100.63
20.000	46.400	928.000	18560.000	209.50
22.500	32.900	740.250	16655.625	308.63
25.000	23.500	587.500	14687.500	379.13
27.500	16.600	456.500	12553.750	429.25
30.000	11.800	354.000	10620.000	464.75
32.500	8.500	276.250	8978.125	490.13
35.000	6.000	210.000	7350.000	508.25
37.500	4.100	153.750	5765.625	520.88
40.000	2.600	104.000	4160.000	529.25
42.500	1.500	63.750	2709.375	534.38
45.000	0.800	36.000	1620.000	537.25
47.500	0.400	19.000	902.500	538.75
50.000	0.000	0.000	0.000	539.25



P5.01.09. RESPONSE FUNCTIONS FROM C_δ DATA

Tracer impulse input data are given in the first two columns. Find various response functions and make plots of $F(t)$ and $\Lambda(t_r)$.

Integrals are evaluated trapezoidally.

$\int_0^\infty C_\delta dt = 25.78$, $\int_0^\infty tC_\delta dt = 130.75$, $\int_0^\infty t^2 C_\delta dt = 813.77$, $\bar{t} = 130.75/25.78 = 5.07$, $C^\circ = 25.785/5.07 = 5.08$, $t_r = t/5.07$, $E(t) = C_\delta/25.78$, $E(t_r) = C_\delta/C^\circ = C_\delta/5.08$, $F(t) = C_\delta/\int_0^t C_\delta dt$ (tabulated), $\Lambda(t_r) = E(t_r)/[1-F(t)]$ (tabulated).

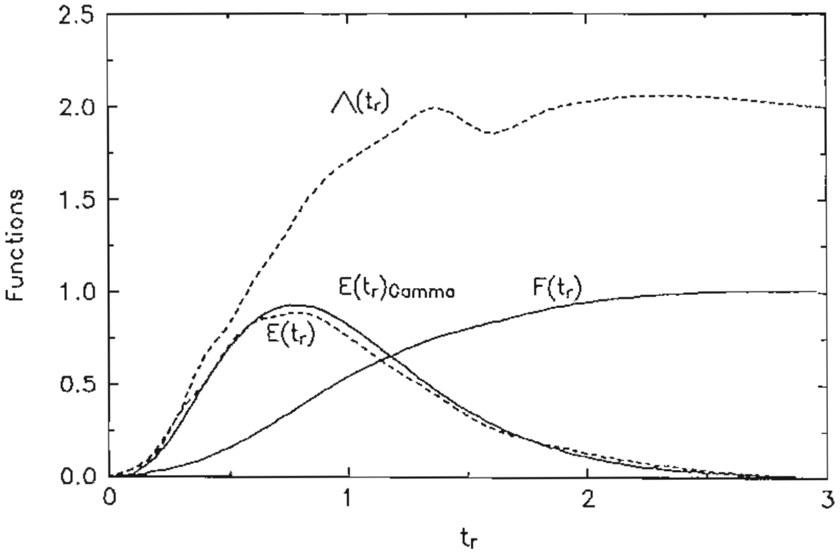
$$\sigma^2(t_r) = -1 + \frac{813.77}{(5.07)^2(25.78)} = 0.228,$$

$n = 1/0.228 = 4.385$, $\Gamma(4.385) = 9.93$

$$E(t_r)_{\text{Gamma}} = \frac{4.385^{4.385}}{9.93}\, t_r^{3.385}\exp(-4.385t_r)$$

This value of $E(t_r)$ is compared on the graph with the tabulated values obtained directly from the data.

t	C_δ	$F(t_r)$	$\Lambda(t_r)$
0	0	0	0
0.5	0.2	0.002	0.041
1	0.7	0.018	0.137
1.5	1.8	0.035	0.365
22	2.6	0.078	0.653
2.5	3.6	0.138	0.821
3	4.2	0.213	1.049
3.5	4.4	0.297	1.232
4	4.5	0.383	1.435
4.5	4.3	0.468	1.592
5	3.9	0.548	1.698
6	3.0	0.682	1.856
7	2.2	0.783	1.993
8	1.4	0.852	1.861
9	1.0	0.899	1.947
10	0.7	0.932	2.023
15	0	1.000	



P5.01.10. RESPONSES TO INPUTS OF SIMPLE GEOMETRIC SHAPES

Responses C_δ to inputs to several vessels are represented by the figures and the tabulation [for case (e)]. Various response functions will be derived with the formulas of Table 5.2. The equations for C_δ are as follows:

a. $C_\delta = 1.5(1-0.1t)$ when $0 \le t \le 10$; $= 0$ elsewhere.

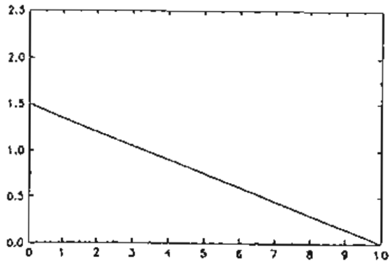
b. $C_\delta = 0.4t$ when $0 \le t \le 5$; $= 2$ when $5 \le t \le 7.5$; $= 0$ when $t \ge 7.5$.

c. $C_\delta = \sqrt{3t-t^2}$ when $0 \le t \le 3$; $= 0$ elsewhere.

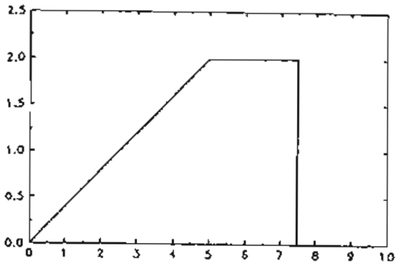
d. $C_\delta = 0.5\sqrt{2-t}$ when $0 \le t \le 2$; $= 0$ elsewhere.

e. C_δ is given tabularly as a function of t.
The various integrals are evaluated numerically and the results are tabulated. The RTD and the Age Fnction then are found from $E(t_r) = C_\delta/C^\circ$ and $F(t_r) = \int_0^{t_r} E(t_r)dt_r$ after substitution of the equations for C_δ.

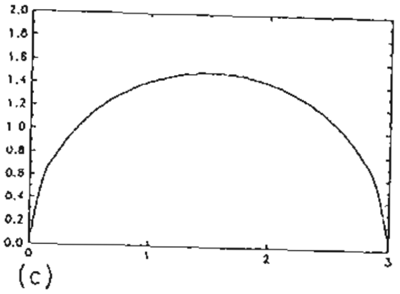
Function	a	b	c	d	e
$\int_0^\infty C_\delta dt$	7.5	10	3.53	0.943	1.48
$\int_0^\infty tC_\delta dt$	25	47.02	5.29	0.754	1.48
$\int_0^\infty t^2C_\delta dt$	125	260.4	9.90		1.97
$\bar{t}$	3.33	4.79	1.50	0.8	1.00
C°	2.25	2.09	2.36	1.18	1.48
$\sigma^2(t)$	5.56	3.08	0.551	0.274	0.332
$\sigma^2(t_r)$	0.5	0.134	0.245	0.429	0.332



(a)



(b)



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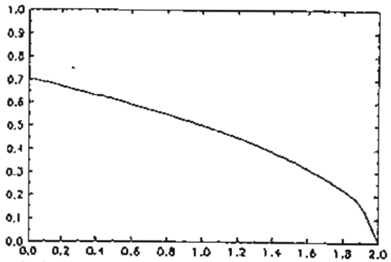
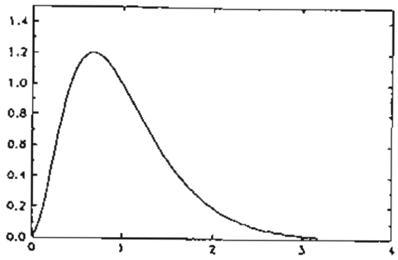


(d)



(e)

t	C_δ	t	C_δ
0	0	1.6	0.42
0.2	0.44	1.8	0.29
0.4	0.96	2.0	0.20
0.6	1.19	2.5	0.075
0.8	1.16	3	0.020
1.0	1.00	4	0.002
1.2	0.79	5	0.0002
1.4	0.59		

(e, data)

P5.01.11. SQUARE PULSE INPUT.

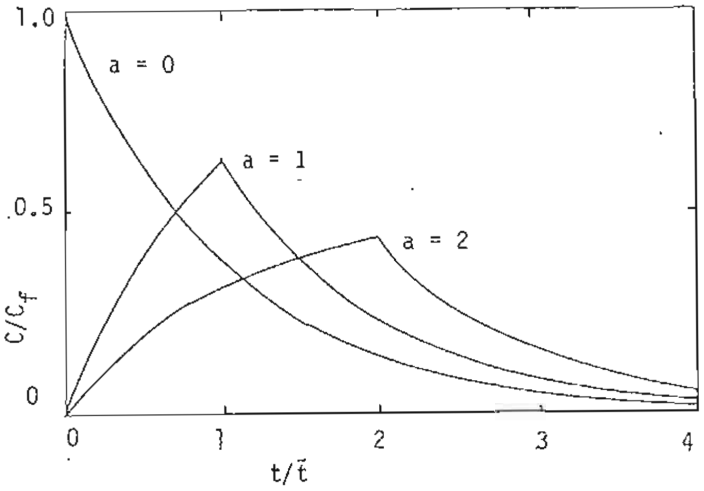
A square pulse of tracer of magnitude C_f/a and of duration a units of time is charged to a CSTR, starting at t = 0. Prepare plots of $C_{effluent}/C_f$ against $t/\bar{t}$ for a = 0, 1 or 2.

Input = $(C_f/a)[u(t)-u(t-a)]$

Output $C/C_f = \{1-\exp(-t/\bar{t}) + [1-\exp((t-a)/\bar{t})]\}/a$

This equation holds for t ≥ a. Note that as a ⇒ 0,

$$\lim \frac{u(t)-u(t-a)}{a} = \delta(t).$$



P5.01.12. INPUT OF ELLIPTICAL SHAPE

The response to impulse input of tracer to a vessel is shaped like an ellipse with equation $C_\delta = \sqrt{1-0.25(t-2)^2}$. Various RTD functions will be found. The trapezoidal rule is used for integration.

$$\int_0^\infty C_\delta dt = 3.14,\ \int_0^\infty tC_\delta dt = 6.28,\ \int_0^\infty t^2C_\delta dt = 15.68$$

Then

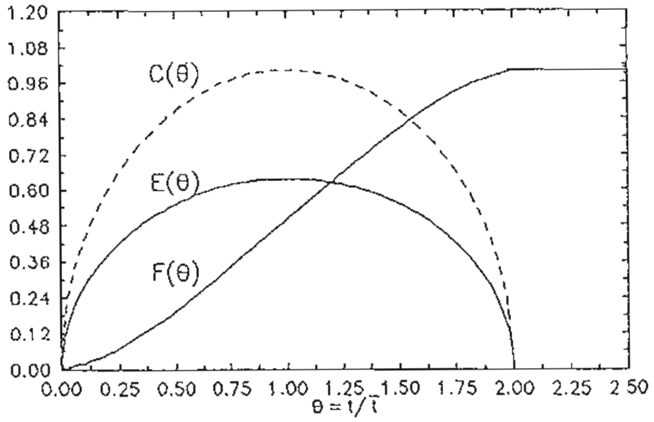
$$\bar{t} = 6.28/3.14 = 2.00,\ C^\circ = m/V_r = \int_0^\infty C_\delta dt/\bar{t} = 3.14/2 = 1.57$$

$$\vartheta = t_r = t/\bar{t} = 0.5t$$

$$E(\vartheta) = C_\delta/C^\circ = \sqrt{1-0.25(2\vartheta-2)^2}/1.57$$

$$F(\vartheta) = \int_0^\vartheta E(\vartheta)d\vartheta$$

The numerical values are plotted.



P5.01.13. RESPONSE TO A STEP INPUT MADE UP OF TWO QUARTER CIRCLES

The response to a step input is made up of horizontal lines connected by two quarter circles as shown on the first figure. The equations are

$$C_u = \left| 0, \text{ when } t \le 1 \right.$$

$$\begin{array}{|l} 2-\sqrt{4-(t-1)^2},\ \text{when } 1\le t\le 3 \\ 2+\sqrt{4-(t-5)^2},\ \text{when } 3\le t\le 5 \\ 4,\ \text{when } t \ge 5 \end{array}$$

Since the limiting concentration is $C_f = 4$, the Age Function is

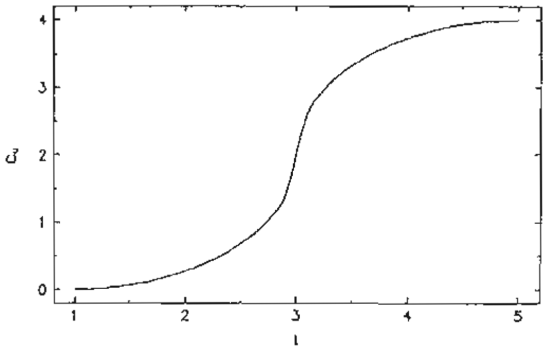
$$F(t) = C_u/4$$

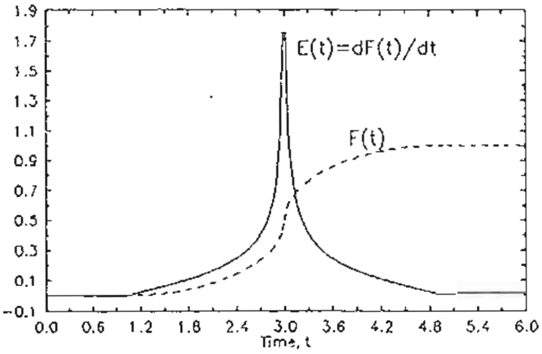
Also,

$$E(t) = \frac{dF(t)}{dt} = \frac{dC_u}{C_f dt}$$

$$= \begin{array}{|l} 0,\ \text{when } t\le 1 \text{ and } t\ge 5 \\ \dfrac{t-1}{4\sqrt{4-(t-1)^2}},\ \text{when } 1\le t\le 3 \\ \dfrac{5-t}{4\sqrt{4-(5-t)^2}},\ \text{when } 3\le t\le 5 \end{array}$$

The plot shows E(t) going to infinity at t = 3.



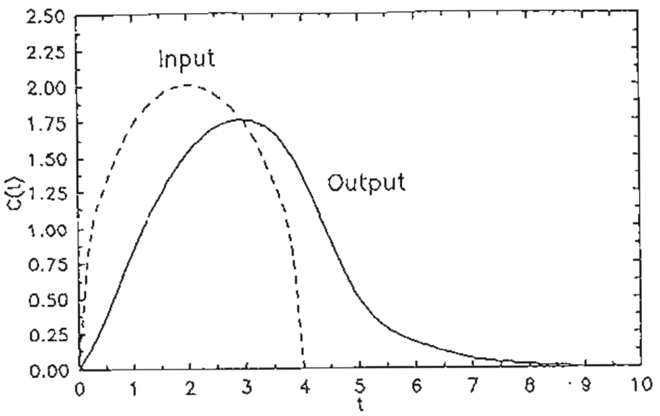


P5.01.14. SEMICIRCULAR INPUT OF TRACER TO A CSTR

Input of tracer concentration to a CSTR is semicircular in shape with equation $C_f = \sqrt{4-(t-2)^2}$ when $0\le t\le 4$ and = 0 elsewhere. The residence time is $\bar{t} = V_r/V' = 1$. The output concentration profile is to be found.

The material balance is

$$\bar{t}\,\frac{dC}{dt} + C = C_f,$$ with C = 0 when t = 0 and C = 1.35 when t = 4. The latter value is obtained from the solution over the range $0\le t\le 4$. After this time the tracer is simply elutriated from the vessel. The differential equation is linear and could be solved analytically, but here it is solved numerically with the result that is graphed.



P5.01.15. PARABOLIC SHAPED RESPONSE CURVE

A test with an impulse input of tracer gave a parabolic response curve with equation $C = (t-2)^2$ when $0 \le t \le 2$ and $C = 0$ elsewhere. Find: (a) the mean residence time; (b) equations of the functions $E(t)$, $E(t_r)$ and $F(t)$; (c) conversion under segregated flow conditions of a reaction with rate equation $r = kC$.

The required quantities are

$$\int_0^\infty C dt = \int_0^2 (2-t)^2 dt = 8/3,\quad \int_0^\infty tC dt = \int_0^2 t(t-2)^2 dt = 4/3,$$

$$\bar{t} = (4/3)/(8/3) = 0.5,\quad E(t) = C/\int_0^\infty C dt = 0.375(t-2)^2,$$

$$E(t_r) = \bar{t}E(t) = (3/16)(t-2)^2$$

$$F(t) = \int_0^t E(t)dt) = 0.125[(t-2)^3+8]$$

In segregated flow,

$$(C/C_0)_{seg} = \int_0^\infty \exp(-kt)E(t)dt = 0.375\int_0^2 \exp(-kt)(t-2)^2 dt$$

Analytical integrals are known, but when k is known numerical integration is convenient.

$$\int xb^{ax}dx = \frac{xb^{ax}}{a \ln b} - \frac{b^{ax}}{a^2(\ln b)^2}$$

$$\int x^n e^{ax}dx = \frac{1}{a} x^n e^{ax} - \frac{n}{a} \int x^{n-1}e^{ax}dx, \text{ (n positive)}$$

P5.01.16. TRIANGULAR RESPONSE CURVE

The response curve to an impulse input of tracer is a triangle with the equations

$$C = \begin{vmatrix} t, \text{ when } 0 \le t \le 2 \\ 2(3-t), \text{ when } 2 \le t \le 3 \\ 0 \text{ elsewhere} \end{matrix}$$

Find (a) the normalized response $E(t_r)$; (b) segregated conversion of a reaction with rate equation $r = 0.6C$.

The required quantities are

$\int_0^\infty Cdt = 3$, area of triangle

$$\int_0^\infty tC dt = \int_0^2 t^2 dt + \int_2^3 2t(3-t)dt = 5$$

$$\bar{t} = 5/3,\quad t_r = t/(5/3) = 0.6t,\quad C^\circ = \int_0^\infty C dt/\bar{t} = 9/5$$

When $0 \le t_r \le 1.2$, $E(t_r) = C/C_0 = (5/9)t = (5/9)(3t_r/5) = t_r/3$

When $1.2 \le t_r \le 1.8$, $E(t_r) = 2(5/9)(3-t) = (10/9)(3-9t_r/5)$.

In segregated flow,

$$(C/C_0)_{seg} = \int_0^\infty \exp(-0.6\bar{t}t_r)E(t_r)dt_r = 0.3954$$

The integration is done numerically after substituting $\bar{t}$ = 5/3 and the given expressions for $E(t_r)$.

P5.01.17. ISOSCELES RIGHT TRIANGLE. RESPONSE FUNCTIONS

Find the response functions when the response to an impulse input has the equations

$$C = \left| \begin{array}{l} t, \text{ when } 0 \le t \le a \\ 2a-t, \text{ when } a \le t \le 2a, \text{ and } = 0 \text{ elsewhere} \end{array} \right.$$

The various quantities are

$$\int_0^\infty C dt = a^2, \text{ area of triangle}$$

$$\int_0^\infty tC dt = \int_0^a t^2 dt + \int_a^{2a} t(2a-t)dt = a^3$$

$$\int_0^\infty t^2 C dt = \int_0^a t^3 dt + \int_a^{2a} t^2(2a-t)dt = 7a^4/6$$

$$\bar{t} = a^3/a^2 = a$$

$$E(t) = C/\int_0^\infty C dt = C/a^2 = \left| \begin{array}{l} t/a^2, \text{ when } 0 \le t \le a \\ \\ (2a-t)/a^2, \text{ when } a \le t \le 2a \end{array} \right.$$

$$\sigma^2(t) = [\int_0^a (t-a)^2 dt + \int_a^{2a} (2a-t-a)^2 dt]/a^2 = \frac{8a^3-6}{3a^2}$$

$$\sigma^2(t_r) = \sigma^2(t)/\bar{t}^2 = \frac{8a^3-6}{3a^4}.$$

P5.01.18. INPUT OR OUTPUT RESPONSE CURVES, RAMP SHAPE

Part (a) The input to a stirred tank is represented by $C_f = 0.5(t-1)$, for $1<t<3$ and zero elsewhere, and the mean residence time is $\bar{t}$ = 1. Find the output up to t = 6.

The material balance on the vessel is
$dC/dt + C = 0.5(t-1)$, for $1<t<3$.

Over the interval $1<t<3$, the solution of this first order linear equation is
$Ce^t = 0.5\int e^t(t-1)dt + I = 0.5[e^t(t-1)-e^t] + I$
When t=1, C = 0 and I = e. Therefore,
$C = 0.5(e^{1-t} + t-2)$, $1<t<3$

Beyond t = 3, the differential equation is
$dC/dt + C = 0$, with C = 0.5377 when t = 3. The integral is
$\ln(C) + t = I = \ln(0.5677) + 3 = \ln(11.4019)$
The overall solution consequently is
$C = 0.5(e^{1-t} +t - 2)$, for $1<t<3$

$11.4019\ e^{-t}$
The input and response curves are plotted.

Part (b). When the response to an impulse input has the same shape as the plot of Part (a), find the response functions.

The various functions are evaluated.

$\int_0^\infty Cdt = 1$ (area of the triangle), $\int_0^\infty tCdt = 0.5\int_1^3 t(t-1)dt = 7/3$,

$\int_0^\infty t^2Cdt = 0.5\int_1^3 t^2(t-1)dt = 17/3$, $\bar{t} = \int_0^\infty tCdt/\int_0^\infty Cdt = 7/3$,

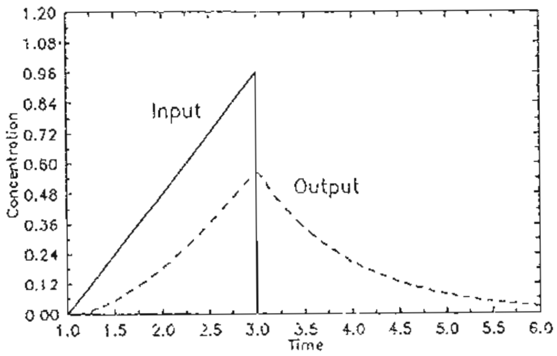
$t_r = 3t/7$, $C^0 = \int_0^\infty Cdt/\bar{t} = 3/7$,

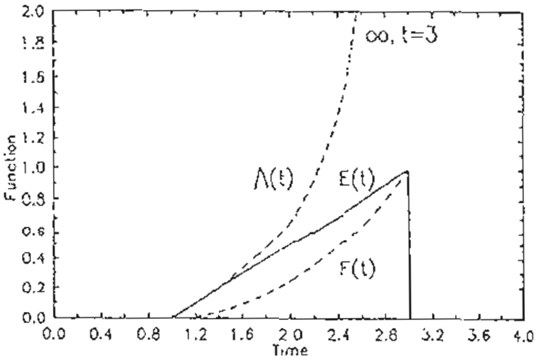
$E(t_r) = C/C^0 = (7/3)(0.5)(t-1) = (7/6)(7t_r/3 - 1)$, for $1<t<3$ or $3/7<t_r< 9/7$.

$E(t) = E(t_r)/\bar{t}$, $F(t) = \int_0^t Et)dt = 0.25(t^2-2t+1)$,

$$\Lambda(t) = E(t)/[1-Ft)] = \frac{2(t-1)}{3-t^2+2t}$$

The plots show E(t), F(t) and Λ(t) against t_r.





P5.01.19. RESPONSE CURVE IN THE SHAPE OF A TRAPEZOID

The response to an impulse input has the shape of a trapezoid with equations

$$C = \begin{cases} t-2, \text{ when } 2\le t\le 5 \\ 3, \text{ when } 5\le t\le 8 \\ 11-t, \text{ when } 8\le t\le 11, \text{ and } = 0 \text{ elsewhere} \end{cases}$$

The residence time $\bar{t}$ and the residence time distribution E(t) are to be found. The required integrals and functions are,

$\int_0^\infty Cdt = 18$, the area of the figure

$\int_0^\infty tCdt = \int_2^5 (t-2)dt + \int_5^8 3tdt + \int_8^{11} t(11-t)dt = 117$

$\bar{t} = 117/18 = 6.5$

$$E(t) = C/\int_0^\infty Cdt = C/18 = \begin{cases} (t-2)/18, \text{ when } 2\le t\le 5 \\ 3/18, \text{ when } 5\le t\le 8 \\ (11-t)/18, \text{ when } 8\le t\le 11 \\ 0, \text{ elsewhere} \end{cases}$$

P5.01.20. A STRAIGHT LINE AND A SEMICIRCLE

The effluent curve of a vessel to which an impulse of tracer has been injected has a straight line portion and a semicircle. E(t) and F(t) are to be found. The equations of the input are,

$$C = \begin{cases} 0, \text{ when } t \le 1 \text{ and } t \ge 5 \\ 0.75(t-1), \text{ when } 1 \le t \le 3 \\ 1.5+\sqrt{1-(t-4)^2}, \text{ when } 3 \le t \le 5 \end{cases}$$

Numerical integration is used to find,

$$\int_0^5 C\,dt = 6.071, \quad \int_0^\infty tC\,dt = \int_1^3 + \int_3^5 = 3/5 + 16.9 = 21.4$$

Accordingly,

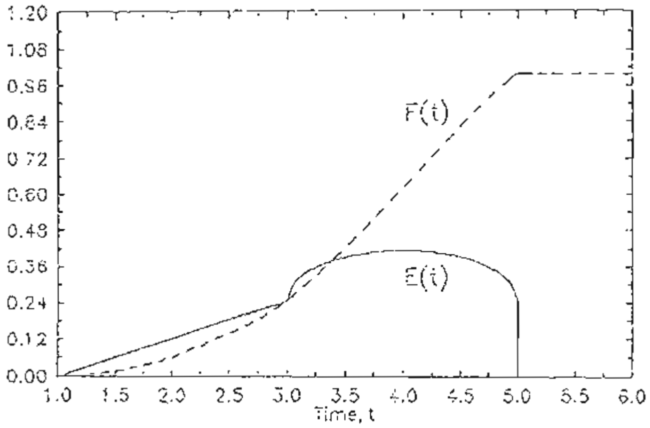
$$E(t) = C/\int_0^\infty C\,dt = C/6.071$$

$$F(t) = \int_0^t E(t)\,dt = \int_0^t C\,dt/6.071$$

The last two functions are plotted against t. If it is desired to express the results in terms of t_r, the residence time is

$$\bar{t} = 21.4/6.071 = 3.52$$

$$t_r = t/3.52$$



P5.01.21. INTENSITY FUNCTION $\Lambda(t_r)$ OF THE n-STAGE CSTR BATTERY

Equations for $E(t_r)$ and $F(t_r)$ are derived in problem P5.01.02. The intensity function is $\Lambda(t_r) = E(t_r)/[1-F(t_r)]$. Equations and curves are shown for several stages.

$n = 1, \ \Lambda(t_r) = 1$

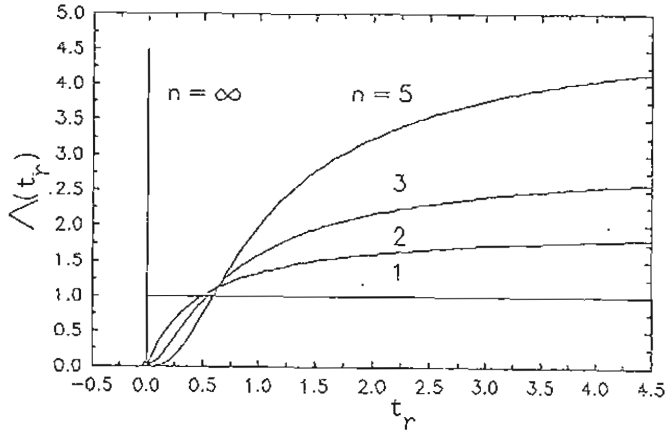
2 $\qquad \dfrac{2t_r}{1+2t_r}$

3 $\qquad \dfrac{13.5t_r^2}{1+3t_r+(3t_r)^2/2!}$

5 $\qquad \dfrac{130.2t_r^4}{1+5t_r+(5t_r)^2/2! + (5t_r)^3/3! + (5t_r)^4/4!}$

$\infty \qquad \infty$

Also of interest is the relation, $\Lambda(\infty) = n$.



P5.01.22. FINITE PULSE INPUT

The profile of a tracer input is represented by a trapezoid with the given equations and with $V_r/V' = 2$. Plot the outlet concentration against time. The equations of the input are,

$$C_f = \begin{cases} 2t/3, \text{ when } 0 \le t \le 3 \\ 2, \text{ when } 3 \le t \le 7 \\ 2(10-t)/3, \text{ when } 7 \le t \le 10, \text{ and zero elsewhere} \end{cases}$$

The material balance of a CSTR is

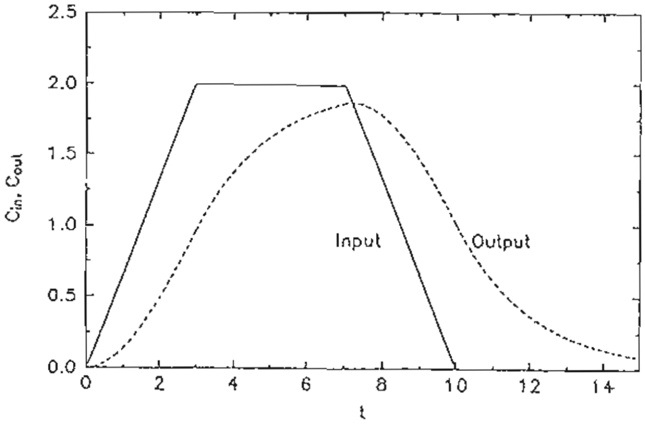
$$V_r \frac{dC}{dt} + V'C = V'C_f$$

This is a linear differential equation whose solution is

$$C \exp(t/\bar{t}) = \int \frac{C_f}{\bar{t}} \exp(t/\bar{t})\, dt + \text{Integration constant}$$

The results are in terms of $t_r = t/\bar{t} = t/2$.

$$C = \begin{cases} (4/3)[t_r - 1 + \exp(-t_r)], \text{ when } 0 \le t \le 3 \\ 2 - 4.6421 \exp(-t_r), \text{ when } 3 \le t \le 7 \\ 6.67 - 1.33(t_r - 1) - 48.797 \exp(-t_r), \text{ when } 7 \le t \le 10 \\ 149.088 \exp(-t_r), \text{ when } t \le 10. \end{cases}$$



P5.01.23. A POLYGONAL TRACER INPUT CURVE

The response curve to an impulse input has the equations

$$C = \begin{cases} t-2, \text{ when } 5 \le t \le 8 \\ 14-t, \text{ when } 8 \le t \le 11, \text{ and } = 0 \text{ elsewhere} \end{cases}$$

Various response functions are to be found. The integrals are found numerically,

$$\int_0^\infty Cdt = 27,\ \int_0^\infty tCdt = 216,\ \int_0^\infty t^2Cdt = 1796.5,\ \bar{t} = 216/27 = 8,$$

$$\sigma^2(t_r) = -1+\int_0^\infty t^2Cdt/\bar{t}^2\int_0^\infty Cdt = -1+1795.6/(8)^2(27) = 0.0391$$

$$n = 1/0.0391 = 25.6$$

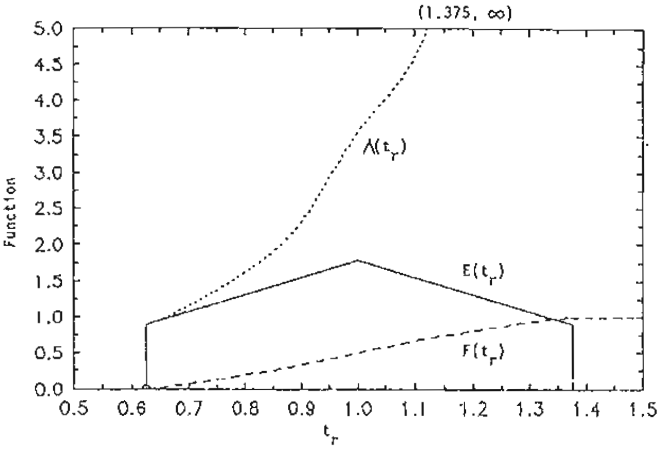
$$E(t_r) = \bar{t}C/\int_0^\infty Cdt = \begin{cases} 0.2963t-0.5926, \text{ when } 5\le t\le 8 \\ 4.1482-0.2963t, \text{ when } 8\le t\le 11 \end{cases}$$

$$= \begin{cases} 2.3704t_r-0.5926, \text{ when } 0.625\le t_r\le 1 \\ 4.1482-2.3704t_r, \text{ when } 1\le t_r\le 1.375 \end{cases}$$

$$F(t_r) = \int_0^{t_r} E(t_r)dt_r,\quad \Lambda(t_r) = E(t_r)/[1-F(t_r)]$$

The results are tabulated and plotted.

t_r	$E(t_r)$	$F(t_r)$	$\Lambda(t_r)$
0.625	0	0	0
0.625	0.889	0	0.889
0.650	0.948	0.023	0.971
0.7	1.067	0.073	1.151
0.8	1.304	0.192	1.613
0.9	1.541	0.334	2.314
1.0	1.778	0.500	3.556
1.1	1.541	0.665	4.599
1.2	1.304	0.808	6.797
1.3	1.067	0.927	14.55
1.375	0.889	1.000	∞
1.375	0		



P5.01.24. TRAPEZOIDAL SHAPED RESPONSE CURVE

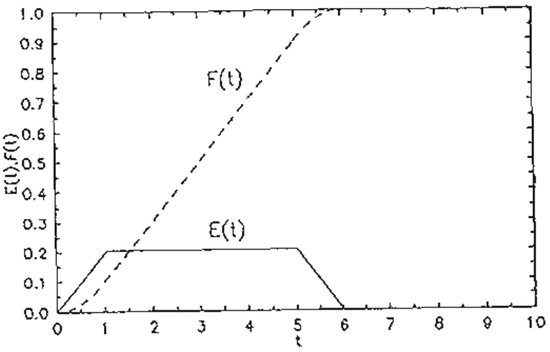
The response curve of an impulse input has the shape of a trapezoid with equations,

$$C = \begin{cases} 4t, \text{ when } 0\le t\le 1 \\ 4, \text{ when } 1\le t\le 5 \\ 4(6-t), \text{ when } 5\le t\le 6, \text{ and } = 0 \text{ elsewhere} \end{cases}$$

The functions E(t) and F(t) will be found. The area of the figure is $\int_0^\infty Cdt = 20$. Accordingly,

$$E(t) = C/20$$

$$F(t) = \int_0^t Cdt/20 = \begin{cases} \int_0^t 0.2tdt, \text{ when } 0\le t\le 1 \\ 0.1+\int_1^t 0.2dt, \text{ when } 1\le t\le 5 \\ 0.9+\int_5^t 0.2(6-t)dt, \text{ when } 5\le t\le 6 \\ 1, \text{ when } t\ge 6 \end{cases}$$



P5.01.25. STEP INPUT OF TRACER

Response to a step input of tracer is given in the first two columns of the table. The mean residence time $\bar{t}$ and the functions $E(t_r)$ and $F(t_r)$ are to be found.

From the table, the limiting value is $C_f = 8.0$ as $t \Rightarrow \infty$. Accordingly $F(t_r) = C_u/C_f = C_u/8$. The data are curve-fitted, $C_u = f(t)$, as a ratio of polynomials, as shown on the first graph. Then the derivative is evaluated and tabulated. The mean residence time is

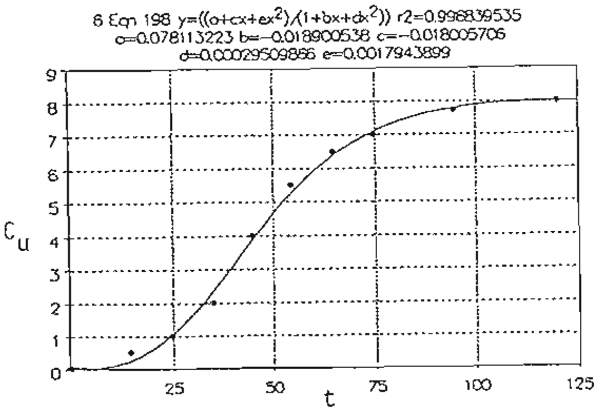
$$\bar{t} = \int_0^1 t\,d(C_u/C_f) = 0.125\int_0^8 t\,dC_u = 48.2$$

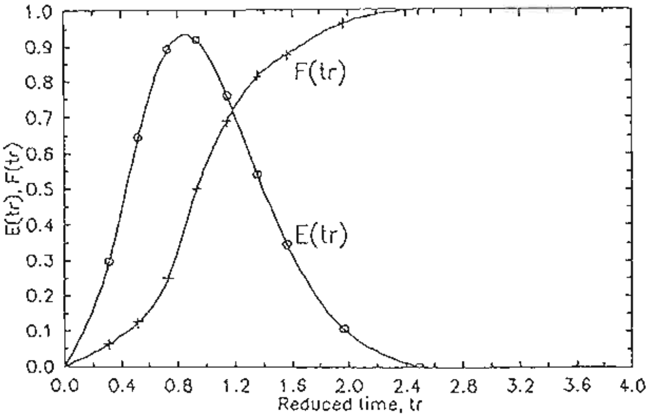
and

$$E(t_r) = \frac{dF(t_r)}{dt_r} = \frac{\bar{t}\,dC_u}{C_f dt} = \frac{48.2dC_u}{8dt}$$

The calculated values are tabulated and plotted.

t	C_u	dC_u/dt	t_r	$E(t_r)$	$F(t_r)$
0	0	-0.0167	0	-0.1(0)	0
15	0.5	0.0492	0.31	0.2965	0.063
25	1	0.1068	0.52	0.6436	0.125
35	2	0.1478	0.73	0.8904	0.250
45	4	0.1522	0.93	0.9171	0.500
55	5.5	0.1261	1.14	0.7597	0.688
65	6.5	0.0896	1.35	0.5397	0.813
75	7	0.0572	1.56	0.3446	0.875
95	7.7	0.0177	1.97	0.1069	0.963
120	8	-0.0004	2.49	-0.02(0)	1.000
∞	8				





P5.01.26. STEP INPUT. EQUIVALENT CSTR BATTERY

The data of the first two columns are derived from a step input of tracer, and show the values of F(t) as a function of time. The variance is to be found, then $E(t_r)$ for the equivalent Gamma distribution. That value of $E(t_r)$ is to be compared with the one found directly from the data.

Integration is done numerically.

$$\bar{t} = \int_0^1 t\,dF = 0.4983,\ t_r = t/0.4983,\ \sigma^2(t_r) = \int_0^1 (t_r-1)^2 dF = 0.3442.$$

The equivalent CSTR battery or Gamma distribution has

$$n = 1/0.3442 = 2.9053,\ \Gamma(2.9053) = 1.8918,$$

$$E(t_r) = \frac{2.905^{2.905}}{1.8918} t_r^{1.905}\exp(-2.905t_r)$$

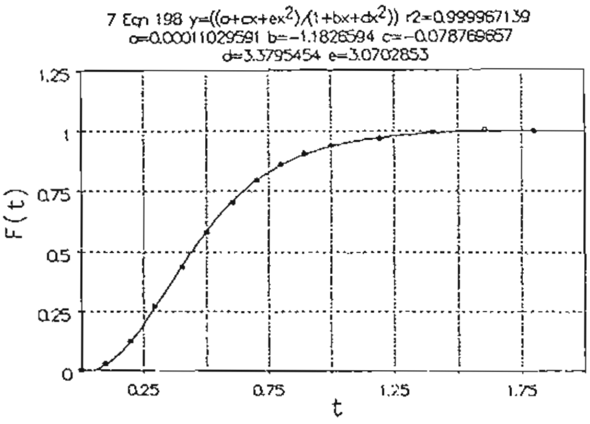
$$= 11.71t_r^{1.905}\exp(-2.905t_r) \qquad (1)$$

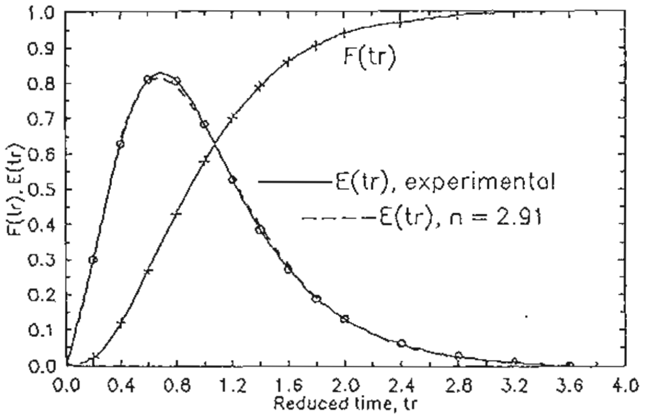
The $E(t_r)$ also is found from the original data. The original data are curve-fitted on graph 1, then differentiated, thus

$$E(t_r) = dF(t_r)/dt_r = \bar{t}dF(t)/dt \qquad (2)$$

The two plots of $E(t_r)$ agree closely.

t	F(t)	t_r	Eqn 2
0	0	0	-0.04
0.1	0.023	0.2	0.299
0.2	0.12	0.4	0.628
0.3	0.27	0.6	0.810
0.4	0.43	0.8	0.807
0.5	0.58	1.0	0.684
0.6	0.70	1.2	0.520
0.7	0.79	1.4	0.385
0.8	0.86	1.6	0.273
0.9	0.91	1.8	0.190
1.0	0.94	2.0	0.132
1.2	0.97	2.4	0.062
1.4	0.99	2.8	0.027
1.6	0.996	3.2	0.010
1.8	0.999	3.6	0.0005





P5.01.27. EXPERIMENTAL RTD COMPARED WITH THAT OF AN IDEAL CSTR

The data of the first two columns are of response to impulse input to a reactor. The RTD is to evaluated and compared with that of an ideal CSTR with the same residence time.

Integrations are done with the trapezoidal rule.

$$\int_0^\infty C_\delta dt = 1.004,\ \int_0^\infty tC_\delta dt = 4.852,\ \bar{t} = 4.852/1.004 = 4.833$$

Then the RTD is

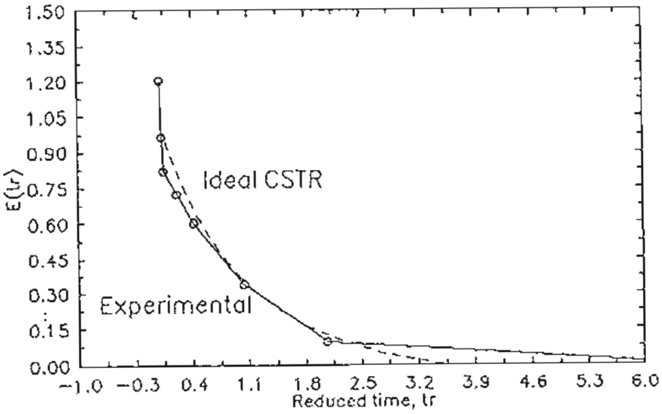
$$E(t_r) = \frac{\bar{t}C_\delta}{\int_0^\infty C_\delta dt} = \frac{4.833}{1.004} C_\delta = 4.814C_\delta \qquad (1)$$

For an ideal stirred tank with $\bar{t}$ = 4.833,

$$E(t_r) = \exp(-t/4.833) \qquad (2)$$

Except for the tails, the plots of Equations (1) and (2) are close.

t	C_δ	t_r	Eqn 1
0	0.25	0	1.2034
0.1	0.20	0.0207	0.9627
0.2	0.17	0.0414	0.8183
1	0.15	0.2069	0.7221
2	0.125	0.4138	0.6017
5	0.07	1.0346	0.3370
10	0.02	2.0691	0.0963
30	0.001	6.2073	0.0048



P5.01.28. SINUSOIDAL INPUT OF TRACER

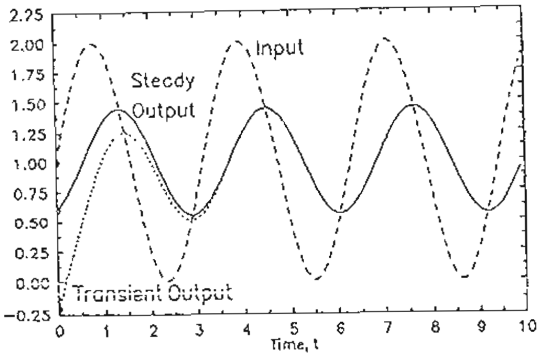
Tracer input to a CSTR is sinusoidal with equation $C/C_f = 1+\sin(\omega t)$. Transient and steady output concentrations are to be found. The unsteady material balance is

$$\bar{t}\frac{dC}{dt} + C = C_f[1+\sin(\omega t)]$$

Taking the transform,

$$(\bar{t}s+1)\bar{C} = C_f(\frac{1}{s} + \frac{\omega}{s^2+\omega^2})$$

$$\bar{C}/C_f = \frac{1}{\bar{t}s+1}(\frac{1}{s} + \frac{\omega}{s^2+\omega^2})$$



The inverse is

$$C/C_f = 1-\exp(-t/\bar{t})+\frac{\exp(-t/\bar{t})}{\bar{t}(\omega^2+1/\bar{t}^2)} + \frac{1}{\bar{t}\sqrt{w^2+1/\bar{t}^2}}\sin[\omega t-\arctan(\omega t)]$$

With the numerical values $\bar{t}$ = 1, ω = 2 and arctan(2) = -1.107,

$$C/C_f = 1-\exp(-t)+0.2\exp(-t)+0.4472\ \sin(2t-1.107)$$

Beyond t = 4, the exponential term disappears; then the output is called "steady". The input, the transient output and the steady output are plotted.

P5.01.29. FREQUENCY RESPONSE AND TRANSFER FUNCTIONS

Frequency response testing mesures the amplitude, r, and the phase angle, ϑ. These involve the parameters of the transfer function so this mode of testing can identify two such parameters. The relationship depends on the properties of complex numbers.

In a transfer function G(s) replace $s = j\omega$ and rearrange the complex number into a standard form.

$$G(j\omega) = a+jb$$

In polar form,

$$a+jb = r(\cos\vartheta + j\sin\vartheta) = r\exp(j\vartheta)$$

$$r = \sqrt{a^2+b^2}, \text{ called Amplitude or Gain}$$

$$\vartheta = \arctan(b/a), \text{ called Angle or phase angle}$$

As an example take $G(s) = 1/(Ts+1)$ and substitute $s = j\omega$,

$$G(j\omega) = \frac{1}{j\omega T+1} = \frac{j\omega T-1}{-\omega^2T^2-1} = \frac{1}{\omega^2T^2+1} - j\frac{\omega T}{\omega^2T^2+1}$$

Accordingly,

$$r = 1/\sqrt{\omega^2T^2+1}, \quad \vartheta = \arctan(-\omega T)$$

Measurements of either r or ϑ at a particular frequency ω can establish the value of T. With a more complex transfer function, two parameters can be established by such measurements.

P5.01.30. FREQUENCY RESPONSE OF A CSTR BATTERY

The Gain and phase angle will be found for several ideal stirred tanks in series. For such a series of vessels, the overall transfer function is the product of the individual transfer functions, that is,

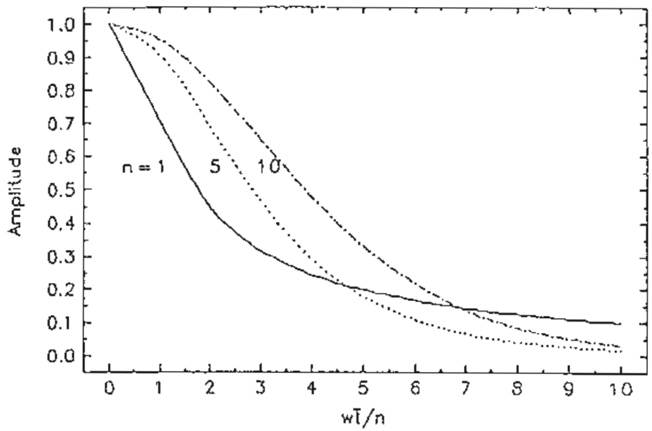
$$G(s) = G_1(s)G_2(s)\ldots G_n(s)$$

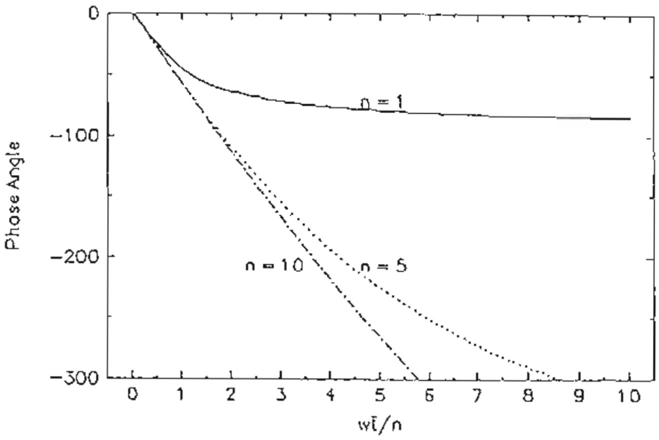
It follows that the overall Gain is the product of the individual gains and the overall angle is the sum of the individual angles. When these rules are applied to n equal CSTR stages,

$$\text{Gain} = \frac{1}{[1+(\omega\bar{t}/n)^2]^{n/2}}$$

$$\text{Angle} = -\,n\arctan(\omega\bar{t}/n)$$

These functions are plotted in their dependence on the frequency term $\omega\bar{t}/n$ for several values of n. The results appear to be quite distinctive functions of the number of stages in the battery.





P5.01.31. A CSTR WITH BYPASS. FREQUENCY RESPONSE

A CSTR is believed to be operating with a fraction α of the flow in bypass. Frequency response testing with ω - 2/sec gave a Gain $r = \sqrt{a^2+b^2} = 0.4$ and a phase angle $\vartheta = \arctan(b/a) = 2.5$ radians. The transfer function of the CSTR is

$$G(s) = G_1(s) = 1/(Ts+1)$$

The material balance with bypass in terms of transforms is

$$\bar{C} = [(1-\alpha)G_1+\alpha]\bar{C}_f$$

whence

$$G(s) = \frac{1-\alpha}{Ts+1} + \alpha$$

and on replacing $s = j\omega$,

$$G(j\omega) = \frac{1-\alpha}{j\omega T+1} + \alpha = \frac{(1-\alpha)(j\omega T-1)}{-\omega^2T^2-1} + \alpha = \frac{1+\alpha\omega^2T^2}{\omega^2T^2+1} - j\,\frac{(1-\alpha)\omega T}{\omega^2T^2+1}$$

The equations to be solved for α and T are,

$$a = \frac{1+\alpha\omega^2T^2}{\omega^2T^2+1}$$

$$b = \frac{-(1-\alpha)\omega T}{\omega^2T^2+1}$$

$$a^2+b^2 = (0.4)^2$$

$$b/a = \tan(2.5)$$

The numerical results with $\omega = 2$ are: $a = 0.321$, $b = -0.239$, $\alpha = 0.236$, $T = 1.419$.

P5.01.32. CSTR WITH BYPASS AND A PFR IN SERIES. FREQUENCY RESPONSE

A CSTR is operated in series with a PFR, with a fraction α of the flow in bypass around the CSTR. Equations are to be found for the Gain and phase angle of a frequency response.

The transfer function of the CSTR is $G_1 = 1/(T_1s+1)$ and that of the PFR is $G_2 = \exp(-T_2s)$. Overall,

$$G(s) = [(1-\alpha)G_1+\alpha]G_2 = \left(\frac{1-\alpha}{T_1s+1} + \alpha\right)\exp(-T_2s) = \frac{\alpha T_1s+1}{T_1s+1}\exp(-T_2s)$$

On substituting $s = j\omega$,

$$G(j\omega) = \frac{-(j\alpha\omega T_1+1)(j\omega T_1-1)}{\omega^2T_1^2+1}\exp(-j\omega T_2)$$

Reduction to the standard form, $G(j\omega) = a+jb$, can be accomplished after making the further substitution,

$$\exp(-j\omega T_2) = \cos(-\omega T_2) + j\sin(-\omega T_2)$$

However, there are three unknown parameters: α, T_1 and T_2, so measurements of Gain and Angle at a given frequency will not suffice for their determination.

P5.02.01. MOMENTS FROM TRANSFER FUNCTIONS

For a model with a known transfer function the several moments can be obtained directly without need for inversion of the transform. This a consequence of a property of the derivative of the Laplace transform, namely certain limits as $s \Rightarrow 0$:

$$\text{limit } \frac{d^nG(s)}{ds^n} = \text{limit } \int_0^\infty t^n e^{-st} G(t)dt = (-1)^n \int_0^\infty t^n G(t)dt$$

(a) The several derivatives of the transfer function with respect to s are formed together with their limits as s goes to zero. Designate these derivatives as G_0', G_0'', G_0''', etc. The formulas for the first three moments are,

Moment	Equation
$\mu(t)$	$-G_0'$
$\mu(t_r)$	$-G_0'/\bar{t}$
$\sigma^2(t)$	$G_0''-(G_0')^2$
$\sigma^2(t_r)$	$[G_0''-(G_0')^2]/\bar{t}^2$
$\gamma^3(t_r)$	$[-G_0'''+3G_0'G_0''-2(G_0')^3]/\bar{t}^3$

(b) As the first example, take the Gamma distribution.

$$G(s) = \frac{1}{(1+\bar{t}s/n)^n}$$

$$G_0' = \text{limit } \frac{-\bar{t}}{(1+\bar{t}s/n)^{n+1}} = -\bar{t}$$

$$G_0'' = \text{limit } \frac{(n+1)\bar{t}^2/n}{(1+\bar{t}s/n)^{n+2}} = (n+1)\bar{t}^2/n$$

$$G_0''' = \text{limit } \frac{-(n+1)(n+2)\bar{t}^3}{(1+\bar{t}s/n)^n n^2} = \frac{-(n+1)(n+2)\bar{t}^3}{n^2}$$

$\sigma^2(t_r) = 1/n$

$\gamma^3(t_r) = 2/n^2$

(c) As another example take an n-stage CSTR battery with recycle to the first stage. β = recycle flow rate/fresh feed rate. The transfer function is

$$G(s) = \frac{1}{(1+\beta)(1+\bar{t}s/n)^n-\beta}$$

where $\bar{t}$ = reactor volume/fresh feed rate. The first derivative is

$$\frac{dG}{ds} = \frac{-(1+\beta)(1+\bar{t}s/n)^{n-1}\bar{t}}{[(1+\beta)(1+\bar{t}s/n)^n-\beta]^2}$$

so that

$$G_0' = -(1+\beta)\bar{t}$$

Similarly,

$$G_0'' = \bar{t}^2(1+\beta)^2(1+1/n+2\beta)$$

Then the moments become

$$\sigma^2(t_r) = (1+\beta)^2(1/n + 2\beta)$$

$$\mu(t_r) = 1+\beta$$

When $\beta = 0$, these moments do reduce to the corresponding ones for the n-stage CSTR without recycle.

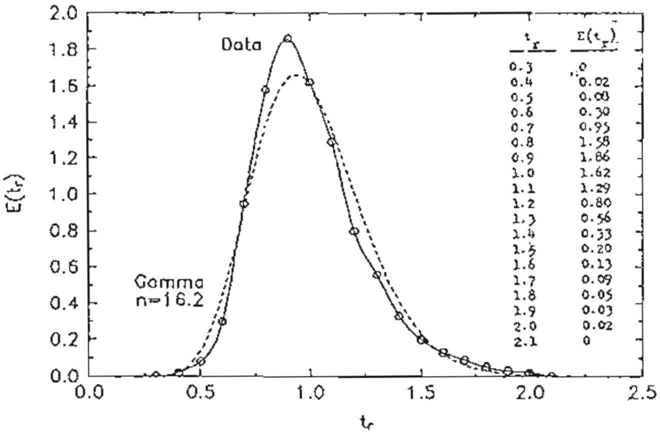
P5.02.02. CURVE FITS OF HYDRODESULFURIZER RTD DATA

For a commercial hydrodesulfurizer, $E(t_r)$ data are tabulated and plotted on the first figure. The variance was calculated as $\sigma^2(t_r) = 0.0618$, which makes the parameter of a Gamma distribution $n = 1/0.0618 = 16.2$. Accordingly,

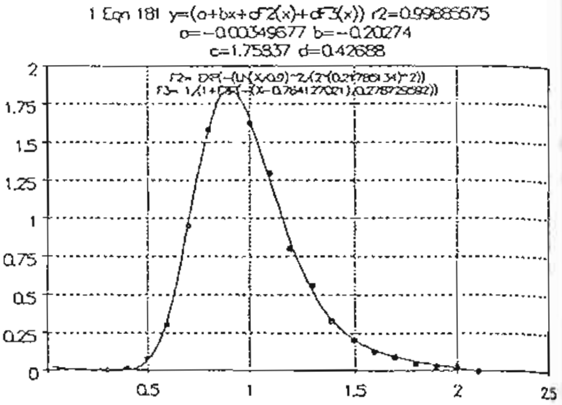
$$E(t_r)_{Gamma} = 1.733(10^7)t_r^{15.2}\exp(-16.2t_r)$$

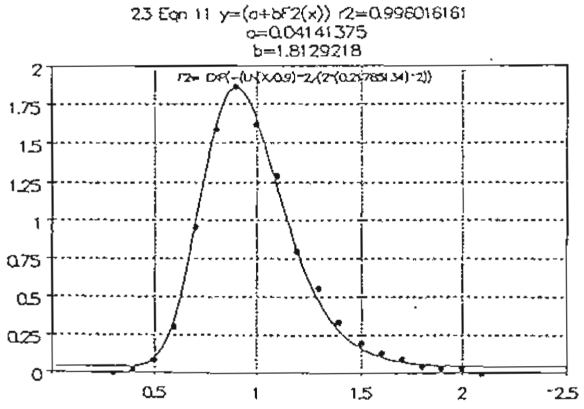
The first figure compares the plot of this equation with a cubic spline fit of the original data.

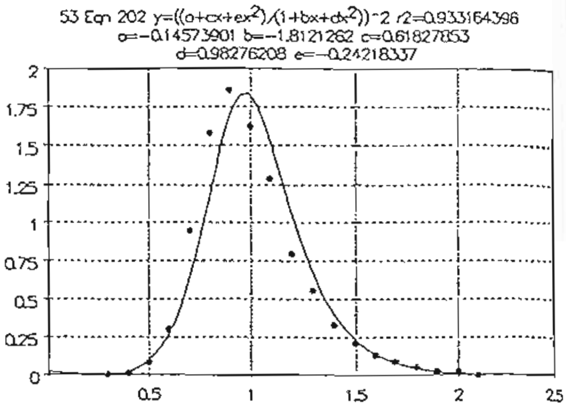
The other plots are made with the software TABLECURVE. The special function F2 used there is a log-normal relation and F3 is a sine-wave function. Usually a ratio of low degree polynomials also provides a good fit to bell-shaped curves; here five constants are needed. The Gamma distribution needs only one constant, but the fit is not as good as some of the other curves. The peak, especially, is missed.



t_r	$E(t_r)$
0.3	0
0.4	0.02
0.5	0.08
0.6	0.30
0.7	0.95
0.8	1.58
0.9	1.86
1.0	1.62
1.1	1.29
1.2	0.80
1.3	0.56
1.4	0.33
1.5	0.20
1.6	0.13
1.7	0.09
1.8	0.05
1.9	0.03
2.0	0.02
2.1	0







P5.02.03. GAMMA DISTRIBUTION FOR NON-INTEGRAL n

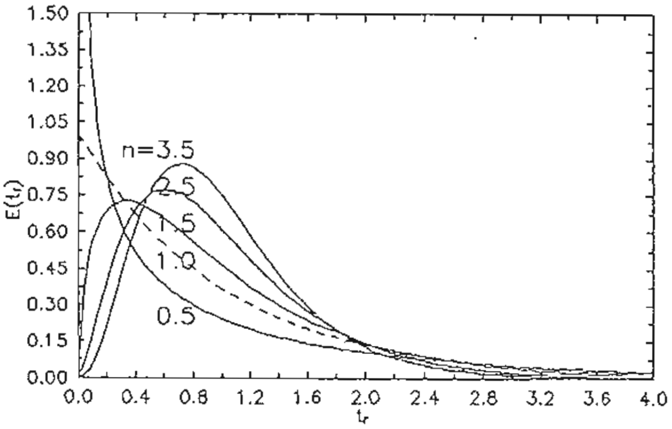
The equation is

$$E(t_r) = \frac{n^n}{\Gamma(n)} t_r^{n-1}\exp(-nt_r)$$

Values of the Gamma function are

n	0.5	1	1.5	2.5	3.5
$\Gamma(n)$	1.7724	1	0.8862	1.3293	3.233

Note that $E(0) \Rightarrow \infty$ when $n < 1$. Plots for integral values of n are in problem P5.01.02.



P5.02.04. LINEARIZED PLOT OF GAMMA RTD

Data of a pilot plant hydrodesulfurizer (Sherwood, 1963) are to be fitted to a Gamma model. That equation is rearranged into a linear form as

$$\ln[t_rE(t_r)] = \ln[n^n/\Gamma(n)] + n\ \ln[t_r\exp(-t_r)]$$

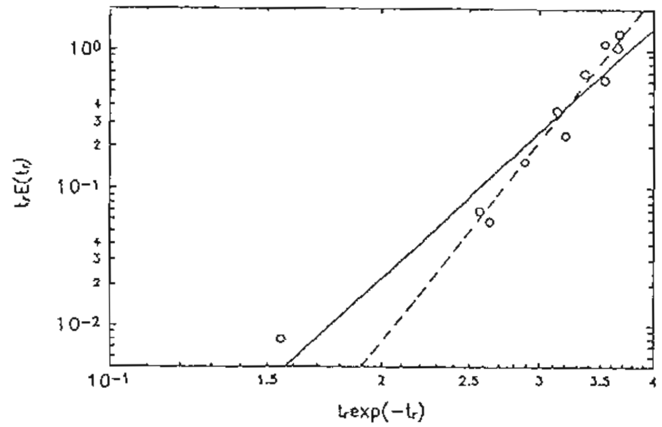
Ignoring the first point, the equation of the dashed line is

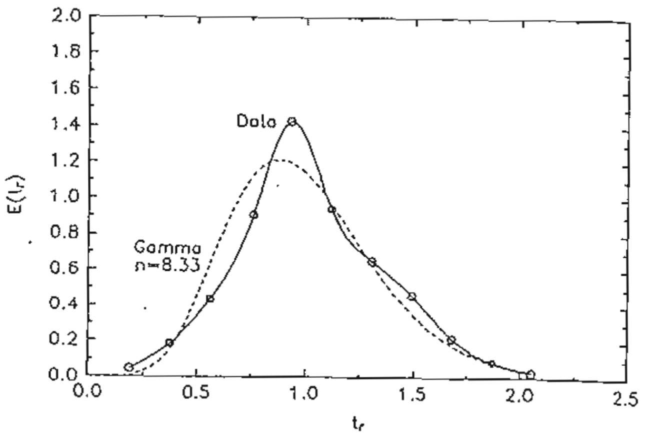
$$\ln(y) = 8.53 + 8.33\ \ln(x)$$

so the value of the Gamma parameter is $n = 8.33$. Plots of the tabulated data and the data predicted by the Gamma correlation are compared. The equation is

$$E(t_r) = \frac{8.33^{8.33}}{9875}\ t_r^{7.33}\exp(-8.33t_r)$$

t_r	$E(t_r)$	$t_rE(t_r)$	$t_r\exp(-t_r)$
0.187	0.042	0.008	0.155
.0373	0.185	0.069	0.257
0.560	0.435	0.244	0.312
0.746	0.903	0.614	0.354
0.933	1.426	1.331	0.367
1.119	0.940	1.052	0.366
1.306	0.852	1.113	0.354
1.493	0.458	0.684	0.336
1.679	0.218	0.366	0.313
1.886	0.083	0.155	0.289
2.052	0.028	0.058	0.264





P5.02.05. LINEARIZED GAMMA PLOT. HYDRODESULFURIZATION DATA

Data of tracer impulse input to a hydrodesulfurizer are cited by Sherwood (1963) and listed in the first two columns. The following functions are derived.

$\int_0^\infty C\,dt = 532.5$, $\int_0^\infty tC\,dt = 11978$, $\int_0^\infty t^2C\,dt = 289982$,

$\bar{t} = 11978/532.5 = 22.494$, $\sigma^2(t_r) = -1 + \dfrac{289982}{532.5(22.494)^2} = 0.0763$, $n = 1/\sigma^2(t_r) = 13.1$, $E(t_r) = \bar{t}C/\int_0^\infty C\,dt = 0.0422\,C$

In linearized form the Gamma distribution is

$\ln[t_rE(t_r)] = \ln[n^n/(n-1)!] + n\ln[t_r\exp(-t_r)]$

On the plot the first two points are ignored. In any case they contribute little to segregated conversion. The slope is

$n = 9.9$

which does not agree well with the value n = 13.1 predicted from the variance, although both values approximate plug flow.

The desulfurization process is first order with k = 0.371/sec. With $\bar{t} = 22.494/n$ in each stage, the fractional conversion is

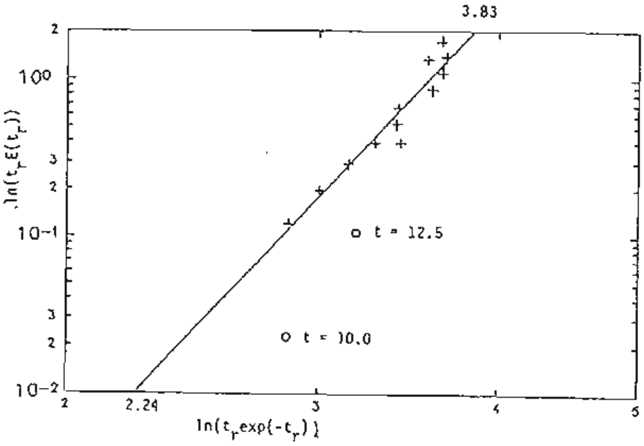
$$x = 1 - C/C_0 = 1 - \left[\frac{1}{1+0.371(22.494/n)}\right]^n$$

$= 0.9984$, with n = 13.1

0.9976, with n = 9.9

In a plug flow unit, $x = 1 - \exp[-0.371(22.049)] = 0.9998$. Taking into consideration the probable inaccuracies of tracer and kinetic data, these three values are in agreement.

t	C	$E(t_r)$	t_r	$t_rE(t_r)$	$t_r\exp(-t_r)$
7.5	0	0	0.333	0	0.2387
10	1.2	0.051	0.445	0.0227	0.2852
12.5	4.5	0.190	0.556	0.1056	0.3189
15	14.2	0.590	0.667	0.3935	0.3423
17.5	40.7	1.718	0.778	1.3366	0.3574
20	46.4	1.958	0.889	1.7407	0.3654
22.5	32.9	1.388	1.000	1.3884	0.3679
25	23.5	0.992	1.111	1.1025	0.3658
27.5	16.6	0.7	1.223	0.8561	0.3600
30	11.8	0.498	1.334	0.6643	0.3514
32.5	8.5	0.359	1.445	0.5188	0.3407
35	6.0	0.253	1.556	0.3937	0.3283
37.5	4.1	0.173	1.667	0.2884	0.3148
40	2.6	0.1098	1.778	0.1952	0.3004
42.5	1.5	0.0633	1.889	0.1196	0.2857



P5.02.06. LINEARIZED GAMMA PLOT OF CURVE FIT DATA

The impulse response data of a pilot hydrofiner shown with the first figure are fitted by

$$C = (-0.1581+0.7449t-0.2934t^2)/(1-2.0742t+1.4036t^2)$$

Then these data are obtained,

$$\int_0^\infty Cdt = 0.8312, \quad \int_0^\infty tCdt = 0.8408, \quad \int_0^\infty t^2Cdt = 0.9472,$$

$$\bar{t} = 0.8408/0.8312 = 1.0115,$$

$$\sigma^2(t_r) = -1 + \frac{0.9472}{0.8312(1.0115)^2} = 0.1138, \quad n = 1/0.1138 = 8.79$$

$$C^0 = \int_0^\infty Cdt\ /\bar{t} = 0.8312/1.0115 = 0.8217$$

$$E(t_r) = C/C^0 = C/0.8217, \quad t_r = t/1.0115$$

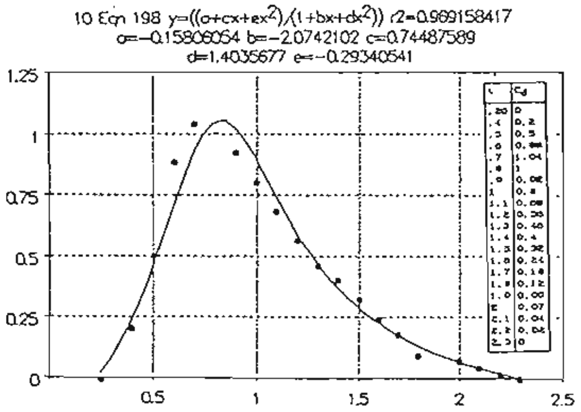
The linearized form of the Gamma distribution is

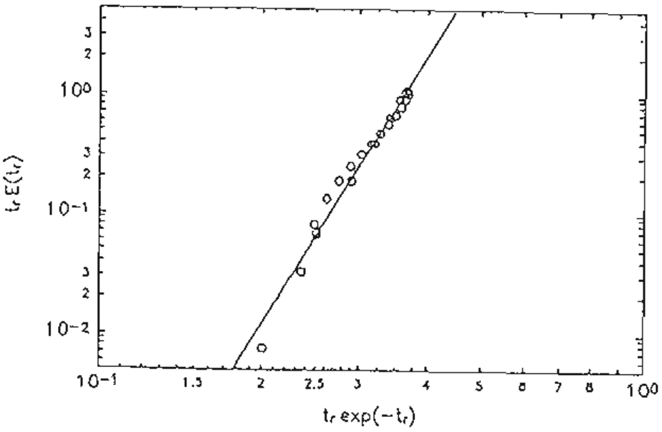
$$\ln[t_rE(t_r)] = \ln[n^n/(n-1)!] + n\ln[t_r\exp(-t_r)]$$

The data plotted this way have the equation

$$\ln(y) = 15.89 + 7.63\ln(x)$$

Accordingly n = 7.63, a value in rough agreement with n = 8.79 found from the variance.





P5.02.07. GAMMA DISTRIBUTION WITH TIME DELAY

A generalization of the Gamma distribution is obtained by incorporatinbg a time delay, $t_D = \tau\bar{t}$, where τ is a fraction. This model corresponds to a Gamma vesel in series with a PFR whose volume is a fraction τ of the total. Accordingly, $\bar{t}_1 = (1-\tau)\bar{t}$ and $\bar{t}_2 = \tau\bar{t}$, so the transfer function is

$$\bar{C}/\bar{C}_f = \frac{\exp(-\tau s)}{[1+(1-\tau)\bar{t}s/n]^n}$$

For an impulse input, $\bar{C}_f = C^o\bar{t}$. Then the inverse transform is

$$E(t_r) = C/C^o = \frac{n^n}{(1-\tau)\Gamma(n)}[\frac{t_r-\tau}{1-\tau}]^{n-1}\exp[-n(\frac{t_r-\tau}{1-\tau})]$$

The variance and skewness are evaluated directly from the transfer function by the method of problem P5.02.01,

$$\sigma^2(t_r) = (1-\tau)^2/n$$

$$\gamma^3(t_r) = 2(1-\tau)^3/n^2$$

from which

$$n = 4(\sigma^2)^3/(\gamma^3)^2$$

$$\tau = 1-2(\sigma^2)^2\gamma^3$$

Thus the two parameters of the distribution can be determined after finding the variance and skewness from the experimental RTD.

For the data cited in problem P5.02.02, the results are:

$\sigma^2 = 0.06178$, $\gamma^3 = 0.01217$, $n = 6.3893$, $\tau = 0.3728$, $\Gamma(6.3693) = 227.67$.

Accordingly for the Gamma with time delay,

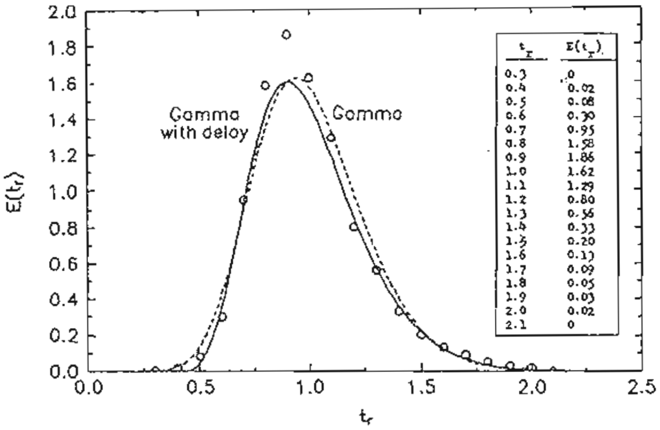
$$E(t_r) = 859.96[\frac{t_r-0.3728}{0.6272}]^{5.3683}\exp[-10.1535(t_r-0.3728)] \quad (1)$$

Without time delay,

$$n = 1/0.06178 = 16.19,\ \Gamma(n) = 221.7(10)^{10}$$

$$E(t_r) = 17.06(10)^6\ t_r^{15.19}\exp(-16.19t_r) \quad (2)$$

These two equations are plotted. The main difference is near the beginning. The great difference in the values of n may be noted.



t_r	$E(t_r)$
0.3	0
0.4	0.02
0.5	0.08
0.6	0.30
0.7	0.95
0.8	1.58
0.9	1.86
1.0	1.62
1.1	1.29
1.2	0.80
1.3	0.56
1.4	0.33
1.5	0.20
1.6	0.13
1.7	0.09
1.8	0.05
1.9	0.03
2.0	0.02
2.1	0

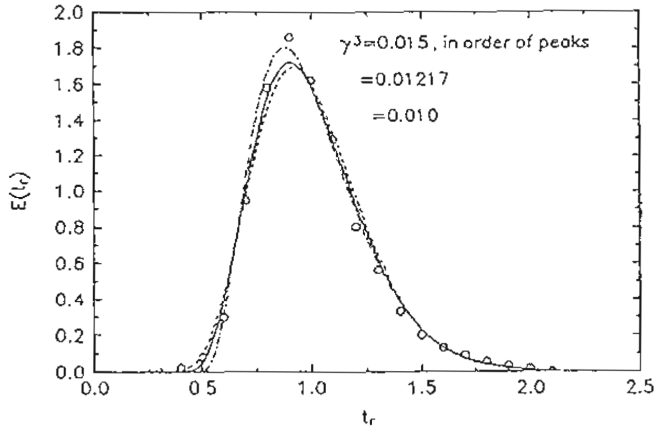
P5.02.07a. SENSITIVITY TO THE THIRD MOMENT

Find the effect of relatively small changes in the value of the third moment on the RTD of problem P5.02.07.

Calculated values of the third moment are often uncertain because of the possible inaccuracy of the measured (C, t) data. The table and the graphs cover a range of possible values of the third moment. It appears that some adjustment of γ^3 can improve correlation of the data which are shown in this case as scattered points.

$$E(t_r) = \frac{n^n}{(1-\tau)\Gamma(n)}\left[\frac{t_r-\tau}{1-\tau}\right]^{n-1}\exp\left[-n\left(\frac{t_r-\tau}{1-\tau}\right)\right]$$

γ^3	τ	n	$\Gamma(n)$	$n^n/(1-\tau)\Gamma(n)$
0.010	0.2366	9.432	101855	20033
0.01217	0.3728	6.368	228	924
0.015	0.4911	4.192	7.616	104.9



P5.02.08. NORMALIZATION OF THE GAUSSIAN DISTRIBUTION

The statistical Gaussian distribution is

$$C(t_r) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(t_r-1)^2}{2\sigma^2}\right], \qquad -\infty < t_r < +\infty$$

When it is restricted to the plus range, $0 < t_r < \infty$, a normalization is required. For the RTD,

$$E(t_r) = C/\int_0^\infty C\,dt_r$$

The value of the integral is given by Abramowitz & Stegun (Section 7.1.22, 1964). Then the result becomes

$$E(t_r) = f(\sigma)\exp\left[-\frac{(t_r-1)^2}{2\sigma^2}\right]$$

where

$$f(\sigma) = \frac{\sqrt{2/\pi\sigma^2}}{1+\mathrm{erf}(1/\sigma\sqrt{2})}$$

For convenience, these approximations have been obtained by curve fitting and apply over the range $0.1 < \sigma^2 < 1.0$.

$$f(\sigma) \cong \sqrt{0.07105 + 0.1516/\sigma^2} \qquad 0.1<\sigma^2<1.0$$

$$f(\sigma) \cong \frac{1 + 1.5410\sigma^2}{0.4510 + 4.8860\sigma^2} \qquad 0.1<\sigma^2<1.0$$

$$f(\sigma) = 1/\sigma\sqrt{2\pi} \qquad \sigma^2 < 0.1$$

The normalization factor is tabulated.

σ^2	$1/f(\sigma)$
0.1	0.9992
0.2	0.9872
0.3	0.966
0.4	0.9429
0.5	0.9213
0.6	0.9015
0.7	0.8839
0.8	0.8682
0.9	0.8540
1.0	0.8413

P5.02.09. GAUSSIAN DISTRIBUTION, RESPONSE FUNCTIONS

The Age $F(t_r)$ and intensity $\Lambda(t_r)$ functions will be derived for the Gaussian distribution. From problem P5.02.08,

$$z = (t_r-1)/\sqrt{2\sigma^2}$$

$$E(t_r) = \frac{\sqrt{2/\pi\sigma^2}}{1+\mathrm{erf}(1/\sigma\sqrt{2})} \exp(-z^2)$$

The Age function becomes

$$F(t_r)_{\mathrm{Gauss}} = \int_0^{t_r} E(t_r)dt_r = \frac{\mathrm{erf}(\ 0.707/\sigma)+\mathrm{erf}(z)}{1+\mathrm{erf}(0.707/\sigma)}$$

This integration is given by Abramovitz & Stegun (1964). The intensity function becomes,

$$\Lambda(t_r)_{\mathrm{Gauss}} = \frac{E(t_r)}{1-F(t_r)} = \frac{\sqrt{2/\pi\sigma^2}}{\sigma[1-\mathrm{erf}(z)]} \exp(-z^2)$$

Application of L'Hopital's Rule leads to the result

$$\Lambda(\infty) \Rightarrow \infty$$

Some evaluatioons of these functions when $\sigma^2 = 0.2$ are given by these formulas and in the table:

$$z = (t_r-1)/\sqrt{0.4}$$

$$\mathrm{erf}(1/0.2\sqrt{0.2}) = 0.97465$$

$$E(t_r) = 0.9035 \exp(-z^2)$$

$$F(t_r) = \frac{0.97465+\mathrm{erf}(z)}{1.97465}$$

$$\Lambda(t_r) = \frac{1.7841 \exp(-z^2)}{1-\mathrm{erf}(z)}$$

In the table, the quantities in parentheses are obtained by extrapolation of a curve fit of the preceding data.

t_r	z	erf(z)	$E(t_r)$	$F(t_r)$	$\Lambda(t_r)$
0	-1.5811	-0.9745	0.07417	0	0.07417
0.25	-1.1858	-0.9065	0.2214	0.0345	0.2294
0.5	-0.7921	-0.7361	0.4824	0.1208	0.5487
1	0	0	0.9035	0.4936	1.7841
1.5	0.7921	0.7361	0.4824	0.8664	3.0696
2	1.5811	0.9745	0.07417	0.9871	5.3437
2.265	2.000	0.9953	0.0165	0.9976	6.692
2.5	2.3716	1.0000	0.00326	1.0000	(8.06)
3					(10.3)
3.5					(12.3)
4					(13.7)

P5.02.10. GAUSS AND GAMMA FUNCTIONS WITH $\sigma^2(t_r) = 0.5$

The Gamma functions are

$$E(t_r) = 4\ t_r\exp(-2t_r)$$

$$F(t_r) = \int_0^{t_r} E(t_r)dt_r = 1 - (1+2t_r)\exp(-2t_r)$$

$$\Lambda(t_r) = 4t_r/(1 + 2t_r)$$

$$\Lambda(\infty) \Rightarrow \infty$$

The Gauss functions are

$$E(t_r) = \frac{1+1.541(0.5)}{0.451+4.886(0.5)} \exp[-(t_r-1)^2]$$

$$= 0.6118 \exp([-(t_r-1)^2]$$

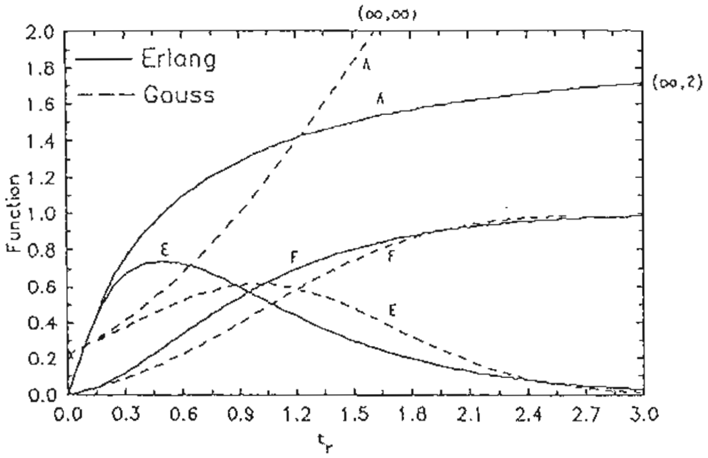
$$F(t_r) = \int_0^{t_r} E(t_r)dt_r, \quad \text{by numerical integration}$$

$$\Lambda(t_r) = E(t_r)/[1-F(t_r)]$$

$$\Lambda(\infty) \Rightarrow \infty$$

The data of the table are of the Gaussian functions.

t_r	$E(t_r)$	$F(t_r)$	$\Lambda(t_r)$
0	0.225	0	0.225
0.2	0.323	0.054	0.341
0.4	0.427	0.130	0.490
0.6	0.521	0.225	0.672
0.8	0.588	0.336	0.886
1.0	0.612	0.457	1.126
1.2	0.588	0.578	1.392
1.4	0.521	0.689	1.677
1.6	0.427	0.784	1.979
1.8	0.323	0.859	2.293
2	0.225	0.914	2.611
2.2	0.145	0.951	2.928
2.4	0.086	0.973	3.216
2.6	0.047	0.986	3.452



P5.02.11. COMPARISON OF GAMMA AND GAUSSIAN RTD'S

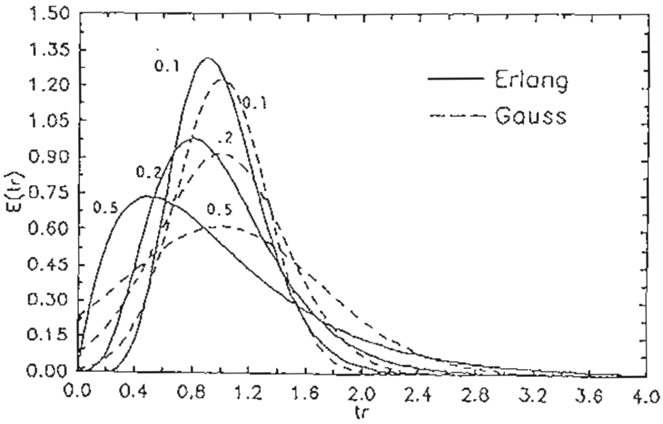
The plots of $E(t_r)$ are compared for $\sigma^2(t_r) = 0.1$, 0.2 and 0.5; or n = 10, 5 and 2. The Gamma function is

$$E(t_r) = \frac{n^n}{(n-1)!}\, t_r^{n-1}\exp(-nt_r)$$

and the Gaussian,

$$E(t_r) = \sqrt{0.07105+0.1516/\sigma^2}\ \exp[-(t_r-1)^2/2\sigma^2]$$

At larger values of σ^2 the Gaussian $E(t_r)$ is increasingly non-zero at the origin, whereas the Gamma always is zero.



P5.02.12. PEAK VALUES OF GAMMA AND GAUSSIAN RTD'S

The maximum value of an $E(t_r)$ profile is conveniently recognizable, and is related to the variance in both distributions.

For the Gamma,

$$E(t_r) = \frac{n^n}{\Gamma(n)}\, t_r^{n-1}\exp(-nt_r)$$

For the maximum,

$$\frac{dE(t_r)}{dt_r} = 0$$

$$= \frac{n^n}{\Gamma(n)}\exp(-nt_r)[(n-1)t_r^{n-2} - nt_r^{n-1}]$$

Whence,

$$t_r = (n-1)/n$$

$$E(t_r)_{max} = \frac{n(n-1)^{n-1}}{\Gamma(n)}\exp(1-n), \qquad n = 1/\sigma^2$$

For the Gaussian,

$$E(t_r) = f(\sigma)\exp[-(t_r-1)^2/2\sigma^2]$$

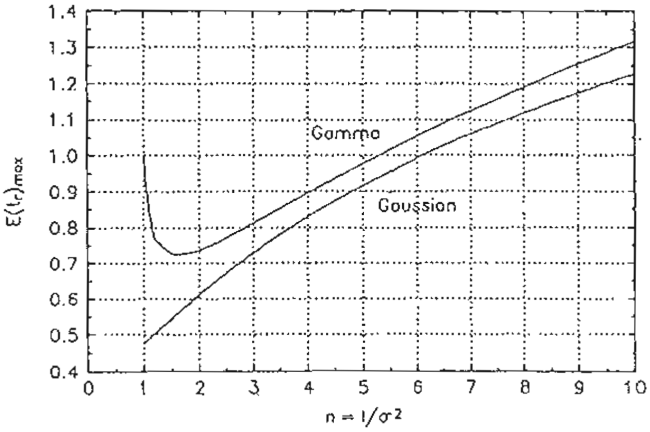
For the maximum,

$$\frac{dE(t_r)}{dt_r} = 0$$

$$= f(\sigma)\ [-\frac{2(t_r-1)}{2\sigma^2}\exp[-(t_r-1)^2/2\sigma^2]$$

Whence $t_r = 1$ and

$E(t_r) = f(\sigma) \cong \sqrt{0.0715 + 0.1516/\sigma^2}$, $0.1 < \sigma^2 < 1.0$
Other expressions for $f(\sigma)$ are in problem p5.02.08.



P5.02.13. TRIANGULAR RESPONSE. EQUIVALENT GAMMA AND GAUSSIAN RTD'S

A triangular shaped tracer response has the equation $C_\delta = 2.5 - 0.5t$, for $1 \le t \le 5$ and zero elsewhere. The Gamma and Gaussian $E(t_r)$ with the same variance will be found.

These quantities are evaluated,

$$\int_0^\infty C dt = 4, \quad \int_0^\infty tC dt = 9.333, \quad \int_0^\infty t^2 C dt = 25.333,$$

$$\bar{t} = 9.333/4 = 2.333, \quad C^0 = 4/2.333 = 1.7143, \quad t_r = t/2.333$$

$$\sigma^2(t_r) = -1 + \frac{25.333}{4(2.333)^2} = 0.1633, \quad n = 1/0.1633 = 6.125,$$

$$\Gamma(6.125) = 148.73$$

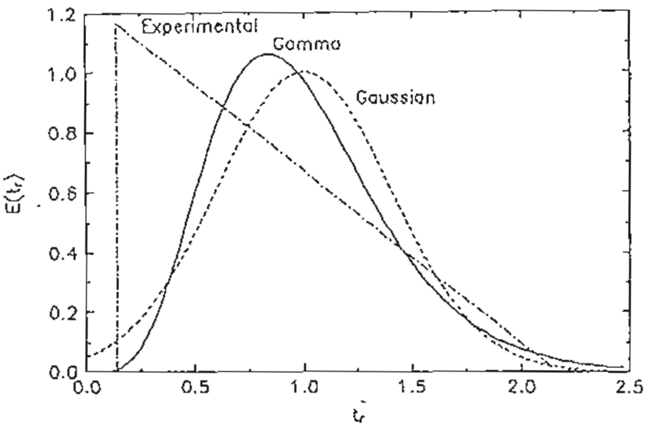
$$E(t_r)_{data} = C_\delta/C^0 = (2.5-1.167t_r)/1.7143, \quad 3/7 \le t_r \le 15/7$$

$$E(t_r)_{Gamma} = 445.26\, t_r^{5.125} \exp(-6.125 t_r)$$

$$E(t_r)_{Gauss} = \frac{1+1.5411\sigma^2}{0.451+4.886\sigma^2} \exp[-(t_r-1)^2/2\sigma^2]$$

$$= 1.0022 \exp[-3.0618(t_r-1)^2]$$

The three profiles of $E(t_r)$ are compared.



P5.02.14. PARABOLIC RESPONSE. EQUIVALENT GAMMA AND GAUSSIAN

The response curve to an impulse input has the parabolic equation,

$C_\delta = 5 - 1.25(t-2.5)^2$, $0.5 \le t \le 4.5$ and zero elsewhere
The RTD's, $E(t_r)$, are to be made for Gamma and Gauss as well as the direct data.

These quantities are found,

$$\int_0^\infty C dt = 13.33, \quad \int_0^\infty tC dt = 33.33, \quad \int_0^\infty t^2 C dt = 94.00,$$

$\bar{t} = 33.33/13.33 = 2.5$, $t_r = t/2.5$, $C^0 = 13.33/2.5 = 5.33$,
$\sigma^2(t) = 94/13.33 - (2.5)^2 = 0.8018$, $\sigma^2(t_r) = 0.8018/(2.5)^2 = 0.1283$, $n = 1/0.1283 = 7.795$, $\Gamma(7.795) = 3345.4$

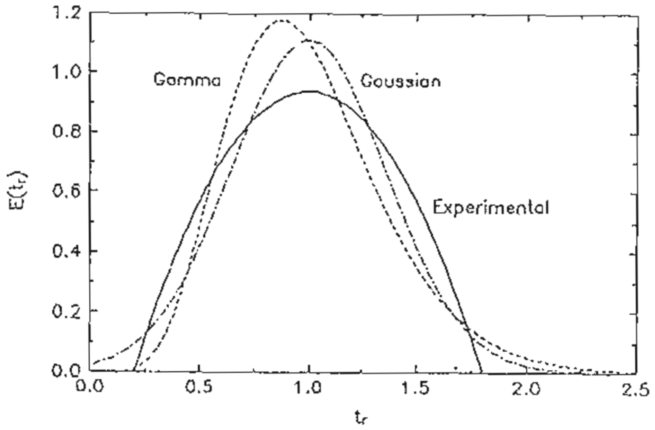
$$E(t_r)_{data} = C_\delta/C^0 = 0.1876\ [5 - (2.5t_r-2.5)^2], \quad 0.2 \le t_r \le 1.8$$

$$E(t_r)_{Gamma} = 2674.6\ t_r^{6.795}\exp(-7.795t_r),$$

$$E(t_r)_{Gauss} = \frac{1+1.5411\sigma^2}{0.451+4.886\sigma^2}\exp[-(t_r-1)^2/2\sigma^2]$$

$$= 1.1112\ \exp[-3.8971(t_r-1)^2]$$

The three profiles are only roughly similar.



P5.02.15. GRAM-CHARLIER DISTRIBUTION

The Gram-Charlier series (Kendall, Advanced Theory of Statistics, volume 1, 1958) is an infinite series whose coefficients involve the Gaussian distribution and its derivatives. The derivatives in turn are expressed in terms of the moments. The series truncated at the coefficient involving the fourth moment is:

$$E(t_r)_{GC} = E(t_r)_{Gauss}[1 - m_3(3z-z^3)/6 \quad (m_4-3)(z^4-6z^2+3)/24]$$

where

$$z = (t_r-1)/\sigma, \quad \sigma^2 = \int_0^\infty (t_r-1)^2 E(t_r)dt_r,$$

$$m_3 = (\gamma/\sigma)^3 = \int_0^\infty \left(\frac{t_r-1}{\sigma}\right)^3 E(t_r)dt_r,$$

$$m_4 = (\delta/\sigma)^4 = \int_0^\infty \left(\frac{t_r-1}{\sigma}\right)^4 E(t_r)dt_r.$$

In this problem the Gram-Charlier will be compared with the Gamma Gauss distributions for an impulse response curve with the equation

$C_\delta = 0.4\ t^{0.5}(3-t)$, $0 \le t \le 3$, and zero elsewhere
The integrals are found trapezoidally,

$$\int_0^\infty C dt = 1.6623, \quad \int_0^\infty tC dt = 2.1378, \quad \bar{t} = 2.1378/1.6623 = 1.286,$$

$t_r = t/1.286$,

$$E(t) = C_\delta/1.6623 = 0.2406\ t^{0.5}(3-5)$$

$$\sigma^2(t_r) = (1/\bar{t}^2)\int_0^\infty (t-\bar{t})^2 E(t)dt = 0.2959,$$

$$\gamma^3(t_r) = (1/\bar{t}^3)\int_0^\infty (t-\bar{t})^3 E(t)dt = 0.0360,$$

$$\delta^4(t_r) = (1/\bar{t}^4)\int_0^\infty (t-\bar{t})^4 E(t)dt = 0.1874$$

For the original data,

$$E(t_r)_{data} = \bar{t}C_\delta/\int_0^\infty Cdt = 0.4512\ t_r^{0.5}(2.333-t_r),\ 0\le t_r \le 2.333 \qquad (1)$$

For the Gamma distribution,

$$n = 1/0.2959 = 3.3792,\ \Gamma(n) = 2.915,$$

$$E(t_r)_{Gamma} = 21.01\ t_r^{2.379}\exp(-3.379t_r) \qquad (2)$$

For the Gaussian,

$$E(t_r)_{Gauss} = \frac{1+1.541\sigma^2}{0.451+4.886\sigma^2}\exp[-(t_r-1)^2/2\sigma^2]$$

$$= 0.7676\ \exp[-1.6898(t_r-1)^2] \qquad (3)$$

For the Gram-Charlier,

$$m_3 = 0.2237,\ m_4 = 2.1403,\ z = 1.8383(t_r-1)$$

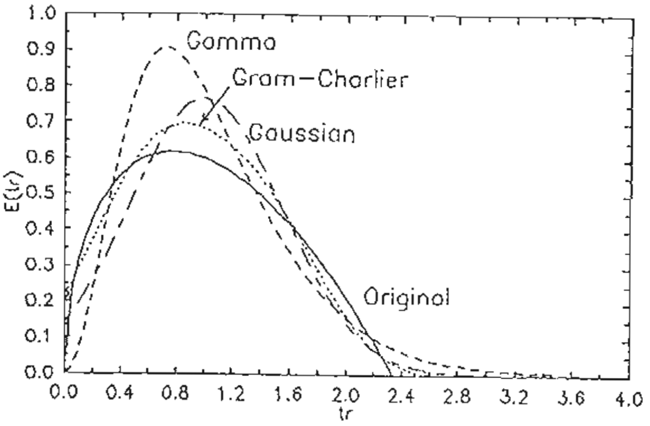
$$E(t_r)_{GC} = E(t_r)_{Gauss}[1-0.2237(3z-z^2)/6 + (2.1403-3)(z^4-6z^2+3)/24)] \qquad (4)$$

Plots of Equations (10-(4) reveal the Gram-Charlier to be closest to the original data, except near $t_r = 0$.

Another comparison is afforded by calculating the segregated conversion of a first order reaction. Results are tabulated for two values of $k\bar{t}$.

$$(C/C^0)_{segregated} = \int_0^\infty \exp(-k\bar{t}t_r)E(t_r)dt_r$$

	C/C_0	
Model	$k\bar{t} = 1.5$	$k\bar{t} = 3$
Original	0.3013	0.1408
Gamma	0.2891	0.1168
Gauss	0.2758	0.1148
GC	0.3097	0.1418



P5.02.16. GRAM-CHARLIER DISTRIBUTION WITH $\sigma^2 = 0.5$

Construct the third and fourth order Gram-Charlier distributions corresponding to an Erlang with $\sigma^2(t_r) = 0.5$ or $n = 2$.

$$E(t_r)_{Erlang} = 4\ t_r\exp(-2t_r) \qquad (1)$$

$$E(t_r)_{Gauss} = \frac{1+1.5411\sigma^2}{0.451+4.886\sigma^2} \exp[-(t_r-1)^2/2\sigma^2]$$

$$= 0.6118 \exp[-(t_r-1)^2] \qquad (2)$$

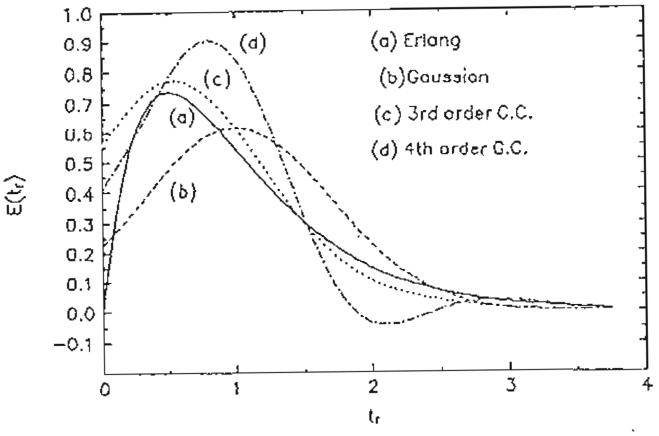
$m_3 = 1.4188$

$m_4 = 6.0282$

$z = \sqrt{.2}(t_r-1)$

$$E(t_r)_{GC} = E(t_r)_{Gauss}[1 - m_3(3z-z^2)/6 + (m_4-3)(z^4-6z^2+3)/24] \qquad (3,\ 4)$$

The third order Gram-Charlier approximates the Erlang more closely than does the fourth order.



P5.02.17. COMPARISON OF THREE DISTRIBUTIONS

The response to an impulse input to a vessel has the properties: $\bar{t} = 2$, $\sigma^2(t) = 1$, $\gamma^3(t_r) = 0.075$. Prepare $E(t_r)$ for Gamma, Gaussian and third order Gram-Charlier.

$\sigma^2(t_r) = \sigma^2(t)/\bar{t}^2 = 0.25$, $n = 4$

$$E(t_r)_{Gamma} = (4^4/3!)\ t_r^3 \exp(-4t_r) \qquad (1)$$

$$E(t_r)_{Gauss} = \frac{1+1.541\sigma^2}{0.451+4.886\sigma^2} \exp[-(t_r-1)^2/2\sigma^2]$$

$$= 0.8283 \exp[-2(t_r-1)^2] \qquad (2)$$

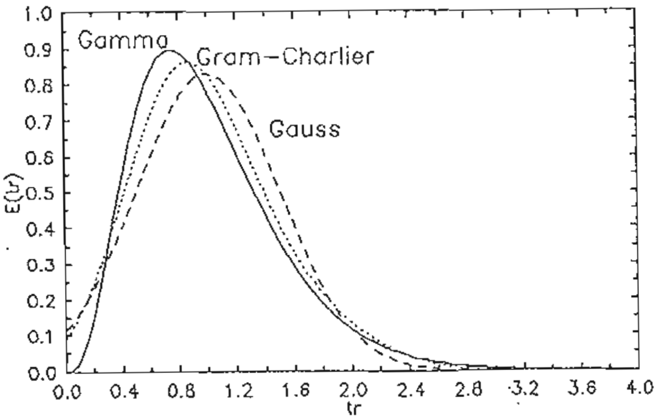
$m_3 = (\gamma/\sigma)^3 = 0.6$

$z = (t_r-1)/\sigma(t_r) = 2(t_r-1)$

$\psi = 1 - m_3(3z-z^2)/6 = 1 - 0.1(3z-z^2)$

$$E(t_r)_{GC} = E(t_r)_{Gauss}[1 - 0.1(3z-z^2)] \qquad (3)$$

The plots are only roughly in agreement.



P5.02.18. WEIBULL DISTRIBUTION

The known data about a response to an impulse input of tracer are that the peak of the curve is at $t = 0.6$ and that the variance is $\sigma(t) = 0.64$.

(a) Fit a Weibull distribution to these results,

$C = (\eta/\sigma)(t/\sigma)^{\eta-1} \exp[-(t/\sigma)^{\eta}]$

(b) Find C/C_0 for a second order reaction with $kC_0 = 5$, assuming segregated flow, with both Weibull and Gamma distributions.

First find the parameter η. Let $z = t/\sigma$. Find the maximum of the curve which is at $t = 0.6$ or at $z = 0.6/0.8 = 0.75$. On differentiating for the maximum, the equation to be solved is

$-\eta(0.75)^{\eta} + \eta - 1 = 0$, with the result $\eta = 2.16$. The correlation becomes

$$C(t) = (2.16/0.8)\ (1.25t)^{1.16}\exp[-(1.25)^{2.16}]$$
$$= 3.498\ t^{1.16}\exp(-1.6193\ t^{2.16})$$

Proceeding further,

$\int_0^{\infty} Cdt = 1.000,\quad \int_0^{\infty} tCdt = 0.7085,\quad \bar{t} = 0.7085,\quad t_r = t/0.7085$

$$E(t_r)_{Weibull} = \bar{t}E(t) = \bar{t}C(t)$$
$$= 2.3452\ t_r^{1.16} \exp(-0.7692\ t_r^{2.16}) \qquad (1)$$

For the Gamma distribution,

$n = 1/\bar{t}^2\sigma^2(t) = 1/(0.7085)^2(0.64) = 3.11,\ \Gamma(3.11) = 2.219$

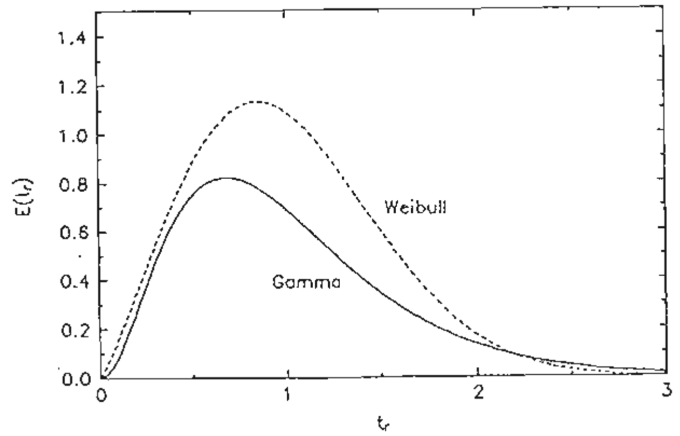
$E(t_r)_{Gamma} = 15.36\ t_r^{2.11} \exp(-3.11\ t_r) \qquad (2)$

In segregated flow reaction,

$$C/C_0 = \int_0^{\infty} \frac{E(t_r)}{1+0.7085(5)t_r}\, dt_r = 0.3675, \quad \text{Weibull}$$

0.2666, Gamma

0.2201, Plug flow



P5.03.01. TRANSFER FUNCTION OF A COMPLEX NETWORK

Find the transfer fuction, $G_5 = \bar{C}_5/\bar{C}_0$, of the given network, and the result when the individual transfer functions all have the form $G_i(s) = 1/(s+\alpha)$.

The several relations are:

$$(\beta V'\bar{C}_0 + R\bar{C}_4)G_1G_2 = (\beta V' + R)\bar{C}_2$$

$$(\beta V' + R)\bar{C}_2 + [(1-\beta)V' - R)\bar{C}_3 = V'\bar{C}_5$$

$$\bar{C}_0G_3 = \bar{C}_3$$

$$\bar{C}_3G_4 = \bar{C}_4 = \bar{C}_0G_3G_4$$

$$\bar{C}_2 = \frac{(\beta V'\bar{C}_0 + R\bar{C}_4)G_1G_2}{\beta V' + R} = \frac{[\beta\bar{C}o + (R/V')\bar{C}4]G1G^2}{\beta + R/V'}$$

$$= \frac{[\beta + (R/V')G_3G_4]G_1G_2\bar{C}o}{\beta + R/V'}$$

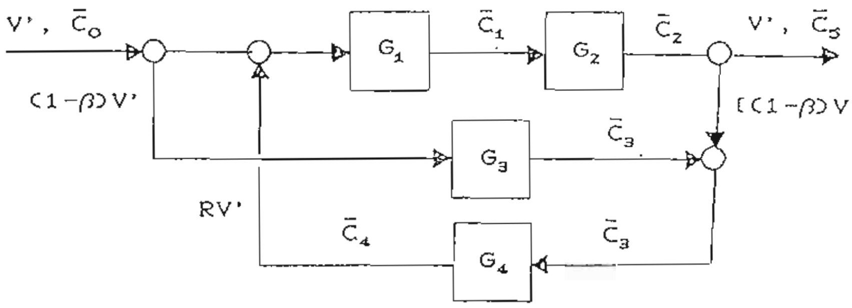
$$\bar{C}_5 = (\beta + R/V')\bar{C}_2 + (1-\beta-R/V')\bar{C}_3$$

$$G_5 = \bar{C}_5/\bar{C}_0 = [\beta + (R/V')G_3G_4]G_1G_2 + (1-\beta-R/V')G_3$$

When $G_i(s) = 1/(s+\alpha)$,

$$G_5(s) = [\ \frac{A}{(s+\alpha)^4} + \frac{B}{(s+\alpha)^2} + \frac{C}{s+\alpha}\ ]\ \bar{C}_0(s)$$

These relatively simple transforms can be inverted to find $C_5(t)$ when $\bar{C}_0(s)$ is known.



P5.03.02. STIRRED VESSEL WITH TWO IMPELLERS

A deep stirred vessel is provided with two impellers on a single shaft. Feed is between the impellers. A plausible model for such a vessel is two CSTR's partly in parallel and partly in series, followed by a PFR, as indicated on the sketch. Let α be the fraction of the total feed that goes to the first CSTR, and let β and γ be the fractions of the volume occupied by each of the CSTRs. Find the transfer function of the whole vessel and the response to impulse input.

The individual residence times are expressed in terms of the overall residence time $\bar{t} = V_r/V'$ as,

$$\bar{t}_1 = (\beta/\alpha)\bar{t},\quad \bar{t}_2 = \gamma\bar{t},\quad \bar{t}_3 = (1-\beta-\gamma)\bar{t}.$$

The individual transfer functions are,

$$G_1 = 1/(1+\bar{t}_1 s),\ G_2 = 1/(1+\bar{t}_2 s),\quad G_3 = \exp(-\bar{t}_3 s).$$

Overall,

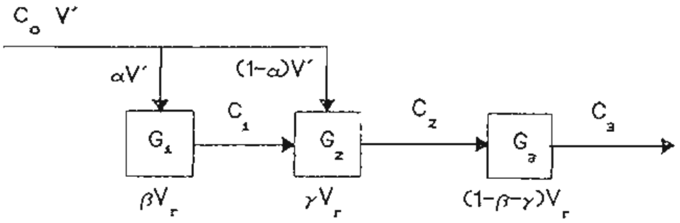
$$[\alpha G_1 + (1-\alpha)]\bar{C}_0 G_2 G_3 = \bar{C}_3$$

Upon making substitutions,

$$\bar{C}_3/\bar{C}_0 = \frac{\alpha\ \exp(-\ \bar{t}_3 s)}{(1+\bar{t}_1 s)(1+\bar{t}_2 s)} + \frac{(1-\alpha)\ \exp(-\ \bar{t}_3 s)}{1+\bar{t}_2 s}$$

For impulse input, $\bar{C}_0 = C^0\bar{t}$. When inverting, note that

$$\mathcal{L}^{-1}F(s)\ e^{-as} = f(t-a),\quad t\geq a$$



P5.03.03. MODEL OF A FLUIDIZED BED REACTOR

A fluidized bed reactor has a substantial free space above the main level of the catalyst for purpose of disengaging entrainment. In this region plug flow may be assumed to prevail. An overall appropriate model accordingly will consist of well mixed and bypass zones in parallel followed by a plug flow zone. The fraction of flow in bypass is 1-α and the fraction of vessel volume in plug flow is β. Find the transfer function and equations for the responses to step and impulse inputs of tracer.

The individual residence times and transfer functions are,

$$\bar{t}_1 = \frac{(1-\beta)V_r}{\alpha V'} = \frac{(1-\beta)\bar{t}}{\alpha}$$

$$\bar{t}_2 = \beta\bar{t}$$

$$G_1 = 1/(1+\bar{t}_1 s)$$

$$G_2 = \exp(-\bar{t}_2 s)$$

The overall material balance results in

$$\bar{C} = [\alpha G_1 + (1-\alpha)]\bar{C}_0 G_2$$

For step input, $\bar{C}_0 = C_0/s$. Acccordingly,

$$\bar{C}/C_0 = [\frac{\alpha}{s(1+\bar{t}_1 s)} + \frac{1-\alpha}{s}]\ \exp(-\bar{t}_2 s)$$

The inverse is

$$C(t)/C_o = \{(\alpha/\bar{t}_1)[1-\exp(-t/\bar{t}_1)] + (1-\alpha)\}u(t-\bar{t}_2)$$

$$= \quad (\alpha/\bar{t}_1)[1-\exp(-\frac{t-\bar{t}_2}{\bar{t}_1}), \text{ when } t\ge\bar{t}_2$$

$$0, \text{ when } t\le\bar{t}_2$$

For impulse input, replace $\bar{C}_0 = C^0\bar{t}$. Then the inverse is

$$C/C^o = (\alpha/\bar{t}_1)\exp(-\frac{t-\bar{t}_2}{\bar{t}_1}) + (1-\alpha)\ \delta(t-\bar{t}_2), \text{ when } t\ge\bar{t}_2.$$

P5.03.04. BYPASS AND STAGNANCY OF A STIRRED VESSEL

Flow to a vessel is bypassed with a fraction α and a fraction $1-\beta$ of the volume is stagnant. Find the transfer function and the response to step input, $C_f u(t-a)$.

$\bar{t}_1 = (\beta/\alpha)\bar{t}$, in the active zone

$\bar{t}_2 = 0$, in the stagnant zone

$G_1 = 1/(1+\bar{t}_1 s)$, active zone
$G_2 = 0$, stagnant zone
$G_3 = 1$, bypass

The material balance results in

$$\bar{C} = \bar{C}_f(\alpha G_1 + 1 - \alpha) = C_f(\frac{\alpha}{\bar{t}_1 s+1} + 1 - \alpha)\ \frac{\exp(-as)}{s}$$

Inverting,

$$C(t)/C_f = \{\alpha[1 - \exp(-t/\bar{t}_1)] + 1 - \alpha\}\ u(t-a)$$

$$= \alpha[1 - \exp(-\frac{t-a}{\bar{t}_1}) + 1 - \alpha, \qquad t \ge a$$

P5.03.05. THREE UNITS IN PARALLEL

The dynamic behavior of a particular vessel is equivalent to that of three elements in parallel with equal flows to each. Responses of the individual branches to a tracer impulse input have been measured and are represented by the equations

$$C_1 = \exp(-0.5t),\ C_2 = t\ \exp(-t),\ C_3 = t^2\ \exp(-2t) \qquad (1)$$

Find (a) the residence time in the whole vessel; (b) the hypothetical initial concentration, $C^o = m/V_r$; (c) equations for $E(t_r)$, $E(t)$ and $F(t_r)$.

For the entire vessel, the effluent concentration is

$$C = (C_1+C_2+C_3)/3 \qquad (2)$$

The required integrals are found numerically.

$$\int_0^\infty C dt = 1.0832,\ \int_0^\infty tC dt = 2.1247$$

$$\bar{t} = 2.1247/1.0832 = 1.9615,\ t_r = t/1.9615$$

$$C^o = \int_0^\infty C dt/\bar{t} = 1.0832/1.9615 = 0.5522$$

The desired functions are evaluated:

$$E(t) = C/\int_0^\infty C dt = C/1.0832$$

$$E(t_r) = C/C^\circ = C/0.5522$$

$$F(t_r) = F(t) = \int_0^t E(t)dt = \frac{1}{1.0832}\int_0^t C dt \qquad (3)$$

Substitute (1) and (2) into (3) and complete the integration.

P5.03.06. RTD OF A THREE VESSEL NETWORK

The model of a reaction vessel is made up of three CSTRs as shown on the sketch. One of the elements in parallel is twice the size of the other and the element in series with the pair is the same size as the smaller one. Flow is split equally between the parallel elements. The initial average concentration is $C^0 = m/V_r$, where m is the amount of tracer impulsed to the whole vessel of volume V_r. Find the equation of the response, C_4/C°, and its variance. Compare the plot with that of a single CSTR.

Various times and concentrations are,

$$\bar{t} = V_r/V',\quad \bar{t}_1 = \bar{t}/2,\quad \bar{t}_2 = \bar{t},\quad \bar{t}_3 = \bar{t}/4$$

$$C^0 = m/V_r,\quad C_1^0 = 2C^0,\quad C_2^0 = C^0,$$

$$C_1 = C_1^0 \exp(-t/\bar{t}_1) = 2C^0 \exp(-2t_r)$$

$$C_2 = C^0 \exp(-t_r)$$

$$C_3 = 0.5(C_1 + C_2) = 0.5C^0[2\exp(-2t_r) + \exp(-t_r)]$$

The material balance on vessel 3, with $C_4 = 0$ when $t = 0$ is,

$$C_4 + \bar{t}_3 \frac{dC_4}{dt} = C_3$$

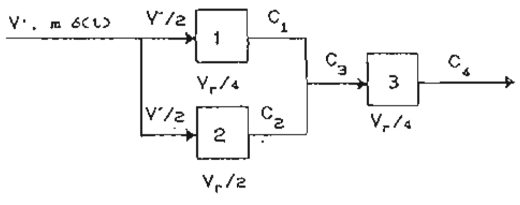
$$0.25\frac{dC_4}{dt_r} + C_4 = 0.5C^0\,[2\exp(-2t_r) + \exp(-t_r)]$$

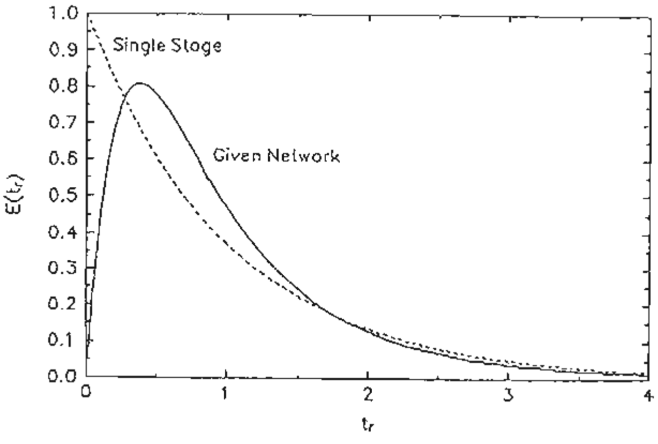
Transforming and solving for the transform,

$$\bar{C}_4 = \frac{4(0.5C^0)}{s+4}\left[\frac{2}{s+2} + \frac{1}{s+1}\right]$$

The inverse is

$$C_4 = 2C^0\left\{\exp(-2t_r) - \exp(-4t_r) + \frac{1}{3}[\exp(-t_r) - \exp(-4t_r)]\right\}$$





P5.03.07. VARIABLE INPUT OF TRACER TO A CSTR

The concentration, C_f, of tracer input to a CSTR varies with time as given in the first two columns of the first table. The outlet concentration profile will be found for two values of the residence time, $\bar{t} = V_r/V' = 5$ or 10.

The material balance of the tracer is

$$V'C_f = V'C + V_r dC/dt$$

or

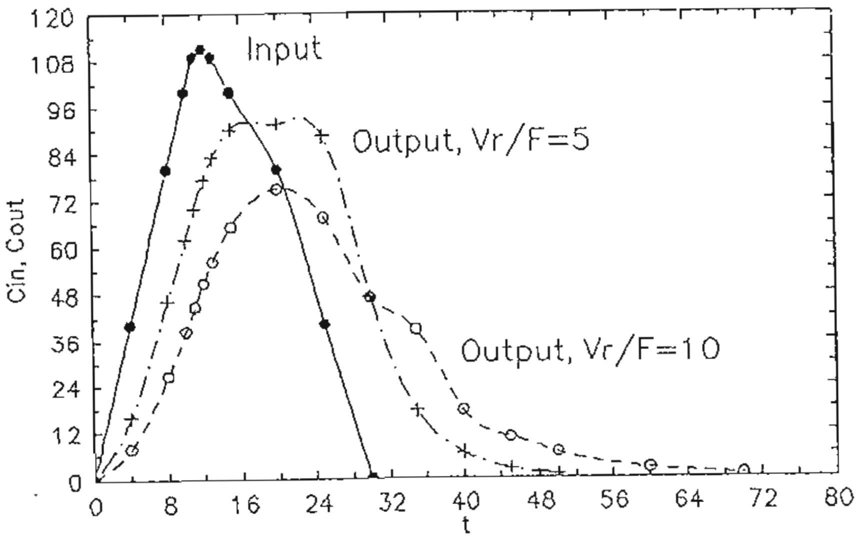
$$\bar{t}\frac{dC}{dt} + C = C_f$$

The solution of this linear first order equation is, for $C_0 = 0$,

$$C = \frac{\exp(-t/\bar{t})}{\bar{t}} \int_0^t C_f \exp(t/\bar{t})dt$$

The integrands are tabulated for the two values of $\bar{t}$ and the values of C are tabulated and graphed.

The various properties of the input and output curves are in the second table. All three values of $\int_0^\infty Cdt$ should be the same; the differences probably are due to errors of trapezoidal integration.



t	C_f	I_{10}	C_{10}	I_5	C_5
0	0	0	0	0	0
4	40	59.7	8.00	89.0	16.0
8	80	178.0	26.7	396.2	46.4
10	100	271.8	38.4	738.9	61.8
11	109	327.5	44.7	983.7	69.7
12	111	368.5	51.0	1223.6	77.1
13	109	400.0	56.4	1467.5	83.1
15	100	448.2	65.3	2008.6	90.3
20	80	591.	74.8	4368.0	91.6
25	40	487.3	67.5	5936.0	88.4
30	0	0	47.0	0	32.5
35			28.5		12.0
40			17.3		4.4
45			10.5		1.6
50			6.4		.6
60			2.3		.08
70			0.9		.01

Function	Input	$\bar{t}=10$	$\bar{t}=5$
$\int C dt$	1883.5	1877.5	2039
$\int tC dt$	26707	44521	38602
$\int t^2 C dt$	443405	1288733	854231
$\bar{t}$	14.2	23.7	18.9
$\sigma^2(t_r)$		0.222	0.169

P5.03.08. TRIANGULAR SHAPED TRACER INPUT TO A CSTR

The curve representing tracer input to a CSTR has the equations $C_f = 0.06t$ when $0 \le t < 5k$ and $C_f = 0.06(10-t)$ when $5 < t < 10$. Find the output concentration as function of time.

The differential equation is

$$\bar{t}\frac{dC}{dt} + C = C_f$$

Three ranges are involved for the solution: $0 \le t \le 5$, $5 \le t \le 10$ and $t \ge 10$.

Over the interval $0 \le t \le 5$,

$$\bar{t}\frac{dC}{dt} + C = 0.06t, \text{ with } C = 0 \text{ when } t = 0$$

The solution by Laplace transform is

$$C = 0.06\bar{t}[t/\bar{t} - 1 + \exp(-t/\bar{t}]$$

$$C(5) = 0.110$$

Over the interval $5 \le t \le 10$,

$$\bar{t}\frac{dC}{dt} + C = 0.06(10-t), \text{ with } C = C_5 = 0.110 \text{ when } t = 5$$

Transforming,

$$\bar{t}(s\bar{C} - C_5) + \bar{C} = 0.06(10/s + 1/s^2)$$

Isolating the $\bar{C}$ and carrying out the inversion yields

$$C = 0.110 \exp(-\frac{t-5}{\bar{t}}) + 0.3[1 - \exp(-\frac{t-5}{\bar{t}})]$$

$$-0.06\bar{t}[\frac{t-5}{\bar{t}} - 1 + \exp(-\frac{t-5}{\bar{t}})] \geq 10,$$

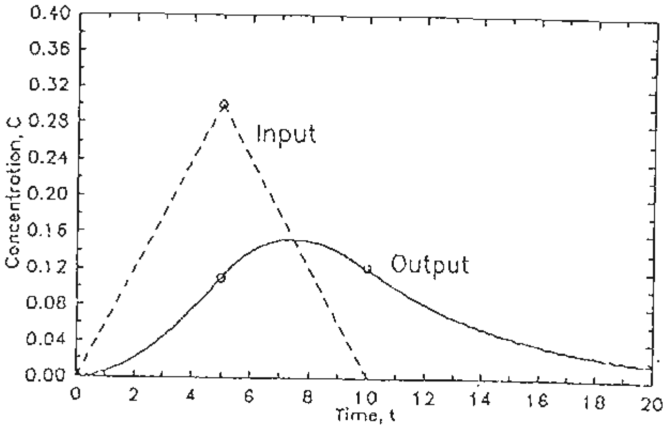
$$C = C_{10} = 0.122 \text{ when } t = 10.$$

Beyond $t = 10$,

$$\bar{t}\frac{dC}{dt} + C = 0, \text{ with } C = C_{10} = 0.122 \text{ when } t = 10$$

The variables are separable, with the solution

$$C = 0.122 \exp(-\frac{t-10}{\bar{t}})$$



P5.03.09. PLUG FLOW REACTOR WITH RECYCLE

A plug flow reactor is operated with a ratio $\beta = R'/V'$ of recycle flow to fresh flow. The reaction is first order. Find the ratio C_r/C_f of the effluent and feed concentrations.

The true residence time is

$$\bar{t} = V_r/(V'+R') = \bar{t}_0/(1+\beta), \quad \bar{t}_0 = V_r/V'$$

The material balance over an element dV_r of the reactor is

$$-V'(1+\beta)\,dC = kC\,dV_r$$

The integral is

$$-\frac{kV_r}{V'(1+\beta)} = -k\bar{t} = \ln(C) + I$$

At the inlet,

$$V_r = 0 \text{ and } (1+\beta)C = C_f + \beta C_r \text{ or } C = (C_f + \beta C_r)/(1+\beta)$$

Evaluating the integration constant and placing $C = C_r$ at the outlet of the reactor, the integral becomes

$$C_r/C_f = \frac{1}{-\beta + (1+\beta)\exp(\frac{k\bar{t}_0}{1+\beta}}$$

For limiting values of β:

$$C_r/C_f = \exp(-kV_r/V'), \quad \text{when } \beta = 0$$

$$1/(1 + kV_r/V'), \quad \text{when } \beta \Rightarrow \infty$$

The last result becomes evident after expansion of the exponential in a power series, $e^x = \sum_0^\infty x^n/n!$.

P5.03.10. GAMMA DISTRIBUTION WITH TIME DELAY AND BYPASS

A vessel with a Gamma RTD is in series with a PFR whose volume is a fraction τ of the total, with bypass of a fraction $1-\beta$ of the total flow. The variance and the skewness of the response to an impulse input are to be found.

The individual residence times are

$$\bar{t}_1 = (1-\tau)V_r/\beta V' = [(1-\tau)/\beta]\bar{t}, \quad \bar{t}_2 = \tau\bar{t}.$$

and the individual transfer functions are

$$G_1 = \frac{1}{(1+\bar{t}_1 s/n)^n} = \frac{1}{[1+(1-\tau)\bar{t}s/\beta n]^n}$$

$$G_2 = \exp(-\bar{t}_2) = \exp(-\tau\bar{t}s)$$

Overall,

$$\bar{C}/\bar{C}_f = \beta G_1 G_2 + (1-\beta)G_2$$

For impulse input, $C_f = C^0\bar{t}\delta(t)$ and $\bar{C}_f = C^0\bar{t}$. Consequently the transform of $E(t_r)$ is

$$E(s) = \beta\left[\frac{1}{1+(1-\tau)\bar{t}s/\beta n}\right]^n \exp((-\tau\bar{t}s) + (1-\beta)\exp(-\tau\bar{t}s)$$

The variance and skewness are derived from this transform by the formulas of problem P5.02.01 with these results.

$$\sigma^2(t_r) = (1-\tau)^2\left(\frac{n+1}{\beta n} - 1\right)$$

$$\gamma^3(t_r) = (1-\tau)^3\left[2 - \frac{3(n+1)}{\beta n} + \frac{(n+1)(n+2)}{(\beta n)^2}\right]$$

When experimental $E(t_r)$ data are known, the time delay τ is the value of t_r when $E(t_r) = 0$. The moments also are obtained from the data. Then values of the other parameters, n and β, can be deduced from the given equations. Some numerical examples are tabulated.

τ	$\sigma^2=0.25$, $\gamma^3=0.02$		$\sigma^2=.25$, $\gamma^3=0.05$		$\sigma^2=0.10$, $\gamma^3=0.02$	
	n	β	n	β	n	β
0.2	5.98	0.839	4.76	0.870	6.82	0.992
0.3	6.4	0.766	4.76	0.801	5.57	0.979
0.4	8.42	0.660	5.47	0.698	4.57	9.53
0.45	11.6	0.594				
0.5	24.0	0.521	9.00	0.555	3.90	0.897

P5.03.11. SQUARE PULSE INPUT TO TWO STAGES

Concentration of tracer input to a two stage CSTR is represented by $C_f = 2.0$ when $1 \le t \le 3$ and zero elsewhere. The residence time in each stage is $\bar{t}_i = 1$. Find the concentrations of effluents from both vessels.

First stage material balance is

$$C_f = C_1 + \bar{t}_1\frac{dC_1}{dt}, \text{ with } C_f = 2 \text{ and } C_1 = 0 \text{ when } t = 0$$

The integral is

$$C_1 = 2[1 - \exp(1-t)], \text{ when } 1 \le t \le 3. \qquad (1)$$

Beyond $t = 3$, $C_f = 0$ and $C_1(3) = 1.7293$. The variables are separable,

$$C_1 = 1.7293 \exp(3-t). \qquad (2)$$

Second stage:

$$C_1 = C_2 + \frac{dC_2}{dt}, \text{ with } C_2 = 0 \text{ when } t = 0$$

When $1 \le t \le 3$,

$$\frac{dC_2}{dt} + C_2 = 2[1 - \exp(1-t)]$$

The solution of this linear equation is

$$C_2 = 2[1 - t\exp(1-t)] \qquad (3)$$

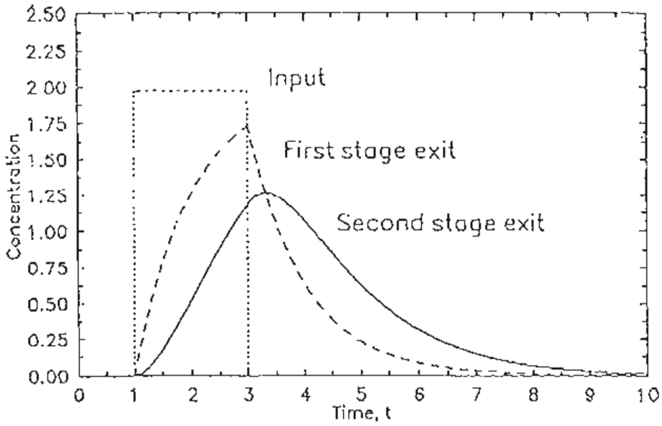
Beyond $t = 3$,

$$\frac{dC_2}{dt} + C_2 = 1.7293 \exp(3-t), \text{ with } C_2(3) = 1.188$$

The solution of this first order linear equation is

$$C_2 = (34.73t - 80.34)\exp(-t) \qquad (4)$$

Equations (1), (2), (3) and (4) are plotted along with square pulse input.



P5.03.12. PARALLEL PFR AND CSTR. IMPULSE, STEP AND SQUARE PULSE

A PFR and a CSTR are operated in parallel with a fraction $\alpha = 0.5$ of the flow going to the PFR. The vessels have equal volumes V_r. Make plots of the responses to the three kinds of inputs: impulse, step, square pulse with duration $a = 1$. The residence times are $\bar{t}_1 = \bar{t}_2 = 1$.

C_1 is the effluent from the PFR, C_2 from the CSTR. In each case,

$$C_3 = \alpha C_1 + (1-\alpha)C_2$$

$$\bar{t}_1 = V_r/\alpha V', \quad \bar{t}_2 = V_r/(1-\alpha)V'$$

(a) Impulse input, $m\delta(t-\bar{t}_1)$

$$C_1 = C_1^o\bar{t}_1\delta(t-\bar{t}_1), \quad C_1^o = m/2V_r$$

$$C_2 = C_2^o \exp(-t/\bar{t}_2), \quad C_2^o = m/2V_r$$

(b) Step input

$C_1/C_f = 1$, when $t \ge \bar{t}_1$ and $= 0$ elsewhere

$C_2/C_f = 1-\exp(-t/\bar{t}_2)$

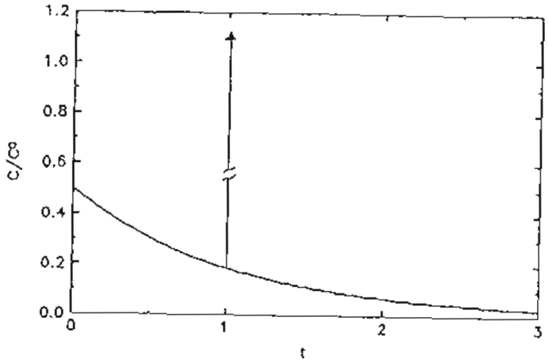
(c) Square pulse

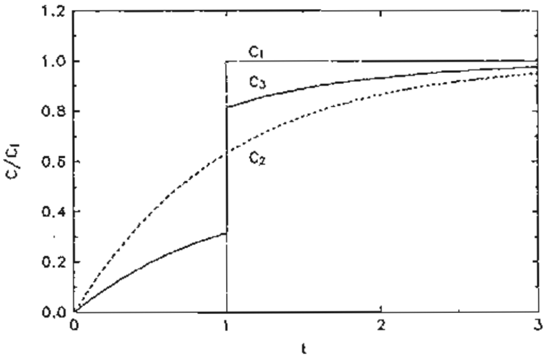
$C_1/C_f = u(t-\bar{t}_1)_{\ t\ge\bar{t}_1} - u(t-a-\bar{t}_1)_{\ t\ge(t-a-\bar{t}_2)}$

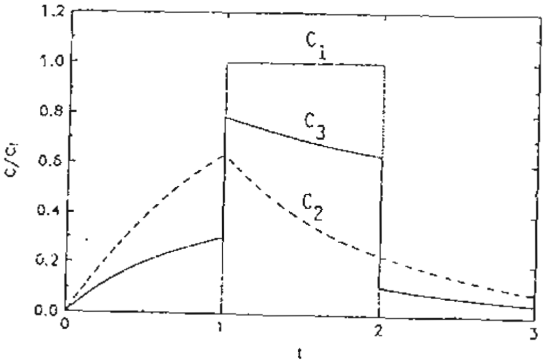
$C_2/C_f = 1-\exp(-t/\bar{t}_2) - [1-\exp(t-a-\bar{t}_2)]$

In the last line, the expression in brackets [] is 0 when $t \le (t-a-\bar{t}_2)$.

The plots show discontinuities at the transition from PFR to CSTR.





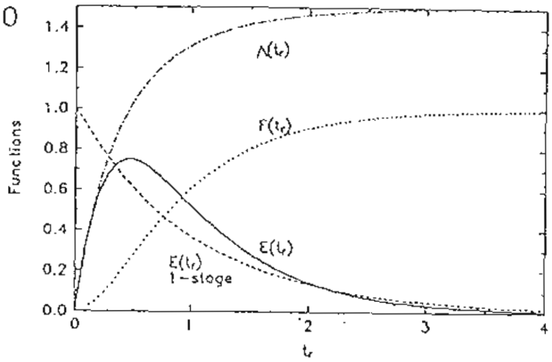


P5.03.13. CSTRS OF DIFFERENT SIZES

A reactor is modelled as two stirred tanks in series, of which the first is half the size of the other. Derive equations for the time distributions $E(t_r)$, $F(t_r)$ and $\Lambda(t_r)$.

With impulse input to the first stage, the material balance is

$$\bar{t}_1\frac{dC_1}{dt} + C_1 = C^0\bar{t}\ \delta(t),\ \text{with } C_1 = 0 \text{ when } t = 0$$



Transforming,

$$\bar{t}_1 s\bar{C}_1 + \bar{C}_1 = C^0\bar{t}$$

$$\bar{C}_1 = C^0\bar{t}/(\bar{t}_1 s+1)$$

Over the second stage,

$$\bar{t}_2\frac{dC_2}{dt} + C_2 = C_1$$

$$\bar{C}_2 = \frac{\bar{C}_1}{\bar{t}_2 s+1} = \frac{C^o\bar{t}}{(\bar{t}_1 s+1)(\bar{t}_2 s+1)}$$

Inverting and rearranging,

$$E(t_r) = C_2/C^0 = \frac{\bar{t}}{\bar{t}_2-\bar{t}_1}[\exp(-1.5t/\bar{t}_2) - \exp(-t/\bar{t}_1)]$$

$$= 3[\exp(-1.5t_r) - \exp(-3t_r)]$$

$$F(t_r) = \int_0^{t_r} E(t_r)dt_r = 1 - 2\exp(-1.5t_r) + \exp(-3t_r)$$

$$\Lambda(t_r) = \frac{E(t_r)}{1-F(t_r)} = \frac{3[1 - \exp(-1.5t_r)]}{2- \exp(-1.5t_r)}$$

The three functions are plotted.

P5.03.14. STEP INPUT TO A TWO-STAGE CSTR

The sketch shows the flow arrangement in a two-stage CSTR battery. The stages are equal. Initial content of tracer in the system is zero. Step input of tracer is entered. Write equations for $C_1(t)$ and $C_2(t)$, and plot them for these numerical values:

$V_r/V' = 1$, $V_1'/V' = 0.2$ and $V_2' = 0$.

Material balances for each of the stages are

$$V'C_f + V_2'C_2 = (V'+V_2')C_1 + V_r\frac{dC_1}{dt}$$

$$C_1 = C_2 + \bar{t}_2\frac{dC_2}{dt}\ ,\quad \bar{t}_2 = V_r/(V'+V_2'-V_1')$$

The transforms are

$$\bar{C}_1 = \frac{V'C_f/s+V_2'\bar{C}_2}{V'+V_2'+V_r s}$$

$$\bar{C}_2 = \frac{\bar{C}_1}{1+\bar{t}_2 s}$$

Solving for $\bar{C}_2$ between these two equations,

$$\bar{C}_2 = \frac{V'}{s[(1+\bar{t}_2 s)(V'+V_2'+V_r s)-V_2']}$$

For the numerical values $V_r/V' = 1$, $V_2' = 0$, $V_1'/V' = 0.2$, $\bar{t}_2=1.25$,

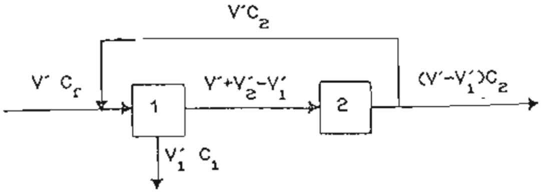
$$\bar{C}_2/C_f = \frac{1}{1.25s(s+0.8)(s+1)}$$

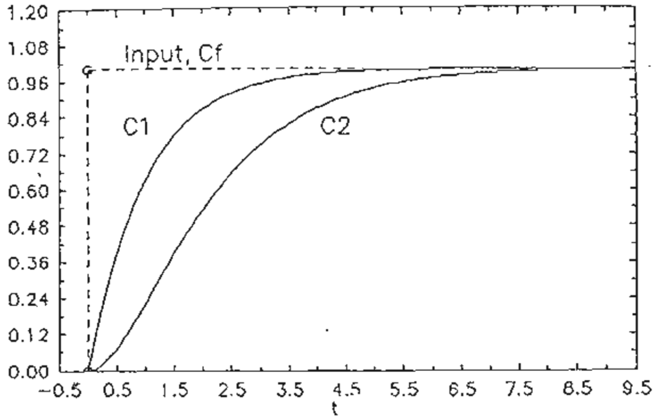
$$\bar{C}_1 = (1+\bar{t}_2 s)\bar{C}_2 = C_f/s(s+1)$$

The inverses are

$$C_2/C_f = 1 - 5\exp(-0.8t) + 4\exp(-t)$$

$$C_1/C_f = 1 - \exp(-t)$$





P5.04.01. A CSTR WITH A STAGNANT ZONE

In an otherwise ideal stirred tank it is estimated that 10% of the volume is occupied by stagnant fluid. If there were no stagnant region, the conversion would be 60%. What conversion is to be expected in the actual reactor.

(a) In the ideal reactor, if first order reaction,

$x = 1-C/C_0 = 0.6 = 1-1/(1+kt)$

$kt = 1.5$

In the actual reactor,

$kt = 0.9(1.5) = 1.35, \quad x = 1-1/(1+1.35) = 0.575$

(b) In the ideal reactor, if second order reaction,

$1 = f + kC_0f^2 \;, \quad f = C/C_0$

$kC_0t = (1-f)/f^2 = 0.6/(0.16) = 3.75$

In the actual reactor,

$kC_0t = 0.9(3.75) = 3.375$

$$f = \frac{-1+\sqrt{1+4(3.375)}}{2(3.375)} = 0.416$$

$x = 1-f = 0.584$

P5.04.01A. CSTR WITH BYPASS OR STAGNANCY

Compare the RTD of an ideal CSTR with cases having 25% bypass or 25% stagnancy.

$1-\alpha$ = fraction of flow in bypass

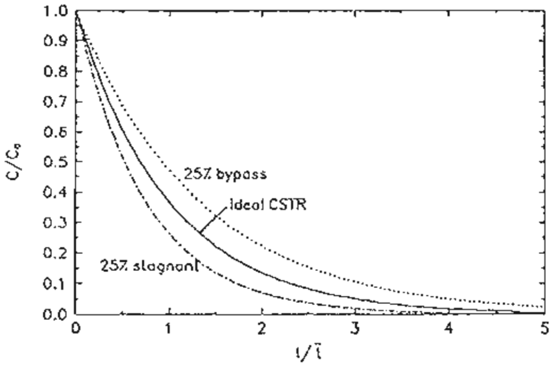
$1-\beta$ = fraction of vessel volume stagnant

The true residence time then becomes

$$\bar{t}^* = \frac{1-\beta}{1-\alpha}\frac{V_r}{V'} = \frac{1-\beta}{1-\alpha}\bar{t}$$

and the effluent concentration ratio,

$$C/C_0 = \exp(-t/\bar{t}^*) = \exp(-\frac{1-\alpha}{1-\beta}\frac{t}{\bar{t}})$$



With 25% bypass, $C/C_0 = \exp(-0.75t_r)$; and with 25% stagnancy, $C/C_0 = \exp(-1.33t_r)$. The concentration falls off less rapidly with bypass.

P5.04.02. STIRRED TANK WITH BYPASS AND DEAD SPACE

The model of a stirred tank reactor has a fraction $1-\alpha$ of the flow in bypass and a fraction $1-\beta$ of the volume inactive. A step input of tracer is entered. Effluent concentrations were measured at high and low agitator speeds and the quantity $1-C/C_f$ was obtained at zero time by extrapolation. The values were 0.89 at high speed and 0.59 at low speed. (a) Find α and β. (b) Compare plots of $E(t_r)$ for the two cases with the ideal CSTR.

In the active portion of the tank, with C_1 as the effluent concentration, the material balance is

$$\alpha V' C_f = \alpha V' C_1 + \beta V_r \frac{dC_1}{dt}$$

The solution by Laplace transform is

$$C_1/C_f = 1 - \exp(- \frac{\alpha t}{\beta \bar{t}})$$

The overall balance is

$$V' C = (1-\alpha)V' C_f + \alpha C_1$$

$$C/C_f = 1 - \alpha \exp(-\alpha t_r/\beta) \qquad (1)$$

$$\alpha = 1 - C/C_f \text{ when } t_r = 0$$

$$\beta = \frac{\alpha t_r}{\ln(\frac{\alpha}{1-C/C_f})}$$

After α has been found by extrapolation of C/C_f, β can be calculated at any value of t_r; when those values are constant, the model is validated. Data for the two cases are in the table.

At high speed, $\alpha = 0.89$, $\beta = 0.8$. At low speed, $\alpha = 0.59$, $\beta = 0.5$.

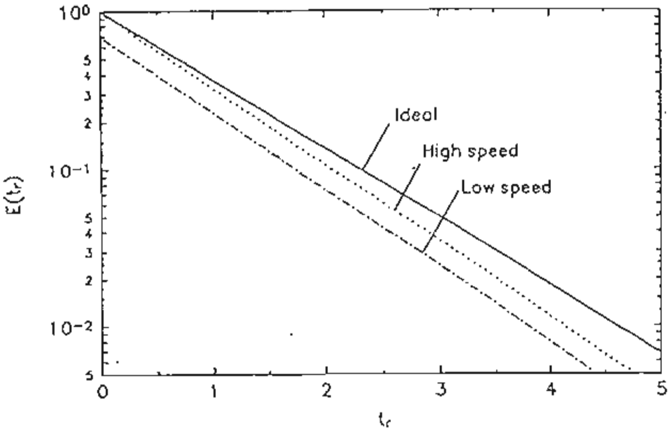
The Age function is given by Equation (1). The RTD then becomes

$$E(t_r) = dF(t_r)/dt_r = (\alpha^2/\beta) \exp(-\alpha t_r/\beta)$$

$$0.990 \exp(-1.113t_r), \text{ at high speed}$$

$$0.696 \exp(-1.118t_r), \text{ at low speed}$$

	$1-C/C_f$		β	
t_r	High	Low	High	Low
0	(0.89)	(0.59)		
0.20	0.72	0.47	0.832	0.529
0.40	0.57	0.37	0.811	0.510
0.60	0.46	0.29	0.804	0.503
0.80	0.37	0.23	0.801	0.500
1.00	0.29	0.18	0.799	0.499
1.20	0.23	0.14	0.798	0.497
1.40	0.19	0.11	0.797	0.497
1.60	0.15	0.09	0.796	0.496
1.80	0.12	0.07	0.796	0.496
2.00	0.09	0.05	0.795	0.495



P5.04.03. A SYSTEM OF THREE VESSELS. TRACER RESPONSE

A reactor is made up of three zones. Zone 1 is a CSTR in parallel with a PFR that is zone 2, and both are in series with zone 3 that is another PFR. The fraction of the flow going to the CSTR is α. Find the response functions $E(t_r)$ and $F(t_r)$.

The individual transfer functions are

$$G_1 = 1/(1+\bar{t}_1 s),\quad G_2 = \exp(-\bar{t}_2 s),\quad G_3 = \exp(-\bar{t}_3 s)$$

The overall transfer function is

$$\bar{C}/\bar{C}_f = [\alpha G_1 + (1-\alpha)G_2]G_3$$

For step input, $\bar{C}_f = C_f/s$. Solving for the transform,

$$\bar{C}/C_f = \frac{1}{s}\left[\frac{\alpha}{1+\bar{t}_1 s} + (1-\alpha)\exp(-\bar{t}_2 s)\right]\exp(-\bar{t}_3 s)$$

The inverse is

$$C/C_f = \alpha\left[1 - \exp\left(-\frac{t-\bar{t}_3}{\bar{t}_1}\right)\right] u(t-\bar{t}_3) + (1-\alpha)\, u(t-\bar{t}_2-\bar{t}_3)$$

Numerical values are obtained for

$$\bar{t}_1 = \bar{t}_2 = \bar{t}_3 = 1,\ \bar{t} = 2 \text{ and } \alpha = 0.5$$

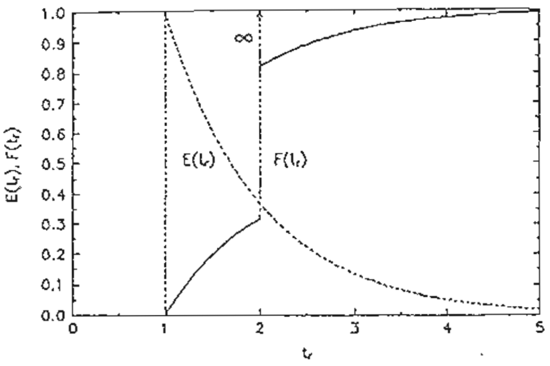
Then for step input

$$F(t_r) = C/C_f = 0.5\{[1 - \exp(1-t)]\, u(t-1)\} + u(t-2)\}$$

For impulse response, replace $C_f = C^0\bar{t} = 2C^0$ and differentiate the preceding equation, with the result

$$E(t_r) = C/C^0 = 0/5(2)[\exp(1-t)\, u(t-1) + \delta(t-2)\}$$

The graph shows a broken line at $t_r = 2$ on the $F(t_r)$ plot and a blip at $t_r = 2$ on the $E(t_r)$ line.



P5.04.04. A TWO STAGE CSTR WITH RECYCLE.

A two stage CSTR is operated with a partial recycle of overall effluent to the first stage. The ratio of recycle to fresh feed is $\beta = R'/V'$. The stages are of equal size. Find $E(t_r)$ for several values of β.

In terms of transforms the material balances are

$$(\bar{C}_f + \beta\bar{C})G_1G_2 = (1+\beta)\bar{C}$$

$$\bar{t}_1 = \bar{t}_2 = \bar{t}/2(1+\beta), \quad \bar{t} = V_r/V'$$

$$G_1 = G_2 = 1/[1+\bar{t}s/2(1+\beta)],$$

$$\bar{C}_f = C_f/s, \text{ for step input}$$

$$C^0\bar{t}, \text{ for impulse input}$$

For impulse input, after substitution of various terms and rearrangement,

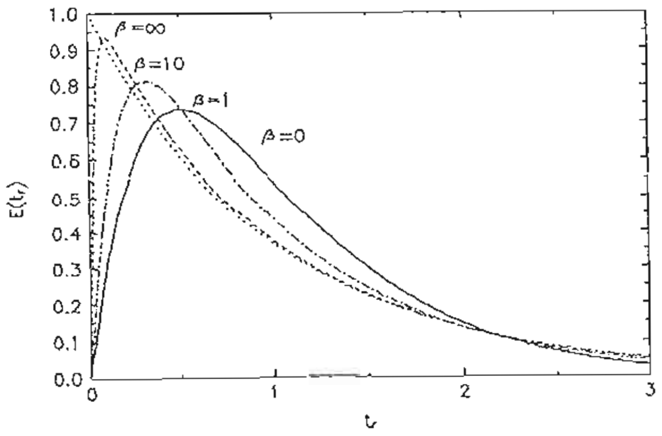
$$\bar{C}/C^0 = \frac{1}{(1+\beta)(1+\frac{\bar{t}s}{2(1+\beta)})^2 - \beta}$$

Inversion of this equation is a bit involved but the result is

$$E(t_r) = \frac{1+\beta}{\sqrt{\beta^2+\beta}}\{\exp[-2t_r(1+\beta-\sqrt{\beta^2+\beta})]$$

$$-\exp[-2t_r(1+\beta+\sqrt{\beta^2+\beta})]\}$$

This is shown plotted for several values of β. Limiting values are $\beta = 0$ for two stage operation and $\beta = \infty$ for one stage operation. Inversion of the transform will give $E(t_r) = C/C^0$ as a function of the recycle ratio, β.



P5.04.05. CSTR WITH BYPASS AND IN SERIES WITH A PFR

An n-stage CSTR is in series with a PFR. A fraction 1-α of the flow is bypassed around the CSTR. The response functions E(t) and F(t) are to be found.

The individual transfer functions are

$$G_1 = 1/\ (1+\bar{t}_1 s/n)^n,\quad G_2 = \exp(-\bar{t}_2 s)$$

Overall,

$$\bar{C}/\bar{C}_f = (\alpha G_1 + 1 - \alpha)G_2$$

For impulse input, $\bar{C}_f = C^o\bar{t}$, so the transform equation becomes

$$\frac{\bar{C}}{C^o\bar{t}} = \frac{\alpha}{(1+\bar{t}_1 s/n)^n}\exp(-\bar{t}_2 s) + (1-\alpha)\exp(-\bar{t}_2 s)$$

Inverting,

$$E(t) = C/C^o\bar{t} = \frac{\alpha n^n}{\bar{t}_1(n-1)!}\left(\frac{t-\bar{t}_2}{\bar{t}_1}\right)^{n-1}\exp[-n(t-\bar{t}_2)/\bar{t}_1]\ u(t-\bar{t}_2)$$

$$+ (1-\alpha)\delta(t-\bar{t}_2)$$

F(t) is found by integration

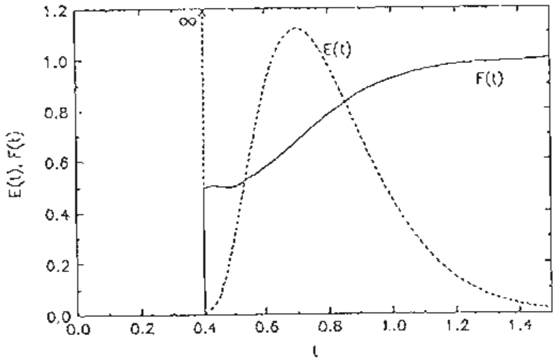
$$F(t) = \int_0^t E(t)dt$$

The curves are drawn for

$$\alpha = 0.5,\ n = 4,\ \bar{t}_1 = \bar{t}_2 = 0.4,\ \bar{t} = 0.8$$

Note that

$$\int_{0.4}^{\infty}(1-\alpha)\delta(t-0.4)dt = 0.5$$



P5.04.06. ARRANGEMENTS OF A CSTR BATTERY AND A PFR

Three different arrangements of a CSTR and a PFR with bypass are shown on the sketch. τ = fraction of total volume occupied by the CSTR battery. β = fraction of the total flow that goes directly to the CSTR. Equations for $E(t_r)$ are to be developed for the three cases.

The individual transfer functions are

$$G_1 = 1/(1+\bar{t}_1 s/n)^n,\quad G_2 = \exp(-\bar{t}_2 s)$$

(a) With bypass around the CSTR battery.

$$\bar{t}_1 = \frac{1-\tau}{\beta}\bar{t},\quad \bar{t}_2 = \tau\bar{t},\ \bar{t} = V_r/V'$$

$$[\beta G_1 + 1-\beta]G_2 = \bar{C}/\bar{C}_f$$

$$E(s) = \bar{C}/\bar{C}_f = \beta\left[\frac{n\beta}{n\beta+(1-\tau)\bar{t}s}\right]^n\exp(-\tau\bar{t}s) + (1-\beta)\exp(-\tau\bar{t}s)$$

For impulse input, $\bar{C}_f = C^0\bar{t}$. Inverting,

$$E(t_r) = C/C^0 = f(t_r-\tau)\ u(t_r-\tau) + (1-\beta)\ \delta(t_r-\tau)$$

where

$$f(t_r-\tau) = \frac{\beta(n\beta)^n}{(1-\tau)\Gamma(n)} \left(\frac{t_r-\tau}{1-\tau} \right)^{n-1} \exp\left[-\beta n\left(\frac{t_r-\tau}{1-\tau} \right)\right]$$

and the relation $\bar{t}\ \delta(t-\tau\bar{t}) = \delta(t_r-\tau)$ has been used.

(b) With bypass about both vessels.

$$(\beta G_1G_2 + 1-\beta) = \bar{C}/\bar{C}_f$$

$$E(s) = \beta\left[\frac{n\beta}{n\beta+(1-\tau)\bar{t}s} \right]^n \exp\left(-\frac{\tau\bar{t}s}{\beta}\right) + 1-\beta$$

$$E(t_r) = f(t_r-\tau)\ u(t_r-\tau) + (1-\beta)\ \delta(t_r)$$

(c) With the bypass stream and the two vessels all in parallel.

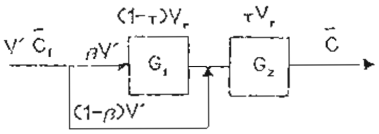
$$\bar{t}_1 = (1-\tau)\bar{t}/\beta, \quad \bar{t}_2 = \tau\bar{t}/\alpha$$

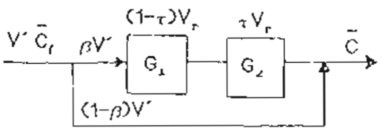
$$[\beta G_1 + \alpha G_2 + 1-\alpha-\beta] = \bar{C}/\bar{C}_f$$

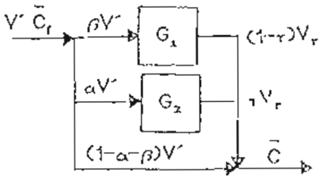
$$E(s) = \beta\left[\frac{n\beta}{n\beta+(1-\tau)\bar{t}s} \right]^n + \alpha\exp(-\tau\bar{t}s/\alpha) + 1-\alpha-\beta$$

$$E(t_r) = \frac{\beta(n\beta)^n}{1-\tau}\left(\frac{t_r}{1-\tau} \right)^{n-1}\exp\left[-\left(\frac{n\beta t_r}{1-\tau}\right)\right]$$

$$+\alpha\ \delta(t_r-\tau/\alpha) + (1-\alpha-\beta)\ \delta(t_r)$$







P5.04.07. CONVERSION IN A KNOWN NETWORK

The system consists of two CSTRs and a PFR hooked up as on the sketch. Equations for chemical conversion will be found for several rate equations.

The individual residence times and transfer functions are,

$$\bar{t}_1 = \bar{\beta}\bar{t}/\alpha\ ,\quad \bar{t}_2 = \frac{1-\beta-\gamma}{1-\alpha}\ \bar{t}, \quad \bar{t}_3 = \gamma t$$

$$G_1 = 1/(1+\bar{t}_1s),\ G_2 = \exp(-\bar{t}_2s),\ G_3 = 1/(1+\bar{t}_3s)$$

Overall,

$$\bar{C}_3/\bar{C}_0 = [\alpha G_1 + (1-\alpha)G_2]G_3$$

$$= \left[\frac{\alpha}{1+\bar{t}_1s} + (1-\alpha)\ \exp(-\bar{t}_2s)\right] \frac{1}{1+\bar{t}_3s}$$

(a) For a first order reaction, replace s in the transfer function by the specific rate, k. Then

$$C_3/C_0 = \left[\frac{\alpha}{1+k\bar{t}_1} + (1-\alpha)\ \exp(-k\bar{t}_2)\right] \frac{1}{1+k\bar{t}_3}$$

(b) For zero order, formulate the material balances.

$$C_0 = C_1 + k\bar{t}_1$$

$$C_1 = C_2 + k\bar{t}_2$$

$$\alpha C_1 + (1-\alpha)C_2 = C_3 + k\bar{t}_3$$

$$\frac{C_3}{C_0} = 1 - (k/C_0)[\alpha\bar{t}_1 + (1-\alpha)\bar{t}_2 + \bar{t}_3]$$

(c) For second order, formulate the material balances.

$$C_1/ C_0 = \frac{-1 + \sqrt{1+4kC_0\bar{t}_1}}{2kC_0\bar{t}_1} \qquad (1)$$

$$C_2/C_0 = \frac{1}{1+kC_0\bar{t}_2} \qquad (2)$$

$$\alpha \frac{C_1}{C_0} + (1-\alpha) \frac{C_2}{C_0} = \frac{C_3}{C_0} + kC_0\bar{t}_3(C_3/C_0)^2 \qquad (3)$$

Solve these three equations for the three concentration ratios.

(d) When the rate equation is $-dC/dt = k_1C/(1+k_2C)$,

$$C_0 = C_1 + k_1\bar{t}_1C_1/(1+k_2C_1) \qquad (4)$$

$$k_1\bar{t}_2 = \int_{C_2}^{C_0}(1/C + k_2)dC = \ln(C_0/C_2) + k_2(C_0-C_2) \qquad (5)$$

$$\alpha C_1 + (1-\alpha)C_2 = C_3 + \frac{k_1\bar{t}_3C_3}{1+k_2C_3} \qquad (6)$$

Only numerical solutions can be obtained for this system of three equations for the three concentrations.

P5.04.08. THREE REACTORS. DIRECT AND SEGREGATED CONVERSION

Flow to a rector system is split into three equal portions in parallel. One portion goes through a PFR with residence time $\bar{t}_1$, another goes to a two stage CSTR each vessel of which has a residence time $\bar{t}_2$ and the third portion bypasses both units. The three portions recombine as they leave the system. Compare conversion in this system with that of segregated flow in the same equipment, for a second order reaction.

In the plug flow unit,

$$C_1/C_0 = 1/(1+kC_0\bar{t}_1) \qquad (1)$$

In the CSTR battery, the material balances are

$$1 = C_2/C_0 + kC_0\bar{t}_2(C_2/C_0)^2 \qquad (2)$$

$$C_2/C_0 = C_3/C_0 + kC_0\bar{t}_2(C_3/C_0)^2 \qquad (3)$$

Solve the last two equations for C_3/C_0. Overall,

$$C/C_0 = \frac{1}{3}\left[1 + \frac{1}{1+kC_0\bar{t}_1} + C_3/C_0\right] \qquad (4)$$

In segregated flow only the CSTR will be different since the PFR is segregated by definition. For the CSTR,

$$E(t_r) = 4t_r\exp(-2t_r),\ t_r = t/2\bar{t}_2 \qquad (5)$$

$$(C_3/C_0)_{seg} = \int_0^\infty \frac{E(t_r)}{1+4kC_0\bar{t}_2 t_r}\, dt_r \qquad (6)$$

Substitute Equation (6) instead of (3) into (4).

For first order,

$$C/C_0 = \frac{1}{3}\,[1 + \exp(-k\bar{t}_1) + \frac{1}{(1+k\bar{t}_2)^2}] \qquad (7)$$

In the segregated CSTR battery,

$$(C_3/C_0)_{seg} = \int_0^\infty E(t_r)\exp(-2k\bar{t}_2 t_r)\, dt_r$$

$$= \int_0^\infty t_r \exp[-2(1+k\bar{t}_2)t_r]\, dt_r$$

$$= \frac{1}{(1+k\bar{t}_2)^2} \qquad (8)$$

Conversion in the segregated vessel is the same as in the CSTR so Equation (7) still holds for overall conversion of a first order.

P5.04.09. A THREE UNIT REACTOR. RTD AND CONVERSION

The model of a reactor consists of two equal sized CSTRs joined by a PFR whose residence time equals that of the combined CSTRs. A second order reaction with $kC_0\bar{t} = 2$ is to be studied. Find the following. (a) The equation of the RTD, $E(t_r)$; (b) The value of $\sigma^2(t_r)$ and the conversion in a reactor with the corresponding Gamma distribution; (c) Conversion in a segregated flow reactor; (d) Conversion in the given sequence of three reactor elements.

The individual residence times are

$\bar{t}_1 = \bar{t}_3 = \bar{t}/4,\ \bar{t}_2 = \bar{t}/2,\ V_{r1} = V_{r2} = V_r/4$

Since the tracer process is first order, the RTD is the same for all series arrangements. Take the CSTRs first. The mean concentration in the system after injection of an impulse is C^0, and in the first stage it is $C_1^0 = 4C^0$. The material balance on the first stage is

$$V_{r1}\frac{dC_1}{dt} + V'C_1 = 4C^0V_{r1}\delta(t),\ \text{with } C_1 = 0 \text{ when } t = 0$$

The transform is

$$\bar{C}_1 = \frac{4C^0}{s+4/\bar{t}}$$

Second stage,

$$V_{r2}\frac{dC_2}{dt} + V'C_2 = V'C_1$$

$$\bar{C}_2 = \frac{\bar{C}_1}{\bar{t}_2 s+1} = \frac{16C^0}{\bar{t}(s+4/\bar{t})^2}$$

Third stage (PFR),

$$\bar{C}_3 = \bar{C}_2\exp(-\bar{t}_3 s) = \bar{C}_2\exp(-\bar{t}s/2)$$

Inverting,

$$E(t_r) = C_3/C^0 = 16\ (t/\bar{t})\exp(-4t/\bar{t})\ u(t-\bar{t}/2) \qquad (1)$$

$$= 16\ (t_r-0.5)\exp[-4(t_r-0.5)] \qquad t_r \ge 0.5$$

The variance is

$$\sigma^2(t_r) = -1 + \int_{0.5}^{\infty} t_r^2\, E(t_r)\, dt_r = 0.1248$$

$$n = 1/0.1248 = 8.013, \text{ say } 8.0$$

The corresponding Gamma distribution is

$$E(t_r) = (8^8/7!)\, t_r^7 \exp(-8t_r) = 3329\, t_r^7 \exp(-8t_r) \qquad (2)$$

Conversion with this model is given by

$$(C/C_0)_{Eq2} = \int_0^{\infty} \frac{E(t_r)}{1+2t_r}\, dt_r = 0.3518 \qquad (3)$$

Conversion with the RTD of Equation (1) is

$$(C/C_0)_{Eq1} = 0.3490 \qquad (4)$$

Conversion in plug flow overall,

$$(C/C_0)_{PFR} = 1/(1+kC_0t) = 0.3333 \qquad (5)$$

In the first stage of the given sequence of reactors,

$$1 = C_1/C_0 + k_1C_0\bar{t}_1(C_1/C_0)^2 = C_1/C_0 + 0.5(C_1/C_0)^2$$

$$C_1/C_0 = 0.7321$$

In the second stage, the PFR,

$$C_2/C_0 = 1/[1+2(0.7321)] = 0.4058$$

In the last stage,

$$0.4058 = C_3/C_0 + 0.5(C_3/C_0)^2$$

$$C_3/C_0 = 0.3460 \qquad (6)$$

Conversions by all models, Equations (3), (4), (5) and (6) are all about the same. The large value of n from the variance indicates that the performance does approximate plug flow.

P5.04.10. CHLORINATION IN A CSTR AND IN BATCH

Benzene is to be chlorinated in a two stage CSTR. The chlorine is sparged directly to each stage and the solutions are essentially saturated with the gas. Rate equations are expressed as first order in terms of mol fractions x_a of benzene and x_b of monochlor. Formation of trichlor is taken negligible.

$$-dx_a/dt = k_1x_a$$

$$dx_b/dt = k_1x_a - k_2x_b$$

$$x_c = x_{dichlor} = 1 - x_a - x_b$$

Specific rates at 55 C are given by Bodman (*Industrial Practice of Chemical Process Engineering*, 1968) as

$$k_1 = 0.412/\text{hr}, \quad k_2 = 0.055/\text{hr}$$

Find (a) the total benzene residence time for 90% conversion in the CSTR battery; (b) the relative size of a batch reactor for the same daily production with one hour between batches.

(a) The material balances with $\bar{t}$ in each stage,

$$x_{a0} = 1 = x_{a1} + k_1\bar{t}x_{a1}$$

$$x_{a1} = \frac{1}{1+k_1\bar{t}}$$

$$x_{a2} = \frac{1}{(1+k_1\bar{t})^2}$$

$$x_{b0} = 0 = x_{b1} + \bar{t}(-k_1x_{a1} + k_2x_{b1})$$

$$x_{b1} = \frac{k_1\bar{t}x_{a1}}{1+k_2\bar{t}} = \frac{k_1\bar{t}}{(1+k_1\bar{t})(1+k_2\bar{t})}$$

$$x_{b1} = x_{b2}+\bar{t}(-k_1x_{a2}+k_2x_{b2})$$

$$x_{b2} = \frac{x_{b1}+k_1\bar{t}x_{a2}}{1+k_2\bar{t}} = \frac{k_1\bar{t}}{(1+k_1\bar{t})(1+k_2\bar{t})^2} + \frac{k_1\bar{t}}{(1+k_1\bar{t})^2(1+k_2\bar{t})}$$

$= 0.1$, for 90% conversion

Substitute $k_1 = 0.412$, $k_2 = 0.055$ and find $\bar{t} = 4.318$ hr, $2\bar{t} = 8.636$ hr.

(b) In a batch reactor,

$-dx_a/dt = k_1x_a$

$$t = \frac{1}{k_1}\ln(1/x_a) = \frac{1}{0.412}\ln(10) = 5.59 \text{ hr}$$

For the same daily production the ratio of reactor volumes is

$V_{r,batch}/V_{r,twostage} = (5.59+1)/8.636 = 0.763$

P5.04.11. TRACER IN LAMINAR FLOW

In laminar flow through a cylindrical tube of radius R and length L the linear velocity depends on the radial position $\beta = r/R$ according to

$$u = u_0(1-\beta^2) = \frac{2V'}{\pi R^2}(1-\beta^2)$$

The time of passage along any streamline is

$t = L/u = L/u_0(1-\beta^2)$

Also,

$$dt = \frac{2L}{u_0(1-\beta^2)^2}\beta d\beta$$

The fraction of the total fluid that passes between r and r+dr,

$$\frac{dV'}{V'} = \frac{u(2\pi r dr)}{V'} = \left(\frac{u}{V'}\right)(2\pi R^2)\beta d\beta$$

$$= \left[\frac{2(1-\beta^2)}{\pi R^2}\right](2\pi R^2)\left[\frac{u_0(1-\beta^2)^2}{2L}\right] dt$$

$$= \frac{2u_0(1-\beta^2)^3}{L} dt = \frac{2u_0(u/u_0)^3}{L} dt$$

Since the times are inversely proportional to the velocities,

$$E(t) = \frac{dV'}{V'} = \frac{2(u/L)^3}{(u_0/L)^2} = 2\frac{(\bar{t}/2)^2}{t^3} = \frac{\bar{t}^2}{2t^3}$$

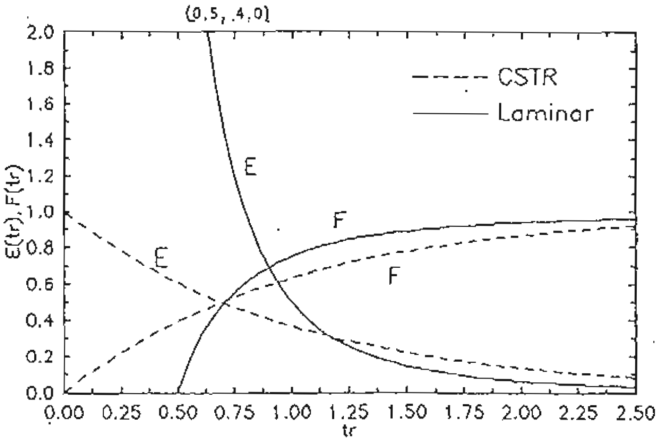
The minimum retention time is $\bar{t}/2$ at the centerline. Accordingly, E(t) when $t \le \bar{t}/2$. The normalized RTD is

$E(t_r) = \bar{t}E(t) = 1/2t_r^3$ when $t_r \geq 0.5$, and = 0 elsewhere.

Also

$F(t_r) = \int_0^{t_r} E(t_r)dt_r = 1-1/4t_r^2$ when $t_r \geq 0.5$ and = 0 elsewhere.

The plots of these functions are compared with those of a CSTR.



P5.05.01. RTD OF A CSTR. VARIOUS REACTION EQUATIONS

In a vessel with the RTD of a CSTR, $E(t_r) = \exp(-t_r)$, conversion under segregated flow conditions is to be found with several different rate equations and compared with that in a CSTR. In segregated flow, conversion is represented by

$$(C/C_0)_{seg} = \int_0^\infty (C/C_0)_{batch}\, E(t_r)\, dt_r$$

(a) First order reaction,

$$(C/C_0)_b = \exp(-kt) = \exp(-k\bar{t}t_r)$$

$$(C/C_0)_{seg} = \int_0^\infty \exp(-k\bar{t}t_r)\exp(-t_r)\, dt_r = 1/(1+k\bar{t})$$

which is the same as the CSTR performance.

(b) Second order reaction,

$$(C/C_0)_b = 1/(1+kC_0\bar{t}t_r)$$

$$(C/C_0)_{seg} = \int_0^\infty \frac{\exp(-t_r)}{1+kC_0\bar{t}t_r}\, dt_r$$

The integration can be done analytically but here it is done numerically and the results compared with conversion in a CSTR..

In a CSTR,

$$C/C_0 = \frac{-1+\sqrt{1+4kC_0\bar{t}}}{2kC_0\bar{t}}$$

	C/C_0	
$kC_0\bar{t}$	CSTR	Segregated
1	0.618	0.596
5	0.358	0.299
10	0.270	0.202

(c) Half order,

$$(C/C_0)_b = (1-k\bar{t}t_r/2\sqrt{C_0}\ )^2$$

In a CSTR the material balance is

$$1 = C/C_0 + \frac{k\bar{t}}{\sqrt{C_0}}\sqrt{\frac{C}{C_0}}$$

from which C/C_0 can be calculated and compared with the value for segregated flow.

	C/C_0	
$k\bar{t}/2\sqrt{C_0}$	CSTR	Segregated
0.5	0.382	0.432
1.0	0.172	0.264
2.5	0.037	0.121
5.0	0.0098	0.0635

(d) Rate equation $-df/dt = kf/(1+5f)$, $f = C/C_0$. The integral is

$$f = \exp[-kt+5(1-f)] \qquad (1)$$

In a CSTR,

$$1 = f + k\bar{t}f/(1+5f) \qquad (2)$$

For segregated flow,

$$f_{seg} = \int_0^\infty f_{Eq1} \exp(-t_r)\, dt_r \qquad (3)$$

f is found from Equation (1), then is substituted into Equation (3) and the integration performed numerically. For instance, values of f_{Eq1} are as follows when $k\bar{t} = 10$,

t_r	0	.2	.4	.6	.8	1	1.2
f_{Eq1}	1	0.555	0.261	0.0890	0.0029	0.0024	0.0002

The CSTR and segregated conversions are compared for several values of $k\bar{t}$.

	C/C_0	
$k\bar{t}$	CSTR	Segregated
2	0.690	0.702
5	0.358	0.453
10	0.282	0.148

P5.05.02. RTD FROM NUMERICAL DATA. SEVERAL REACTION ORDERS

From a pulse input to a vessel the following output signal is obtained

t	1	3	5	7	9	11	13	15
C	0	0	10	10	10	10	0	0

(a) Find the residence time, the variance and the corresponding Gamma distribution. (b) For reactions with k = 1 and $C_0 = 2$, compare conversions in batch and in segregated flow for several orders of reaction.

The required integrals are,

$$\int_0^\infty C dt = 80,\quad \int_0^\infty tC dt = 640,\quad \int_0^\infty t^2 C dt = 5520,\quad \bar{t} = 640/80 = 8,$$

$$\sigma^2(t_r) = -1 + \frac{1}{\bar{t}^2\int_0^\infty C dt} \int_0^\infty \bar{t}^2 C dt = 0.0781,\quad n = 1/0.0781 = 12.8,$$

$$\Gamma(n) = 2.895(10^8)$$

$$E(t_r)_{Gamma} = [n^n/\Gamma(n)]\, t_r^{n-1} \exp(-nt_r)$$

$$= 5.137(10^5)\, t_r^{11.8} \exp(-12.8t_r)$$

In plug flow or batch conversion of reaction of order q,

$$(C/C_0)_{batch} = \exp(-k\bar{t}t_r), \qquad q = 1$$

$$\frac{1}{[1+(q-1)kC_0^{q-1}\,\bar{t}t_r]^{1/(q-1)}}, \qquad q \neq 1$$

In segregated flow,

$$(C/C_0)_{seg} = 5.1365(10^5) \int_0^\infty (C/C_0)_{batch}\, t_r^{11.8} \exp(-12.8t_r) dt_r$$

Results by numerical integration for several orders of reaction are

	C/C_0	
q	batch	segregated
0	0	0
1	0.0003	0.0020
2	0.0588	0.0632
3	0.1240	0.1277

P5.05.03. SPECIFIC RATE WHEN TRACER RESPONSE IS KNOWN

A vessel has a residence time distribution represented by the given equations. A second order reaction with $C_0 = 1$ is conducted in this vessel and attains 90% conversion. Find the specific rate assuming the segregated flow model.

The RTD equations are

$$E(t) = 0.025(t-1),\quad 1 \le t \le 5$$
$$0.1\quad ,\quad 5 \le t \le 13, \text{ and zero elsewhere}$$

For segregated flow,

$$C/C_0 = 0.1 = \int_1^5 \frac{0.025(t-1)}{1+kC_0t}\,dt + \int_0^\infty \frac{0.1}{1+kC_0t}\,dt$$

$$4 = \frac{4}{k} - \left(\frac{1}{k^2} + \frac{1}{k}\right) \ln\left(\frac{1+5k}{1+k}\right) + \frac{4}{k} \ln\left(\frac{1+13k}{1+5k}\right)$$

From which $k = 1.354$.

P5.05.04. SPECIFIC RATE FROM PLUG AND SEGREGATED FLOW DATA

Two tests were made on a vessel packed with catalyst particles. (a) A tracer test that led to the RTD

$$E(t_r) = 7.815\, t_r^2 \exp(-2.5t_r)$$

(b) A first order reaction test that resulted in a conversion of 95%. Compare the values of the specific rate product, $k\bar{t}$, assuming a plug flow or segregated flow mechanism.

For plug flow,

$$k\bar{t} = \ln(C_0/C) = \ln(20) = 2.996$$

For segregated flow,

$$C/C_0 = \int_0^\infty E(t_r)\exp(-t_r)dt_r = 7.815\int_0^\infty t_r^2 \exp[-(2.5+k\bar{t})t_r]dt_r$$

$$= \frac{7.815(2)}{(2.5+k\bar{t})^3} = 0.05$$

From which $k\bar{t} = 2.886$, which agrees moderately well with the plug flow value. This indefinite integral was used in the evaluation,

$$\int x^2 e^{ax} dx = e^{ax}\left[\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right].$$

P5.05.05. SPECIFIC RATE IN TERMS OF FIFTH ORDER GAMMA RTD

The RTD of a reactor is that of a fifth order Gamma distribution. First and second order reactions conducted there each attain $C/C_0 = 0.3$. Find the two reaction parameters assuming segregated flow.

The RTD is

$$E(t_r) = 130.2\, t_r^4 \exp(-5t_r)$$

For first order,

$$(C/C_0)_{seg} = \int_0^\infty E(t_r)\exp(-k\bar{t}t_r)\, dt_r = 0.3$$

For second order,

$$(C/C_0)_{seg} = \int_0^\infty E(t_r)/(1+kC_0\bar{t}t_r)\, dt_r = 0.3$$

The parameters $k\bar{t} = 1.36$ and $kC_0\bar{t} = 2.70$ are found by trial. The work is summarized in the table.

First Order Second Order

$k\bar{t}$	C/C_0			$kC_0\bar{t}$	C/C_0	
1.50	0.2693			2.5	0.3151	
1.36	0.3003	check		2.7	0.2994	check
1.30	0.3148			3.0	0.2788	
1.204	0.3	PFR		3.33	0.3	PFR
1.361	0.3	CSTR		2.96	0.3	CSTR

P5.05.06. SPECIFIC RATE WITH A KNOWN RTD

In the vessel for which the tracer data of problem P5.01.09 were obtained, a first order reaction attains 95% conversion. The specific rate is to be found.

The results of P5.01.05 include,

$$\bar{t} = 5.07,\ E(t_r)_{Gamma} = 65.77\ t_r^{3.385}\exp(-4.385t_r)$$

The data also are curve fitted by

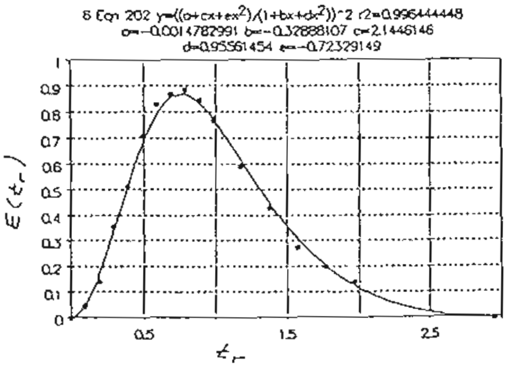
$$E(t_r)_{cf} = [\frac{-0.00148+2.1446t_r-0.7233t_r^2}{1-0.3289t_r+0.9556t_r^2}]^2$$

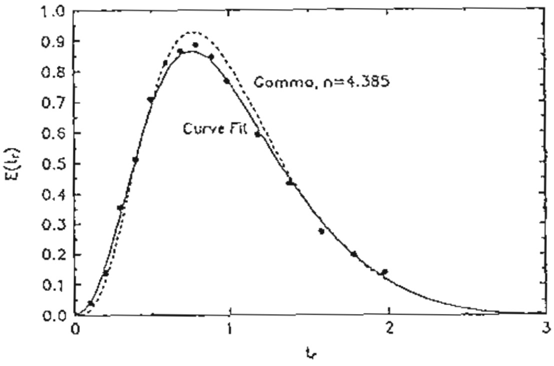
The two RTDs are compared with the original data on the figure. In segregated conversion,

$$C/C_0 = 0.05 = \int_0^\infty E(t_r)\ \exp(-k\bar{t}t_r)\ dt_r,\ \bar{t} = 5.07$$

The values of k are found by trial: k = 0.85 for Gamma, k = 0.882 for curve fit. Judging from the appearance of the $E(t_r)$ plots, an average value, k = 0.866 may be best.

Trial k	Gamma	Curve fit
1.00	0.0344	
0.85	0.05	
0.80	0.0566	
085		0.0538
0.882		0.05
0.90		0.0478





P5.05.07. SPECIFIC RATE WITH TRAPEZOID SHAPED RTD

The impulse tracer response curve of a pilot plant reactor has the shape of a trapezoid with the given equations. A first order reaction conducted in this vessel attained 95% conversion. Assuming segregated flow, find the specific rate.

The equation of the response curve is

$$C(t) = 0.4t, \quad 0 \le t \le 5t$$

$$ 2 \quad\quad 5 \le t \le 7.5, \text{ and zero elsewhere}$$

Since $\int_0^\infty C dt = 10$,

$$E(t) = C(t)/10$$

In segregated flow reaction,

$$C/C_0 = 0.05 = \int_0^\infty E(t) \exp(-kt)\, dt$$

$$= 0.04\int_0^5 t \exp(-kt)dt + 0.2\int_5^{7.5} \exp(-kt)\, dt$$

$$= \frac{0.04}{k^2}[1-(5k+1)\exp(-5k)] + \frac{0.2}{k}[\exp(-5k) - \exp(-7.5k)]$$

$$k = 0.8646$$

P5.05.08. SPECIFIC RATE OF HYDRODESULFURIZATION

The residence time distribution of a pilot catalytic hydrodesulfurizer was measured with the results shown in the table. In another test, 40% conversion was attained at a residence time $\bar{t} = 5.3$. The reaction is first order. Find the specific rate.

For segregated flow,

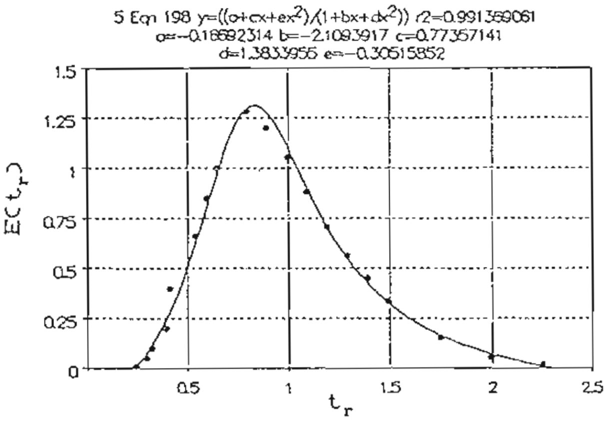
$$C/C_0 = 0.6$$

$$= \int_0^\infty \exp(-kt)E(t)dt = \int_0^\infty \exp(-k\bar{t}t_r)E(t_r)\, dt_r$$

Find k by trial by numerical integration of the $E(t_r)$ data. The solution is easier with a calculator after a curve fit of $(t_r, E(t_r))$. Such a curve fit is given with the attached plot of the data. Another possible curve fit is with the linearized form of the Gamma distribution described with problem P5.02.04 which does not require availability of the software TABLECURVE.

The correct value is k = 0.0764. The sensitivity of the calclulation is indicated by these other trial values: When k = 0.085, $C/C_0 = 0.581$; when k = 0.075, $C/C_0 = 0.603$.

t_r	$E(t_r)$	t_r	$E(t_r)$
0.27	0.01	1	1.05
0.3	0.05	1.1	0.88
0.33	0.1	1.2	0.71
0.4	0.2	1.3	0.56
0.47	0.4	1.4	0.43
0.55	0.65	1.5	0.33
0.6	0.85	1.75	0.153
0.65	1.00	2.00	0.053
0.80	1.28	2.25	0.017
0.90	1.20		



P5.05.09 SPECIFIC RATE OF HYDROFINING

Tracer data of a pilot hydrofiner are tabulated with the plot. When the vessel was used as a reactor, 95% conversion was attained. The reaction is second order. Find the value of kC_0 assuming segregated flow and compare with the plug flow value $kC_0 = 19$.

The data are curve fitted by a ratio of polynomials,

$$\mathrm{Ct)} = \frac{-0.1581+00.7449t-0.2934t^2}{1-2.0742t+1.4036t^2}$$

With this correlation,

$$\int_0^\infty \mathrm{C}dt = 0.8312,\quad \int_0^\infty t\mathrm{C}dt = 0.8408,\quad \int_0^\infty t^2\mathrm{C}dt = 0.9472$$

$$\bar{t} = 0.8408/0.8312 = 1.0015,\quad \mathrm{E}(t) = \mathrm{C}/0.8312,$$

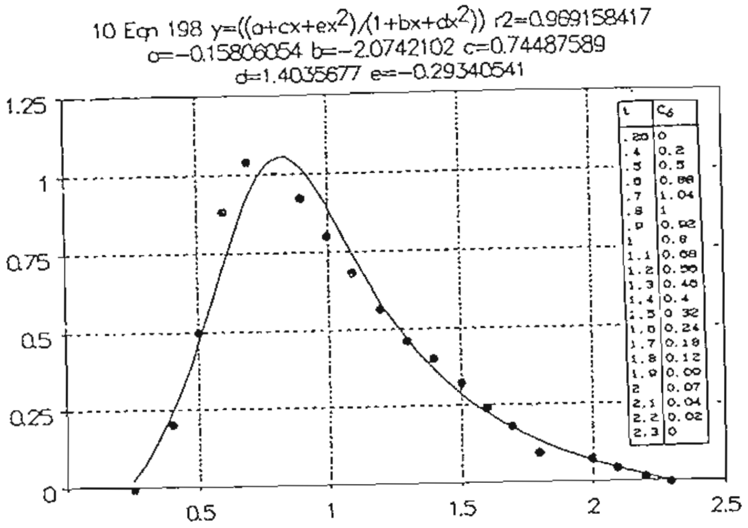
$$\sigma^2(t_r) = -1 + 0.9472/(0.8312(1.0015)^2 = 0.1138,\quad n = 8.79$$

The comparatively large value of n indicates that the flow pattern roughly approximates plug flow.

The segregated yield is given by

$$\mathrm{C/C_0} = 0.05 = \frac{1}{0.8312}\int_{0.26}^{2.3} \frac{\mathrm{C}}{1+k\mathrm{C_0}t}\,dt$$

By trial $k\mathrm{C_0} = 21.98$, compared with 19.0 for plug flow. Other trial results are: When $k\mathrm{C_0} = 25$, $\mathrm{C/C_0} = 0.0443$ and when $k\mathrm{C_0} = 20$, $\mathrm{C/C_0} = 0.0546$.



P5.05.10. A REACTOR WITH A LINEAR SHAPED C_δ CURVE

The curve representing the effluent from an impulse input to a reactor has the equation,

$C_\delta = 2 - 0.4t$, $0 \le t \le 5$, and zero elsewhere.

Find the conversion of a second order reaction for which $k\mathrm{C_0} = 0.2$ in segregated flow (a) when the response is of the given form; (b) when the Gamma distribution with the same variance is applied.

Various function are evaluated.

$\int_0^5 \mathrm{C}dt = 5$, $\int_0^5 t\mathrm{C}dt = 8.333$, $\int_0^5 t^2\mathrm{C}dt = 20.83$, $\bar{t} = 8.33/5 = 1.667$, $t_r = t/1.667$, $\mathrm{C^0} = 5/1.667 = 3.00$, $\sigma^2(t_r) = -1 + 20.83/(1.667)^2(5) = 0.5$, $n = 1/0.5 = 2$.

$$\mathrm{E}(t_r)_{\mathrm{Linear}} = (2-0.4\bar{t}t_r)/\mathrm{C^0} = 0.667 - 0.222t_r,\quad 0 \le t \le 3$$

$$\mathrm{E}(t_r)_{\mathrm{Gamma}} = 4\, t_r \exp(-2t_r),\quad \mathrm{E}(t) = \mathrm{E}(t_r)/\bar{t}$$

Conversion in segregated flow is given by

$$\mathrm{C/C_0} = \int_0^3 \frac{\mathrm{E}(t_r)}{1+0.2(1.667)t_r}\,dt_r$$

= 0.7727 , with the linear RTD (1)
0.7621 , with the Gamma RTD (2)

In a two stage CSTR, not assuming segregated flow, the material balances are, with $f_i = C_i/C_0$,

$$1 = f_1 + \bar{t}_1 k C_0 f_1^2 = f_1 + (1.667/2)(0.2)f_1^2$$

$$f_1 = f_2 + 0.1667f_2^2$$

of which the solution is

$$f_1 = 0.8730,\ f_2 = 0.7607 \qquad (3)$$

Lines (1), (2) and (3) are to be compared.

P5.05.11. CONVERSION WITH TRIANGLE SHAPED C_δ

The curve of tracer response from a reactor is triangular in shape, with the equation given following for C_δ. A second order reaction with $kC_0 = 1.5$ occurs there. Assuming segregated flow, find the conversion (a) when E(t) is represented by the given equation; (b) when the Gamma $E(t_r)$ with the same variance is used.

The equations of the response are,

$$C_\delta = \begin{cases} 1.5(t-1), & 1 \le t \le 3 \\ 5.25-0.75t & 3 \le t \le 7,\ \text{and zero elsewhere} \end{cases}$$

Various functions are obtained by numerical integration,

$$\int_0^\infty C dt = 9,\quad \int_0^\infty tC dt = 33,\quad \int_0^\infty t^2 C dt = 135,\quad \bar{t} = 33/9 = 3.67,$$

$$C^0 = 9/3.67 = 2.455,\ \sigma^2(t_r) = -1 + \frac{135}{(3.67)^2(9)} = 0.1157,$$

$$n = 1/0.1157 = 8.64,\ \Gamma(8.64) = 18807.4,\ n^n/\Gamma(n) = 6564$$

$$E(t_r)_{Gamma} = 6564\, t_r^{7.64} \exp(-8.64t_r)$$

$$E(t_r)_{Triangle} = C_\delta/C^0 = C_\delta/2.455$$

Conversion in segregated flow is given by

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+kC_0\bar{t}t_r} dt_r = \int_0^\infty \frac{E(t_r)}{1+1.5(3.67)t_r} dt_r$$

= 0.1682, with triangular response
0.1672, with Gamma response
0.1538, with plug flow.

P5.05.12. FIRST ORDER REACTION WITH TRIANGULAR TRACER RESPONSE

An impulse tracer tracer test gave the response represented by given equations. A first order reaction with k = 0.8 is conducted in this vessel. Find conversions by three models: (a) segregated flow with the given response curve; (b) segregated flow with a Gamma distribution having the same variance; c) a CSTR battery with the same variance, interpolating linearly when necessary between integral values of n.

The equation representing the tracer response is,

$$C = \begin{cases} 1.667t, & 0 \le t \le 3 \\ 12.5-2.5t, & 3 \le t \le 5,\ \text{and zero elsewhere} \end{cases}$$

Various functions are derived by manipulation of this response,

$$\int_0^\infty C dt = 12.5,\quad \int_0^\infty tC dt = 33.33,\quad \int_0^\infty t^2 C dt = 102.08$$

$$\bar{t} = 33.33/12.5 = 2.667,\ \sigma^2(t_r) = -1 + \frac{102.08}{(2.667)^2(12.5)} = 0.1484,\ n = 6.74,$$

$\Gamma(n) = 443.7,\ n^n/\Gamma(n) = 867.1,$

$$E(t_r)_{Gamma} = 867.1\ t_r^{5.74}\exp(-6.74t_r)$$

$$E(t)_{Triangle} = C/\int_0^\infty Cdt = 0.08C$$

With the Gamma model, segregated flow gives

$$C/C_0 = \int_0^\infty \exp(-k\bar{t}t_r)E(t_r)\ dt_r = \int_0^\infty \exp[-(0.8)(2.67)t_r]E(t_r)dt_r$$

$$= 0.1571 \qquad (1)$$

With the triangular shaped response,

$$C/C_0 = \int_0^\infty \exp(-0.8t)\ E(t)_{Triangle}dt = 0.1667 \qquad (2)$$

In a CSTR battery of n = 6.74 stages,

$$C/C_0 = 1/(1+k\bar{t}/n)^n = \frac{1}{(1+0.8(2.667)/6.74)^{6.74}} = 0.1567 \qquad (3)$$

In plug flow, $C/C_0 = 0.1184$, (4)

Compare the results of lines (1), (2), (3) and (4).

P5.05.13. SEMICIRCULAR SHAPED RESPONSE CURVE

The tracer response curve from an impulse input to a reactor is a semicircle with the equation

$$C = \sqrt{2.25-(t-1.5)^2} = \sqrt{3t-t^2}, \qquad 0 \le t \le 3$$

A second order reaction with $kC_0 = 3.25$ is conducted there. Find the segregated conversion using (a) the experimental E(t); (b) the Gamma distribution with the same variance.

Various functions are evaluated by numerical integration,

$$\int_0^\infty Cdt = 3.534,\quad \int_0^\infty tCdt = 5.293,\quad \int_0^\infty t^2Cdt = 9.865,$$

$$\bar{t} = 5.293/3.534 = 1.5,\ \sigma^2(t_r) = -1 + \frac{9.865}{(1.5)^2(5.293)} = 0.2405,$$

$$n = 1/0.2405 = 4.16,\ \Gamma(n) = 6.35,\ n^n/\Gamma(n) = 59.25$$

$$E(t)_{data} = C/3.534$$

$$E(t_r)_{Gamma} = 59.25\ t_r^{3.16}\ \exp(-4.16t_r).$$

For batch reaction,

$$(C/C_0)_{batch} = 1/(1+kC_0t) = 1/(1+3.25t)$$

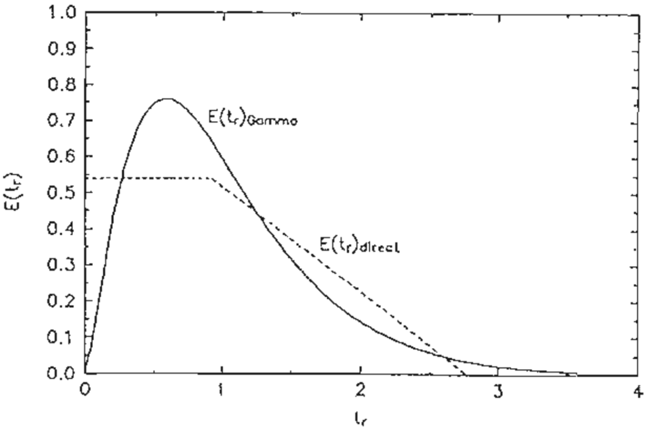
In segregated flow with the direct data,

$$C/C_0 = \int_0^3 (C/C_0)_{batch}E(t)_{data}dt = 0.2183, \qquad (1)$$

In segregated flow with the Gamma distribution,

$$C/C_0 = \int_0^\infty \frac{E(t_r)_{Gamma}}{1+3.25(1.5)t_r}\ dt_r = 0.2329 \qquad (2)$$

The results on lines (1) and (2) are in rough agreement. Plots of the two distributions are shown.



P5.05.14. SEGREGATED MODELS. QUARTER CIRCLE INPUT

A tracer response curve is made up of two quarter circles with the equations

$$C = \begin{cases} 1 - \sqrt{1-t^2}, & 0 \le t \le 1 \\ 1 - \sqrt{1-(2-t)^2}, & 1 \le t \le 2, \text{ and zero elsewhere} \end{cases}$$

A second order reaction with k = 1 and $C_0 = 2$ is to be conducted there. Find the conversion under segregated flow conditions with the direct RTD and Gamma RTD with the same variance.

Pertinent functions are derived as follows,

$$\int_0^2 C dt = 0.4292,\ \int_0^2 tC dt = 0.4298,\ \int_0^2 t^2 C dt = 0.4663,$$

$$\bar{t} = 0.4298/0.4292 = 1.0014, \text{ say } 1.0$$

$$\sigma^2(t_r) = -1 + \frac{0.4663}{(1.0)^2(0.4292)} = 0.0864,$$

$$n = 1/0.0864 = 11.57,\ \Gamma(n) = 1.406(10^7),\ n^n/\Gamma n) = 142810$$

$$E(t) = C/\int_0^\infty C dt = C/0.4292$$

In segregated flow with the original data,

$$(C/C_0)_{batch} = 1/(1+kC_0 t) = 1/(1+2t)$$

$$C/C_0 = \int_0^2 \frac{C}{0.4292(1+2t)} dt = 0.2012 + 0.1468 = 0.3480 \quad (1)$$

In segregated flow with the Gamma distribution,

$$E(t_r)_{Gamma} = 142810\ t_r^{10.57} \exp(-11.57 t_r)$$

$$C/C_0 = \int_0^\infty \frac{E(t_r)_{Gamma}}{1+kC_0 \bar{t} t_r} dt_r = 0.3465\ ,\ kC_0 = 2, \quad (2)$$

The results of lines (1) and (2) agree closely. In plug flow, $C/C_0 = 1/(1+2) = 0.3333$.

P5.05.15. CONSECUTIVE REACTIONS. PARABOLIC RESPONSE CURVE.

The tracer response curve of an impulse input to a reactor has the equation $C = \sqrt{1-0.5t}$. The reaction $A \Rightarrow B \Rightarrow C$ is conducted there. $k_1 = 1.5$, $k_2 = 0.75$. Find conversion under batch and segregated flow conditions.

The required functions are

$$\int_0^2 C dt = 1.3333,\ \int_0^2 tC dt = 1.0658,\ \bar{t} = 1.0658/1.3333 = 0.7994,$$

$$E(t) = C/\int_0^2 C dt = 0.75\sqrt{1-0.5t}$$

In a batch reactor,

$$\frac{dC_b}{dt} = 1.5 C_{a0} \exp(-1.5t) - 0.75 C_b$$

$$(C_b/C_{a0})_{batch} = 2[\exp(-0.75t) - \exp(-1.5t)]$$

In segregated flow

$$(C_b/C_{b0})_{seg} = 0.75(2)\int_0^2 \sqrt{1-0.5t}\ [\exp(-0.75t) - \exp(-1.5t)]dt$$
$$= 0.3907 \qquad (1)$$

In a batch reactor with $\bar{t} = 0.7994$,

$$C_b/C_{a0} = 2[\exp(-0.6) - \exp(-1.2)] = 0.4952 \qquad (2)$$

P5.05.16. BATCH AND SEGREGATED FLOW. SEMICIRCULAR RESPONSE CURVE

The response curve of impulse input to a reactor is semicircular with equation

$$C = -1+\sqrt{10t-t^2}, \quad 0.101\le t\le 9.899$$

A reaction for which the batch conversion equation is

$$(C/C_0)_{batch} = 1/(1+0.2t)$$

is conducted there. Find the conversions under batch and segregated flow conditions.

Required functions are evaluated following.

$$\int_{0.1}^{9.9} Cdt = 28.90,\ \int_{0.1}^{9.9} tCdt = 145.27,\ \bar{t} = 145.27/28.9 = 5.03$$

$$E(t) = C/28.90 = = 0.0346C$$

In segregated flow,

$$C/C_0 = 0.0346 \int_{0.1}^{9.9} \frac{-1+\sqrt{10t-t^2}}{1+0.2t}\,dt = 0.536 \qquad (1)$$

In batch operation with $\bar{t} = 5.03$,

$$C/C_0 = 1/[1+0.2(5.03)] = 0.4985 \qquad (2)$$

P5.05.17. REACTOR WITH A TRAPEZOIDAL RESPONSE CURVE.

The tracer response curve of impulse input to a reactor is a trapezoid with the given equations. For a second order reaction with $kC_0 = 2$, find the conversion (a) in segregated flow; (b) in a CSTR battery having the same variance, interpolating if necessary between integral values of n.

The equation of the response curve is

$$C = \begin{cases} 5t/3, & 0\le t\le 3 \\ 5 & 3\le t\le 5 \\ (40-5t)/3 & 5\le t\le 8, \text{ and zero elsewhere} \end{cases}$$

The required functions are evaluated numerically.

$$\int_0^8 Cdt = 25,\ \int_0^8 tCdt = 100,\ \int_0^8 t^2Cdt = 470.83,\ \bar{t} = 100/25 = 4$$

$$\sigma^2(t_r) = -1 + \frac{470.83}{(4)^2(25)} = 0.1771,\ n = 1/0.1771 = 5.65$$

$$E(t) = C/\int_0^\infty Cdt = 0.04C$$

In segregated flow,

$$C/C_0 = \int_0^8 \frac{0.04C}{1+2t}\,dt = 0.1361 \qquad (1)$$

In a CSTR battery with n between 5 and 6, the material balance is

$$C_{\alpha-1}/C_0 = C_\alpha/C_0 + (kC_0\bar{t}/n)(C_\alpha/C_0)^2,\ \alpha = 1 \text{ to } n,\ n = 5 \text{ or } 6$$

For n = 5, the solution of the preceding equation is $C_5/C_0 = 0.1527$; for n = 6, $C_6/C_0 = 0.1459$. Interpolating linearly,

$$C_{5.65}/C_0 = 0.1483. \qquad (2)$$

In plug flow,

$C/C_0 = 1/(1+2\bar{t}) = 1/9 = 0.1111 \qquad (3)$

Comparison also could be made for segregated conversion with a Gamma distribution having a variance of 0.1771.

P5.05.18. RESPONSE CURVE A RIGHT ANGLED TRAPEZOID

A tracer response curve in the shape of a trapezoid with a right angle has the given equations. Find the conversion of a second order reaction with $kC_0 = 1.25$ under segregated flow conditions (a) with the directly evaluated RTD; (b) with a Gamma RTD having the same variance.

The equations of the response curve are

$$C = \begin{cases} 2 & 0 \le t \le 1 \\ 3-t & 1 \le t \le 3, \text{ and zero elsewhere} \end{cases}$$

Numerical integration results in these values:

$$\int_0^3 C dt = 4.0,\ \int_0^3 tC dt = 4.333,\ \int_0^3 t^2 C dt = 6.667,$$

$$\bar{t} = 4.333/4 = 1.083,\ \sigma^2(t_r) = -1 + \frac{6.667}{(1.083)^2(4)} = 0.4201$$

$$n = 2.38,\ \Gamma(n) = 1.226,\ n^n/\Gamma(n) = 6.423$$

$$E(t) = C/\int_0^3 C dt = 0.25C$$

In segregated flow with this direct RTD,

$$C/C_0 = \int_0^3 \frac{0.25C}{1+1.25t} dt = 0.4922 \qquad (1)$$

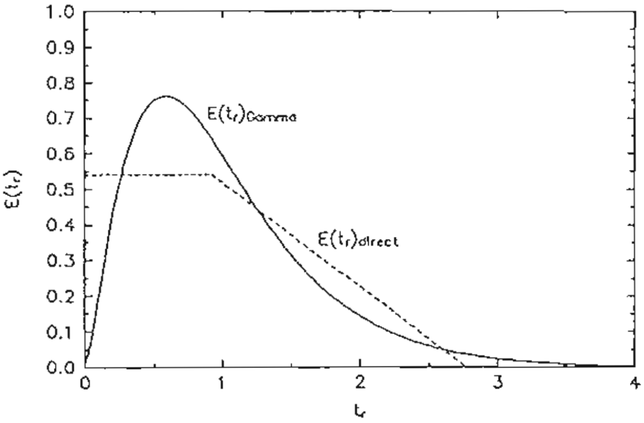
The Gamma distribution with n = 2.38 is

$$E(t_r) = 6.423\ t^{1.38}\exp(-2.38t_r)$$

and the segregated conversion is

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+1.25(1.083)t_r} dt_r = 0.4789 \qquad (2)$$

Plots of $E(t_r)_{Gamma}$ and $E(t_r)_{direct} = \bar{t}E(t)$ show a rough equivalency, as also attested by the closeness of the two conversions.



P5.05.19. COSINUSOIDAL TRACER RESPONSE CURVE

A reactor has a tracer response curve from an impulse input with the equation $C = 0.5\cos(\pi t/4)$ over the range $0 \le t \le 2$. A reaction A⇒B⇒C with k_2 =

$k_1/2$ attains 70% conversion of A under plug flow conditions. Find the concentration of B under segregated flow conditions.

The required functions are

$$\int_0^2 C dt = 2/\pi = 0.6366,\ \int_0^2 tC dt = 0.4626,\ \int_0^2 t^2 C dt = 0.4823,$$

$$\bar{t} = 0.4626/0.6366 = 0.7267,\ E(t) = C/(2/\pi) = (\pi/4)\cos(\pi t/4)$$

In the plug flow unit,

$$C_a/C_{a0} = 0.3 = \exp(-k_1\bar{t}),\ = \exp(-0.7276k_1),\ k_1 = 1.6568$$

$$C_b/C_{a0} = 2[\exp(-0.8284t) - \exp(-1.6568t)] \quad (1)$$

$$= 0.4995 \text{ with } C_{b0} = 0.4995 \quad (2)$$

In segregated flow,

$$C_b/C_{ao} = \int_0^2 (C_b/C_{a0})_{plugflow} E(t)\ dt$$

$$= (\pi/4) \int_0^2 [\exp(-0.8284t) - \exp(-1.6568t)] \cos(\pi t/4) dt$$

$$= 0.3916 \quad (3)$$

This could be compared with segregated flow and a Gamma distribution for which

$$\sigma^2(t_r) = -1 + \frac{0.4823}{(0.7267)^2(0.6366)} = 0.4350,\ n = 2.299,$$

$$\Gamma(n) = 1.166,\ n^n/\Gamma(n) = 5.815,$$

$$E(t_r)_{Gamma} = 5.815\ t_r^{1.299} \exp(-2.299t_r)$$

P5.05.20. CONVERSION WITH A KNOWN RTD

Values of $E(t_r)$ of a reactor are tabulated. The residence time is $\bar{t} = 5$. Find the conversion in segregated flow of a second order reaction with $kC_0 = 0.04$. Interpret the fact that the variance is greater than unity and that the performance is poorer than that of a single stage CSTR.

The required integrals are found trapezoidally.

$$(C/C_0)_{seg} = \int_0^{10} (C/C_0)_{batch} E(t_r) dt_r = \int_0^{10} \frac{E(t_r)}{1+kC_0\bar{t}t_r} dt_r$$

$$= 0.8692, \text{ with } kC_0 = 0.04.$$

The variance is

$$\sigma^2(t_r) = -1 + \int_0^{10} t_r^2 E(t_r) dt_r = 1.3077$$

Number of stages, $n = 1/1.3077 = 0.765$

In plug flow, $C/C_0 = 1/[1+0.04(5)] = 0.833$

In an ideal CSTR,

$$1 = C/C_0 + kC_0\bar{t}(C/C_0)^2,\ C/C_0 = 0.854$$

The performance poorer than a single stage ideal stirred tank may be accounted for by the occurrence of bypassing or dead volume.

t_r	$E(t_r)$	$t_r^2E(t_r)$	$\frac{E(t_r)}{1+0.2t_r}$
0	1.4	0	1.4
0.1	1.2	0.012	1.143
0.4	0.8	0.128	0.7407
0.8	0.38	0.243	0.3276
1	0.12	0.270	0.0923
1.8	0.08	0.259	0.0588
2.5	0.04	0.250	0.0266
3.7	0.02	0.274	0.0115
4.4	0.015	0.290	0.0080
5.6	0.01	0.314	0.0047
7.1	0.006	0.302	0.0026
10	0	0	0

P5.05.21. CONVERSION WITH A KNOWN RTD

A reactor has an RTD represented by

$$E(t_r) = 13.5t_r^2 \exp(-3t_r)$$

and a mean residence time $\bar{t} = 4.5$. A reaction with rate equation, $-dC/dt = 1.5C^2$, is to be conducted there. Compare the conversions in (a) segregated flow; (a) in plug flow; (c) in a three stage CSTR.

(a) In a batch reactor

$$(C/C_0)_{batch} = 1/(1+1.5t) = 1/[1+1.5(4.5)t_r] = 1/(1+6.75t_r)$$

$$(C/C_0)_{segregated} = \int_0^\infty \frac{E(t_r)}{1+6.75t_r}dt_r = 0.1668 \qquad (1)$$

(b) In plug flow,

$$(C/C_0)_{pf} = 1/[1+1.5(4/5)] = 0.1290 \qquad (2)$$

(c) In a three stage CSTR

$$C_{n-1}/C_0 = C_n/C_0 + kC_0(\bar{t}/3)(C_n/C_0)^2$$

$$= C_n/C_0 + 2.25(C_n/C_0)^2, \text{ with } n = 1, 2, 3$$

Numerical results are

$$C_1/C_0 = 0.4805,\ C_2/C_0 = 0.2906,\ C_3/C_0 = 0.2003 \qquad (3)$$

Lines (1), (2) and (3) are to be compared.

P5.05.22. DATA OF TRACER RESPONSE. FIRST ORDER REACTION

Flow characteristics of a continuous reactor are studied by sudden introduction of miscible tracer into the feed stream. These data of the effluent concentration were taken,

t	0.1	0.2	1	2	5	10	30
C	0.20	0.17	0.15	0.125	0.070	0.020	0.001

What conversion can be expected in segregated flow of a first order reaction with specific rate k = 0.15?

The data are fitted by the empirical equation

$$t = -9.881 - 5.6374\ln(C)$$

$$C = 0.1733\exp(-t/5.6374)$$

NumericaL integration then gives these values,

$$\int_0^\infty Cdt = 0.5745,\ \int_0^\infty tCdt = 1.2267,\ \int_0^\infty t^2Cdt = 3.7707,$$

$$\bar{t} = 1.2267/0.5745 = 2.135$$

$$E(t) = C/0.5745 = 0.3017\exp(-t/5.6374)$$

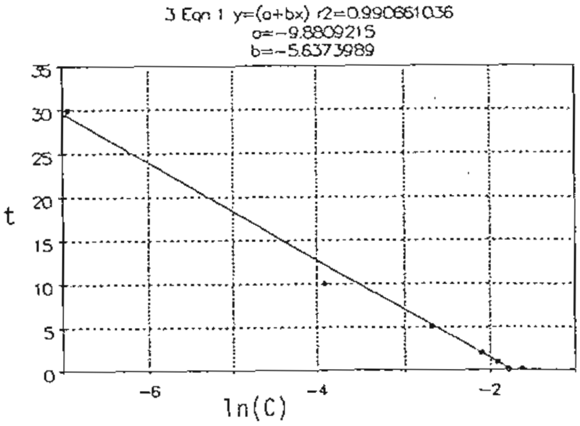
In segregated flow,

$$C/C_0 = \int_0^\infty (C/C_0)_{batch} E(t)\,dt$$

$$= 0.3017\int_0^\infty \exp(-0.15t)\exp(-t/5.6374)\,dt = 0.7421 \quad (1)$$

For comparison, in plug flow,

$$C/C_0 = \exp(-kt) = \exp[0.15(2.135)] = 0.7260 \quad (2)$$



P5.05.23. NORMALIZED DATA OF TRACER RESPONSE

A tracer test on a packed vessel with "closed ends" gave the data of the first two columns of the table. Find conversion of a second order reaction with $kC_0 = 2$ in segregated flow (a) with the direct data; (b) with a Gamma distribution of the same variance.

In segregated flow,

$$(C/C_0)_{direct} = \int_0^\infty \frac{E(t_r)}{1+kC_0\bar{t}t_r}\,dt_r = \int_0^\infty \frac{E(t_r)}{1+2t_r}\,dt_r = 0.3455 \quad (1)$$

The integrand is tabulated and the integration is with the trapezoidal rule.

The variance is

$$\sigma^2(t_r) = -1 + \int_0^\infty t_r^2 E(t_r)\,dt_r = 0.0677,\ n = 1/0.0677 = 14.77,\ \Gamma(n) = 4.695(10^{10}),\ n^n/\Gamma(n) = 3.982(10^6).$$

The integrand is tabulated and the integration is done trapezoidally. Accordingly,

$$E(t_r)_{Gamma} = 3.982(10^6)\,t_r^{13.77}\exp(-14.77t_r)$$

$$(C/C_0)_{seg} = \int_0^\infty \frac{E(t}{1+2t_r}\,dt_r = 0.3452 \quad (2)$$

Results on lines (1) and (2) are in agreement.

t_r	$E(t_r)$	$t_r^2E(t_r)$	$\frac{E(t_r)}{1+2t_r}$
0	0	0	0
.35	0	0	0
.5	.09	.0225	.045
.55	.15	.0454	.0714
.6	.32	.1152	.1455
.6	.55	.2324	.2391
.75	.95	.4655	.3958
.7	1.3	.7313	.52
.85	1.59	1.0176	.6115
.8	1.78	1.2644	.6593
.95	1.85	1.4985	.6607
.95	1.82	1.6426	.6276
1	1.7	1.7	.5667
1.05	1.52	1.6758	.4903
1.1	1.3	1.573	.4063
1.15	1.06	1.4019	.3212
1.2	.85	1.224	.25
1.25	.68	1.0625	.1943
1.3	.56	.9464	.1556
1.35	.45	.8201	.1216
1.4	.33	.6468	.0868
1.45	.26	.5467	.0667
1.5	.2	.45	.05
1.6	.13	.3328	.031
1.7	.09	.2601	.0205
1.8	.06	.1944	.013
1.9	.04	.1444	.0083
2	.02	.08	.004
2.1	0	0	0

P5.05.24. CONVERSION WITH A RIGHT TRIANGLE RESPONSE CURVE

The response curve of impulse input to a reactor has the equation

$C = 0.5(5-t)$, $1 \le t \le 5$, and zero elsewhere

A second order reaction with $kC_0 = 0.5$ is to be conducted there. Find the following (a) The RTD, $E(t_r)_{Gamma}$, of the Gamma distribution with the same variance as the data; (b) segregated conversion with the direct data; (c) segregated conversion with the Gamma distribution.

These functions are evaluated,

$\int_1^5 Cdt = 4$, $\int_1^5 tCdt = 9.333$, $\int_1^5 t^2Cdt = 25.33$,

$\bar{t} = 9.333/4 = 2.333$, $C^0 = \int_1^5 C\,dt/\bar{t} = 1.7143$,

$$\sigma^2(t_r) = -1 + \frac{25.33}{(2.333)^2(4)} = 0.1633,\ n = 6.125,\ \Gamma(n) = 132.2,$$

$n^n/\Gamma(n) = 500.95$

$$E(t_r)_{data} = C/C^0 = 0.2917(5-t_r), \qquad 0.428 \le t_r \le 2.143 \qquad (1)$$

$$E(t_r)_{Gamma} = 500.95\ t_r^{5.125}\exp(-6.125t_r) \qquad (2)$$

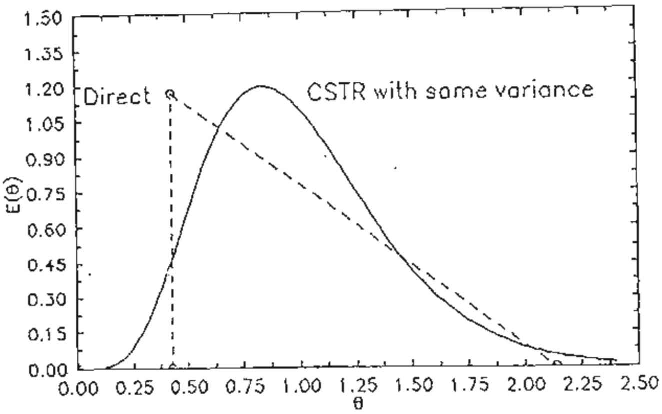
In segregated conversion,

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+kC_0\bar{t}t_r}\,dt_r = \int_0^\infty \frac{E(t_r)}{1+0.5(2.333)t_r}\,dt_r$$

$= 0.483$, with Equation (1)

0.543, with Equation (2)

The RTDs of Equations (1) and (2) are compared on the plots.



P5.05.25. ORDER AND SPECIFIC RATE OF A REACTION

A reactor has a residence time distribution

$$E(t_r) = 13.5\ t_r^2\exp(-3t_r)$$

A reaction with $C_0 = 1$ is conducted there at several residence times with the results of the first two rows:

$\bar{t}$	0.5	1.0	2.0	3.0
C/C_0	0.40	0.23	0.12	0.070
k	2.800	2.640	2.683	2.793

The numbers of the last row are calculated here. On the assumption of segregated flow, show that the order of the reaction is 1.5.

In batch reaction of order q = 1.5,

$$(C/C_0)_{batch} = \frac{1}{[1+(q-1)kC_0^{q-1}\bar{t}t_r]^{1/(q-1)}} = \frac{1}{[1+0.5k\bar{t}t_r]^2}$$

In segregated flow,

$$C/C_0 = \int_0^\infty (C/C_0)_{batch}E(t_r)\,dt_r$$

The procedure is: At each residence time of the data, assume a value of k until one is found to satisfy the given value of C/C_0.

The values of the third row of the preceding table are nearly enough constant to substantiate the assumption of the order q = 1.5. The several trial values are summarized following.

$\bar{t}$	k	C/C_0	
0.5	3.0	0.382	
	2.80	0.400	check
1	3.00	0.219	
	2.80	0.233	
	2.84	0.230	check
2	2.80	0.1140	
	2.60	0.1243	
	2.683	0.120	check
3	3.0	0.0638	
	2.8	0.0698	
	2.793	0.0700	check

P5.05.26. A SECOND ORDER REACTION

Tracer response of an impulse input to a reactor has the equation C = 5 t exp(-2.5t). What conversion is attained in segregated flow by a second order reaction with $kC_0 = 23.75$?

The following numbers are derived,

$$\int_0^\infty C dt = 0.8,\quad \int_0^\infty tC dt = 0.64,\quad \bar{t} = 0.64/0.8 = 0.8,$$

$$E(t) = C/\int_0^\infty C dt = 6.25\ t \exp(-2.5t)$$

$$(C/C_0)_{batch} = 1/(1+23.75t)$$

In segregated flow,

$$C/C_0 = \int_0^\infty (C/C_0)_{batch} E(t)\ dt = 0.0831$$

P5.05.27. A SECOND ORDER REACTION

Tracer response of an impulse input to a reactor has the equation C = 5 t exp(-2.5t). What conversion is attained in segregated flow by a second order reaction with $kC_0 = 23.75$?

The following numbers are derived,

$$\int_0^\infty C dt = 0.8,\quad \int_0^\infty tC dt = 0.64,\quad \bar{t} = 0.64/0.8 = 0.8,$$

$$E(t) = C/\int_0^\infty C dt = 6.25\ t \exp(-2.5t)$$

$$(C/C_0)_{batch} = 1/(1+23.75t)$$

In segregated flow,

$$C/C_0 = \int_0^\infty (C/C_0)_{batch} E(t)\ dt = 0.0831$$

P5.06.01. SEGREGATED AND CSTR SIZES

A reactor has a residence time distribution like that of that of two equal completely mixed tanks in series. The rate equation is $-dC/dt = 0.5C^{1.5}$. Inlet concentration is $C_0 = 1.2$ lbmol/cuft and the feed rate is 10 lbmol reactant/min. Conversion required is 95%. Find the reactor volume needed (a) assuming segregated flow; (b) in a two stage CSTR.

The RTD is

$$E(t_r) = 4\ t_r \exp(-2t_r)$$

The volumetric flow rate is

$$V' = 10/1.2 = 8.33 \text{ cfm}$$

and the reactor volume is related to the residence time by

$$V_r = V'\bar{t} = 8.33\bar{t}$$

For a batch reaction of order q = 1.5,

$$(C/C_0)_{batch} = \frac{1}{[1+(q-1)kC_0^{q-1}\bar{t}t_r]^{1/(q-1)}} = \frac{1}{[1+0.5k\bar{t}C_0^{-0.5}t_r]^2}$$

In segregated flow,

$$C/C_0 = \int_0^\infty (C/C_0)_{batch}E(t_r)dt_r = 0.05$$

By trial,

$$k\bar{t}/C_0^{0.5} = 13.88$$

$$\bar{t} = 13.88\sqrt{1.2}\,/0.5 = 30.41$$

$$V_r = V'\bar{t} = 8.33(30.41) = 253.3 \text{ cuft}$$

Material balances in the two stage CSTR,

$$1.2 = C_1 + 0.5(\bar{t}/2)C_1^{1.5} \tag{1}$$

$$C_1 = 0.06 + 0.5(\bar{t}/2)(0.06)^{1.5} \tag{2}$$

Solving these equation simultaneously,

$$C_1 = 0.2105$$

$$\bar{t} = 40.97$$

$$V_r = 341.3 \text{ cuft}$$

P5.06.02. PILOT AND COMMERCIAL REACTORS

(a) An impulse tracer test was made on a pilot reactor. The effluent concentration curve is represented by the equations following. Subsequently a second order reaction was performed in this vessel and 75% conversion was attained. Find kC_0, assuming segregated flow.

(b) The same reaction is to be carried out in a commercial size vessel whose RTD is a sixth order Erlang. The initial concentration is the same as in the pilot run. Find the conversion attained with a residence time $\bar{t} = 0.5$.

The pilot effluent curve equations are,

$$C = \begin{cases} 8t & 0 \le t \le 0.25 \\ 3-4t & 0.25 \le t \le 0.75, \text{ and zero elsewhere} \end{cases}$$

Properties of this relation are,

$$\int_0^\infty Cdt = 0.75,\ \int_0^\infty tCdt = 0.25,\ \bar{t} = 0.25/0.75 = 1/3,$$

$$C^0 = 0.75/(1/3) = 2.25,$$

$$E(t_r) = \begin{cases} C/C^0 = 8\bar{t}t_r/2.25 = 1.1852t_r & 0 \le t_r \le 0.75 \\ (3-4\bar{t}t_r)/2.25 = 1.333-1.5926t_r & 0.75 \le t_r \le 2.25 \end{cases}$$

In segregated flow in the pilot reactor,

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+kC_0\bar{t}t_r}dt = 0.25$$

By trial,

$$kC_0\bar{t} = 3.706$$

$$kC_0 = 3.706(3) = 11.12$$

(b) In the commercial unit,

$$E(t_r) = 388.8\ t_r^5 \exp(-6t_r)$$

In segregated flow with $\bar{t} = 0.5$

$$C/C_0 = 388.8 \int_0^\infty \frac{t_r^5 \exp(-6t_r)}{1+11.18(0.5)t_r}\,dt_r = 0.1710 \qquad (1)$$

For comparison, in plug flow,

$$C/C_0 = 1/[1+11.18(0.5)] = 0.1525 \qquad (2)$$

P5.06.03. SEVERAL MECHANISMS, SEVERAL CONTACT TIMES

A second order reaction undergoes conversion under three conditions: (a)under segregated flow, with $E(t_r) = 4t_r \exp(-2t_r)$; (b) in a two stage CSTR; (c) in plug flow. Compare conversions over a range of $kC_0\bar{t}$.

(a) In segregated flow, $C/C_0 = \int_0^\infty \frac{4t_r\exp(-2t_r)}{1+kC_0\bar{t}t_r}\,dt_r$

(b) Solve the equations of the material balances on the two stages, with $f_i = C_i/C_0$,

$$1 = f_1 + (kC_0\bar{t}/2)f_1^2\ ,\quad f_1 = f_2 + (kC_0\bar{t}/2)f_2^2$$

(c) In plug flow, $C/C_0 = 1/(1+kC_0\bar{t})$

The results are tabulated over a range of the parameter. Segregated performance is intermediate.

C/C_0

$kC_0\bar{t}$	Segregated	CSTR	Plug Flow
5	0.2328	0.2747	0.1667
10	0.1405	0.1857	0.0909
40	0.0438	0.0781	0.0244
100	0.0188	0.0423	0.0099
1000	0.0020	0.0084	0.0010

P5.06.04. SEGREGATED AND CSTR PERFORMANCE

A reactor has a residence time distribution

$$E(t_r) = 24.63\ t_r^2 \exp[-3(t_r+0.2)]$$

A second order reaction is conducted there; it has the properties: $k = 0.5$, $C_0 = 3$ and $\bar{t} = 3$. Find the conversion (a) under segregated flow conditions ; (b) in a CSTR battery with the same variance.

Under segregated flow conditions,

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+kC_0\bar{t}t_r}\,dt_r = \int_0^\infty \frac{E(t_r)}{1+0.5(3)(3)t_r}\,dt_r = 0.2264 \qquad (1)$$

The variance is

$$\sigma^2(t_r) = \int_0^\infty (t_r-1)^2 E(t_r)\,dt_r = 0.3337$$

$$n = 1/3.337 = 2.997,\ \text{say } 3.0$$

The given RTD is not quite that of a three stage CSTR but the variance is very nearly the same. The material balances on a three stage CSTR are

$$f_i = C_i C_0$$

$$1 = f_1 + (kC_0\bar{t}/3)f_1^2 = f_1 + 1.5f_1^2$$

$$f_1 = f_2 + 1.5f_2^2$$

$$f_2 = f_3 + 1.5f_3^2$$

The solution is

$$f_1 = 0.5486,\ f_2 = 0.3572,\ f_3 = 0.2576 \qquad (2)$$

Lines (1) and (2) are to be compared.

P5.06.05. A REVERSIBLE REACTION

A reactor has a tracer response, $C = 1 - 0.25t^2$. A reaction with a rate equation,

$$-dA/dt = 3.2[A - (A_0-A)/4],$$

is to be processed there. Find $f = A/A_0$ at the outlet in segregated flow.

The rate equation is rewritten as

$$-df/dt = 3.2[f - (1-f)/4]$$

In a batch reactor,

$$f_{batch} = 0.2 + 0.8\exp(-4t)] \qquad (1)$$

Pertinent functions of the tracer response are,

$$\int_0^2 C\,dt = 1.333,\ \int_0^2 tC\,dt = 1.000,\ \int_0^2 t^2C\,dt = 1.067,$$

$$\bar{t} = 1/1.333 = 0.75$$

$$E(t) = C/\int_0^\infty C\,dt = 0.75C = 0.75(1-0.25t^2) \qquad (2)$$

In segregated flow,

$$f_{out} = \int_0^\infty f_{batch}E(t)\,dt = 0.3454 \qquad (3)$$

In plug flow or batch reaction with $\bar{t} = 0.75$, using Eq (1),

$$f = 0.2 + 0.8\exp(-3)] = 0.2398 \qquad (4)$$

Lines (3) and (4) are to be compared.

P5.06.06. CONSECUTIVE REACTIONS

The curve of a tracer response has the equation

$$C = \sqrt{1-0.5t}$$

A reaction $A \xrightarrow{2k} B \xrightarrow{k} C$ is to be conducted in this vessel with $C_{b0} = 0$. In plug flow at the residence time in this vessel conversion of A would be 70%. What is the concentration of B at the outlet of this reactor in segregated flow?

Pertinent functions of the tracer response are

$$\int_0^2 C\,dt = 1.333,\ \int_0^2 tC\,dt = 1.067,\ \bar{t} = 1.067/1.333 = 0.80$$

$$E(t) = C/\int_0^\infty C\,dt = 0.75\sqrt{1-0.5t} \qquad (1)$$

In a plug flow reactor,

$$k = \frac{1}{2\bar{t}}\ln(C_{a0}/C_a) = \ln(0.3)/1.6 = 0.75$$

In a batch reactor,

$$-dC_b/dt = 2kC_a - kC_b = 2kC_{a0}\exp(-2kt) - kC_b$$

$$(C_b/C_{a0})_{batch} = 2[\exp(-0.75t) - \exp(-1.5t)] \qquad (2)$$

With $\bar{t} = 0.8$,

$$(C_b/C_{a0})_{batch} = 0.4952 \qquad (3)$$

In segregated flow, using Equations (1) and (2),

$$C_b/C_{a0} = \int_0^\infty (C_b/C_{a0})_{batch}E(t)\,dt = 0.391 \qquad (4)$$

Lines (3) and (4) are to be compared.

P5.06.07. A SECOND ORDER REVERSIBLE REACTION. TABULAR DATA

The rate equation of a reversible reaction is

$-dC/dt = 0.25[C-(1-C)/8]$

The integral for a batch reaction is tabulated in the first two columns. A potential reactor has the residence time distribution E(t) given in column 3. Find the outlet concentration in segregated flow.

In segregated flow,

$$C_{seg} = \int_0^\infty C_{batch}E(t)dt = 0.511$$

The integrand is in column 4 of the table and the integration is accomplished with the trapezoidal rule.

t	C_{batch}	E(t)	$C_{batch}E(t)$
0	1	0	0
1	.8029	.0307	.0246
2	.6758	.1103	.0746
3	.5881	.167	.0984
4	.525	.1782	.0935
5	.478	.1564	.0748
6	.4421	.1214	.0537
7	.4143	.0866	.0359
8	.3923	.0581	.0228
9	.3749	.0372	.0139
10	.3609	.0229	.0083
11	.3495	.0137	.0048
12	.3403	.0080	.0027
13	.3327	.0046	.0015
14	.3265	.0026	.0008
15	.3214	.0014	.0005
16	.3172	.00077	.0002
17	.3137	.00042	.00013
18	.3109	.00022	.00007
19	.3085	.00012	0
20	.3065	.00006	0

P5.06.08. NON-INTEGRAL REACTION ORDER

A reactor has the residence time distribution

$$E(t) = \begin{cases} 0.25 & 0 \le t \le 2 \\ (3-0.5t)/8 & 2 \le t \le 6\text{, and zero elsewhere} \end{cases} \qquad (1)$$

A reaction with rate equation, $-dC/dt = 0.6C^{0.8}$, and with initial concentration $C_0 = 2.5$ is to be processed there. What will be the effluent concentration?

The residence time is

$$\bar{t} = \int_0^\infty tE(t)\,dt = 2.166$$

The integral of the rate equation is

$$(C/C_0)_{batch} = [1 - \frac{0.6t}{5C_0^{0.2}}]^5 = (1 - 0.1t)^5 \qquad (2)$$

In batch or plug flow with $\bar{t} = 2.166$,

$$C/C_0 = (1-0.2166)^5 = 0.2951 \qquad (3)$$

In segregated flow, using Equations (1) and (2),

$$C/C_0 = \int_0^\infty (C/C_0)_{batch}E(t)dt = 0.3857 \qquad (4)$$

Lines (3) and (4) are to be compared.

P5.06.09. A THIRD ORDER REACTION

The data of the first two columns of the table are of effluent concentration data obtained in response to a pulse of tracer added to the feed to a reactor. A third order reaction with $kC_0^2 = 0.15$ is to be treated here. (a) Compare the $E(t_r)$ from these data with that of a Gamma distribution of the same variance; (b) find the segregated conversion with the Gamma distribution .

The pertinent functions are,

$$\int_0^\infty Cdt = 100,\ \int_0^\infty tCdt = 1467,\ \int_0^\infty t^2Cdt = 27750.$$

A curve fit (C,t) of the data appear on the second graph. The three integrals obtained with that curve fit are 100.27, 1501.2 and 27323, quite close to the preceding.

$$\bar{t} = 1467/100 = 14.67$$

$$E(t_r) = \bar{t}C/\int_0^\infty Cdt = 0.1467C \qquad (1)$$

$$\sigma^2(t_r) = -1 + \frac{27750}{(14.67)^2(100)} = 0.2894$$

$$n = 1/0.2894 = 3.45,\ \Gamma(n) = 3.149,\ n^n/\Gamma(n) = 22.767$$

$$E(t_r)_{Gamma} = 22.767\ t_r^{2.45} \exp(-3.45t_r) \qquad (2)$$

Plots of Equations (1) and (2) are shown.

For a third order reaction,

$$(C/C_0)_{batch} = \frac{1}{\sqrt{1+2kC_0^2\bar{t}t_r}} = \frac{1}{\sqrt{1+2(0.15)(14.67)t_r}} = \frac{1}{\sqrt{1+4.4t_r}} \qquad (3)$$

For segregated conversion, apply Equations (2) and (3),

$$(C/C_0)_{seg} = \int_0^\infty (C/C_0)_{batch}E(t_r)_{Gamma}dt_r = 0.4613 \qquad (4)$$

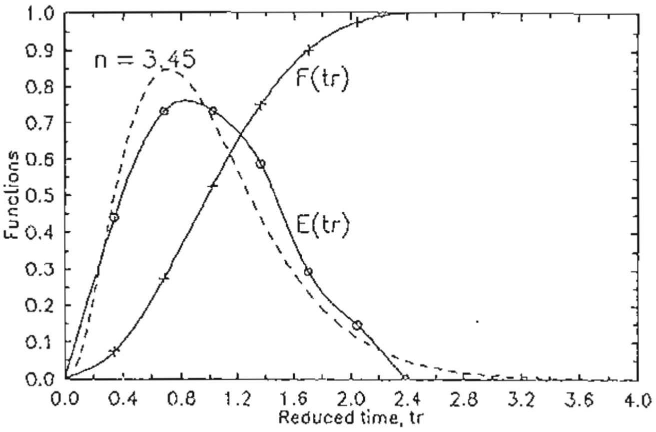
For comparison, batch conversion with t = 14.67 is

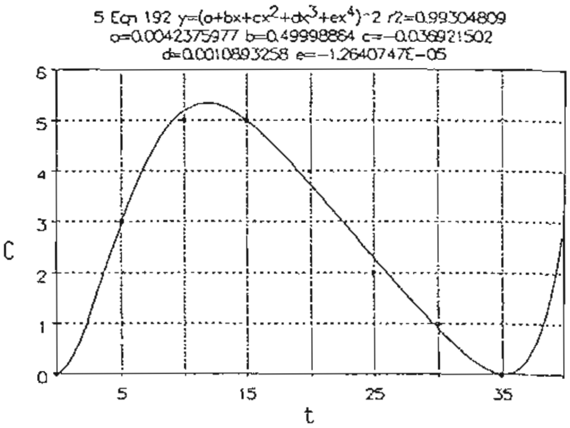
$$C/C_0 = 1/\sqrt{1+4.4} = 0.4303 \qquad (5)$$

Some other segregated yields are,

$2kC_0^2$	0.1	0.3	0.5	0.7	0.9
C/C_0	0.659	0.461	0.376	0.327	0.292

t	C	tC	t^2C
0	0	0	0
5	3	15	75
10	5	50	500
15	5	75	1225
20	4	80	1600
25	2	50	1250
30	1	30	900
35	0	0	0





P5.06.10. THIRD ORDER REACTION WITH EMPIRICAL AND GAMMA RTDs

An effluent response to an impulse input is represented by the equations

$$C = t \qquad 0 \le t \le 1$$

$$\exp(1-t) \qquad t \ge 1 \tag{1}$$

A third order reaction with $kC_0^2 = 1.0$ is to be carried out in this vessel. Find segregated conversion (a) with the RTD of these data; (b) with the Gamma distribution having the variance of these data.

The pertinent functions are,

$$\int_0^\infty Cdt = 1.5, \quad \int_0^\infty tCdt = 2.333, \quad \int_0^\infty t^2Cdt = 5.69, \quad \bar{t} = 1.556$$

$$\sigma^2(t_r) = -1 + \frac{5.69}{(1.556)^2(1.5)} = 0.5677,$$

$$n = 1/0.5677 = 1.762, \quad \Gamma(n) = 0.9219, \quad n^n\Gamma(n) = 2.943$$

$$E(t_r)_{\text{Gamma}} = 2.943\ t_r^{0.762}\exp(-1.762t_r) \tag{2}$$

$$E(t_r)_{\text{data}} = \bar{t}C/\int_0^\infty Cdt = 0.964C \tag{3}$$

In a batch reactor,

$$(C/C_0)_{\text{batch}} = \frac{1}{\sqrt{1+2kC_0\bar{t}t_r}} = \frac{1}{\sqrt{1+3.112t_r}} \tag{4}$$

In segregated flow,

$$C/C_0 = \int_0^\infty (C/C_0)_{batch} E(t_r) dt_r$$

$$= \begin{cases} 0.549, & \text{with the Gamma RTD, Equation (2)} \quad (5) \\ 0.534, & \text{with the data RTD, Equation (3)} \quad (6) \end{cases}$$

For comparison, in a batch reactor Equation (4) gives for $t_r = 1$

$$C/C_0 = 1/\sqrt{4.112} = 0.493 \quad (7)$$

P5.06.11. DISSOCIATION OF NITRIC ACID

The dissociation of nitric acid has a rate equation

$$-d(HNO_3)/dt = 0.32(HNO_3)/[1+3.8(NO_2)/(HNO_3)] \text{ gmol/liter sec}$$

The process is to be conducted in a vessel with a tracer input response given by

$$C = 0.5t, \quad 0 \le t \le 4, \text{ and zero elsewhere} \quad (1)$$

Find the conversion in segregated flow.

Let C = concentration of HNO_3

C_0-C = concentration of NO_2

The rate equation becomes

$$-\frac{dC}{dt} = \frac{0.32C^2}{3.8C_0-2.8C}$$

The integral is

$$t = 11.875(C_0/C - 1) - 8.75 \ln(C_0/C) \quad (2)$$

Values from this solution are tabulated.

From the tracer data,

$$\int_0^\infty C dt = 4, \quad \int_0^\infty tC dt = 10.67, \quad \bar{t} = 10.67/4 = 2.67$$

$$E(t) = 0.5t/\int_0^\infty C dt = 0.125t \qquad 0 \le t \le 4 \quad (3)$$

The segregated conversion is given by

$$C/C_0 = \int_0^4 (C/C_0)_{batch} E(t) dt = 0.6535 \quad (4)$$

The integrand is tabulated and the trapezoidal rule is used.

For comparison, when $t = \bar{t} = 2.67$, the batch conversion obtained from the table is

$$(C/C_0)_{batch} = 0.647 \quad (5)$$

C/C_0	t	$(C/C_0)E(t)$
1	0	0
0.9	0.3975	0.0447
0.8	1.0162	0.1016
0.7	1.968	0.1722
0.647	2.67	0.2159
0.6	3.447	0.2585
0.572	4.000	0.2860

P5.06.12. REACTORS WITH CSTR, ERLANG AND GAUSSIAN BEHAVIOR

Compare conversions in CSTRs and in segregated flow with Erlang or Gaussian RTDs, for $\sigma^2 = 1$ and 0.2, and for first and second order reactions.

The two values of n are 1 and 5. The material balance equations for the CSTRs are

$$f_{k-1} = f_k + (kC_0^{q-1}/n)f_k^q, \qquad k = 1,\ldots,n \qquad (1)$$

k is the stage number, q is the order of the reaction, n is the total number of stages and $f = C/C_0$.

For batch reaction,

$$f_{batch} = \left|\begin{array}{ll} \exp(-k\bar{t}t_r) & \text{first order} \qquad (2) \\ 1/(1+kC_0\bar{t}t_r) & \text{second order} \qquad (3) \end{array}\right.$$

The RTDs,

$$E(t_r)_{Erlang} = \frac{n^n}{(n-1)!} t_r^{n-1}\exp(-nt_r) \qquad (4)$$

$$E(t_r)_{Gaussian} = \sqrt{0.07105+0.1516/\sigma^2}\ \exp\{-0.5[(t_r-1)/\sigma]^2\} \qquad (5)$$

Segregated flow,

$$f = \int_0^\infty f_{batch}E(t_r)\, dt_r \qquad (6)$$

For first order the Erlang yields are the same as those of the CSTRs. The results are summarized in the tables.

First Order

$\sigma^2 = 1$ $\sigma^2 = 0.2$

$k\bar{t}$	CSTR	Gauss	CSTR	Gauss
0.5	0.667	0.5619	0.621	0.6207
1	0.5	0.3586	0.4020	0.3997
2	0.333	0.1876	0.1860	0.1876
3	0.250	0.1205	0.0954	0.1018
4	0.200	0.0872	0.0529	0.0623
5	0.167	0.0678		

Second Order, $\sigma^2 = 0.2$, n = 5

$kC_0\bar{t}$	CSTR	Gauss	Erlang	PFR
1	0.5315	0.5253	0.5237	0.500
3	0.2997	0.2830	0.2778	0.250
5	0.2132	0.1970	0.1915	0.167
10	0.1293	0.1140	0.1079	0.091
50	0.0355	0.0284	0.0242	0.020

P5.06.13. THREE REACTORS IN SERIES

Impulse tracer response of a reactor made up of two equal stirred tanks connected by a long pipeline is represented by the equation

$$C = 20\ t^2\exp(-3.5t)$$

The rate equation of a reaction to be conducted there is

$$-dC/dt = 0.5C/(1+0.3C)$$

with $C_0 = 2$. Find (a) the segregated conversion; (b) overall conversion when the stirred tanks are ideal and the pipeline is a PFR with 20% of the residence time and the total residence time corresponds to the original tracer response.

(a) From the response data,

$$\int_0^\infty C dt = 0.9329, \quad \int_0^\infty tC dt = 0.7996, \quad \bar{t} = 0.8571,$$

$$E(t) = C/\int_0^\infty C dt = 21.434\ t^2 \exp(-3.5t)$$

In a batch reactor,

$$f = C/C_0$$

$$-df/dt = 0.5f/(1+0.6f)$$

$$0.5t = \ln(1/f_b) + 0.6(1-f_b) \quad (1)$$

In segregated flow,

$$C/C_0 = \int_0^\infty f_{batch} E(t) dt = 0.729 \quad (2)$$

Corresponding values from Equation (1) and the integrand of Equation (2) are tabulated and the integration is with the trapezoidal rule.

(b) In the ideal system,

$$\bar{t}_1 = \bar{t}_3 = 0.4(0.8569) = 0.3428, \quad \bar{t}_2 = 0.1714$$

In stage 1 (CSTR),

$$1 = f_1 + \frac{0.5(0.3428)f_1}{1+0.6f_1}, \quad f_1 = 0.8998$$

In stage 2 (PFR),

$$\bar{t}_2 = 0.1748 = \int_{f_2}^{0.8998} (2/f1.2)df$$

$$= 2\ \ln(0.8998/f_2) + 1.2(0.8998-f_2)$$

$$f_2 = 0.8506$$

In stage 3 (CSTR),

$$f_2 = 0.8506 = f_3 + \frac{0.5(0.3428)f_3}{1+0.6f_3}$$

$$f_3 = 0.7610 \quad (3)$$

Line (3) is slightly poorer performance than line (2).

t	f_{batch}	$E(t)$	$f_b E(t)$
0	1	0	0
0.5	0.8514	0.9312	0.7928
1	0.7183	0.6472	0.4649
1.5	0.6003	0.2531	0.1519
2	0.4974	0.0782	0.0383
2.5	0.4085	0.0212	0.0087
3	0.3329	0.0053	0.0018
3.5	0.2694	0.0013	0.0004
4	0.2166	0.0003	0

P5.06.14. CONVERSION WITH GAMMA AND ORIGINAL RTD

The response to a tracer input is represented by the equation,

$$E(t_r) = 0.2917(5-2.333t_r), \quad 0.4286 \le t_r \le 2.1428 \quad (1)$$

A second order reaction with $kC_0\bar{t} = 1.167$ is to be checked in segregated flow with this RTD and with a Gamma RTD of the same variance.

The variance is

$$\sigma^2(t_r) = \int_{0.4286}^{2.1428} (t_r-1)^2 E(t_r)\, dt_r = 0.1633$$

$$n = 1/0.1633 = 6.125,\ \Gamma(n) = 132.2,\ n^n/\Gamma n) = 500.95$$

$$E(t_r)_{\text{Gamma}} = 500.95\ t_r^{5.125}\exp(-6.125t_r) \qquad (2)$$

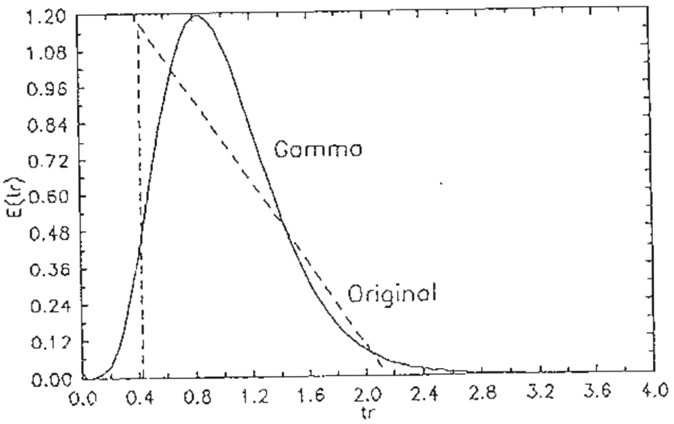
In segregated flow,

$$f_{\text{batch}} = C/C_0 = 1/(1+kC_0\bar{t}t_r) = 1/(1+1.167t_r)$$

$$(C/C_0)_{\text{effluent}} = \int_0^\infty f_{\text{batch}} E(t_r)\, dt_r$$

$$= \left| \begin{array}{ll} 0.4828, \text{ original RTD} & (3) \\ 0.5035, \text{ Gamma RTD} & (4) \end{array} \right.$$

The two RTDs are plotted.



P5.06.15. STEP INPUT OF TRACER TO TWO STAGES. RTD AND CONVERSION

Data of response to step input of tracer are

t	0.5	1	1.5	2	2.5	3	3.5	4	5	6	10
C/C_f	0	.12	.31	46	.58	.68	.75	.80	.88	.93	.99

The reactor is believed equivalent to a PFR in series with a CSTR. A second order reaction with $kC_0 = 2.5$ is to be processed there. Find (a) the residence time in each element; (b) conversion in segregated flow; (c) ideal conversion with the PFR first in series; (d) ideal conversion with the CSTR first in series.

The PFR has $\bar{t}_1$ and the CSTR has $\bar{t}_2$. The material balance in terms of transforms is

$$\bar{C}/C_f = \frac{\exp(-\bar{t}_1 s)}{s(1+\bar{t}_2 s)}$$

Inverting,

$$C/C_f = [1 - \exp(-t/\bar{t}_2)]\ u(t-\bar{t}_1)$$

$$= 1 - \exp[-(t-\bar{t}_1)/\bar{t}_2], \qquad t \geq \bar{t}_1$$

The original data are curve fitted to this form of equation as shown on the graph. Thus,

$$\ln(1 - C/C_f) = -0.4942t + 0.3617$$

so that

$$\bar{t}_1 = 0.732,\ \bar{t}_2 = 2.024,\ \bar{t} = 2.756 \qquad (1)$$

The Age function is

$$F(t_r) = C/C_f = 1 - \exp(0.3617 - 1.3617t_r),\quad t_r \geq 0.2656$$

The RTD becomes

$$E(t_r) = dF(t_r)/dt_r = 1.3617\exp(0.3617-1.3617t_r)$$

In a batch reactor,

$$(C/C_0)_{batch} = 1/(1+kC_0\bar{t}t_r) = 1/[1+2.5(2.756)t_r]$$

In segregated flow,

$$C/C_0 = \int_{0.2656}^{\infty} \frac{E(t_r)}{1+6.89t_r} = 0.1708 \qquad (2)$$

In the sequence PFR-CSTR,

$$C_1/C_0 = 1/[1+2.5(0.732] = 0.3534$$

$$0.3534 = C_2/C_0 + 2.5(2.024)(C_2/C_0)^2,$$

$$C_2/C_0 = 0.1833 \qquad (3)$$

In the sequence CSTR-PFR,

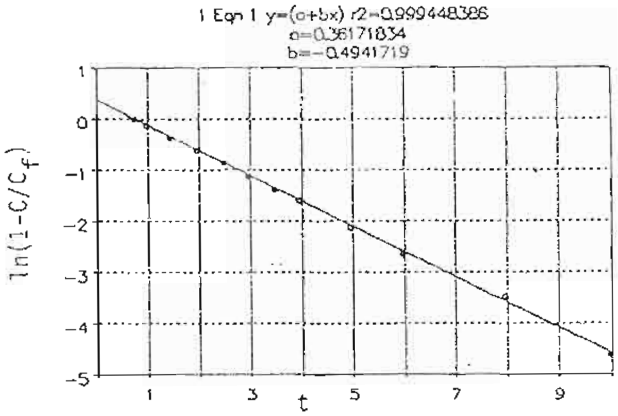
$$1 = C_1/C_0 + 2.5(2.024)(C_1/C_0)^2$$

$$C_1/C_0 = 0.3566$$

$$C_2/C_0 = (C_1/C_0)(C_2/C_1) = 0.3566\left[\frac{1}{1+kC_0(C_1/C_0)\bar{t}_1}\right]$$

$$= \frac{0.3566}{1+2.5(0.3566)(0.732)} = 0.2165 \qquad (4)$$

Lines (2), (3) and(4) are to be compared.



P5.06.16. EMPIRICAL AND GAMMA RTDS

The response to tracer impulse input is represented by

$$C = \begin{cases} 1.333(t-0.5) & 0.5\leq t\leq 2 \\ \sqrt{4-(t-2)^2} & 2\leq t\leq 4,\ \text{and zero elsewhere} \end{cases}$$

The rate equation is $-dC/dt = 0.25C/(1+0.05C)$ with inlet concentration $C_0=1.5$. Find segregated conversions with the original RTD and with the Gamma RTD of the same variance.

From the response data,

$$\int_{0.5}^{4} Cdt = 4.6416,\quad \int_{0.5}^{4} tCdt = 11.1790,\quad \int_{0.5}^{4} t^2Cdt = 29.8541$$

$$\bar{t} = 11.1790/4.6416 = 2.4084$$

$$E(t)_{data} = C/4.6416 \qquad (1)$$

$$\sigma^2(t_r) = -1 + \frac{29.8541}{(2.4084)^2(4.6416)} = 0.1089$$

$$n = 1/0.1089 = 9.18,\ \Gamma(n) = 59438,\ n^n/\Gamma(n) = 11605$$

$$E(t_r)_{Gamma} = 11605\ t_r^{8.18}\exp(-9.18t_r) \qquad (2)$$

$$E(t)_{Gamma} = E(t_r)/\bar{t} = 4819(t/2.4084)^{8.18}\exp(-3.812t) \qquad (3)$$

In a batch reactor, integrating the rate equation,

$$t = -4\ \ln(C/C_0) + 0.3(1-C/C_0) \qquad (4)$$

This is solved for C/C_0 at specified values of t. The results are tabulated.

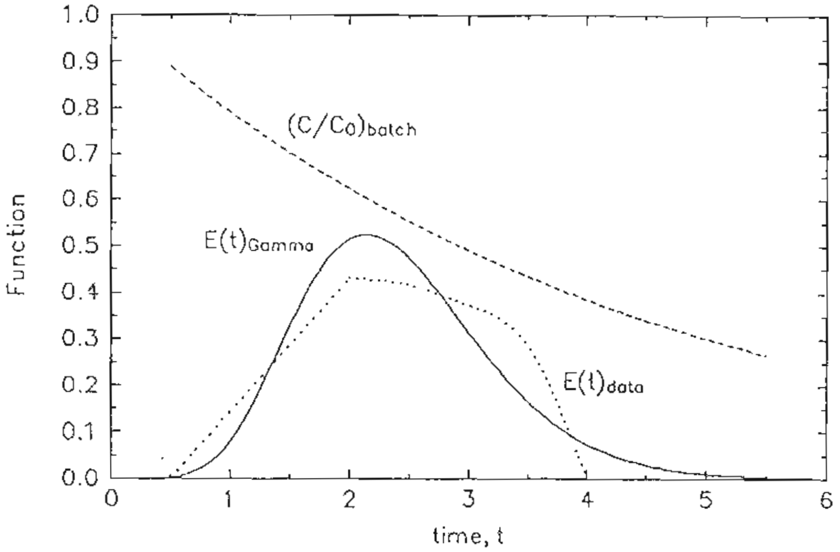
In segregated flow,

$$C/C_0 = \int_0^\infty (C/C_0)_{batch}E(t)dt$$

$$= \begin{vmatrix} 0.5755 & \text{with original RTD} & (5) \\ 0.5730 & \text{with Gamma RTD} & (6) \end{vmatrix}$$

The integrands are tabulated and the integrations are with the trapezoidal rule.

		Data		Gamma	
t	C/C_0	E(t)	$(C/C_0)E(t)$	E(t)	$(C/C_0)E(t)$
0.5	0.8899	0	0	0.0018	0.0017
1	0.7911	0.1437	0.1137	0.0804	0.0636
1.5	0.7028	0.2873	0.2091	0.3296	0.2316
2	0.6244	0.4310	0.2691	0.5155	0.3219
2.5	0.5536	0.4171	0.2309	0.4756	0.2833
3	0.4904	0.3731	0.1830	0.3142	0.1541
3.5	0.4345	0.2849	0.1238	0.1649	0.0716
4	0.3852	0	0	0.0731	0.0282
4.5	0.3412			0.0285	0.0097
5	0.3019			0.0100	0.0030
5.5	0.2671			0.0032	0.0009



P5.06.17. LABORATORY AND COMMERCIAL REACTORS

(a) A laboratory reactor has the RTD

$E(t_r) = 4t_r\exp(-2t_r)$

A first order reaction in this vessel attains 95% conversion at a residence time $\bar{t} = 5$. From this information the specific rate is to be found.

(b) The same reaction is to be conducted in a commercial vessel for which impulse tracer response data were obtained as tabulated. The segregated conversion is to be found and compared with that in a CSTR battery with the same variance.

For segregated reaction of the first order,

$$C/C_0 = \int_0^\infty \exp(-k\bar{t}t_r)E(t_r)dt_r = 4\int_0^\infty t_r\exp[-(2+5k)t_r]dt_r$$

$$= 4/(2+5k)^2 = 0.05$$

$$k = 1.389 \tag{1}$$

From the tabulated response data,

$$\int_0^{15} Cdt = 25.78,\quad \int_0^{15} tCdt = 130.75,\quad \int_0^{15} t^2Cdt = 813.78,$$

$$\bar{t} = 130.75/25.78 = 5.07$$

$$\sigma^2(t_r) = -1 + \frac{813.78}{(5.07)^2(25.78)} = 0.2280$$

$$n = 1/0.2280 = 4.385$$

$$E(t) = C/25.78$$

In segregated flow,

$$C/C_0 = \int_0^\infty \exp(-kt)E(t)dt = \frac{1}{25.78}\int_0^{15} C\exp(-1.389t)dt$$

$$= 0.0175 \tag{2}$$

The integrand is tabulated and the integration is done numerically.

For comparison, in a CSTR battery, assuming validity of non-integral numbers of stages,

$$C/C_0 = 1/(1+k\bar{t}/n)^n = 1/[1+1.389(5.07)/4.385]^{4.385}$$

$$= 0.015 \tag{3}$$

t	c	tC	t^2C	C exp(-1.389T)
0	0	0	0	0
.5	0.2	.1	.05	0.0999
1	0.7	.7	.7	0.1745
1.5	1.8	2.7	4.05	0.2241
2	2.6	5.2	10.4	0.1616
2.5	3.6	9.0	22.5	0.1117
3	4.2	12.6	37.8	0.0651
3.5	4.4	15.4	53.9	0.0341
4	4.5	18.0	72.0	0.0174
4.5	4.3	19.4	87.1	0.0083
5	3.9	19.5	97.5	0.0038
6	3.0	18.0	108.0	0.0007
7	2.2	15.4	107.8	0.0001
8	1.4	11.2	89.6	0
9	1.	9.0	81.0	
10	0.7	7.0	70.	
15	0	0	0	

P5.06.18. PILOT AND COMMERCIAL UNITS

Tracer response data of pilot and commercial reactors are represented by the relations

Pilot $C = 1.5$, $0.5 \le t \le 2.5$ and zero elsewhere

Commercial $E(t_r) = t_r \quad 0 \le t_r \le 1$

$2-t_r \ldots 1 \le t_r \le 2$ and zero elsewhere

A first order reaction conducted in the pilot unit attained 75% conversion. Find (a) the specific rate of the reaction; (b) the conversion in the commercial reactor with a residence time $\bar{t} = 2$. Segregated flow is assumed for both reactors.

From the pilot data,

$$\int_{0.5}^{2.5} Cdt = 3,\quad \int_{0.5}^{2.5} tCdt = 4.5,\quad \bar{t} = 4.5/3 = 1.5,\quad C^0 = 3/1.5 = 2$$

$$E(t_r) = C/2 = 0.75, \quad 1/3 \le t_r \le 5/3 \quad \text{and zero elsewhere}$$

In segregated flow in the pilot unit,

$$C/C_0 = \int_{1/3}^{5/3} 0.75\exp(-k\bar{t}t_r)dt_r = \frac{0.75}{k\bar{t}}[\exp(-5k\bar{t}/3)-\exp(-k\bar{t}/3)]$$

$$= 0.25$$

$$k\bar{t} = 1.56,\quad k = 1.56/1.5 = 1.04 \qquad (1)$$

In the commercial unit, in segregated flow,

$$C/C_0 = \int_0^\infty \exp(-k\bar{t}t_r)E(t_r)dt_r$$

$$= \int_0^1 t_r\exp(-2.04t_r)dt_r + \int_1^2 (2-t_r)\exp(-2.04t_r)dt_r$$

$$= 0.1769 \qquad (2)$$

For comparison, in plug flow, $t_r = 1$

$$C/C_0 = \exp(-2.08) = 0.1249 \qquad (3)$$

In a CSTR,

$$C/C_0 = 1/(1+2.08) = 0.3247 \qquad (4)$$

P5.06.19. SEGREGATED AND CSTR BATTERY PERFORMANCE

Compare conversions of first and second order reactions in a four stage CSTR with segregated flow in a Gamma vessel having the same variance. For first order $k = 0.5$; for second order $kC_0 = 0.8$, and $\bar{t} = 5$ for both orders.

In the four stage Gamma vessel,

$$E(t_r) = \frac{n^n}{(n-1)!}\, t_r^{n-1}\exp(-nt_r) = 42.67\ t_r^3\exp(-4t_r) \qquad (1)$$

For first order,

$$(C/C_0)_{cstr} = 1/(1+k\bar{t}/4)^4 = 1/(1+0.5(5)/4)^4 = 0.1434 \qquad (2)$$

$$(C/C_0)_{batch} = \exp(-k\bar{t})$$

$$(C/C_0)_{seg} = \int_0^\infty (C/C_0)_{batch}E(t_r)dt_r = 0.1434 \qquad (3)$$

For second order, in a CSTR battery, the material balances are

$$f_{n-1} = f_n + (k\bar{t}/4)f_n^2, \qquad f = C/C_0,\ n = 1,\ 2,\ 3,\ 4$$

The successive values are

$$C_n/C_0 = 0.6180,\ 0.4317,\ 0.3257,\ 0.2587 \qquad (4)$$

In segregated flow,

$$(C/C_0)_{batch} = 1/(1+kC_0\bar{t}t_r) = 1/(1+4t_r)$$

$$(C/C_0)_{seg} = \int_0^\infty \frac{E(t_r)}{1+4t_r}\, dt_r = 0.2340 \qquad (5)$$

Lines (2) and (3) are to be compared, and line (4) with (5).

P50620. STIRRED TANK DATA

The following concentration readings are of response to an impulse input of tracer,

t	10	20	30	40	50	60	70	80
C	0	3	5	5	4	2	1	0
C exp(-0.1153t)	0	0.301	0.159	0.050	0.012	0.002	0.000	0.000

The third line is of calculations made for the solution of this problem. What conversion can be expected in this reactor of a first order reaction that has a conversion of 82.18% in an ideal CSTR at the same residence time?

From the response data,

$$\int_0^{80} Cdt = 200,\ \int_0^{80} tCdt = 8000,\ \bar{t} = 8000/200 = 40$$

$$E(t) = C/\int_0^\infty Cdt = 0.005C \qquad (1)$$

In an ideal CSTR,

$$C/C_0 = 0.1782 = 1/(1+k\bar{t}) = 1/(1+40k)$$

$$k = 0.1153 \qquad (2)$$

The segregated conversion is given by

$$C/C_0 = \int_0^\infty \exp(-kt)E(t)dt = 0.005\int_0^8 C\exp(-0.1153t)dt$$

$$= 0.0262,\ \text{or } 97.38\% \qquad (3)$$

P5.06.21. CONVERSION WITH GAUSSIAN AND GAMMA RTDS

Find segregated conversion when the Gaussian or Gamma residence time distributions hold, for a range of variances and a range of $kC_0\bar{t}$ of second order reactions.

For the Gaussian distribution,

$$E(t_r)_{Gauss} = \sqrt{0.07105+0.1516/\sigma^2}\ \exp[-(t_r-1)^2/2\sigma^2]$$

and for the Gamma distribution,

$$E(t_r)_{Gamma} = \frac{n^n}{(n-1)!}\ t_r^{n-1}\ \exp(-nt_r),\quad n = 1/\sigma^2$$

Segregated conversion is

$$(C/C_0) = \int_0^\infty \frac{E(t_r)}{1+kC_0\bar{t}}\, dt_r$$

Results of these integrations are tabulated for the two cases for ranges of $kC_0\bar{t}$ and $n = 1/\sigma^2$.

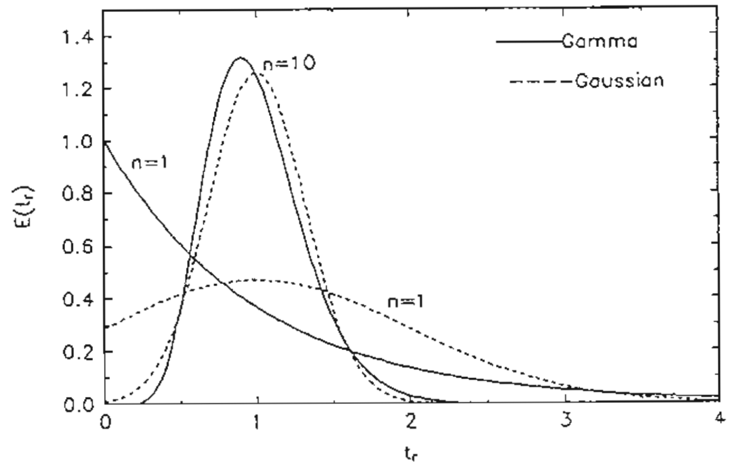
Gaussian

n	$kC_0\bar{t}=1$	2	5	10	50
10	0.5119	0.349	0.181	0.1011	0.0226
5	0.525	0.365	0.197	0.114	0.0278
3	0.5252	0.3702	0.2052	0.1221	0.0321
1	0.4922	0.3485	0.1982	0.1216	0.0350

Gamma

n	$kC_0\bar{t}=1$	2	5	10	50
10	0.512	0.3481	0.1787	0.0989	0.0217
5	0.5237	0.3626	0.1915	0.108	0.0242
3	0.5381	0.3814	0.2094	0.1215	0.0285
1	0.5954	0.4610	0.2988	0.2019	0.0708

The two sets of results disagree most at large values of σ^2 or small values of n. This is also true of the plots of $E(t_r)$, as appears on the graph. Plots for other values of n are in problem P5.02.11.



P5.06.22. REACTION WITH GAUSSIAN AND GAMMA RTDS

The tracer response curve of a reactor has a variance $\sigma^2(t_r) = 0.56$. A second order reaction with parameter $kC_0\bar{t} = 4$ is to be conducted there. Find the segregated conversion with a Gaussian or a Gamma $E(t_r)$.

For the Gaussian distribution see problem P5.02.08,

$$f(\sigma) = \frac{1+1.541\sigma^2}{0.451+4.886\sigma^2} = 0.585$$

$$E(t_r)_{Gauss} = 0.585\exp[-(t_r-1)^2/2(0.56)] \qquad (1)$$

For the Gamma distribution,

$$n = 1/0.56 = 1.786,\ \Gamma(n) = 0.929,\ n^n/\Gamma(n) = 3.033$$

$$E(t_r)_{Gamma} = 3.033\, t_r^{0.786}\exp(-1.786t_r) \qquad (2)$$

In segregated flow,

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+4t_r}\,dt_r$$

$$= \left|\begin{array}{lll} 0.2385 & \text{Gaussian} & (3) \\ 0.2767 & \text{Gamma} & (4) \end{array}\right.$$

P5.06.23. GRAM-CHARLIER CONVERSION

Find second order segregated conversion with $kC_0\bar{t} = 10$. The reactor has a Gram-Charlier distribution with the same first three moments as a third order Erlang distribution.

The moments of the Erlang distribution are derived in problem P5.02.01. For n = 3 they are

$$\sigma^2(t_r) = 1n = 0.333,\ \gamma^3(t_r) = 2/n^2 = 0.2222,\ \sigma = 0.5774,$$

$$z = (t_r-1)/0.5774$$

$$f(\sigma) = \sqrt{0.07105+0.1516/\sigma^2} = 0.7252$$

$$E(t_r)_{Gauss} = 0.7252\exp(-z^2/2) \qquad (1)$$

$$E(t_r)_{GC} = E(t_r)_{Gauss}[1 - (\gamma/\sigma)^3(3z-z^3)/6]$$

$$= E(t_r)_{Gauss}[1-0.1924(3z-z^3)] \qquad (2)$$

$$E(t_r)_{Erlang} = 13.5t_r^2\exp(-3t_r) \qquad (3)$$

In segregated flow,

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+10t_r}\,dt_r$$

$$= \left|\begin{array}{lll} 0.1220 & \text{Gaussian} & (4) \\ 0.1331 & \text{Gram-Charlier} & (5) \\ 0.1215 & \text{Erlang} & (6) \end{array}\right.$$

In plug flow,

$$C/C_0 = 1/(1+10) = 0.0909 \qquad (7)$$

In a three stage CSTR the material balances are

$$C_{n-1}/C_0 = C_n/C_0 + (10/3)(C_n/C_0)^2,\quad n = 1,\ 2,\ 3$$

These have the solution,

0.418, 0.235 and 0.1547 (8)

Lines (4), (5), (6(), (7) and (8) are to be compared.

P5.06.24. COMPARISON OF MODELS

For a tracer response curve with $\sigma^2(t_r) = 0.2$ compare segregated conversions with Erlang, Gaussian and Gram-Charlier with a third moment, as well as with plug flow and a five stage CSTR battery. The reaction is second order.

Auxiliary quantities are,

$$n = 1/\sigma^2 = 5$$

$$f(\sigma) = \sqrt{0.07105+0.1516/0.2} = 0.9105$$

$$z = (t_r-1)/\sqrt{0.2}$$

$$\sigma^2(t_r) = 1/n = 0.2,$$

$$\gamma^3(t_r) = 2/n^2 = 0.08,$$

The several RTDs are,

$$E(t_r)_{Erlang} = 130.2\ t_r^4 \exp(-5t_r)$$

$$E(t_r)_{Gauss} = 0.9105 \exp(-0.5z^2)$$

$$E(t_r)_{Gram-Charlier} = E(t_r)_{Gauss}[1-(\gamma/\sigma)^3(3z-z^3)/6]$$

$$= E(t_r)_{Gauss}[1-0.1491(3z-z^3)]$$

In segregated conversion,

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+kC_0\bar{t}t_r}\ dt_r$$

In plug flow,

$$C/C_0 = 1/(1+kC_0\bar{t})$$

In the five stage CSTR,

$$C_{n-1}/C_0 = C_n/C_0 + (kC_0\bar{t}/5)(C_n/C_0)^2, \quad n = 1,\ 2,\ 3,\ 4\ ,5$$

The tabulation summarizes the values of C/C_0 for two values of the reaction parameter $kC_0\bar{t}$.

$kC_0\bar{t}$	Erlang	Gauss	GC	PFR	CSTR
9	0.1307	0.1406	0.1423	0.1000	0.1527
19	0.0606	0.0704	0.0684	0.0500	0.0786

The segregated conversions are intermediate to plug flow and CSTR battery. The only way to tell which of the segregated models is superior is to check them with actual conversion data.

5.07.01. DERIVATION OF THE MAXIMUM MIXEDNESS EQUATION

The model is a reactor in plug flow with inlet flows on the side programmed to result in a particular RTD. The relation between the distribution functions is

$$F(t_r) = \int_0^{t_r} E(t_r)dt_r$$

A material balance on the reactant is made over the shaded element of volume in which the life expectancy change by an amount dt. The life expectancy t_e and elapsed time t have the same distribution functions. The rate of reaction per unit volume is r_c.

The accumulated flow rate in the reactor is

$$Q\int_\infty^t E(t)dt = Q[1-F(t_e)] = Q[1-F(t)]$$

The elements of the material balace on the flowing reactant are

Mass input at t+dt = $Q(1-F)C + d[(1-F)C]$

Input through the wall = QC_0Edt

Output at t = $Q(1-F)C$

Reaction sink $r_cdV_r = r_cQ(1-F)dt$

The material balance is

$$(1-F)C + d[(1-F)C] + C_0Edt = (1-F)C + r_c(1-F)dt$$

Utilizing the relation $dF = Edt$ yields the result,

$$\frac{dC}{dt} = r_c - \frac{E(t)}{1-F(t)}(C_0-C) \tag{1}$$

The boundary condition is

$$\frac{dC}{dt} = 0 \text{ for } t = \infty \tag{2}$$

In terms of a power law rate equation, $r_c = kC^q$, and $f = C/C_0$,

$$\frac{df}{dt} = kC_0^{q-1}f^q - \Lambda(t)(1-f) \tag{3}$$

where $\Lambda(t) = E(t)/[1-F(t)]$. The boundary condition results in

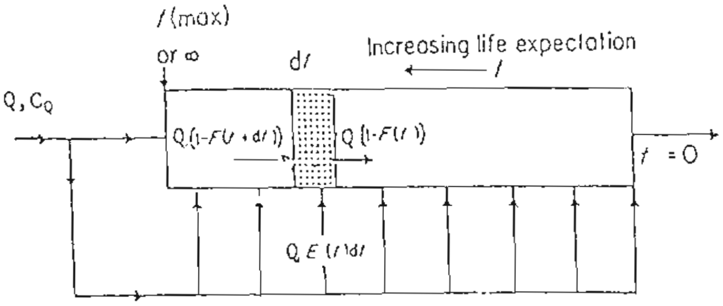
$$kC_0^{q-1}f_\infty^q - \Lambda(\infty)(1-f_\infty) = 0 \tag{4}$$

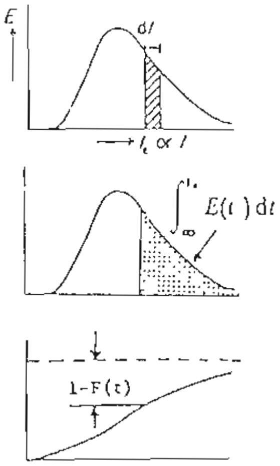
Convenient forms of these relations are expressed in terms of reduced time, $t_r = t/\bar{t}$, and by noting that $E(t_r) = \bar{t}E(t)$, $F(t_r) = F(t)$ and $\Lambda(t_r) = \bar{t}\Lambda(t)$. Then

$$\frac{df}{dt_r} = k\bar{t}C_0^{q-1}f^q - \Lambda(t_r)(1-f) \tag{3a}$$

$$k\bar{t}C_0^{q-1}f_\infty^q - \Lambda(\infty)(1-f_\infty) = 0 \tag{4a}$$

The conversion achieved in the vessel is the solution of Equation (3) or (3a) at the exit of the vessel where $t = 0$. The starting point for the integration is f_∞ at $t = \infty$. In practice, however, the levelling off of the RTD as $t_r \Rightarrow \infty$ is attained by the time t_r becomes 3 or 4. The integral beyond this point is nil. Accordingly the initial condition for integration is (f_∞, t_r = 3 or 4) and the end point is ($f_{effluent}$, $t_r = 0$). f_∞ is found from Equation (4) or (4a).





P5.07.02. FIRST ORDER REACTIONS

Show that for a first order reaction, segregated and maximum mixed conversion are the same.

Note that

$$\Lambda = E/(1-F) = \frac{1}{1-F}\frac{dF}{dt} = -\frac{d[\ln(1-F)]}{dt}$$

For first order reaction the Zwietering equation is

$$\frac{dC}{dt} = kC - \Lambda(C_0 - C)$$

or

$$\frac{dC}{dt} - (k + \frac{d[\ln(1-F)]}{dt}) = -\Lambda C_0$$

This is a first order linear equation for which

$$z = -\int[k + \frac{d[\ln(1-F)]}{dt}]dt = -kt + \ln(1-F)$$

The integrating factor is

$$\exp(z) = (1-F)\exp(-kt)$$

and the solution is

$$C(1-F)\exp(-kt)\Big|_t^{\infty} = -C_0\int_t^{\infty}(1-F)\exp(-kt)\Lambda\, dt$$

or

$$C = \frac{C_0\exp(kt)}{1-F}\int_t^{\infty}\exp(-kt)E dt$$

The concentration at the exit is found when t = 0. Since F = 0 at that time, the final result is

$$C_{exit}/C_0 = \int_0^{\infty}\exp(-kt)E(t)dt$$

which is the segregated conversion equation.

P5.07.03. NUMERICAL INTENSITY FUNCTION DATA

The intensity function of tracer flow in a reactor has these values,

t_r	0	0.5	1	1.5	2	3	4	5	6+
$\Lambda(t_r)$	0	1	2.2	2.8	3.2	3.5	3.6	3.7	4.0

Find the yield of a second order reaction with $kC_0\bar{t} = 10$ under plug flow and under MM flow conditions.

The data are fitted on the plot by the equation

$$\Lambda(t_r) = 3.449+0.0554t_r+0.00076t_r^3-3.5927\exp(-t_r)$$

By inspection of the data, $\Lambda(\infty) = 4$, and the starting value is found from the boundary condition

$$k\bar{t}C_0(1-x_{\infty})^2 - 4x_{\infty} = 0$$

$$x_{\infty} = 0.537$$

The MM equation is

$$\frac{dx}{dt_r} = -10(1-x)^2 + \Lambda(t_r)x$$

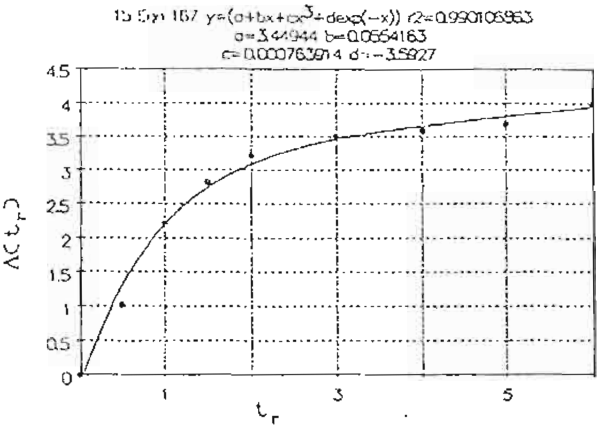
The terminal points for the integration are (0.537, 4) and (x_{exit}, 0).

For plug flow,

$$x = 1-C/C_0 = 1-1/(1+kC_0\bar{t})$$

The solutions are tabulated for several values of the reaction parameter.

$kC_0\bar{t}$	x_{∞}	x, MM	x, PF
1	0.1715	0.4072	0.500
5	0.4200	0.7200	0.833
10.	0.5370	0.8139	0.909



P5.07.04. MM AND SEGREGATED FLOW MODELS. NUMERICAL TRACER RESPONSE DATA

Data of tracer concentration in effluent of impulse input to a reactor are given in the first two columns (Fogler, 1992). A second order reaction with $C_0 = 8$ and several values of specific rate is to be carried out here. Find conversion under max mixed and segregated flow conditions.

Required functions are evaluated,

$$\int_0^\infty C dt = 4026, \quad \int_0^\infty tC dt = 145885, \quad \bar{t} = 36.23,$$

$$E(t) = C/4026$$

$$F(t) = \int_0^t E(t) dt$$

$$\Lambda(t) = E(t)/[1-F(t)]$$

The last values are tabulated and fitted by the equation,

$$\Lambda(t) = \frac{1}{35.63+0.1405t+0.000364t^2-8.107(E-6)t^3}$$

The MM equation with specific rate k is

$$\frac{dC}{dt} = kC^2 - \Lambda(t)(8-C)$$

At about $t/\bar{t} = 4$, $\Lambda(t) = 0.0221$, so the starting value of C is obtained from

$$kC_\infty^2 = 0.0221(8-C_\infty)$$

$$C_\infty = 3.242, \quad k = 0.01$$

$$1.672, \quad k = 0.05$$

Consequently the integration limits are from $(t_\infty, C_\infty) = (4\bar{t}, 3.242 \text{ or } 1.672)$ to $(0, C_{exit})$. Results are shown in the second table for several starting values of t, and appear to be quite insensitive to those values. The second figure also shows that quite different starting values result in essentially the same effluent composition.

In segregated flow,

$$C/C_0 = \int_0^{200} \frac{E(t)}{1+kC_0\bar{t}} dt = \int_0^{200} \frac{E(t)}{1+8(36.2)k} dt$$

$$= 0.39 \quad \text{with } k = 0.01$$

$$0.181 \quad \text{with } k = 0.05$$

In plug flow,

$$C/C_0 = \frac{1}{1+8(36.2)k} = 0.345 \quad \text{with } k = 0.04$$

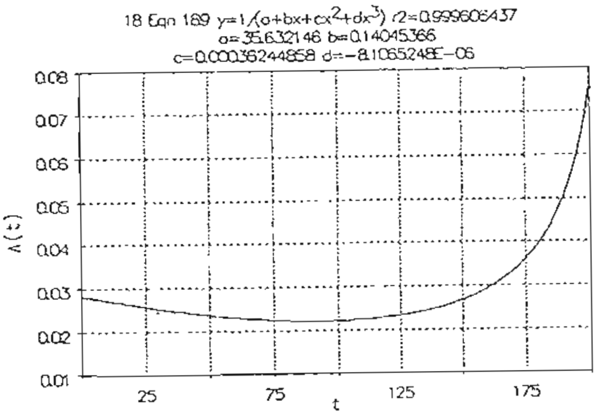
$$0.065 \quad \text{with } k = 0.05$$

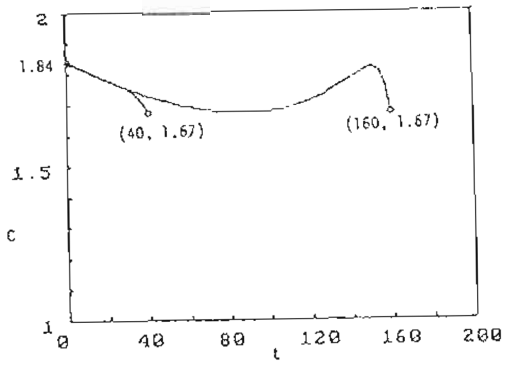
The MM results are

t_∞	k=0.01	k=0.05
160	0.4360	0.2303
100	0.4360	0.2303
40	0.4358	0.2303

The tracer response data are

t	C	Λ(t)
0	112	0.0280
5	95.8	0.0276
10	82.2	0.0271
15	70.6	0.0267
20	60.9	0.0260
30	45.6	0.0242
40	34.5	0.0244
50	26.3	0.0237
70	15.7	0.0226
100	7.67	0.0221
150	2.55	0.0266
200	0.90	0.0750





P5.07.05. RELATIVE SIZES OF SEGREGATED AND MM REACTORS

The relative sizes of segregated and max mixed reactors are to be found on the basis of Gamma or Erlang distributions. Reaction orders are to be 2 and 0.5. For first order the ratio of sizes is unity.

For maximum mixedness the equations are

$$\frac{df}{dt_r} = Rf^q - \Lambda(t_r)(1-f)$$

$$R = kC_0^{q-1}\bar{t}, \qquad f = C/C_0$$

$$Rf_\infty^q - n(1-f_\infty) = 0, \qquad n = 1/\sigma^2 t_r)$$

The starting value for the integration is $(f, t_r) = (f_\infty$, 3 or 4) and the endpoint is $(f_{exit}, 0)$.

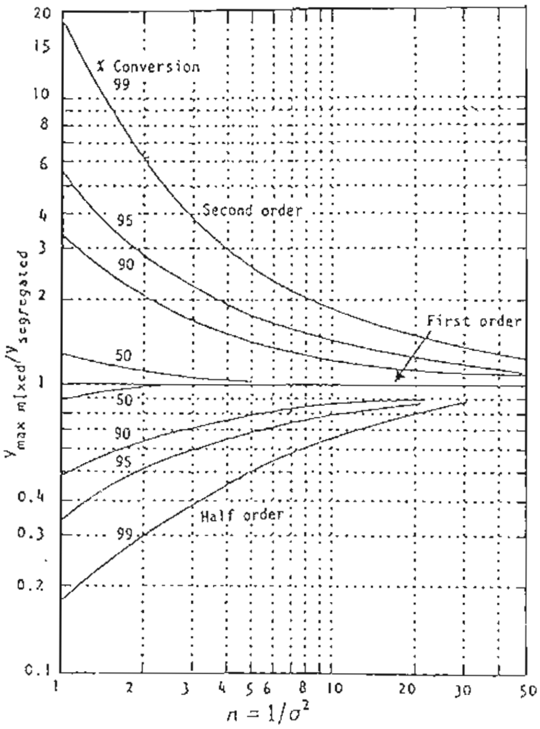
For segregated flow,

$$f = \int_0^\infty E(t_r)\left[\frac{1}{1+(q-1)Rt_r}\right]^{1/(q-1)} dt_r$$

$\Lambda(t_r)$ and $E(t_r)$ are functions of $n = 1/\sigma^2(t_r)$. At each value of n, values of R are assumed, the integrations for $f = C/C_0$ are completed and the results interpolated to the values of f shown on the curves.

The ratio of reactor volumes is

$$V_{MM}/V_{seg} = R_{MM}/R_{seg} = \bar{t}_{MM}/\bar{t}_{seg}$$



P5.07.06. ERLANG DISTRIBUTION. CONVERSION IN MAXIMUM MIXEDNESS OR SEGREGATION.

The pertinent distribution functions are

$$E(t_r) = \frac{n^n}{(n-1)!}\, t_r^{n-1} \exp(-nt_r) \tag{1}$$

$$F(t_r) = 1 - \exp(-nt_r) \sum_{j=1}^{n} \frac{(nt_r)^{j-1}}{(j-1)!} \tag{2}$$

$$\Lambda(t_r) = \frac{E(t_r)}{1-F(t_r)}$$

$$= \frac{n^n t_r^{n-1}}{(n-1)!} [1+ nt_r + \frac{1}{2!}(nt_r)^2 + ..+ \frac{1}{(n-1)!} (nt_r)^{n-1}] \quad (3)$$

$$\Lambda(\infty) = n \quad (4)$$

In terms of $f = C/C_0$, the maximum mixedness (Zwietering) equation for a reaction of order q is

$$\frac{df}{dt_r} = k\bar{t}C_0^{q-1}f^q - \Lambda(t_r)(1-f) \quad (5)$$

The starting value, f_∞, for the integration is established by the boundary condition

$$k\bar{t}C_0^{q-1}f_\infty^q - n(1-f_\infty) = 0 \quad (6)$$

The starting value of time t_r for the integration is 3 or 4 ; anything beyond these values ordinarily does not affect the result. Integrate to $t_r = 0$. Thus the integration range is from $(f_\infty,\ t_r = 3\ t0\ 4)$ to $(f_{exit},\ t_r = 0)$.

In segregated flow,

$$(C/C_0)_{batch} = \exp(-k\bar{t}t_r) \qquad \text{first order} \quad (7)$$

$$\frac{1}{[1+(q-1)kC_0^{q-1}\ \bar{t}t_r]^{1/(q-1)}}, \quad \text{.other orders} \quad (8)$$

$$(C/C_0)_{segregated} = \int_0^\infty (C/C_0)_{batch}E(t_r)dt_r \quad (9)$$

P5.07.07 CONVERSION WITH MAXIMUM MIXEDNESS OR SEGREGATION, ERLANG DISTRIBUTION, NUMERICAL SOLUTIONS.

The two modes are compared for a second order reaction, q = 2, over a range of $R = kC_0\bar{t}$ and for n = 2 to 5. Formulas are taken from other problems. Intensity functions are

$n = 2,\ \Lambda(t_r) = 4t_r/(1+2t_r)$

3 $\quad 13.5t_r^2/(1+3t_r+4.5t_r^2)$

4 $\quad 42.67t_r^3/(1+4t_r+8t_r^2+10.67t_r^3)$

5 $\quad 130.21t_r^4/(1+5t_r+12.5t_r^2+20.83t_r^3+26.04t_r^4)$

The starting values, x_∞, for the MM solution are in Table 1. Conversions by the two modes are in Table 2. Some of these data are plotted and compared with plug flow conversion.

At high conversions, MM reactor size is significantly larger than segregated. For n = 5 at 95% conversion, the abscissas are 4.15 and 2.3, corresponding to a reactor volume ratio of 1.8.

Table 1. Starting values, x_∞

$kC_0\bar{t}$	n=2	n=3	n=4	n=5
0.5	0.1716	0.1270	0.1010	0.0830
1	0.2679	0.2087	0.1716	0.1459
2	0.3820	0.3139	0.2679	0.2344
3	0.4514	0.3820	0.3333	0.2967
4	0.5000	0.4313	0.3820	0.3441
5	0.5367	0.4693	0.4202	0.3820
10	0.6417	0.5821	0.5367	0.5000
20	0.7298	0.6808	0.6417	0.6096
30	0.7730	0.7298	0.6955	0.6667
50	0.8190	0.7832	0.7543	0.7298

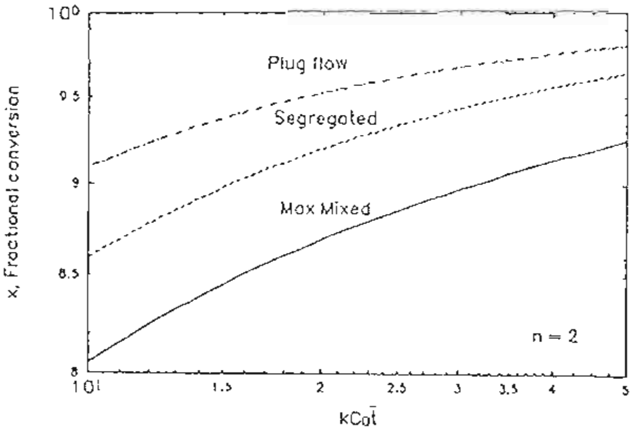
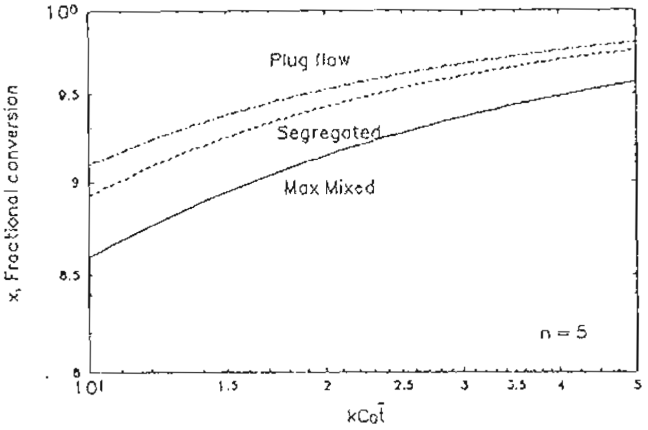
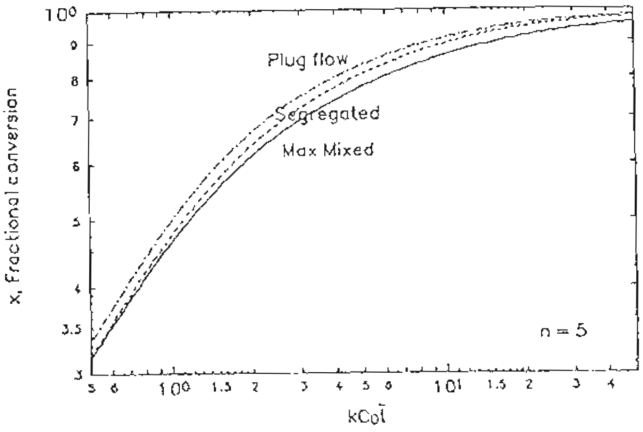


Table 2. Conversion, x

	Maximum Mixed				Segregated			
$kC_0\bar{t}$	n=2	n=3	n=4	n=5	n=2	n=3	n=4	n=5
0.5	0.2946	0.3056	0.3117	0.3155	0.3012	0.3111	0.3163	0.3194
1	0.4277	0.4472	0.4581	0.4651	0.4449	0.4618	0.4708	0.4763
2	0.5635	0.5904	0.6057	0.6155	0.5959	0.6185	0.6303	0.6374
3	0.6365	0.6662	0.6828	0.6953	0.6777	0.7018	0.7140	0.7212
4	0.6838	0.7144	0.7314	0.7423	0.7302	0.7542	0.7661	0.7731
5	0.7175	0.7483	0.7652	0.7761	0.7672	0.7905	0.8019	0.8085
10	0.8053	0.8342	0.8496	0.8593	0.8592	0.8785	0.8872	0.8920
20	0.8692	0.8938	0.9064	0.9142	0.9196	0.9333	0.9391	0.9422
30	0.8972	0.9190	0.9298	0.9364	0.9433	0.9540	0.9582	0.9605
50	0.9247	0.9438	0.9516	0.9567	0.9639	0.9715	0.9744	0.9758





P5.07.08. SEVERAL CONVERSIONS AND SEVERAL VARIANCES

The relation between conversion and reaction parameter R is to be developed with Erlang parameters n = 2 and n = 3. Second order reaction.

For n = 2,

$E(t_r) = 4t_r\exp(-2t_r)$

$\Lambda(t_r) = 4t_r/(1+2t_r)$

$\Lambda(\infty) = 2$

For n = 3,

$E(t_r) = 13.5t_r^2\exp(-3t_r)$

$\Lambda(t_r) = 13.5t_r^2/(1+3t_r4.5t_r^2)$

$\Lambda(\infty) = 3$

For maximum mixedness, $f= C/C_0$, $R = kC_0\bar{t}$,

$$\frac{df}{dt_r} = Rf^2 - \Lambda(t_r)(1-f) \qquad (1)$$

$$Rf_\infty^2 - n(1-f_\infty) = 0 \qquad (2)$$

The starting conditions for integration of Equation (1) are $f = f_\infty$ and $t_r = 3$ or 4 and the ending condition is $f = f_{exit}$ and $t_r = 0$. Values of f_∞ are found by solving Equation (2) and are tabulated for the several cases. The solutions f_{exit} are tabulated and plotted.

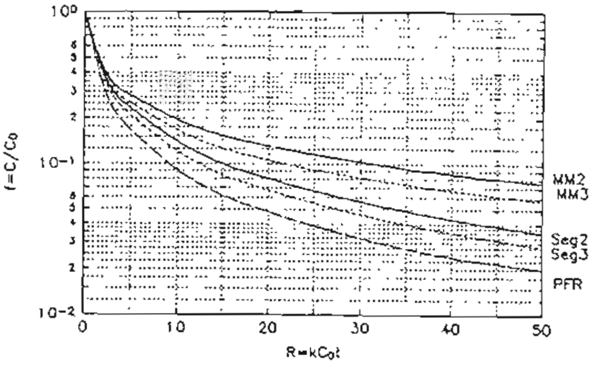
For segregated flow,

$$f = \int_0^\infty \frac{E(t_r)}{1+Rt_r}\,dt_r \qquad (3)$$

These exit concentrations also are tabulated and plotted.

The ratio of MM and segregated reactor volumes at a given conversion can be read off the graph as $V_{MM}/V_{seg} = R_{MM}/R_{seg}$. A few values are,

	V_{MM}/V_{seg}	
C/C_0	n=2	n=3
0.2	1.55	1.40
0.1	2.10	1.75
0.07	2.50	2.05
0.05		2.15



	f_{exit}						
	n = 2		n = 3			y_∞	
R	MM	Seg	MM	Seg	PFR	n=2	n=3
0.000	1.000	1.000	1.000	1.000	1.000		
2.000	0.436	0.403	0.410	0.381	0.333	0.618	0.684
5.000	0.282	0.232	0.252	0.209	0.167	0.463	0.531
10.000	0.195	0.140	0.166	0.121	0.091	0.358	0.418
20.000	0.131	0.080	0.106	0.067	0.048	0.270	0.319
30.000	0.103	0.056	0.081	0.046	0.032	0.227	0.270
40.000	0.086	0.043	0.067	0.035	0.024	0.200	0.239
50.000	0.075	0.035	0.057	0.028	0.020	0.181	0.217

P5.07.09. CONVERSIONS AND REACTOR VOLUMES IN SEVERAL MODES

A second order reaction is to be checked under plug flow, max mixed and segregated flow conditions when $E(t_r)$ of the reactor is Erlang with n = 3. (a) When conversion in a PFR is 90%, what are the other conversions? (b) Find the relative reactor volumes when all three conversions are 90%.

Use the graph of problem P5.07.08, or interpolate in the table given there.

(a) $R = C_0/C - 1 = 9$ At this abscissa and n = 3, the ordinates are f = 0.18 for MM and 0.13 for segregated.

(b) At the ordinate $C/C_0 = 0.9$, the abscissas are $R_{PFR} = 9.0$, $R_{seg} = 12.5$ and $R_{MM} = 31.0$. The relative reactor volumes are in the ratio of the R's.

P5.07.10. TWO CSTRs AND A PFR IN SERIES

The model of a reactor consists of two equal sized CSTRs joined by a PFR whose residence time equals that of the combined CSTRs. A second order reaction with $kC_0t = 2$ is to be studied by the maximum mixedness mechanism. More details of this problem are in problem P5.04.09 where the RTD is developed as

$$E(t_r) = 16(t_r-0.5)\exp(-4(t_r-0.5), \qquad t_r \geq 0.5$$

Other required functions are

$$F(t_r) = \int_{0.5}^{\infty} E(t_r)dt_r = 1 - (4t_r-1)\exp[-4(t_r-0.5)]$$

$$\Lambda(t_r) = \frac{16(t_r-0.5)}{4t_r-1}$$

$$\Lambda(\infty) = 4$$

The starting value for the integration of the Zwietering equation is f_∞ which is obtained by solving

$$kC_0\bar{t}f_\infty^2 + \Lambda(\infty)(f_\infty-1) = 0$$

$$2f_\infty^2 + 4(f_\infty-1) = 0,$$

$$f_\infty = 0.732$$

The equation for the effluent concentration is

$$\frac{df}{dt_r} = 2f^2 + \frac{16(t_r-0.5)}{4t_r-1}(f-1)$$

The starting value for the numerical integration is $f_\infty = 0.732$ and any value of t_{r0} greater than 2 or so. Integrate to $t_r = 0.5$.

Results with several values of t_{r0} are

t_{r0}	0.6	0.8	1.0	1.5	2 and greater
f	0.6073	0.5742	0.5708	0.5721	0.5723

The effluent thus is f = 0.5723. This does not compare favorably with the value $f_{segregated} = 0.3489$ found in problem P5.04.09.

P5.07.11. SEVERAL RTDs, SEVERAL REACTION MODES

Concentration responses to impulse inputs of tracers of cases (a), (b) and (c) are represented by the sketches and the equations given subsequently. Find conversions of a second order reaction with $kC_0 = 2$ in these reaction modes: (1) plug flow; (2) CSTR battery with the variance of the response curve; (3) segregated flow; (4) maximum mixedness, assuming the behavior to be like that of a Gamma distribution with the same variance, and using the results of problem p5.07.07.

(a) The equation of the line is

$$C = 1.5 - 0.3t$$

Derived quantities are,

$$\int_0^5 Cdt = 3.75,\ \int_0^5 tCdt = 6.25,\ \int_0^5 t^2Cdt = 15.625,\ \bar{t} = 1.667,$$

$$\sigma^2(t_r) = -1 + \frac{15.625}{(1.667)^2(3.75)} = 0.500,\ n = 2$$

$$E(t) = C/\int_0^\infty Cdt = 0.4 - 0.08t$$

In plug flow, $C/C_0 = 1/(1+2\bar{t}) = 0.2308$ (a1)

In a two stage CSTR,

$$kC_0\bar{t}/2 = 0.883$$

$$1 = C_1/C_0 + 0.883(C_1/C_0)^2,\quad C_1 = C_2 + 0.883(C_2/C_0)^2$$

$$C_2/C_0 = 0.339 \quad \text{(a2)}$$

In segregated flow,

$$C/C_0 = \int_0^5 \frac{E(t)}{1+2t}dt = 0.328 \quad \text{(a3)}$$

In max mixed flow, interpolating in the table of problem P.07.07,

$$kC_0\bar{t} = 3.33,\ n = 2,\ C/C_0 = 0.348 \quad \text{(a4)}$$

(b) Parabolic response,

$C = 2(4t-t^2-3)$

$\int_1^3 Cdt = 2.667,\ \int_1^3 tCdt = 5.333,\ \int_1^3 t^2Cdt = 11.20,\ \bar{t} = 2.00,$

$$\sigma^2(t_r) = -1 + \frac{11.20}{(2)^2(2.667)} = .0500,\ n = 20.$$

In plug flow, $C/C_0 = 1/[1+2(2)] = 0.20$ (b1)

In CSTR, with n this large, the behavior will be essentially plug flow, with $C/C_0 = 0.20$ (b2)

In segregated flow,

$E(t) = C/2.667$

$$C/C_0 = \int_1^3 \frac{E(t)}{1+2t}\,dt = 0.2068 \qquad \text{(b3)}$$

In max mixed flow, with this large value of n conversion will be the same as segregated.

(c) The equations of the curve are

$$C = \left|\begin{array}{ll} 5(t-0.5) & 0.5\le t\le 1 \\ 2 & 1\le t\le 3 \\ 5(1.5-t) & 3\le t\le 3.5,\ \text{and zero elsewhere} \end{array}\right.$$

$\int_{0.5}^{3.5} Cdt = 6.25,\ \int_{0.5}^{3.5} tCdt = 10.5,\ \int_{0.5}^{3.5} t^2Cdt = 24.05,\ \bar{t} = 1.68,\ \sigma^2(t_r) =$

$$-1 + \frac{24.05}{(1.68)^2(10.5)} = 0.363,\ n = 1/0.363 = 2.75$$

In plug flow, $C/C_0 = 1/[1+2(1.68)] = 0.2294$ (c1)

In the CSTR battery, solve for integral values and interpolate to n = 2.75.

$f_n = C_n/C_0,\ f_0 = 1$

$f_{n-1} = f_n + (2\bar{t}/n)(C_n/C_0)^2$

These integral and interpolated values are found,

n	1	2	2.75	3	4
f_n	0.4167	0.3377	(0.3115)	0.3056	0.2880

The interpolated value is

$C/C_0 = 0.3115$ (c2)

In segregated flow,

$E(t) = C/\int_0^\infty Cdt = C/6.25$

$$C/C_0 = 0.16\left[\int_{0.5}^{1} \frac{5(t-0.5)}{1+2t}\,dt + \int_1^3 \frac{2}{1+2t}\,dt\right.$$

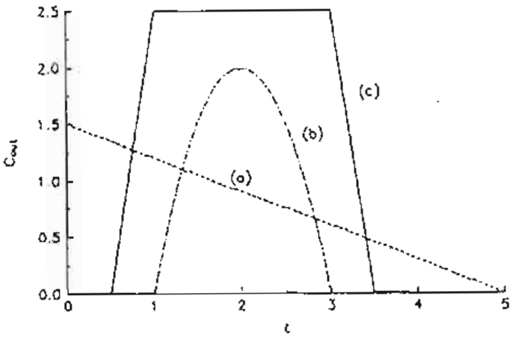
$$\left. + \int_3^{3.5} \frac{5(3.5-t)}{1+2t}\,dt\right] = 0.187 \qquad \text{(c3)}$$

(Note: This value should not be smaller than that in plug flow, but the error has proven elusive).

In max mixed flow, employ double interpolation for x as tabulated.

The interpolated values are x = 0.676 and $C/C_0 = 0.324$.

R	n=2	n=2.75	n=3
3	0.6365		0.6662
3.36	0.6535	0.676	0.6836
4	0.6838		0.7144



P5.07.12. CONVERSION WITH SEVERAL MODELS

The reaction is second order and the RTD is the Erlang with n = 3. A range of values of reaction parameter $R = kC_0\bar{t}$ is to be examined and the models are to be maximum mixed, segregated, three stage CSTR and plug flow.

The distribution functions are

$$E(t_r) = 13.5t_r^2 \exp(-3t_r)$$

$$\Lambda(t_r) = \frac{13.5t_r^2}{1+3t_r+4.5t_r^2}$$

$$\Lambda(\infty) = 3$$

(a) Maximum mixedness. The differential equation and the boundary condition are

$$\frac{df}{dt_r} = Rf^2 - \frac{13.5t_r^2}{1+3t_r+4.5t_r^2}(1-f),\quad f = C/C_0$$

$$Rf_\infty^2-3(1-f_\infty) = 0$$

$$f_\infty = \frac{-3+\sqrt{9+12R}}{2R}$$

Integration starts at $(f_\infty, t_r=4)$, although $t_r=2$ or 3 give essentially the same result. Results are obtained over a range of R.

(b) Segregated flow,

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1+Rt_r}\,dt_r$$

These results also obtained over a range of R.

(c) Three stage CSTR. The given RTD does not apply to this configuration but the results are obtained for comparison. The material balances are

$$f_{n-1} = f_n\ (R/3)f_n^2,\quad n = 1,\ 2,\ 3$$

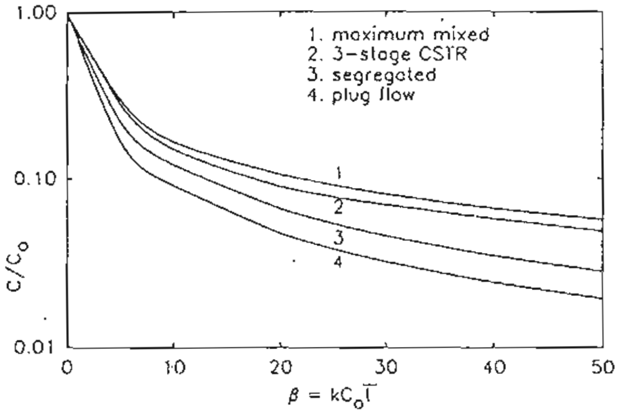
These three equations are solved simultaneously for the conversion out of the third stage as a function of R.

(d) Plug flow. The given RTD does not apply to this model but the results are given for comparison.

$$C/C_0 = 1/(1+R)$$

All four cases are plotted. The required reactor volumes at a given value of f are in the ratios of the corresponding values of $R = kC_0\bar{t}$. At f = 0.06, for instance

Type	$kC_0\bar{t}$	V/V_{pf}	V/V_{seg}
MM	46	2.88	1.48
Seg	31	1.94	1.00
3-stage	22	1.38	
Plug	16	1.00	



P5.07.13. A THIRD ORDER REACTION

A third order reaction with $kC_0^2\bar{t} = 1.5$ is to be conducted in vessel that has an Erlang RTD with n = 5. Compare segregated and max mixed conversions.

The distribution functions are

$$E(t_r) = 130.2\ t_r^4\exp(-5t_r)$$

$$\Lambda(t_r) = \frac{130.2t_r^4}{1+5t_r+(5t_r)^2/2+(5t_r)^3/6+(5t_r)^4/24}$$

$$\Lambda(\infty) = 5$$

In segregated flow,

$$(C/C_0)_{batch} = \frac{1}{(1+2kC_0^2\bar{t}t_r)^{0.5}} = \frac{1}{(1+3t_r)^{0.5}}$$

$$(C/C_0)_{seg} = \int_0^\infty (C/C_0)_{batch}\ E(t_r)dt_r = 0.5208 \qquad (1)$$

In max mixed flow,

$$Rf_\infty^3 = \Lambda(\infty)(1-f_\infty) \text{ or } 1.5f_\infty^3 = 5(1-f_\infty),\ f_\infty = 0.829$$

$$\frac{df}{dt_r} = 1.5f^3 - \Lambda(t_r)(1-f)$$

Integrate over the range $(0.829, t_{r0})$ to $(f_{exit}, 0)$. The results with several values of t_{r0} show insensitivity of the result beyond $t_{r0} = 2$.

t_{r0}	5	3	2	1	0.5	0.1
f_{exit}	0.5414	0.5414	0.5414	0.5465	0.5950	0.7549

So the max mixed result is

$$C/C_0 = 0.5414 \qquad (2)$$

Lines (1) and (2) are to be compared.

P5.07.14. GAUSSIAN DISTRIBUTION

A second order reaction with $kC_0 = 1.5$ is to be processed under segregated or max mixed conditions. The RTD is Gaussian with variance $\sigma^2(t_r) = 0.2$.

The Gaussian distribution functions are

$$f(\sigma) = \frac{1+1.541(0.2)}{0.451+4.886(0.2)} = 0.9160$$

$$E(t_r) = 0.916\ \exp(-2.5(t_r-1)^2)$$

The intensity function $\Lambda(t_r)$ was evaluated numerically in problem P5.02.09. It is curve fitted, as shown on the graph, by

$$\Lambda(t_r) = 0.09036+1.9829t_r^2 - 0.2830t_r^3$$

A starting value f_∞ for integration of the max mixedness equation is found by solving

$$1.5f_\infty^2 - \Lambda(t_{r0})(1-f_\infty)$$

The equation to be integrated is

$$\frac{df}{dt_r} = 1.5f^2 - \Lambda(t_r)(1-f)$$

starting with (f_∞, t_{r0}) and proceeding to $(f_{exit}, 0)$. Results with several trial values of t_{r0} are tabulated.

t_{r0}	$\Lambda(t_{r0})$	f_∞	f_{exit}
1.5	3.61	0.76	0.4437
2	5.74	0.8231	0.4445
2.5	8.06	0.8617	0.4451
3	10.30	0.8857	0.4458
3.5	12.25	0.9007	0.4464
4	13.71	0.9095	0.4471
∞	∞	1	overflow

Although the values do not strictly converge, an appropriate value may be

$$(C/C_0)_{MM} = 0.446 \qquad (1)$$

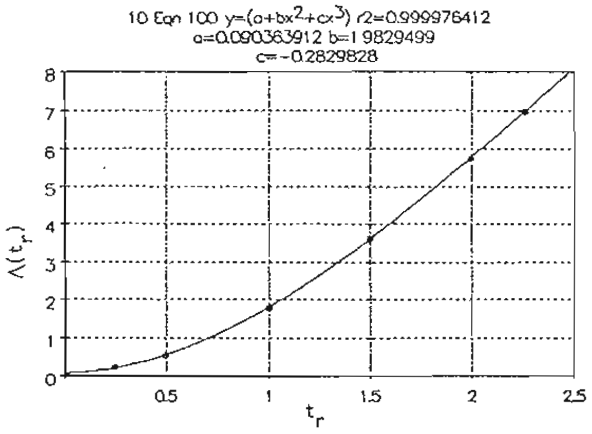
In segregated flow,

$$(C/C_0)_{seg} = \int_0^\infty \frac{E(t_r)}{(1+1.5t_r} dt_r = 0.4327 \qquad (2)$$

Also,

$$(C/C_0)_{plug} = 1/(1+1.5) = 0.4000 \qquad (3)$$

Lines (1), () and (3) are to be compared.



P5.07.15. SEMICIRCULAR SHAPED TRACER RESPONSE CURVE

The response curve of tracer response is a semicircle with equation

$$C = \sqrt{2.25-(t-1.5)^2}$$

For a second order reaction with $kC_0 = 0.25$, find conversion in segregated and max mixed flows.

The required quantities are,

$\int_0^3 C\,dt = 3.534$, $\bar{t} = 1.5$, by reason of symmetry

$E(t) = C/3.534$

$\Lambda(t)$ is evaluated numerically in the first table and is curve fitted by

$\Lambda(t) = (0.1646 + 0.1690t)/(1-0.3244t)$

In plug flow,

$$(C/C_0)_{pf} = 1/[1+0.25(1.5)] = 0.7273 \qquad (1)$$

In segregated flow,

$$(C/C_0)_{seg} = \int_0^3 \frac{E(t)}{1+0.25t}\,dt = 0.7404 \qquad (2)$$

In max mixed flow, the starting point f_∞ is found from

$$0.25f_\infty^2 = \Lambda(t_{r0})(1-f_\infty)$$

The Zwietering equation,

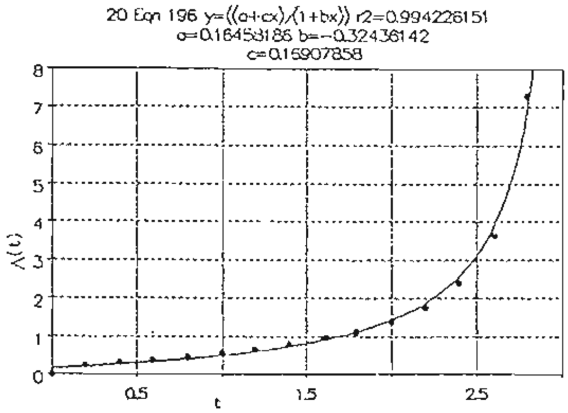
$$\frac{df}{dt} = 0.25f^2 - \Lambda(t)(1-f)$$

then is integrated over the range $(f_\infty,\ t_{r0})$ to $(f_{exit}, 0)$. Several values of t_{r0} and corresponding f_∞ are summarized in the table, together with the corresponding f_{exit}. The converged value seems to be about

$$(C/C_0)_{MM} = 0.738 \qquad (3)$$

This value is between the plug flow and segregated values as it ordinarily is.

t	E(t)	F(t)	$\Lambda(t)$	f_∞	f_{exit}
0	0	0	0		
.2	.2117	.0286	.2172		
.4	.2885	.0792	.3133		
.6	.3395	.1423	.3958		
.8	.3753	.214	.4775		
1	.4001	.2917	.5649	.7506	.6904
1.2	.4158	.3734	.6636	.7742	.7089
1.4	.4234	.4575	.7805	.7967	.7166
1.6	.4234	.5423	.9312	.8196	.723
1.8	.4158	.6263	1.1127	.8411	.7278
2	.4001	.708	1.3702	.8638	.7318
2.2	.3753	.7857	1.748	.8874	.7347
2.4	.3395	.8574	2.3808	.9726	.7367
2.6	.2885	.9204	3.6244	.9392	.7379
2.8	.2117	.971	7.3	.9679	.7379
3	0	1	∞	1	



P5.08.01. DERIVATION OF THE DISPERSION EQUATION

A basis is Fick's diffusion law adapted to dispersion which states that the rate of mass transfer by dispersion is proportional to the concentration gradient. A material balance is made on a hollow cylindrical element of radii r and r+dr and length dx. This element is sketched.

$$\text{Input} = (uC-D_x\frac{\partial C}{\partial x})2\pi r dr - D_r(2\pi r dx)\frac{\partial C}{\partial r}$$

$$\text{Output} = \text{Input} + d[\text{Input}]$$

$$\text{Sink} = R_c dv_r = R_C(2\pi r dx dr)$$

$$\text{Accumulation} = 2\pi r dx dr\frac{\partial C}{\partial t}$$

Combining these four terms,

$$d[uC-D_x\frac{\partial C}{\partial x}](2\pi r dr) - 2\pi D_r dx d(r\frac{\partial C}{\partial r}) + 2\pi r dx dr(R_c+\frac{\partial C}{\partial t}) = 0$$

which rearranges to

$$\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} + \frac{D_r}{r}\frac{\partial}{\partial r}(r\frac{\partial C}{\partial r}) - u\frac{\partial C}{\partial x} - R_c \quad (1)$$

When only axial dispersion is significant,

$$\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - R_c \quad (2)$$

In terms of the normalized coordinates

$$t_r = t/\bar{t} = tu/L,\ z = x/L,\ L = \text{reactor length}$$

$$\frac{\partial C}{\partial t_r} = \frac{1}{Pe}\frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} - R_C\bar{t} \quad (3)$$

where $Pe = uL/D_x$ is the Peclet number.

For power law kinetics of order n at steady state,

$$\frac{d^2C}{dz^2} = Pe[\frac{dC}{dz} - k\bar{t}C^n] \quad (4)$$

and with $f = C/C_0$,

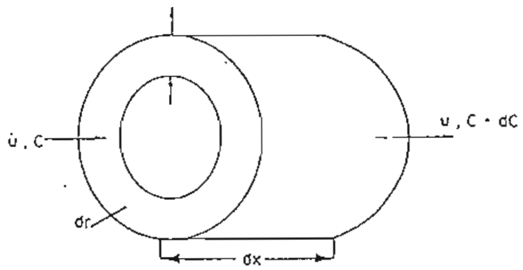
$$\frac{d^2f}{dz^2} = Pe[\frac{df}{dz} - k\bar{t}C_0^{n-1}f^n] \quad (5)$$

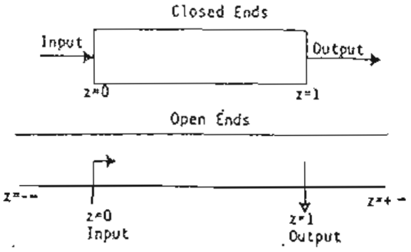
Two sets of boundary conditions for Equations (3) or (4) are

$$\text{"Closed Ends"},\ uC_0 = (uC-D_z\frac{\partial C}{\partial z})_{z=0} \text{ and } (\frac{\partial C}{\partial z})_{z=1} = 0 \quad (6)$$

$$\text{"Open Ends"},\ C(\pm\infty,\ t) = 0,\ C(0,t) = C(t) \quad (7)$$

Closed ends normally applies to reactor operation. Open ends may be used with tracer studies when tracer is injected and sampled some distances from the ends of the vessel. The figures show these two cases.





P5.08.02. TWO SETS OF BOUNDARY CONDITIONS

Solve the dispersion equation for several values of Pe for both closed and open end boundary conditions for a second order reaction with $kC_0\bar{t} = 1$.

The dispersion equation and its equivalent as two first order equations are

$$\frac{d^2f}{dz^2} = Pe[\frac{df}{dz} + kC_0\bar{t}f^2], \; df/dz = p, \; dp/dz = Pe(p+f^2) \qquad (1)$$

The closed end conditions are

$$1 = f-(df/dz)/Pe \text{ at } z = 0, \text{ and } df/dz = 0 \text{ at } z = 1 \qquad (2)$$

The open conditions are

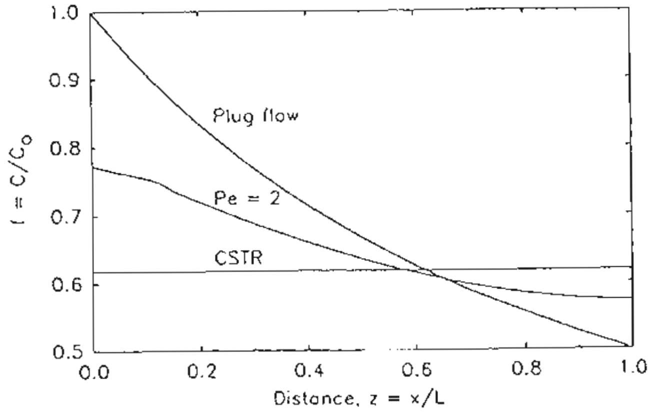
$$f = 1 \text{ at } z = 0, \text{ and } df/dz = 0 \text{ at } z = 1 \qquad (3)$$

For this two point boundary value problem, the following procedure will be used:

1. Estimate f_0 at $z = 0$
2. The derivative at $z = 0$ then will be $f'_0 = Pe(f_0-1)$
3. Solve the pair of first order differential equations numerically and note if $df/dz = 0$ at $z=1$.

The table shows final results for several values of Pe and also a comparison with CSTR at Pe = 0 and PFR at Pe = ∞.

	Closed Ends				Open	
Pe	f_0	$-f'_0$	f_1		f_0	f_1
0			0.618			
0.5	0.684	0.158	0.603			
1	0.731	0.269	0.590		1	0.77
2	0.794	0.413	0.573		1	0.68
4	0.859	0.565	0.552		1	0.61
∞			0.500			



Since the values f_1 of the open end configuration do not fall within the yields of the CSTR and PFR, that boundary condition is not valid. The PFR and CSTR profiles are compared on the figure with the closed end result at Pe = 2.

P5.08.03. TWO POINT BOUNDARY CONDITIONS. SEVERAL VALUES OF R AND Pe

Solve the dispersion equation for a second order reaction for several values of $R = kC_0\bar{t}$ and $Pe = uL/D$.

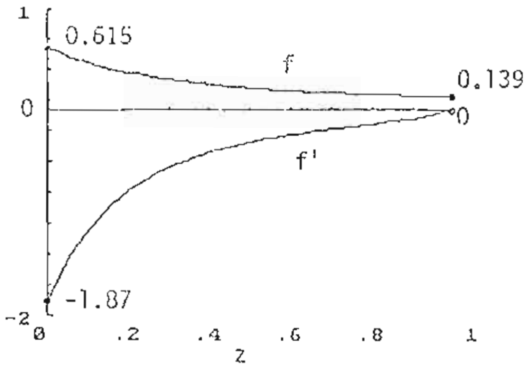
The equation and the boundary conditions are

$$\frac{d^2f}{dz^2} = Pe\left(\frac{df}{dz} + Rf^2\right),\quad 1 = (f-f'/Pe)_{z=0},\quad (df/dz)_{z=1} = 0$$

The procedure is to assume a value of f(1), solve the differential equation for f(0) and f'(0) and check the value of $(f-f'/Pe)_{z=0} \overset{?}{=} 1$.

The figure shows final profiles of f and f' when R = 10 and Pe = 5. The table shows several trial values and the final one for each case. Usually two trials and a linear interpolation suffice.

R	Pe	f_1	f_0	$-f'_0$	$-f'_0/Pe$	Sum
1	1	0.60	0.7459	0.2791	0.2791	1.0250
		0.59	0.7308	0.2692	0.2692	1.0 Check
1	5	0.50	0.7719	.4840	.0968	0.868
		0.58	0.9670	0.7327	0.1465	1.1135
		0.5453				1.0 Check
10	1	0.20	0.4106	0.5304	0.5304	0.9410
		0.22	0.4858	0.6975	0.6975	1.1833
		0.205				1.0 Check
10	5	0.15	0.782	2.850	0.570	1.352
		0.138	0.597	1.806	0.361	0.958
		0.1393				1.0 Check



P5.08.04. RTD AND VARIANCE OF THE DISPERSION MODEL

For impulse input of tracer to a vessel with closed ends, the solution has been found by Otake & Kunigata [Kagaku Kogaku 22 144 (1958)]. The condition is unsteady state and is represented by the partial differential equation

$$\frac{\partial f}{\partial \vartheta} = \frac{\partial f}{\partial z} + \frac{1}{Pe}\frac{\partial^2 f}{\partial z^2},\quad f = C/C_0,\quad \vartheta = t/\bar{t}$$

At $z = 0$, $f_0 = [f-(\partial f/\partial z)/Pe]_{z=0}$

At $z = 1$, $\partial f/\partial z = 0$

The solution is

$$E(\theta) = \exp\left[\frac{Pe}{2}\left(1-\frac{\theta}{2}\right)\right]\sum_{n=1}^{\infty}\frac{\delta_n[Pe\sin\delta_n + 2\delta_n\cos\delta_n]}{\left[\delta_n^2+\left(\frac{Pe}{2}\right)^2+Pe\right]}\times\exp\left[-\frac{\delta_n^2\theta}{Pe}\right],$$

Where δ_n is given by the nth root of the transcendental equation

$$\cot\delta_n = \frac{\delta_n}{Pe} - \frac{Pe}{4\delta_n}.$$

Plots of this solution are shown. They are bell shapes resembling Gamma and Gaussian distributions except that they apparently possess time delay.

The variance is a function of Pe alone and is derived most readily from the transfer function by the method of problem P5.02.01. The result for closed ends is

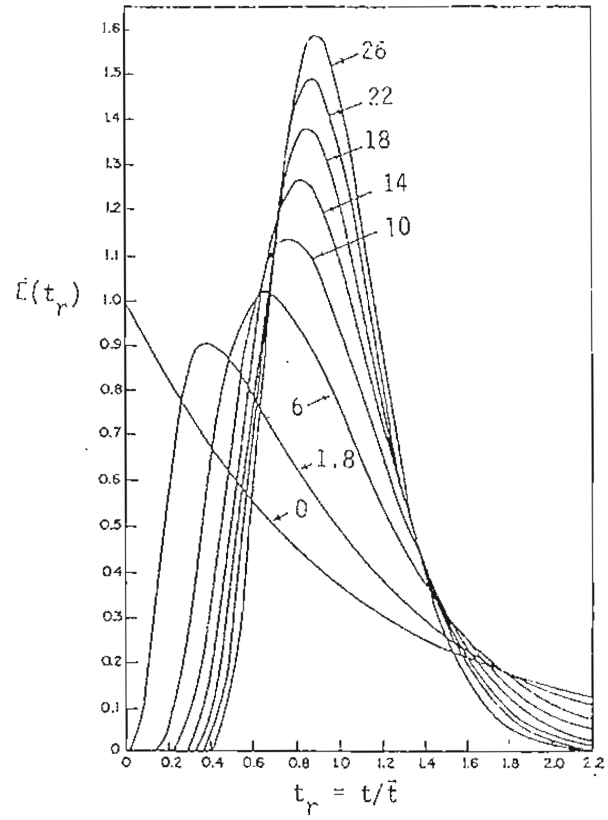
$$\sigma^2(\vartheta) = \sigma^2(t_r) = \frac{2[Pe - 1 + \exp(-Pe)]}{Pe^2}$$

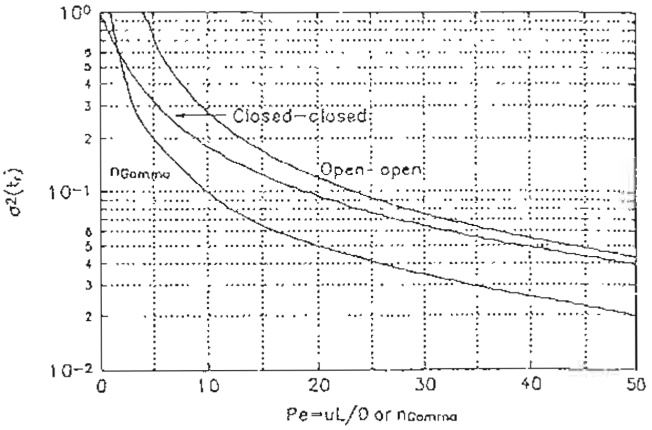
The corresponding relation for open ends is

$$\sigma^2(t_r) = \frac{2(Pe+4)}{Pe^2}$$

Plots of these functions are shown together with the Erlang or Gamma result, $n = 1/\sigma^2$. Equating the variances provides a relation between n and Pe. For both boundary conditions, $n \Rightarrow Pe/2$ at large values. Plots of these relations are shown.

The open ends boundary conditions apply when the measuring points are some distances from the ends. Such an arrangement is used in making accurate measurements of dispersion coefficients.





P5.08.05. PECLET NUMBER FROM THE VARIANCE

Readings off an enlargement of the figure in problem P5.08.04 for Pe = 6 are tabulated here. The data are for closed end conditions. Find the variance of these data and the equivalent number of Gamma stages. Also find Pe from the variance by the two correlations cited in problem P5.08.04.

From the tabular data,

$$\int_{0.13}^{2.4} C\,dt = 0.9745,\quad \int_{0.13}^{2.4} tC\,dt = 0.9121,\quad \int_{0.13}^{2.4} t^2C\,dt = 1.0334$$

$$\bar{t} = 0.936,\quad \sigma^2(t_r) = -1 + \frac{1.0334}{(0.936)^2(0.9745)} = 0.2105,$$

$$n = 4.75$$

For the two kinds of end conditions

$$n = \frac{Pe^2}{2[Pe-1+\exp(-Pe)]} = 4.75,\quad Pe = 8.37,\ \text{closed ends}$$

$$n = Pe^2/(2Pe+8) = 4.75,\quad Pe = 12.5,\ \text{open ends}$$

Neither of these checks the original value Pe = 6. The relation (Pe, σ^2) is quite sensitive so σ^2 data must be accurate for good evaluation of Pe. Some inaccuracy resulted in this case from reading the plot of $E(t_r)$, evidently since $\int_{0.13}^{2.4} E\,dt$ is not quite unity.

t_r	$E(t_r)$	tE	t^2E
0.13	0	0	0
0.2	0.07	0.014	0.0028
0.4	0.67	0.268	0.1072
0.6	0.99	0.594	0.3564
0.8	0.93	0.744	0.5952
1	0.74	0.74	0.74
1.2	0.53	0.636	0.7632
1.4	0.38	0.532	0.7448
1.6	0.26	0.416	0.6656
1.8	0.18	0.324	0.5832
2	0.11	0.22	0.44
2.2	0.07	0.154	0.1388
2.4	0	0	0

P5.08.06. FIRST AND SECOND ORDER REACTIONS. TABLES AND GRAPHS

The dispersion equation

$$\frac{d^2f}{dz^2} = Pe\left(\frac{df}{dz} + kC_0^{n-1}\bar{t}\,f^n\right)$$

is to be solved for n = 1 and n = 2 at a range of values of Pe and $kC_0^{n-1}\bar{t}$.

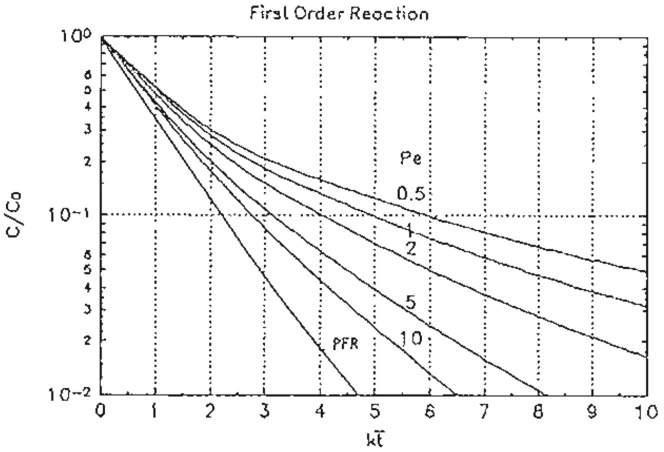
Trial values of the effluent yield, f_1, are assumed until one is found that results in satisfaction of the condition at $z = 0$ by backward integration.

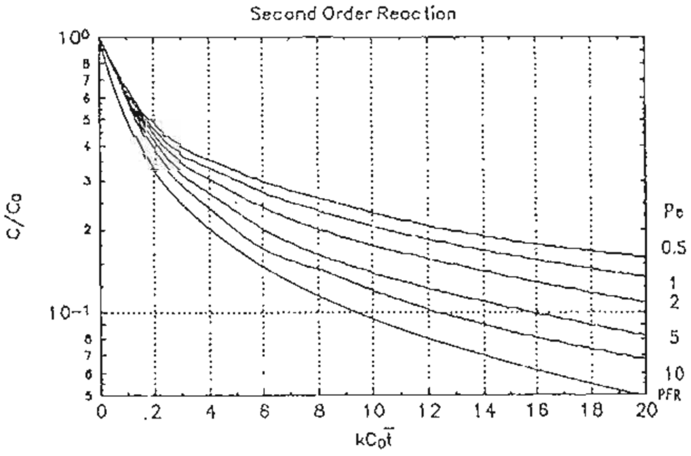
At $z = 1$, $df/dz = 0$; at $z = 0$, $1 = (f-f'/Pe)_{z=0}$.

The results are tabulated and plotted. For comparison, the performance of plug flow is included.

First Order

$k\bar{t}$ \ Pe	0.5	1	2	5	10	PFR
0	1	1	1	1	1	1
2	0.302	0.280	0.249	0.201	0.177	0.1353
4	0.159	0.133	0.102	0.064	0.0442	0.0183
6	0.0993	0.0754	0.0502	0.0245	0.0133	0.0025
8	0.0678	0.0472	0.0277	0.0107	0.0046	0.0003
10	0.0492	0.0314	0.0164	0.0051	0.0018	





P5.08.07. DISPERSION MODEL. ANALYTICAL SOLUTION FOR FIRST ORDER

Solve the dispersion equation for first order reaction for several values of dispersion coefficient D, with $u = L = k\bar{t} = 1$.

The differential equation is

$$\frac{D}{uL}\frac{d^2C}{dz^2} - \frac{dC}{dz} - k\bar{t}C = 0 \quad \text{or} \quad D\frac{d^2C}{dz^2} - \frac{dC}{dz} - C = 0$$

The roots of the auxiliary equation are

$$m_1,\ m_2 = \frac{1 \pm \sqrt{1+4D}}{2}$$

The solution is continued with $D = 2$, $m_1 = 1.0$ and $m_2 = -0.5$.

$$C = A\exp(z) + B\exp(-0.5z)$$

$$\frac{dC}{dz} = A\exp(z) - 0.5B\exp(-0.5z)$$

At $z = 1$, $dC/dz = 0$, so that

$$0 = 2.7183A - 0.3038B, \quad B = 8.963A \tag{1}$$

At $z = 0$, $C_0 = [C-D(dC/dz)]_{z=0}$, which becomes

$$C_0 = A+B-2(A-0.5B) = 16.9267A \tag{2}$$

From (1) and (2),

$A = 0.0591C_0$, $B = 0.5295C_0$

and the solution becomes

$$C/C_0 = 0.0591\exp(z) + 0.5295\exp(-0.5z)$$

The effluent concentration is attained at $z = 1$. Thus,

$$(C/C_0)_{exit} = 0.4819$$

When $D = 0$, the reactor is a PFR and

$$(C/C_0)_{pfr} = \exp(-k\bar{t}) = 0.3678$$

When $D \Rightarrow \infty$, the reactor is a CSTR and

$$(C/C_o)_{cstr} = 1/(1+k\bar{t}) = 0.500$$

Results for several values of D are tabulated.

D	m_1	m_2	C/C_0
0			0.3678 PFR
1	1.618	-0.618	0.4675
2	1.000	-0.500	0.4819
3	0.7575	-0.4343	0.4872
∞			0.5000 CSTR

P5.08.08. FIRST ORDER DISPERSION REACTION. GENERAL SOLUTION

Find the general solution of the equations of first order reaction with dispersion, closed end conditions.

The equation and the boundary conditions are,

$$\frac{d^2f}{dz^2} - Pe\left(\frac{df}{dz} + k\bar{t}f\right) = 0 \qquad (1)$$

$$\text{At } z = 1,\ df/dz = 0.\ \text{At } z = 0,\ 1 = \left(f - \frac{1}{Pe}\frac{df}{dz}\right)_{z=0} \qquad (2)$$

The general solution of this linear equation with constant coefficients is

$$f = A\exp(m_1 z) + B\exp(m_2 z) \qquad (3)$$

$$m_1,\ m_2 = (Pe/2)(1 \pm a) \qquad (4)$$

$$a = \sqrt{1+4k\bar{t}/Pe} \qquad (5)$$

$$\frac{df}{dz} = A\,m_1\exp(m_1 z) + B\,m_2\exp(m_2 z) \qquad (6)$$

Apply the boundary conditions to find the integration constants A and B. At z = 1,

$$A\,m_1\exp(m_1) + B\,m_2\exp(m_2) = 0 \qquad (7)$$

At z = 0,

$$[A(1 - m_1/Pe)\exp(m_1 z) + B(1-m_2/Pe)\exp(m_2 z)]_{z=0}$$
$$= A(1 - m_1/Pe) + B(1 - m_2/Pe) = 1 \qquad (8)$$

Solve Equations (7) and (8) for A and B, then substitute into Equation (3) which becomes,

$$C/C_0 = 2\exp\left\{\frac{Pe}{2}z\right\} \times \left[\frac{(1+a)\exp\left\{a\frac{Pe}{2}(1-z)\right\} - (1-a)\exp\left\{-a\frac{Pe}{2}(1-z)\right\}}{(1+a)^2\exp\left\{a\frac{Pe}{2}\right\} - (1-a)^2\exp\left\{-a\frac{Pe}{2}\right\}}\right] \qquad (9)$$

The effluent yield occurs at $z = 1$. Then

$$C_1/C_0 = \frac{4a}{(1+a)^2 \exp\left\{-\frac{uL}{2D}(1-a)\right\} - (1-a)^2 \exp\left\{-\frac{uL}{2D}(1+a)\right\}} \qquad (10)$$

P5.08.09. FIRST ORDER DISPERSION AND PLUG FLOW

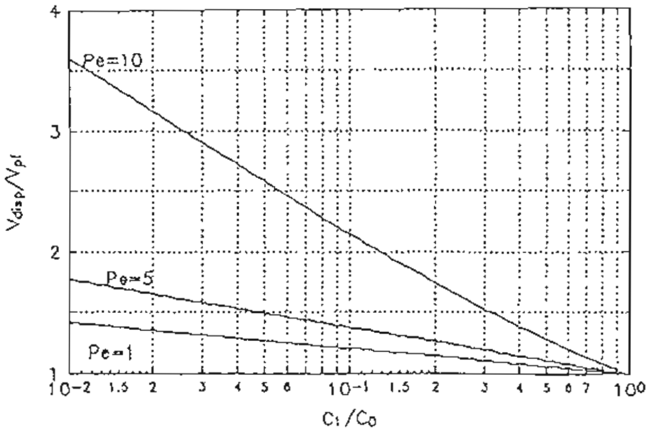
Find the ratio of reactor volumes or residence times of reactions under dispersion conditions or plug flow over a range of Peclet numbers. Use the result of problem P5.08.08.

The calculation procedure will be,

1. Specify C_1/C_0 and evaluate $k\bar{t}_{pf} = \ln(C_0/C_1)$
2. Specify Pe
3. Find $a = \sqrt{1+4k\bar{t}/Pe}$ with Equation (10) of problem P.08.08.
4. For dispersion, find $k\bar{t}$ from Equation (5)
5. The relative reactor volumes are in the ratio $V_{disp}/V_{pf} = \bar{t}_{disp}/\bar{t}_{pf}$.

The results are tabulated and plotted.

Pe	C_1/C_0	a	$k\bar{t}_{disp}$	$k\bar{t}_{pf}$	V_d/V_{pf}
1	.01	8.296	16.597	4.605	3.604
	.05	5.652	7.736	2.996	2.582
	.10	4.559	4.946	2.303	2.148
	.5	2.136	.8908	.693	1.285
	.9	1.992	.1095	.105	1.039
	1.0				1
5	.01	2.744	8.163	R	2.744
	.05	2.142	4.483	E	2.142
	.1	1.882	3.176	P	1.882
	.5	1.272	.7709	E	1.272
	.9	1.042	.1064	A	1.042
	1.0			T	1
10	.01	1.901	6.532	R	1.418
	.05	1.589	3.809	E	1.271
	.1	1.454	2.782	P	1.208
	.5	1.138	.737	E	1.062
	.9	1.021	.1064	A	1.009
	1			T	1



P5.08.10. SECOND ORDER REACTION WITH DISPERSION

The dispersion-reaction equation is to be solved for a second order reaction over a range of $R = kC_0\bar{t}$ and Peclet numbers.

The equation

$$\frac{d^2f}{dz^2} = Pe\left(\frac{df}{dz} + Rf^2\right) \qquad (1)$$

is solved as the pair

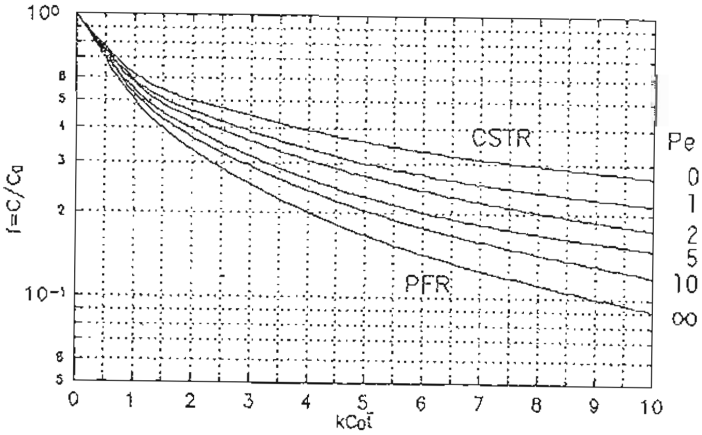
$$\frac{df}{dz} = f', \quad \frac{df'}{dz} = Pe(f' + R f^2) \qquad (2)$$

At $z = 1$, $df/dz = 0$ (3)

At $z = 0$, $(f - f'/Pe)_{z=0} = 1$ (4)

Values of f at z = 1 are found by trial that will result in satisfaction of the condition at z = 0 by backward integration. The table and graph show these values of f(1).

R Pe	0	1	2	5	10
0(CSTR)	1	.618	.500	.358	.270
1	1	.590	.458	.300	.215
2	1	.572	.432	.269	.176
5	1	.545	.394	.227	.150
10	1	.527	.370	.204	.120
∞(PFR)	1	.500	.333	.169	.091



P5.08.11. CLOSED OR OPEN END CONDITIONS. SECOND ORDER REACTION

For both closed end and open end boundary conditions, solve the dispersion equation for second order reaction with Pe = 5 and $kC_0\bar{t} = 5$.

The equation is

$$\frac{d^2f}{dz^2} = 5\left(\frac{df}{dz} + 5f^2\right)$$

For closed end conditions,

at $z = 1$, $df/dz = 0$; at $z = 0$, $[f - (1/5)df/dz]_{z=0} = 1$

For open end conditions,

at $z = 1$, $df/dz = 0$; at $z = 0$, $f = 1$

The procedure is to assume a value f_1 at $z = 1$, then to integrate backwards to $z = 0$ and check the other boundary condition. Some of the trial values and the final values are tabulated. For the closed end condition, $f_1 = 0.2276$ results in $0.9971 \cong 1.000$ for the condition at the other end. For the open end condition, $f_1 = 0.260$ results in $f_0 = 1.002 \cong 1.000$.

An open end condition may exist in a reactor with a catalytic section some distances from the ends and with the same hydrodynamic behavior.

f_{exit}	f_0	$-f'_0$	$(f-f'/5)_0$
0.20	0.5233	0.8674	0.6968
0.2276	0.7058	1.4563	0.9971(check)
0.25	0.8988	2.2026	1.1901
0.260	1.002(check)		

P5.08.12. CONCENTRATION JUMP AT THE INLET WITH DISPERSION

Show the discontinuity that exists at the inlet of a reactor with dispersion and closed ends, for a second order reaction with $R = kC_0\bar{t} = 5$, and for several values of Pe including those of CSTR and PFR.

The differential equation is

$$\frac{d^2f}{dz^2} = Pe(\frac{df}{dz} + 5f^2)$$

with the boundary conditions,

at $z = 1$, $f' = df/dz = 0$

at $z = 0$, $(f - f'/Pe)_{z=0} = 1$

The shooting method of solution is employed. Values of f at z = 1 are tried until one is found that results in satisfaction of the requirement at the other end after backward integration.

For a CSTR, the material balance is.

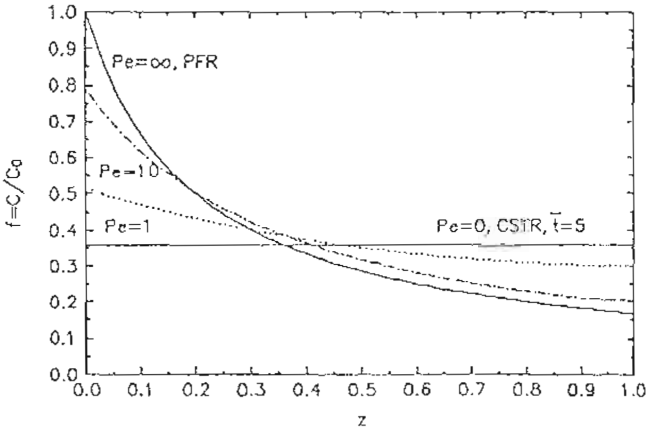
$1 = f_1 + 5f_1^2$, $f_1 = 0.358$

For a PFR,

$f_1 = 1/(1 + R) = 0.167$

The yields are tabulated for several values of Pe. The graph is of concentration profiles and reveals the sudden drop in concentration at the inlet for all cases but the PFR.

Pe	f_1	f_0	$-f'_0$	$(f-f'/Pe)_0$
0	0.358	1, 0.358		CSTR
1	0.300	0.5145	0.4865	1.001
10	0.2036	0.7878	2.1068	0.999
∞	0.167	1		PFR



P5.08.13. DISPERSED AND SEGREGATED FLOW. FIRST ORDER REACTION

Impulse tracer response data are fitted by the empirical equation

$$C = 163.9 + 2.314t - 39.08\sqrt{t} - 333.8\exp(-t), \quad 0 \le t < 60$$

The vessel is of the closed ends type. A first order reaction with $k\bar{t} = 4.6$ is to be conducted there. Find the following. (a) the variance; (b) the Peclet number; (c) conversion under dispersion conditions; (d) conversion in segregated flow.

For the variance,

$$\int_0^{60} C\,dt = 1551,\quad \int_0^{60} tC\,dt = 25393,\quad \int_0^{60} t^2C\,dt = 615790,$$

$$\bar{t} = 16.38,\ \sigma^2(t_r) = -1 + \frac{615790}{(16.38)^2(1551)} = 0.480 \qquad (a)$$

For the Peclet number use the correlation of problem P5.08.04

$$\sigma^2(t_r) = \frac{2[\mathrm{Pe} - 1 + \exp(-5\,\mathrm{Pe})]}{(\mathrm{Pe})^2} = 0.480$$

$$\mathrm{Pe} = 2.51 \qquad (b)$$

For dispersion reaction, apply Equation (10) of problem P5.08.08.

$$a = \sqrt{1 + 4k\bar{t}/\mathrm{Pe}} = \sqrt{1 + 4(4.6)/2.51} = 2.886$$

$$(C_1/C_0)_{disp} = 0.0717 \qquad (c)$$

For segregated flow,

$$E(t) = C/\int_0^{\infty} C\,dt = C/1551$$

$$(C/C_0)_{batch} = \exp(-kt) = \exp(-\frac{k\bar{t}}{\bar{t}}\,t) = \exp(-\frac{4.6}{16.38}\,t)$$

$$(C/C_0)_{seg} = \int_0^{60} (C/C_0)_{batch}E(t)\,dt = 0.0762 \qquad (d)$$

5.08.14. CORRELATIONS OF DISPERSION (PECLET NUMBER) DATA

Rough correlations of Peclet numbers for dispersion are given by Wen (in Petho & Noble, *Residence Time Distribution in Chemical Engineering*, 1982) Those for axial dispersion are quoted. Others given there are for fluidized beds and for radial dispersion.

1. Axial dispersion in empty tubes,

$$\frac{1}{\mathrm{Pe}} = \frac{1}{(\mathrm{Re})(\mathrm{Sc})} + \frac{(\mathrm{Re})(\mathrm{Sc})}{192}, \qquad 1 \le \mathrm{Re} \le 2000,\ 0.2 \le \mathrm{Sc} \le 1000$$

$$\frac{1}{\mathrm{Pe}} = \frac{3(10^7)}{(\mathrm{Re})^{2.1}} + \frac{1.35}{(\mathrm{Re})^{0.125}}, \qquad \mathrm{Re} \ge 2000$$

2. Axial dispersion of gases in packed tubes,

$$\frac{1}{\mathrm{Pe}} = \frac{0.3}{(\mathrm{Re})(\mathrm{Sc})} + \frac{0.5}{1 + \frac{3.8}{(\mathrm{Re})(\mathrm{Sc})}}, \qquad 0.008 \le \mathrm{Re} \le 400,\ 0.28 \le \mathrm{Sc} \le 2.2$$

$\mathrm{Pe} = d_p u_0/\varepsilon D$, Peclet number
$\mathrm{Re} = d_p u_0/\nu$, Reynolds number
$\mathrm{Sc} = \nu/D$, Schmidt number
D = axial dispersion coefficient
d_p = diameter of particle or empty tube
ε = fraction voids in packed bed
u_0 = superficial velocity in vessel

Find the following: (a) the values of (Re)(Sc) when Pe = 1, 5 and 10; (b) the values of Re when Pe = 0.3, 0.5 and 1.0; (c) the values of (Re)(Sc) in a packed tube when Pe = 1, 2 and 3.

(Answers: (a) 191, 32.5, 17.7; (b) 2220, 2994, 4905; (c) 0.311, 0.713, 1.647).

P5.08.15. APPLICATION OF CORRELATIONS OF PECLET NUMBERS

Conversions will be found for the following cases, using the correlations of problem P5.08.14:

(a) A first order reaction with $k\bar{t} = 4$ in an empty tube with Re = 2500. From problem P5.08.14,

$$1/Pe = 1/(2500)^{2.1} + 1.35/(2500)^{0.125}$$

$$Pe = 1.97$$

$$a = \sqrt{1+4k\bar{t}/Pe} = 3.02$$

$C_1/C_0 = 0.1022$, using Equation (10) of problem P5.08.08.

(b) A first order reaction with $k\bar{t} = 4$, flow of gas in a packed tube with Re = 100 and Sc = 0.5.

$$1/Pe = 0.3/(100)(0.5) + 0.5/[1 + 3.8/(100)(0.5)]$$

$$Pe = 2.125$$

$$a = \sqrt{1+4k\bar{t}/Pe} = 2.92$$

$C_1/C_0 = 0.0989$, using Equation (10) of problem P5.08.08.

(c) Same as part (a) except second order reaction with $kC_0\bar{t} = 5$.

Pe = 1.97 as in part (a). Solve the differential equation by the shooting method.

$$\frac{d^2f}{dz^2} = 1.97\left(\frac{df}{dz} + 5f^2\right)$$

Boundary conditions: at z = 1, $f' = df/dz = 0$; at z = 0, $(f-f'/1.97)_{z=0} = 1$. Results with several trial values of f at z = 1 are in the table. Final result is $C_1/C_0 = 0.27$.

(d) Same as part (b) except second order reaction with $kC_0\bar{t} = 5$. The equation to be solved is

$$\frac{d^2f}{dz^2} = 2.125\left(\frac{df}{dz} + 5\,f^2\right)$$

with $df/dz = 0$ at z = 1 and $(f - f'/2.125)_{z=0} = 1$. Several trial values are in the table. The final result is $C_1/C_0 = 0.266$.

f_1	f_0	$-f'_0$	$(f-f'/Pe)_0$
0.309	0.7229	1.1247	1.2938
0.25	0.5157	.6392	0.8402
0.27	0.5923	.8067	1.002 check
0.25	0.5349	0.6979	0.8634
0.27	0.6167	0.8867	1.0340
0.266			1.00 check

P5.08.16. REACTION IN A PACKED VESSEL

Tracer tests on a packed open end vessel has an RTD with a variance $\sigma^2(t_r) = 0.3$. A reaction with rate equation

$$r = k_1f/(1+k_2C_0f)$$

with $k_1\bar{t} = 2.0$ and $k_2C_0 = 0.5$ is to be conducted in a closed end vessel under the same hydrodynamic conditions as the tracer test. Find the exit value of $f = C/C_0$.

From the correlation of problem p5.08.04,

$$\sigma^2 t_r) = 0.3 = \frac{2(Pe+4)}{Pe^2}$$

Pe = 9.5

The dispersion-reaction equation is

$$\frac{d^2f}{dz^2} = 9.5\left(\frac{df}{dz} + \frac{2f}{1+0.5f}\right)$$

with the conditions: $f' = df/dz = 0$ at $z = 1$; $(f-f'/9.5)_{z=0} = 1$, at $z = 0$. The table shows that the trial value, $f_1 = 0.244$, satisfies the boundary conditions

f_1	f_0	$-f'_0$	$(f-f'/9.5)_0$
0.25	0.9862	0.1912	1.0063
0.24	0.9762	0.1912	0.9963
0.244			1.00 check

P5.08.17. DISPERSION AND SEGREGATION COMPARED

A vessel 2 cm in diameter with "closed ends" is operated at a linear velocity of 5.2 cm/sec. Kinematic viscosity of the fluid is 0.0018 sqcm/sec. A second order reaction with $kC_0\bar{t} = 4$ is to be conducted here. Find the following: (a) the dispersion coefficient; (b) the chemical conversion by the dispersion model; (c) the variance of the RTD resulting from impulse input of tracer; (d) the Gamma distribution with the same variance; (e) segregated conversion with the Gamma distribution.

(a) The Reynolds number is $Re = d_t u/\nu = 2(5.2)/0.0018 = 5778$. Use this correlation from problem P5.08.14,

$$1/Pe = D/ud_t = \frac{3(10^7)}{Re^{2.1}} + \frac{1.3}{Re^{0.125}}$$

Pe = 1.197

D = 2(5.2)/1.197 = 8.69 sqcm/sec (a)

(b) To find the conversion, either solve the differential equation with its boundary conditions, or use the results of problem P5.08.06. That plot for second order conversion gives

$f = C/C_0 = 0.3$ when R = 4 and Pe = 1.197. . . . .(b)

(c) From problem P5.08.04 for closed ends,

$$\sigma^2(t_r) = \frac{2[Pe - 1 + \exp(-Pe)]}{Pe^2} = 0.6967 \qquad (c)$$

(d) For the Gamma distribution,

$n = 1/0.6967 = 1.4354$, $\Gamma(n) = 0.8859$,

$$E(t_r) = \frac{n^n}{\Gamma(n)} t_r^{n-1}\exp(-nt_r) = 1.8964\, t_r^{0.4354}\exp(-1.4354\, t_r)$$

(d)

(e) For segregated second order reaction with $kC_0\bar{t} = 4$,

$$C/C_0 = \int_0^\infty \frac{E(t_r)}{1 + 4\, t_r}\, dt_r = 0.2957 \qquad (e)$$

In plug flow, for comparison,

$C/C_0 = 1/(1 + kC_0\bar{t}) = 0.2000$

P5.08.18. DISPERSION IN A PACKED BED REACTOR

A solution of concentration C_0 is pumped at a velocity u through a catalyst bed in which the dispersion coefficient is D and the rate equation is $r = 0.001(C-C_e)$ where C_e is constant. For a boundary condition, note that C will remain constant as distance $z \Rightarrow \infty$. Find the reactor lengths z that will reduce the displacement of concentration from the equilibrium value by 50% under steady state conditions when (a) D = 0.2 and u = 0.05; (b) D = 0.2 and u = 0; (c) D = 0 and u = 0.05.

The steady state equation is

$$D\frac{d^2C}{dz^2} - u\frac{dC}{dz} - k(C-C_e) = 0$$

or

$$D\frac{d^2w}{dz^2} - u\frac{dw}{dz} - kw = 0,\ w = C-C_e$$

The auxiliary of this linear DE and its roots are

$$Dm^2 2 - um - k = 0$$

$$m_1,\ m_2 = \frac{u \pm \sqrt{u^2+4Dk}}{2D}$$

In view of the finiteness condition, only the root with the negative sign is applicable. Accordingly the solution is

$$w = w_0 \exp[(u-\sqrt{u^2+4Dk}\ (\frac{z}{2D})]$$

$$z = \ln(w/w_0)\frac{2D}{u-\sqrt{u^2+4Dk}}$$

When $w/w_0 = 0.5$, D = 0.2, u = 0.05, k = 0.001, z = 37.2 (a)

When $w/w_0 = 0.5$, D = 0.2 and u = 0, z = 9.8 (b)

When D = 0 and u = 0.05, the differential equation becomes

$$u\frac{dw}{dz} + kw = 0$$

and has the solution

$$z = (u/k)\ln(w_0/w) = 34.7 \qquad (c)$$

P5.08.19. TWO DIFFERENT INLET CONCENTRATIONS

A second order reaction with $kC_0\bar{t} = 5$ is conducted in a vessel with Pe = 10. The feed is partially converted with $f_{inlet} = 0.8$. Find the effluent yield, and compare with the yield when $f_{inlet} = 1.0$. Closed end boundary conditions.

The differential equation is

$$\frac{d^2f}{dz^2} = 10(\frac{df}{dz} + 5f^2)$$

At the outlet where z = 1, $f' = df/dz = 0$. At the inlet, z = 0,

$$(f-f'/10)_{z=0} = 0.8 \text{ or } 1.0$$

The value f_1 at the exit is established by trial to satisfy the boundary condition at the inlet.The results are summarized in the table

f_{inlet}	f_1	f_0	f'_0	$(f-f'/Pe)_0$
1.0	0.2036	0.3878	2.1068	0.999 check
0.8	0.1910	0.6522	1.5062	0.8003 check

The two effluent yields are 0.2036 with inlet 1.0 and 0.191 with inlet 0.8.

P5.08.20. DISPERSION AND OTHER MECHANISMS

A second order reaction is to be conducted in a vessel whose RTD is an Erlang with n = 3. Find conversion with the dispersion and other models for several values of $R = kC_0\bar{t}$.

From problem P5.08.04,

$$n = 3 = \frac{Pe^2}{2[Pe-1+\exp(-Pe)]}, \quad Pe = 4.75$$

The dispersion equation is

$$\frac{d^2f}{dz^2} = 4.75(\frac{df}{dz} + Rf^2)$$

with the conditions: at z = 1, $f' = df/dz = 0$; at the other end, $(f-f'/4.75)_{z=0} = 1$. The two steps of the solution procedure are (i) estimate f_1 at the outlet where z = 1; (ii) integrate back to z = 0 and note if the boundary condition there is satisfied. The second order DE is solved as the first order pair,

$$\frac{df}{dz} = f', \quad \frac{df'}{dz} = 4.75(f' + Rf^2)$$

The dispersion yields are compared in the table with those found by other models in other problems. For the given RTD, at least, the dispersion results fall between those with segregation and maximum mixing.

f_{exit}

$kC_0\bar{t}$	Disp	MM	Seg	3-Stg	PFR
1	0.5462	0.5528	0.5280	0.5496	0.5000
5	0.2300	0.2517	0.2094	0.2417	0.1667
10	0.1415	0.1658	0.1215	0.1547	0.0909

P5.08.21. DISPERSION AND SEGREGATED REACTION WITH RTD KNOWN

Tracer response data of impulse input are given in the table. They are fitted by the equation shown with the graph. For a first order reaction, $k\bar{t} = 4.605$. Find the conversion in (a) dispersed flow; (b) in segregated flow; (c) in segregated flow with a Gamma distribution of the same variance; (d) in a CSTR battery of the same variance.

Various integrals are found with the curve fit equation.

$$\int_0^\infty Cdt = 1585, \quad \int_0^\infty tCdt = 25262, \quad \int_0^\infty t^2Cdt = 698954, \quad \bar{t} = 15.93,$$

$$\sigma^2(t_r) = -1 + \frac{698954}{(15.93)^2(1585)} = 0.7373, \quad n = 1.356, \quad \Gamma(n) = 0.8905, \quad n^n/\Gamma(n)$$

= 1.6971.

The Peclet number for closed ends is found with the equation from problem P5.08.04,

$$n = 1.356 = \frac{Pe^2}{2[Pe-1+\exp(-Pe)]}$$

$$Pe = 1.01$$

(a) for dispersed flow, use Equation (10) of problem P5.08.08.

$$a = \sqrt{1+4k\bar{t}Pe} = \sqrt{1+4(4.605)(1.01)} = 4.425$$

$$(C/C_0)_{disp} = 0.1107 \qquad \text{(a)}$$

(b) in segregated flow,

$$(C/C_0)_{batch} = \exp(-kt) = \exp[-(k\bar{t}/\bar{t})t] = \exp[-(4.605/15.93)t]$$
$$= \exp(-0.289t)$$

$$E(t) = C/\int_0^\infty C dt = C/1585$$

$$(C/C_0)_{seg} = \int_0^\infty (C/C_0)_{batch}E(t) = 0.1105 \qquad \text{(b)}$$

(c) with the Gamma distribution,

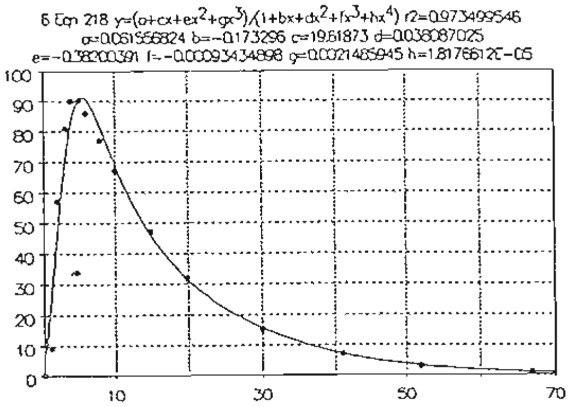
$$E(t_r) = 1.6971\ t_r^{0.356}\exp(-1.356t_r)$$

$$(C/C_0)_{seg} = \int_0^\infty \exp(-4.605t_r)E(t_r) = 0.1313 \qquad \text{(c)}$$

(d) CSTR battery, assuming that the first order equation holds for fractional values of n,

$$C/C_0 = \frac{1}{(1+k\bar{t}/n)^n} = \frac{1}{(1+4.605/1.356)^{1.356}} = 0.1325$$

t	C	t	C
1	9	10	67
2	57	15	47
3	81	20	32
4	90	30	15
5	90	41	7
6	86	52	3
8	77	67	1



P5.08.22. APPLICATION OF EARLIER RESULTS

First and second order reactions done in a continuous intensively stirred laboratory reactor both attained 60% conversion at contact times $\bar{t} = 5$. They are to be done in a larger unit that has an impulse response curve with the equations,

$$C = \begin{cases} 0.4t & 0 \le t \le 5 \\ 3-0.2t & 5 \le t \le 15, \text{ and zero elsewhere} \end{cases}$$

Find the conversions under dispersion or segregated flow conditions.

The specific rates are

$$k = \frac{1/f-1}{\bar{t}} = \frac{1/0.4-1}{5} = 0.333, \text{ for first order}$$

$$kC_0 = \frac{1-f}{\bar{t}f^2} = \frac{1-0.4}{5(0.4)^2} = 0.75, \text{ for second order}$$

The properties of the impulse response are,

$$\int_0^{15} C dt = 15,\ \int_0^{15} tC dt = 100,\ \int_0^{15} t^2 C dt = 812.5,\ \bar{t} = 6.67,$$

$$\sigma^2(t_r) = -1 + \frac{812.5}{(6.67)^2(15)} = 0.2188$$

$$E(t) = C/\int_0^{\infty} C dt = C/15$$

From problem P5.08.04,

$$0.2188 = \frac{2[Pe - 1 + \exp(-Pe)]}{Pe^2},$$

$$Pe = 8.00$$

First order dispersion reaction, using P5.08.06 or the method of P5.08.08,

$$k\bar{t} = 0.333(6.67) = 2.22,\ Pe = 8,\ f \cong 0.16 \qquad (1)$$

Second order dispersion reaction, using P5.08.06 or P5.08.10, or integrating the dispersion equation,

$$kC_0\bar{t} = 0.75(6.67) = 0.5,\ Pe = 8,\ f \cong 0.22 \qquad (2)$$

First order segregated flow reaction,

$$C/C_0 = \int_0^{15} E(t)\exp(-0.333t)dt = 0.1191 + 0.0537 = 0.1728 \qquad (3)$$

Second order segregated flow reaction,

$$C/C_0 = \int_0^{15} \frac{E(t)}{1+0.75t} dt = 0.1039 + 0.0973 = 0.2012 \qquad (4)$$

P5.08.23. SPECIFIC RATE WHEN DISPERSION EXISTS

A second order liquid phase reaction in a packed bed attains 90% conversion. The axial Peclet number is Pe = 12. Find $R = kC_0\bar{t}$.

The dispersion equation is

$$\frac{d^2f}{dz^2} = 12(\frac{df}{dz} Rf^2)$$

The boundary conditions are:

At the outlet, $z = 1,\ f = 0.1,\ f' = df/dz = 0$

At the inlet, $z = 0,\ f = 1,\ (f-f'/Pe)_{z=0} = 1$

The second order equation is solved as the pair,

$df/dz = f'$

$df'/dz = 12(f' + Rf^2)$

The shooting method is used. The procedure is,

1. Assume a value of R
2 Start at $z = 1$ where $f' = 0$ and $f = 0.1$
3. Integrate backward to $z = 0$
4. Evaluate $(f-f'/Pe) \overset{?}{=} 1$ at $z = 0$
5 Repeat with values of R until item 4 is satisfied.

Several trials are summarized in the table. The correct value is $R = kC_0\bar{t} = 11.98$

R	f_0	$-f_0'$	$(f-f'/12)_0$
10	0.413	1.194	0.5125
11	0.5307	1.9992	0.6973
11.98	0.7090	3.5190	1.0023 check
12	0.7136	3.5626	1.0105

P5.08.24. SPECIFIC RATE OF A SECOND ORDER REACTION

A reacting gas flows through a packed bed that has a Peclet number Pe = 12. The reaction is second order and attains 95% conversion. Find $R = kC_0\bar{t}$.

The dispersion equation is

$$\frac{d^2f}{dz^2} = 12(\frac{df}{dz} + Rf^2)$$

with the conditions,

at z = 1, f = 0.05, f' = df/dz = 0

at z = 0, $(f-f'/12)_{z=0} = 1$

Trial values of R are assumed and the solution procedure described in problem P5.08.23 is followed. The table shows several such trial values. The correct one is obtained by interpolation, R = 26.8.

R	f_0	$-f_0'$	$(f-f'/12)_0$
25	0.4231	2.4551	0.6277
26.7	0.5923	4.5318	0.9700
26.8			1.00 interp
27	0.6333	5.1057	1.0588

P5.08.25. A SPECIFIC RATE

A second order reaction in a packed bed attains 80% conversion at a contact time $\bar{t}$ = 200. The Peclet numbert is Pe = 12. Find kC_0 of this operation.

The applicable equation is

$$\frac{d^2f}{dz^2} = 12(\frac{df}{dz} + 200kC_0f^2)$$

with the conditions,

at z = 1, f' = df/dz = 0, f = 0.2

at z = 0, $(f-f'/12)_{z=0} = 1$

The solution procedure outlined in problem P5.08.23 is followed.

Results with several trial values of $R = 200kC_0$ are tabulated. The correct one is R = 4.955, whence

$kC_0 = 4.955/200 = 0.0248$

R	f_0	$-f_0'$	$(f-f'/12)_0$
5.00	0.8260	2.3878	1.0250
4.955	0.8091	2.2849	0.9995 check
4.90	0.7891	2.1660	0.9696

P5.08.26. SPECIFIC RATE OF A FIRST ORDER REACTION

A first order reaction attains 80% conversion in a vessel that has a Peclet number Pe = 12. Find $R = k\bar{t}$.

The dispersion equation is

$$\frac{d^2f}{dz^2} = 12(\frac{df}{dz} + Rf)$$

The solution of problem P5.08.08 will be applied.

$$a = \sqrt{1+4R/Pe} = \sqrt{1+R/3} \quad (1)$$

Equation (10) of P5.08.08 becomes

$$4a(C_0/C) = 20a = (1+a)^2\exp[-6(1-a)] - (1-a)^2\exp[-6(1+a)] \quad (2)$$

The solution of these two equations is

$$a = 1.266,\ R = k\bar{t} = 1.808 \quad (3)$$

For comparison, in plug flow, $R = \ln(C_0/C) = \ln(5) = 1.61$ (4)

P5.08.27. LAMINAR FLOW WITH DISPERSION

A first order reaction takes place under laminar conditions. The data of the reactor are

$u = 10([1-(r/R)^2]$ ft/sec

$L = 20$ ft

$D = 400$ sqft/sec

$k = 0.5$/sec

Find the average value of C/C_0 at the exit, and compare with that at the average velocity, and with that at plug flow.

The solution of the dispersion equation along a stream line is given in problem P5.08.08. That Equation (10) can be written in the form

$$(C/C_0)_{SL} = \frac{4a\exp(b)}{(1+a)^2\exp(ab)-(1-a)^2\exp(-ab)} \quad (1)$$

$$a = \sqrt{1+4k\bar{t}D/uL} = \sqrt{1+4kD/u^2} = \sqrt{1+4kDt^2/L^2} = \sqrt{1+2t^2} \quad (2)$$

$$b = Pe/2 = uL/2D = L^2/2Dt = 1/2t \quad (3)$$

In problem P4.08.01 it is shown that in laminar flow the average concentration over the cross section is

$$(C/C_0)_{avg} = 2t_0^2 \int_{t_0}^{\infty} (C/C_0)_{SL} (\frac{1}{t^3})\, dt \quad (4)$$

where the residence time at the center line is

$$t_0 = \bar{t}/2 = L/u_0 = 20/10 = 2$$

The integrand is tabulated and the integration with the trapezoidal rule gives $(C/C_0)_{avg} = 0.369$. (5)

At the average velocity with dispersion,

$\bar{t} = 4$, $a = \sqrt{33} = 5.745$, $b = 0.125$,

$$C/C_0 = \frac{4(5.745)\exp(0.125)}{(6.745)^2\exp(0.7181)-(4.745)^2\exp(-0.7181)}$$

$$= 0.316 \quad (6)$$

In plug flow,

$$C/C_0 = \exp(-k\bar{t}) = \exp[-0.5(4)] = 0.135 \quad (7)$$

Lines (5), (6) and (7) are to be compared.

t	integrand
2	0.4718
3	0.1132
4	0.0395
5	0.0173
6	0.008
7	0.0049
8	0.0029
9	0.0019
10	0.0012
10+	0.000

P5.08.28. THE METHOD OF LINES FOR AN UNSTEADY STATE

Apply the method of lines to the solution of the unsteady state dispersion reaction equation with closed end boundary conditions for which the partial differential equation for a second order reaction is,

$$\frac{\partial f}{\partial t_r} = \frac{1}{\mathrm{Pe}}\frac{\partial^2 f}{\partial z^2} - \frac{\partial f}{\partial z} - k\bar{t}\, C_0 f^2 \qquad (1)$$

The finite-difference equivalent at node n is

$$\frac{df_n}{dt_r} = \frac{1}{\mathrm{Pe}}\frac{f_{n+1} - 2f_n + f_{n-1}}{(\Delta z)^2} - \frac{f_{n+1} - f_n}{\Delta z} - k\bar{t}\, C_0 f_n^2 \qquad (2)$$

A grid with 10 nodes will be employed. The inlet boundary condition is

$$\left(\frac{\partial f}{\partial z}\right)_0 = \frac{f_1 - f_0}{\Delta z} = \mathrm{Pe}(f_0 - 1)$$

from which

$$f_1 = f_0 - \mathrm{Pe}\,\Delta z(1 - f_0) \qquad (3)$$

The outlet boundary condition is

$$\left(\frac{\partial f}{\partial z}\right)_1 = \frac{f_{10} - f_9}{\Delta z} = 0$$

from which

$$f_{10} = f_9 \qquad (4)$$

The system of ODEs to be solved is

$$\frac{df_1}{dt_r} = \frac{1}{\text{Pe}}\left(\frac{f_2 - 2f_1 + f_0}{(\Delta z)^2}\right) - \frac{f_2 - f_1}{\Delta z} - k\bar{t}C_0 f_1^2$$

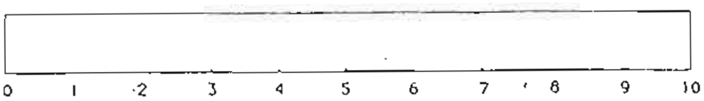
$$\vdots$$

$$\frac{df_9}{dt_r} = \frac{1}{\text{Pe}}\left(\frac{f_{10} - 2f_9 + f_8}{(\Delta z)^2}\right) - \frac{f_{10} - f_9}{\Delta z} - k\bar{t}C_0 f_9^2$$

$$= \frac{1}{\text{Pe}}\left(\frac{-f_9 + f_8}{(\Delta z)^2}\right) - k\bar{t}C_0 f_9^2$$

The solution procedure is

1. Assume a value of f_0.
2. Apply the terminal condition, Eq. (4).
3. Solve the set of nine ODEs.
4. Find f_1 from Eq. (3), and compare with the result found by step 3.
5. Repeat with another estimate of f_0 if necessary.



P5.08.29. STEADY STATE DISPERSION IN TWO DIMENSIONS

Formulate the solution by the method of lines for a steady state flow reaction in a vessel where dispersion occurs radially and axially.

The steady state equation for a second order reaction as obtained from problem P5.08.01 is,

$$\frac{D_r}{r}\frac{\partial}{\partial r}\left(r\frac{\partial f}{\partial r}\right) = -D_x\frac{\partial^2 f}{\partial x^2} + u\frac{\partial f}{\partial x} + k\bar{t}C_0 f^2 \qquad (1)$$

With the substitution

$$\frac{\partial f}{\partial r} = p \qquad (2)$$

the equation becomes

$$\frac{\partial p}{\partial r} = -\frac{p}{r} - \frac{D_x}{D_r}\frac{\partial^2 f}{\partial x^2} + \frac{u}{D_r}\frac{\partial f}{\partial x} + \frac{k\bar{t}C_0}{D_r}f^2 \qquad (3)$$

On replacing the right-hand side with finite differences, Eqs. (2) and (3) become

$$\frac{df_n}{dr} = p_n \qquad (4)$$

$$\frac{dp_n}{dr} = -\frac{p_n}{r} - \frac{D_x}{D_r\Delta x^2}(f_{n+1} - 2f_n + f_{n-1})$$
$$+ \frac{u}{D_r\Delta x}(f_{n+1} - f_n) - \frac{k\bar{t}C_0}{D_r}f_n^2 \qquad (5)$$

Write Eqs. (4) and (5) at each node, say $n = 1$ to 9, for the region shown. The solution procedure can be

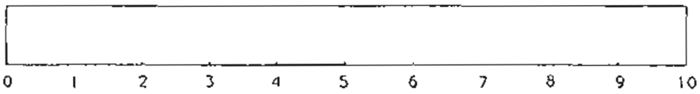
1. Assume a value of f_0.
2. At the inlet,

$$p_0 = \left(\frac{\partial f}{\partial x}\right)_0 = \frac{u}{D_x}(f_0 - 1)$$

3. At the outlet, make $f_{10} = f_9$
4. Solve the system of 18 ODEs for p_1 to p_9 and f_1 to f_9
5. As a check apply the condition,

$$p_0 \overset{?}{=} \frac{f_1 - f_0}{\Delta x}$$

6. If condition 5 is not satisfied, return to step 1 with another estimate of f_0.



CHAPTER 6

REACTIONS WITH SOLID CATALYSTS

THEORY

PROBLEMS

6.1. CATALYTIC PROCESSES

A major class of reactions are those that are influenced by solid catalysts, usually in the form of porous granules that have a large specific surface. Catalysts are substances that react with other participants in a sequence that restores the catalyst to its original chemical identity by the end of the reaction process. The actual mechanism usually is not known positively, but some sequence may be postulated and checked against experimental rate data. In problem P6.03.01 for instance, SO_2 is assumed to be oxidized by oxygen from the solid vanadium catalyst whose oxygen then is replaced from the gas phase. This mechanism together with some other assumptions leads to a rate equation that fits some experimental data. Finding a mechanism in this way is not easy. Usually the existence of unstable intermediates such as free radicals is postulated. Several other examples are shown in Chapter 2.

Correlations of rate data without reference to special chemical mechanisms are more quickly achieved and often suffice over ranges of practical importance. There are two main classes of these methods for solid catalyzed reactions: (1) Power law equations; (2) Adsorption-surface reaction sequences known by the names Langmuir-Hinshelwood, often with the names Hougen-Watson appended, that is, L-H or L-H-H-W.

6.2. POWER LAW EQUATIONS

For a typical reaction, $aA + bB \Leftrightarrow cC + dD$, the rate is assumed to be

$$r = k_1 A^e B^f C^g D^h - k_2 A^{e'} B^{f'} C^{g'} D^{h'} \quad (6.1)$$

where the letters represent partial pressures or concentrations. Reactants and products appear in both terms. The exponents can be zero or negative. If negative, the component is regarded as inhibiting the rate. The reverse term may be left out. The condition of thermodynamic equilibrium requires this relation between the exponents and the stoichiometric coefficients,

$$\frac{e-e'}{a} = \frac{f-f'}{b} = \frac{g-g'}{c} = \frac{h-h'}{d} \qquad (6.2)$$

Data of the irreversible form of the rate equation are analyzed in the linearized form

$$\ln r = \ln k_1 + e \ln A + f \ln B + g \ln C + h \ln D \qquad (6.3)$$

by multilinear reqression.

Over limited ranges of conditions, power law rate equations often are as adequate as those found by detailed chemical or L-H mechanisms.

6.2. LANGMUIR-HINSHELWOOD PROCESSES

Such processes assume that molecules from a fluid phase in contact with a solid catalytic surface combine chemically with catalyst surface molecules and reaction subsequently proceeds between chemisorbed molecules followed by desorption of the products. A large number of different rate equations with varying numbers of constants can be derived by making various auxiliary assumptions and tested against experimental rate data. Since a more or less plausible mechanism is postulated, the feeling is that a chosen rate equation is somewhat extrapolatable outside an experimental range with greater confidence than a power law rate.

6.4. PHYSICAL PROPERTIES OF GRANULAR CATALYSTS

Many solid catalysts are used in the form of porous granules. The size is a compromise between the need for large specific surface and ease of handling. Fluidized bed processes employ particles in the range 20 to 200 microns. Both fixed and moving bed operations are restricted by pressure drop considerations to larger sizes; 4 to 8 mesh is common but may be 1 to 20 mm. Slurry process may employ powders of 400 mesh or so, the limnitation being filterability of the slurry after the reaction is complete.

The most important properties are the specific surface, particle diameter, porosity and pore diameter. The last property determines the accessibility of the surface of the interior which usually is most of it. Specific surface ranges from 1 to 1000 square meters/gram. It is most often measured by adsorption of nitrogen at its atmospheric saturation pressure (-195.8 C), with analysis of the data by the BET adsorption equation (problem P6.01.02). Pore diameters of common catalysts range from 10 to 200 Angstroms (10^{-8} cm); problem P6.01.01 discusses such data. Porosity of a bed of particles consists of the space between their exteriors and of the space within them. The total porosity of a bed of catalytic particles may be 75% or more and that of the particles themselves, 50%.

6.5. ADSORPTION EQUATIONS

An equation relating the amount of adsorption per unit of solid and the partial pressure in contact with the solid at a particular temperature is called an adsorption isotherm. Four of the many kinds of such relations are in common use.

(a) The equation of Freundlich is

$$w = k_1 p^{k_2} \qquad (6.4)$$

or in linearized form

$$\ln w = \ln k_1 + k_2 \ln p \qquad (6.5)$$

Usually k_2 is a fraction. The equation is purely empirical , a tribute to the importance of the logarithm in nature. It applies to both liquid and gas phases, particularly at moderate pressures.

(b) The Temkin equation

$$w = k_1 + k_2 \ln p \qquad (6.6)$$

has a semi theoretical background in that it assumes that the heat of adsorption falls off linearly with the amount of adsorption, and thus recognizes that the solid surface is not uniform.

(c) The Langmuir isotherm is

$$w = \frac{k_1 p}{1+k_2 p} \qquad (6.7)$$

or in linearized form

$$p/w = a + b\,p \qquad (6.8)$$

It is based on a four part mechanism, namely,

(i) A unimolecular layer of adsorbate A is formed

(ii) The rate of adsorption is proportional to the partial pressure and to the amount of free surface,

$$r_a = k_a p_a \vartheta_v = k_a p_a (1-\vartheta_a)$$

where ϑ_v is the fraction of the surface that is unoccupied and ϑ_a is the fraction that is occupied by molecules A.

(iii) The rate of desorption is proportional to the amount that is adsorbed,

$$r_{-a} = k_{-a}\vartheta_a$$

(iv) When adsorptive equilibrium is attained,

$$r_a = r_{-a}$$

and

$$w_a = k'\vartheta_a = \frac{k_1 p_a}{1+k_2 p_a} \qquad (6.7)$$

The relation is readily extended to simultaneous adsorption of several substances.

(d) The BET (Brunauer-Emmett-Teller) isotherm applies even to multilayer adsorption, to pressures approaching liquefaction. The relation is

$$\frac{V}{V_m} = \frac{a(p/p_s)}{(1-p/p_s)[1+(a-1)(p/p_s)]}$$

where a = a constant, V = mass of gas adsorbed by unit mass of adsorbent, V_m = mass of gas adsorbed bky unit mass of adsorbent as a unimolecular layer.

In linearized form,

$$y = \frac{x}{V(1-x)} = \frac{1}{aV_m} + \frac{a-1}{aV_m}x, \quad x = p/p_s \qquad (6.10)$$

At low pressures, $x \ll 1$ and the adsorption tends to unimolecular, this equation reduces to the Langmuir form. It is applied mostly in the determination of specific surfaces of catalysts.

6.6. EXTENSION OF THE LANGMUIR EQUATION

The stoichiometry of Langmuir adsorption of a molecule A can be written

$$A + \sigma \Leftrightarrow A\sigma$$

where σ represents an active site or molecule on the catalyst surface. Application of the law of mass action to the forward and reverse processes results in

$$r_a = k_a p_a \vartheta_v = k_a p_a (1-\vartheta_a)$$

$$r_{-a} = k_{-a}\vartheta_a$$

At eqiuilibrium, as before,

$$w_a = k\vartheta_a = k_1 p_a/(1+k_2 p_a) \qquad (6.7)$$

The mass adsorbed is proportional to the fractional coverage of the surface. The proportionality factor is embodied in the constant of Eq 6.7.

When dissociation of a molecule A_2 accompanies adsorption, the stoichiometry is

$A_2 + 2\sigma \Leftrightarrow 2A\sigma$

and the rate relations at equilibrium are

$k_a p_a \vartheta_v{}^2 = k_a p_a (1-\vartheta_a)^2 = k_{-1}\vartheta_a^2$

and

$$\vartheta_a = \frac{\sqrt{K_a p_a}}{1+\sqrt{K_a p_a}} \qquad (6.11)$$

When two substances are adsorbed on the same surface,

$A + \sigma \Leftrightarrow A\sigma$

$B + \sigma \Leftrightarrow B\sigma$

$k_a p_a \vartheta_v = k_a p_a (1-\vartheta_a-\vartheta_b) = k_{-a}\vartheta_a$

$k_b p_b \vartheta_v = k_b p_b (1-\vartheta_a-\vartheta_b) = k_{-b}\vartheta_b$

whence

$$\vartheta_a = k_a p_a \vartheta_v \qquad (6.12a)$$

$$\vartheta_b = k_b p_b \vartheta_v \qquad (6.12b)$$

$$\vartheta_v = \frac{1}{1+k_a p_a + k_b p_b} \qquad (6.12c)$$

Extension to any number of adsorbates is straightforward,

$$\vartheta_i = k_i p_i \vartheta_v \qquad (6.13a)$$

$$\vartheta_v = 1/(1+\Sigma k_i p_i) \qquad (6.13b)$$

When A_2 dissociates upon adsorption,

$$\vartheta_v = \frac{1}{1+\sqrt{k_a p_a} + k_b p_b} \qquad (6.14a)$$

$$\vartheta_a = \sqrt{k_a p_a}\;\vartheta_v \qquad (6.14b)$$

6.7 RATE WHEN ADSORPTIVE EQUILIBRIUM IS MAINTAINED

In such cases, the overall rate equals the rate of the surface reaction and the surface reaction rate is said to be controlling. The stoichiometric equation is

$A\sigma + B\sigma \Leftrightarrow C\sigma + d\sigma$

with

$\vartheta_i = k_i p_i \vartheta_v$ for every participant

Application of the law of mass action to the reversible reaction is,

$$r = k'(\vartheta_a\vartheta_b - \vartheta_c\vartheta_d/K_e)$$

$$= k(p_a p_b - p_c p_d/K_e)\vartheta_v^2 \qquad (6.15)$$

This may be rearranged to

$$y = \sqrt{\frac{p_a p_b - p_c p_c/Ke}{r}} = (1+\Sigma k_i p_i)/\sqrt{k} \qquad (6.16)$$

When both A and B are in adsorptive equilibrium, but the reaction is between adsorbed A and gas phase B, the stoichiometric and rate equations are

$A\sigma + B \Leftrightarrow$ Products

$$r = k\vartheta_a p_b = k k_a p_a p_b \vartheta_v = \frac{k' p_a p_b}{1+k_a p_a + k_b p_b + \ldots} \qquad (6.17)$$

6.8 SURFACE CHEMICAL REACTION EQUILIBRIUM IS MAINTAINED

In such cases one or more of the participants are not in adsorptive equilibrium and the overall rate is determined by the adsorption rates. Usually only one of the participants is assumed not to be in adsorptive equilibrium, say substance A. Eq 6.12 and analogous others no longer apply. The asterisk, *, is used to identify quantities corresponding to non equilibrium adsorption. From the condition of chemical reaction equilibrium on the surface, the partial pressure of A is

$$p_a^* = \frac{p_c p_d}{K_e p_b} \tag{6.18}$$

Related quantities are

$$\vartheta_a^* = k p_a^* \vartheta_v^* = k\,\frac{p_c p_d}{K_e p_b}\,\vartheta_v^* \tag{6.19}$$

$$\vartheta_v^* = \frac{1}{1+k_a' p_c p_d/p_b + k_b p_b + k_c p_c + k_d p_d + \ldots} \tag{6.20}$$

and the overall rate of the reaction is

$$\begin{aligned} r &= k p_a \vartheta_v^* \\ &= \frac{k p_a}{1+k_a' p_c p_d/p_b + k_b p_b + k_c p_c + k_d p_d + \ldots} \end{aligned} \tag{6.21}$$

Other equations with chemical reaction equilibrium on the surface are summarized in Table 6.2.

6.9 FINDING THE CONSTANTS OF A RATE EQUATION

The data that are required for finding the constants of a rate equation are of the rate as a function of all the partial pressures. When the equilibrium constant also is known, y can be calculated and linear analysis suffices for determination of the constants. Otherwise, nonlinear regression or solution of selected sets of nonlinear equations must be used.

All constants of Langmuir-Hinshelwood rate equations are intrinsically positive so any mechanism that results in any negative constants is regarded as invalid. Although such a result may correlate the data adequately over the experimental range, extrapolation usually is not considered safe.

Often a term for an inert substance may be required in the equation for ϑ_v. Also, one or more of the other terms can be left out, thus giving rise to another rate equation for analysis. For instance, hydrogen, although a reaction participant, often is relatively slightly adsorbed. In such cases, analysis with the complete denominator will not necesssarily give zero for the adsorption constant of the otherwise omittable substance. One of the cases may be preferable statistically.

When more than one equation has all positive constants, the choice will go to the one with the smallest variance.

Table 6.1 summarizes the results obtained here for reactions in which adsorptive equilibrium is maintained

6.10. INTERPRETATION OF DATA

Ordinarily a large number of controlling steps must be investigated by trial. Proper control of the nature of the experimental data - of r as a function of partial pressures - can simplify the problem of equation fitting. Auxiliary experiments on adsorption characteristics may be helpful. For example, on palladium catalyst, hydrogen is not adsorbed, propane is weakly adsorbed and propylene is strongly adsorbed; these data narrow considerably the choice of mechanisms for catalytic dehydrogenation of propane. Stirred tanks or rotating baskets or high recycle reactors give the rates directly without the need for numerical differentiation, moreover at substantially constant temperature.

An often useful discriminant is initial rate data as a function of total pressure. The equations are simpler because terms for the products are absent. Depending on the results of initial rate analysis, the number of complete equations that may need to be investigated could be narrowed. For instance it may be determined initially if a reactant is adsorbed with or without dissociation. Since the number of possible mechanisms sometimes can be 15 or 20 or more, every bit of preliminary assistance is desirable. Typical initial rates as functions of total pressure of some first and second order reactions appear in Figure 6.1.

6.11. SEVERAL CONTROLLING STEPS

All rate equations discussed so far represent single controlling steps. When the equilibrium constant is known, they are linearizable and their constants are relatively easy to find in terms of experimental data. Before going on to more complex mechanisms, it is advisable to exhaust the single step possibilities -, of which the wealth of Tables 6.1 and 6.2 is by means all - before going on to more complex possibilities. A usual next step is to take into account some diffusional resistance for which many mass transfer correlations are existent.

With multiple rate controlling steps, a steady state is postulated, that is, all rates are equated to the overall rate. Equations for the individual steps are formulated in terms of variables such as interfacial concentrations and various coverages ϑ_i of the catalyst surface. Any such variables that are not measurable are eliminated in terms of measurable partial pressures and the rate, as well as various constants to be evaluated from the data. The solved problems deal with several cases; for instance, P6.03.04 has two participants not in adsorptive equilibrium and P6.06.17 treats a process with five steps.

As a typical case take the reaction, $A+B \Leftrightarrow M+N$, in which A is the only participant <u>not</u> in adsorptive equilibrium, and surface chemical reaction is not in equilibrium. Various equations are

$$r = r_{ads} = r_{surf} \qquad \text{(i)}$$

$$= k_1 p_a \vartheta_v - k_2 \vartheta_a = k_3(\vartheta_a \vartheta_b - \vartheta_m \vartheta_n / K_e) \qquad \text{(ii)}$$

$$\vartheta_b = k_4 p_b \vartheta_v \qquad \text{(iii)}$$

$$\vartheta_m = k_5 p_m \vartheta_v \qquad \text{(iv)}$$

$$\vartheta_n = k_6 p_n \vartheta_v \qquad \text{(v)}$$

$$\vartheta_v = 1 - \vartheta_a - \vartheta_b - \vartheta_m - \vartheta_n$$

$$= \frac{1-\vartheta_a}{1+k_4 p_b + k_5 p_m + k_6 p_n} \qquad \text{(vi)}$$

Substitute Eqs (iii) - (vi) into Eq (ii), solve for ϑ_a and formulate the equation for r which will have only the four partial pressures and six constants.

Clearly, such an equation cannot be arranged to make the constants appear linearly. This is usually the case when multiple steps occur.

6.12. WITH DIFFUSIONAL RESISTANCE

The commonest multiple step control mechanism in use is that of diffusion to the surface of the catalyst combined with one of the adsorption or surface reaction steps. Mass transfer by diffusion is proportional to the difference between partial pressures in the bulk of the gas and at the catalyst surface,

$$r_d = k_d(p_g - p_i) \qquad (6.22)$$

The mass transfer coefficient can be found along with other constants from appropriate rate data, or it can be evaluated from an independent known correlation of mass transfer data, of which several are available. In most of the solved problems of this chaper, values of k_d are assumed known. Any brief treatment of mass transfer coefficients in packed beds cannot do justice to the subject, but a typical correlation that may be cited is that of Dwivedi & Upadhyay (IECPDD 16 157, 1977) in terms of Schmidt and Reynolds numbers,

$$k_c = \frac{u}{\varepsilon\ Sc^{2/3}}\left(\frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}\right) \qquad (6.23)$$

k_c has the units of the superficial velocity, u, say cm/sec. This equation is applicable to liquid and gas phases. Problem P6.06.19 is a numerical evaluation.

(a) As an example of a combined model, take control by diffusion of A and by surface reaction. The rate equations are

$$r = r_d = r_{surf}$$

and

$$r_d = k_1(p_{ag}-p_{ai}) \qquad (i)$$

$$r_{surf} = k_2(p_{ai}p_b-p_mp_n/K_e)\vartheta_v^2$$

$$= k_2[(p_{ag}-r/k_1)p_b-p_mp_n/K_e]\vartheta_v^2 \qquad (ii)$$

$$1/\vartheta_v = 1+k_a(p_{ag}-r/k_1)+k_bp_b+k_mp_m+k_np_n \qquad (iii)$$

When k_1 is known, the result can be arranged in a form that is linear in the unknown constants,

$$y = \sqrt{\frac{(p_{ag}-r/k_1)p_b-p_mp_n/K_e}{r}}$$

$$= [1+(k_a(p_{ag}-r/k_1)+k_bp_b+k_mp_m+k_np_n]/\sqrt{k_2} \qquad (iv)$$

Note that when k_1 is large, the last equation reduces to the proper form with surface reaction alone controlling.

(b) As another example take diffusion of A and non equilibrium adsorption of A. The equations are

$$r = k_1(p_{ag}-p_{ai}) = k_2p_{ai}\vartheta_v-k_3\vartheta_a$$

$$= k_2(p_{ag}-r/k_1)\vartheta_v - k_3\vartheta_a \qquad (v)$$

From surface reaction equilibrium,

$$\vartheta_a = k'(p_mp_n/p_b)\vartheta_v \qquad (vi)$$

Also

$$\vartheta_v = 1/(1+k_ap_mp_n/p_b+k_bp_b+k_mp_m+k_np_n) \qquad (vii)$$

Substitution of the last two equations into Eq (v) will find the rate as a function of only measurable quantities and various constants.

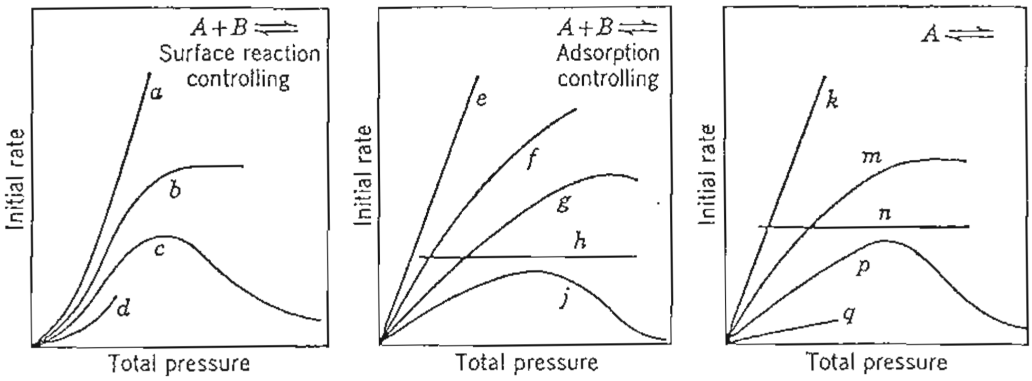


Figure 6.1. Relation between total pressure and initial rate. (*a*) *B* not adsorbed (asymptotic); (*b*) both adsorbed without dissociation (asymptotic); (*c*) both adsorbed, *A* dissociated (asymptotic); (*d*) homogeneous reaction; (*e*) adsorption of *A* controlling, *B* not adsorbed; (*f*) adsorption of *B* controlling, *A* dissociated; (*g*) adsorption of *A* controlling, *B* at equilibrium adsorption (asymptotic); (*h*) desorption of product *R* controlling, irreversible reaction; (*j*) adsorption of *A* controlling with dissociation, *B* at equilibrium adsorption (asymptotic); (*k*) adsorption of *A* controlling; (*m*) surface reaction controlling, single site; (*n*) desorption of product controlling, irreversible reaction; (*p*) surface reaction controlling, dual site; (*q*) homogeneous reaction.

(Hougen, *Chemical Engineering Progress* Monograph No 1, 1951)

Table 6.1. Surface-reaction Controlling (Adsorptive Equilibrium Maintained of All Participants)

	Reaction	Special condition	Basic rate equation	Driving force	Adsorption term
1	$A \rightarrow M + N$	General case	$r = k\theta_a$	p_a	$1 + K_ap_a + K_mp_m + K_np_n$
1a	$A \rightarrow M + N$	Sparsely covered surface	$r = k\theta_a$	p_a	1
1b	$A \rightarrow M + N$	Fully covered surface	$r = k\theta_a$	1	1
2	$A \rightleftharpoons M$	……………………	$r = k_1\theta_a - k_{-1}\theta_m$	$p_a - \frac{p_m}{K}$	$1 + K_ap_a + K_mp_m$
3	$A \rightleftharpoons M + N$	Adsorbed A reacts with vacant site	$r = k_1\theta_a\theta_v - k_{-1}\theta_m\theta_n$	$p_a - \frac{p_mp_n}{K}$	$1 + K_ap_a + K_mp_m + K_np_n)^2$
4	$A_2 \rightleftharpoons M$	Dissociation of A_2 upon adsorption	$r = k_1\theta_a^2 - k_{-1}\theta_m\theta_v$	$p_a - \frac{p_m}{K}$	$(1 + \sqrt{K_ap_a} + K_mp_m)^2$
5	$A + B \rightarrow M + N$	……………………	$r = k\theta_a\theta_b$	p_ap_b	$(1 + K_ap_a + K_bp_b + K_mp_m + K_np_n)^2$
5a	$A + B \rightarrow M + N$	Adsorbed B reacts with A in gas but not with adsorbed A	$r = kp_a\theta_b$	p_ap_b	$1 + K_ap_a + K_bp_b + K_mp_m + K_np_n$
6	$A + B \rightleftharpoons M$	……………………	$r = k_1\theta_a\theta_b - k_{-1}\theta_m\theta_v$	$p_ap_b - \frac{p_m}{K}$	$(1 + K_ap_a + K_bp_b + K_mp_m)^2$
7	$A + B \rightleftharpoons M + N$	……………………	$r = k_1\theta_a\theta_b - k_{-1}\theta_m\theta_n$	$p_ap_b - \frac{p_mp_n}{K}$	$(1 + K_ap_a + K_bp_b + K_mp_m + K_np_n)^2$
8	$A_2 + B \rightleftharpoons M + N$	Dissociation of A_2 upon adsorption	$r = k_1\theta_a^2\theta_b - k_{-1}\theta_m\theta_n\theta_v$	$p_ap_b - \frac{p_mp_n}{K}$	$(1 + \sqrt{K_ap_a} + K_bp_b + K_mp_m + K_np_n)^3$

NOTES: The rate equation is

$$r = \frac{k\ (\text{driving force})}{\text{adsorption term}}$$

When an inert substance I is adsorbed, the term K_ip_i is to be added to the adsorption term.

Table 6.2. Adsorption-rate Controlling (Rapid Surface Reaction)

	Reaction	Special condition	Basic rate equation	Driving force	Adsorption term
1	$A \rightarrow M + N$	…………………	$r = kp_a\theta_v$	p_a	$1 + \frac{K_ap_mp_n}{K} + K_mp_m + K_np_n$
2	$A \rightleftharpoons M$	…………………	$r = k\left(p_a\theta_v - \frac{\theta_a}{K_a}\right)$	$p_a - \frac{p_m}{K}$	$1 + \frac{K_ap_m}{K} + K_mp_m$
3	$A \rightleftharpoons M + N$	…………………	$r = k\left(p_a\theta_v - \frac{\theta_a}{K_a}\right)$	$p_a - \frac{p_mp_n}{K}$	$1 + \frac{K_ap_mp_n}{K} + K_mp_m + K_np_n$
4	$A_2 \rightleftharpoons M$	Dissociation of A_2 upon adsorption	$r = k\left(p_a\theta_v^2 - \frac{\theta_a^2}{K_a}\right)$	$p_a - \frac{p_m}{K}$	$\left(1 + \sqrt{\frac{K_ap_m}{K}} + K_mp_m\right)^2$
5	$A + B \rightarrow M + N$	Unadsorbed A reacts with adsorbed B	$r = kp_a\theta_v$	p_a	$1 + \frac{K_ap_mp_n}{Kp_b} + K_bp_b + K_mp_m + K_np_n$
6	$A + B \rightleftharpoons M$	…………………	$r = k\left(p_a\theta_v - \frac{\theta_a}{K_a}\right)$	$p_a - \frac{p_m}{Kp_b}$	$1 + \frac{K_np_m}{Kp_b} + K_bp_b + K_mp_m$
7	$A + B \rightleftharpoons M + N$	…………………	$r = k\left(p_a\theta_v - \frac{\theta_a}{K_a}\right)$	$p_a - \frac{p_mp_n}{Kp_b}$	$1 + \frac{K_ap_mp_n}{Kp_b} + K_bp_b + K_mp_m + K_np_n$
8	$A_2 + B \rightleftharpoons M + N$	Dissociation of A_2 upon adsorption	$r = k\left(p_a\theta_v^2 - \frac{\theta_a^2}{K_a}\right)$	$p_a - \frac{p_mp_n}{Kp_b}$	$\left(1 + \sqrt{\frac{K_ap_mp_n}{Kp_b}} + K_bp_b + K_mp_m + K_np_n\right)^2$

Adsorption rate of substance A is controlling in each case. When an inert substance I is adsorbed, the term K_ip_i is to be added to the adsorption term.

(From Walas, *Reaction Kinetics for Chemical Engineers*, 1959)

P6.01.01. PORE SIZE DISTRIBUTION BY MERCURY POROSIMETER

Find the pore size distribution of pellets of uranium oxide with these properties. True density = 7.57 g/cc, particle density = 3.2 g/cc, porosity = 57.8% Measurements were made of the penetration of Mercury, cc/gm of pellet, against pressure in psi.

The data are plotted. A relation between the pressure and the pore radius, Å, due to Ritter & Drake (Ind Eng Chem Anal Ed 17 787, 1945) is

$$r = 8.75(10^5)/P$$

Porosity of the pellets is

$$\varepsilon = 0.578/3.2 = 0.1806 \text{ cc/gm}$$

In the plot, both P and r are plotted against cc Hg/gm of pellet.

The pore size distribution may be read off this plot. Some of the values are tabulated.

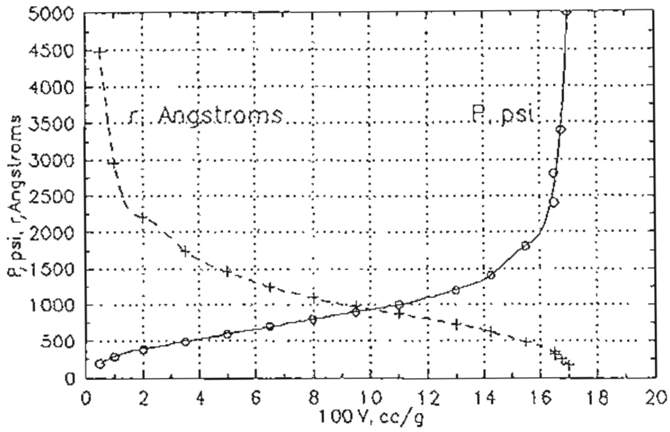
Maximum r, Å	Pores, cc/g	Pores, %
500	0.155	86.0
1000	0.090	49.8
2000	0.028	15.5
3000	0.010	5.5

Note: The quoted equation is derived by equating the force to fill the pores and the opposing surface tension,

$$\pi r^2 \Delta P = -2\pi r\sigma \cos\vartheta,$$

$$r = \frac{2\sigma \cos\vartheta}{\Delta p}$$

For mercury, the surface tension is 480 dynes/cm and the contact angle is $\vartheta = 140°$. The given equation follows in the specified units.



P6.01.02. SPECIFIC SURFACE BY THE BET EQUATION

Adsorption of nitrogen was measured at −195.8 C. Weight of the sample was 50.4 g. The vapor pressure is 760 Torr. Pressures are in Torr and the adsorbate is in cc at STP. The specific surface is to be found.

The BET equation is

$$y = \frac{x}{V(1-x)} = \frac{1}{CV_m} + \frac{C-1}{CV_m}x$$

$x = P/P_s = P/760$

V_m = volume of gas covered by a monolayer, cc/g

The specific surface of nitrogen is

$S_g = 4.35V_m$, m^2/g

The data are plotted. The last four points deviate from the straight line and are omitted. The equation of the straight line is

$1000\ y = 0.0358 + 7.520x$

whence

$CV_m = 1000/0.0358$

$(C-1)/CV_m = 7.520/1000$

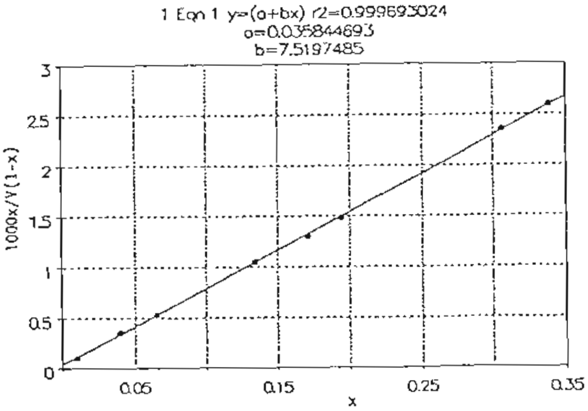
$C = 211.05$, $V_m = 132.3$ cc/50.4 g or 2.626 cc/g

and the specific surface is

$S_g = 4.35(2.626) = 11.4\ m^2/g$

The extrapolation to x = 0 is not highly accurate and may not be reliable.

P	8	30	50	102	130	148	233	258	330	442	480	507	550
V	103	116	130	148	159	163	188	198	221	270	294	316	365



P6.01.03. SPECIFIC SURFACE OF SILICA-ALUMINA

Data for the adsorption of nitrogen on silica-alumina at 77 K are tabulated. V is in cc/g at STP. Find the specific surface by the method of problem P6.01.02.

The equation of the straight line is

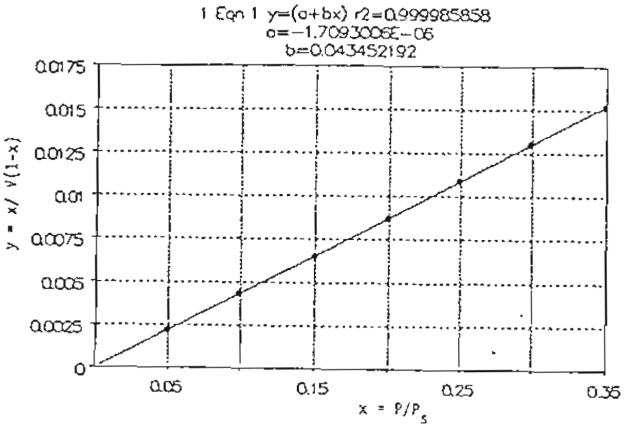
$y = 0 + 0.04345x = 1/CV_m + [(C-1)/VC_m]x$

$$V_m = \frac{1}{\text{Intercept + Slope}} = \frac{1}{0 + 0.04345} = 23.01\ \text{cc/g}$$

and the specific surface is

$S_g = 4.35(23.01) = 100.1\ m^2/g$

P/P_s	0.05	0.10	0.15	0.20	0.25	0.30	0.35
V	24.25	25.60	27.11	28.80	30.58	32.90	35.44



P6.01.04. SURFACE AREA OF SILICA GEL

Data for the adsorption of nitrogen at its atmospheric boiling point on 1.09 g silica gel are correlated by the BET equation as

$$y = \frac{x}{V(1-x)} = \frac{1}{CV_m} + \frac{C-1}{CV_m}x = 0.1 + 17.8x$$

from which

$$V_m = 1/(0.1+17.8) = 55.8 \text{ cc}/1.09 \text{ g}$$

The surface occupied by nitrogen is

$$S = 0.162(10^{-18}) \text{ m}^2/\text{molecule}$$

$$0.162(10^{-18})(6.023)(10^{23}) = 97523 \text{ m}^2/\text{mol}$$

$$97523/22412 = 4.351 \text{ m}^2/\text{cc}$$

Thus the specific surface of the gel is

$$S_g = 4.351(55.8)/1.09 = 222 \text{ m}^2/\text{g}$$

P6.01.05. POROSITY AND DENSITY

A container of V = 50 cc is loaded with W = 53 g of porous pellets. It is first evacuated then connected to a supply of helium. A gas volume $V'+V_g$ = 29 cc is introduced this way. V' is the volume between the pellets and V_g is that of the pores. Then mercury is introduced, the amount to fill the spaces between the pellets being V_g = 19 cc. Find the true density and the porosity of the pellets.

$$\rho_t = \frac{W}{V-(V'+V_g)} = 53/(50-29) = 2.52 \text{ g/cc}$$

$$\vartheta = 1 - \frac{V-(V'+V_g)}{V-V_g} = 1 - \frac{50-29}{50-19} = 0.32, \text{ volume fraction pores}$$

P6.01.06. PORE DIAMETER

Pellets have a porosity ϑ = 0.6 cc/cc, a density of 2.0 g/cc and a specific surface of S = 75 m²/g. Find the average pore diameter.

Assume that the pores are cylindrical with radius R and length h. If the number of pores is N, the volume of the pores will be,

$$V = N\pi R^2 h = 0.6 \text{ cc/cc} = 0.3 \text{ cc/g}$$

and the specific surface,

$$S = N(2\pi R)h = 75 \text{ m}^2/\text{g},\ 75(10^4) \text{ sqcm/g}$$

Therefore,

$$R = 2V/S = 2(0.3/75(10^4) = 8(10^{-7}) \text{ cm},\ 80 \text{ Angstroms}$$

P6.01.07. POROSITY AND PRESSURE DROP IN A BED OF PARTICLES

According to Kozeny (Ber Wien Akad 136A 271, 1927) pressure drop through a bed of spherical particles is expressible in terms of a hydraulic diameter and a travel path $L = \sqrt{2}\,L_s$ where L_s is the depth of the bed. The diameters of the spheres are d, the porosity of the bed is ε and the number of spheres per unit volume of bed is N.

Volume of all spheres,

$$V = 1-\varepsilon = \pi d^3 N/6$$

whence

$$N = 6(1-\varepsilon)/\pi d^3$$

Surface of all spheres,

$$S = \pi d^2 N = 6(1-\varepsilon)/d$$

Hydraulic diameter,

$$D_h = 6V/S = d\varepsilon/(1-\varepsilon)$$

Flow velocity,

$$u = \frac{\text{superficial velocity}}{\varepsilon} = u_s/\varepsilon$$

Travel path,

$$L = \sqrt{2}L_s$$

In laminar flow the friction factor is

$$f = 1/Re = \mu/D_h u\rho$$

Pressure drop,

$$\Delta P = f\rho(u^2/2g)(L/D_h) = \frac{\mu\ u\ L}{2gD_h^2}$$

After the remaining substitutions, the dependence of pressure drop in laminar flow on the porosity becomes,

$$\Delta P = \frac{\mu}{\sqrt{2}g}\ \frac{u_s L_s}{d^2}\ \frac{(1-\varepsilon)^2}{\varepsilon^3}$$

P6.01.08. PORE SIZE

Estimate the voidage and pore size of a catalyst which gave the following results on physical testing: (i) A 50 g sample displaced 110 cc of helium and 130 cc of mercury; (ii) a 3 g sample had a surface area of 1680 m^2.

Volume of particles = 130 cc

Volume of solid = 110 cc

Volume of pores = 20 cc/50 gm, 0.4 cc/g

Surface = 1680/3 = 560 m^2/g, $560(10^4)$ cm^2/g

Assuming the pores to be uniform cylinders, following P6.01.06,

$$r = 2V/S = \frac{2(0.6)}{560(10^4)}(10^8) = 14.3 \text{ Angstroms}$$

P6.01.09. SPECIFIC SURFACE

The tabulated volumes of nitrogen, cc at STP, were adsorbed on the surface of a 2.47 g sample at the pressures indicated at the atmospheric boiling point of nitrogen. Find the specific surface of the solid given that the area occupied by a nitrogen moleclule is $0.162(10^{-18})$ m^2 and that Avogadro's number is $6.023(10^{23})$.

The data are plotted in terms of $x = p/p_s$

$$y = \frac{x}{V(1-x)} = 0.0001576 + 0.01734x$$

From the BET equation, the volume occupied by a monomolecular layer of gas is, as in P6.01.04,

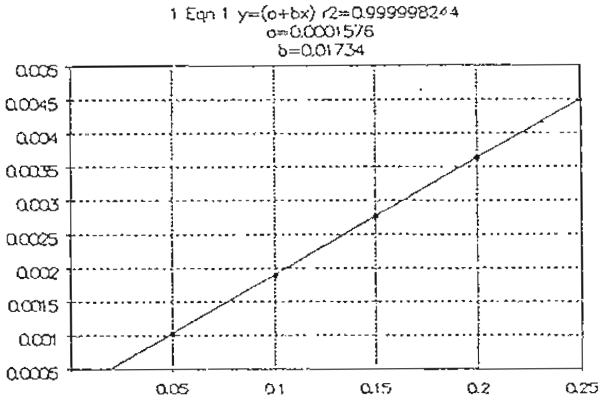
$V_m = 1/(0.0001576+0.01734) = 57.15$ cc/2.47 g, 23.14 cc/g

Surface occupied by nitrogen,

$S_{N2} = 0.162(10^{-18})(6.023)(10^{23})/22412 = 4.351$ m²/ cc @ STP

Specific surface of solid = 23.14(4.351) = 100.7 m²/g

$x=p/p_s$	V	1000y
.05	51.3	1.026
.10	58.8	1.890
.15	64.0	2.757
.20	68.9	3.628
.25	74.2	4.492



P6.02.01. THREE ADSORPTION EQUATIONS

Data for the adsorption of carbon monoxide on charcoal at 273 K are analyzed with three equations in linearized form,

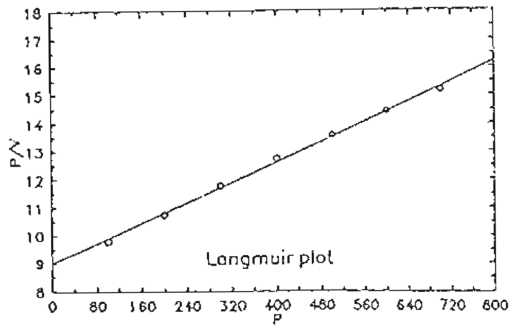
Langmuir, $P/V = k_1 \quad k_2P$

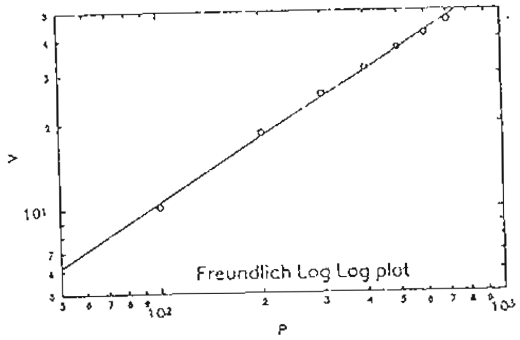
Freundlich, $\ln V = k_1 + k_2 \ln P$

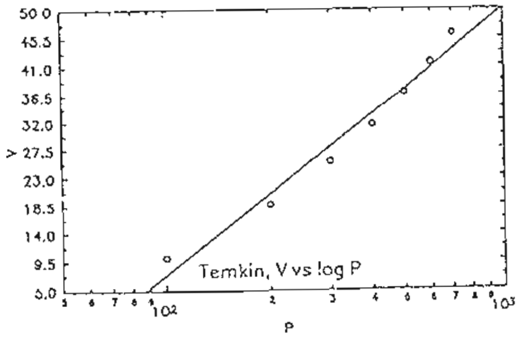
Temkin, $V = k_1 + k_2 \ln P$

The first two plots are nearly linear, but the Temkin is not.

P, Torr	100	200	300	400	500	600	700
V, cc/g	10.2	18.6	25.3	33.4	36.9	41.6	46.1





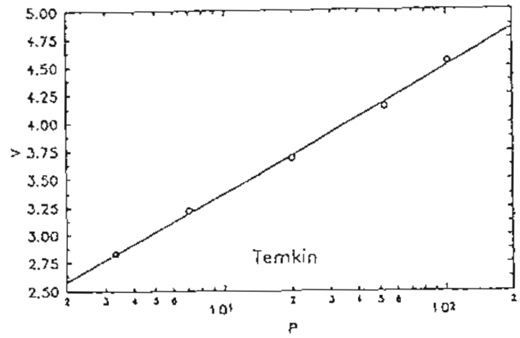


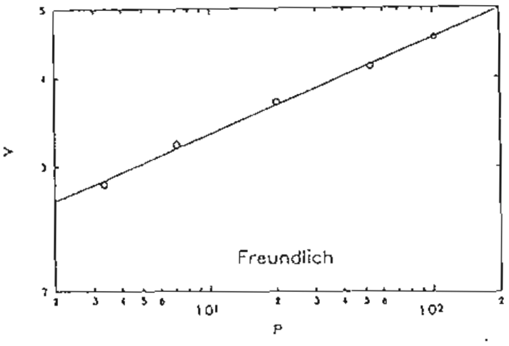
P6.02.02. ADSORPTION OF NITROGEN ON AMMONIA CATALYST

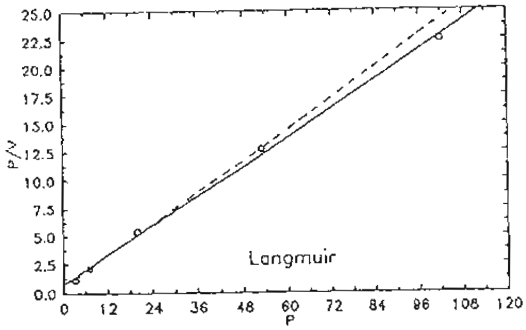
The volume of nitrogen, cc/g at STP, adsorbed on an ammonia synthesis catalyst at 273 K was measured by Brunauer et al (JACS 64 751, 1942).

P, kPa	3.33	7.06	20.0	52.9	102
V, cc/g	2.83	3.22	3.69	4.14	4.55

As the plots show, the Temkin isotherm provides the best fit, although the Freundlich also is close.



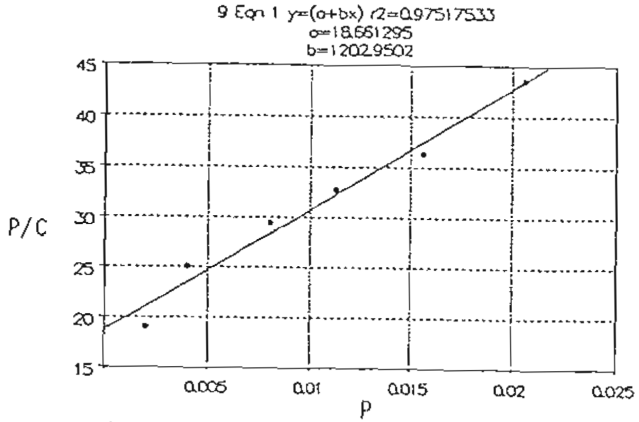




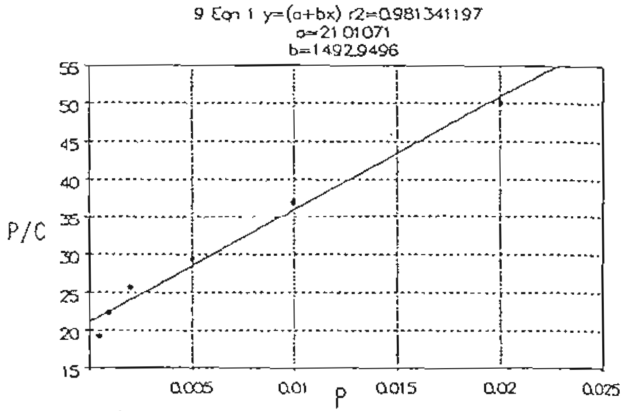
P6.02.03. n-HEXANE ON SILICA GEL

Data were obtained for the equilibrium adsorption of n-hexane on silica gel at 70 C and 110 C. The units are P in atm and adsorption in 10^{-5} gmol/g gel. As the plots show, the Freundlich provides a better fit than the Langmuir at both temperatures.

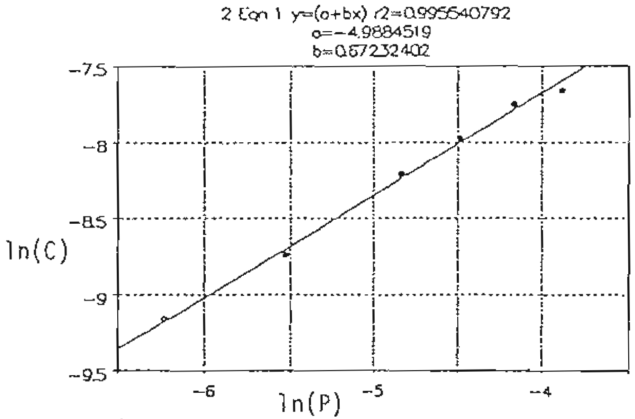
P	w @ 70 C	P	w @ 110 C
0.0020	10.5	0.0005	2.6
0.0040	16.0	0.001	4.5
0.0080	27.2	0.002	7.8
0.0113	34.6	0.005	17.0
0.0156	43.0	0.010	27.0
0.0206	47.3	0.020	40.0



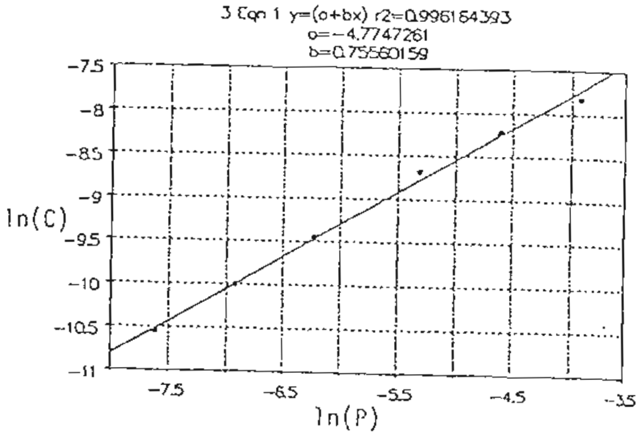
(a) Langmuir at 70 C



(c) Langmuir at 110 C



(b) Freundlich at 70 C

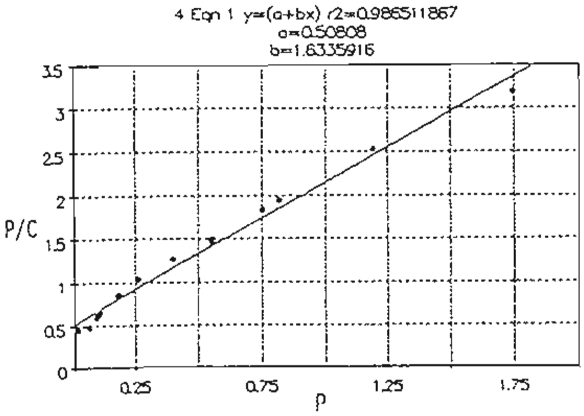


(d) Freundlich at 110 C

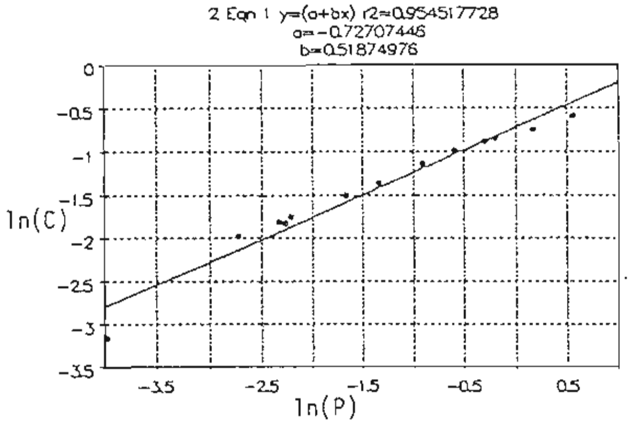
P6.02.04. CHEMISORPTION OF HYDROGEN ON COPPER

Data of the chemisorption of hydrogen on small copper particles were obtained by Ward (Proc Roy Soc London A133 506, 1031) in the units P, Torr, and V in cc/g @ STP. The plots show the Langmuir to be a better fit than the Freundlich.

P	V		P	V
0.0190	0.042		0.405	0.321
0.0660	0.138		0.555	0.371
0.0970	0.163		0.750	0.411
0.1010	0.161		0.815	0.421
0.110	0.171		1.19	0.471
0.190	0.221		1.75	0.550
0.265	0.256			



(a) Langmuir



(b) Freundlich

P6.02.05. NITROUS OXIDE ON CHARCOAL

The adsorption of nitrous oxide by charcoal was measured by McBain & Britton (JACS 52 2198, 1930), in the units P atm and w g NO_2/g C.

P	w	P/w
0.6	0.1525	3.93
4.0	0.1891	21.15
9.7	0.1971	49.21
19.8	0.2064	95.93
38.0	0.2079	182.8

(a) The Langmuir equation in linear form is

$$P/w = 1.916 + 4.763P$$

or

$$w = \frac{0.5219P}{1+2.486P}$$

The fit of the data is quite good.

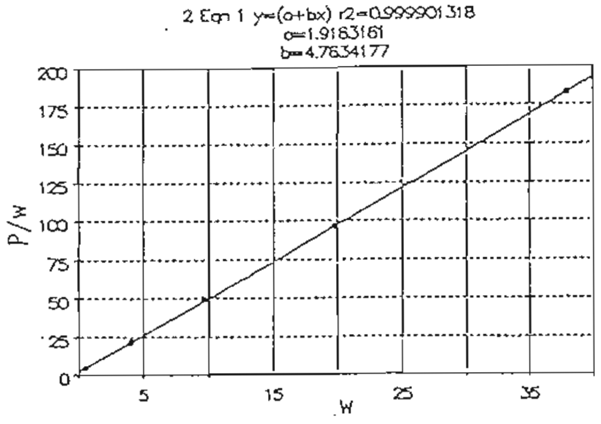
(b) From the second graph the regression line of the Freundlich equation is

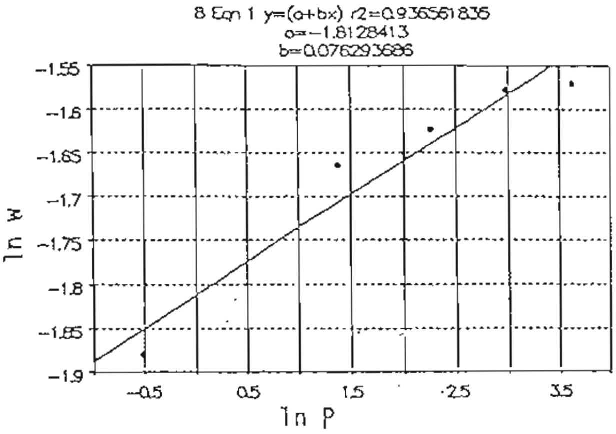
$$\ln w = -1.813 + 0.0763 \ln P$$

or

$$w = 1.632\ P^{0.0763}$$

but the fit is much poorer.





P6.02.06. LANGMUIR ISOTHERM

The following data are of the adsorption of a gas on charcoal.

P, Torr	100	200	500	900
w, mg/g	1.56	1.96	2.29	2.41

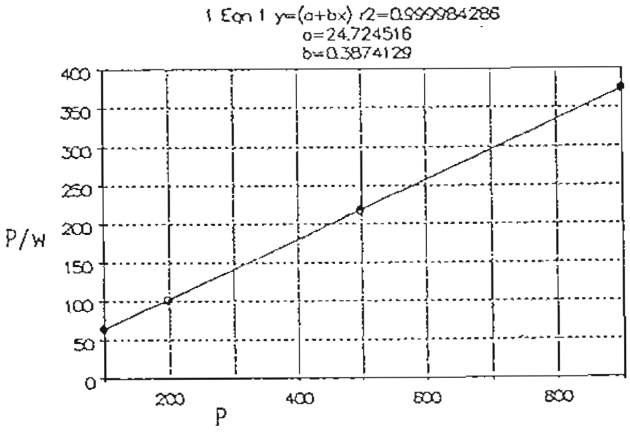
In linearized form the Langmuir isotherm is

$$P/w = \frac{1}{k_1} + \frac{k_2}{k_1} P = 24.72 + 0.387P$$

or

$$w = \frac{k_1 P}{1+k_2 P} = \frac{0.04046P}{1+0.0157P}$$

and is a good fit of the data.



P6.02.07. REACTION OF AMMONIA ON PLATINUM

At low pressures the rate of decomposition of ammonia on a hot platinum wire is proportional to the partial pressure of ammonia and inversely proportional to the partial pressure of hydrogen. Some total pressure data were obtained at 1348 C (Schwab & Schmidt, Z physik Chem B 3 344, 1929) .Check the proposed rate relations.

The partial pressures are

$$P_{NH_3} = 2P_0 - P$$

$$P_{H_2} = 1.5(P-P_0)$$

The rate equation is

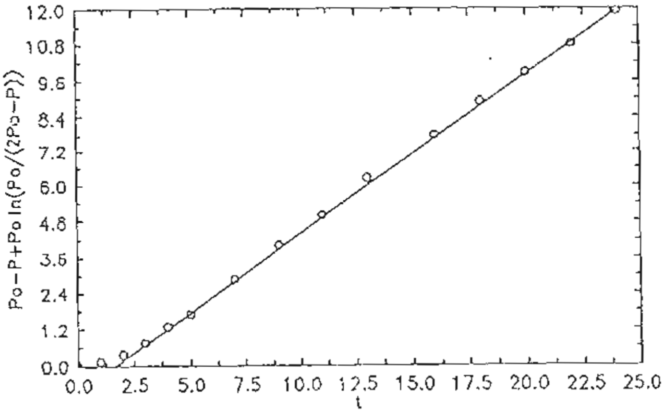
$$-\frac{dP_{NH_3}}{dt} = \frac{dP}{dt} = \frac{k(2P_0-P)}{P-P_0}$$

and the integral is

$$kt = \int_{P_0}^{P} \left(\frac{P}{2P_0-P} - \frac{P_0}{2P_0-P} \right)dP = P_0 - P - P_0 \ln\left(\frac{2P-P_0}{P_0} \right)$$

Except at the shortest times the plot of t against the right hand side is linear, confirming the assumed rate equation. At higher pressures, the adsorption of nitrogen and ammonia also must be taken into account.

t, min	P, Torr		t	P
0	11.00		11	18.45
1	12.72		13	18.98
2	13.66		16	19.50
3	14.56		18	19.80
4	15.48		20	20.02
5	16.01		22	20.22
7	17.14		24	20.42
9	17.93			



P6.02.08. CARBON MONOXIDE ON MICA AT TWO TEMPERATURES

Measurements of the adsorption of carbon monoxide on mica were made at two temperatures (Bawn, JACS 54 72, 1932). A slight correction should be made for adsorption on the glass vessel wall but is not made here. The pressure units are Torr/1000, and the adsorption is (ml @ STP)/100.

At 90 K the Langmuir equation is a good fit with

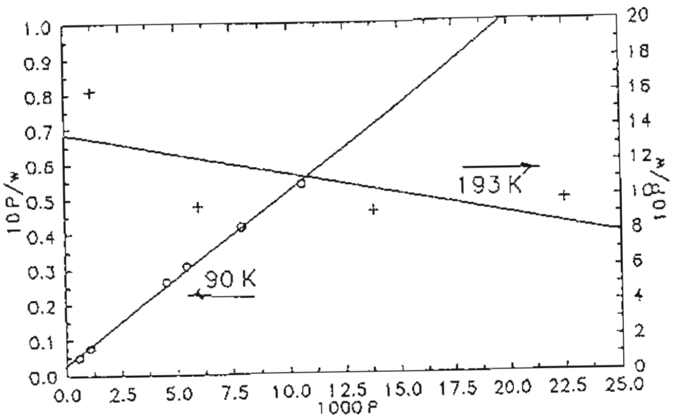
$P/w = 0.004 + 4.83P$

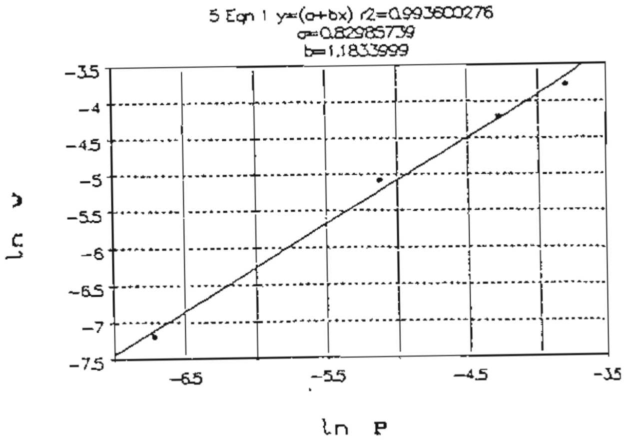
or

$$w = \frac{250P}{1+1207P}$$

At 193 K the Langmuir equation fails., but the Freundlich provides a rough fit.

T	P	w
90	0.56	10.82
	1.05	13.39
	4.53	17.17
	5.45	17.69
	7.91	18.89
	10.59	19.60
193	1.21	0.075
	5.97	0.634
	13.8	1.50
	22.5	2.29





P6.02.09. BET OR LANGMUIR EQUATIONS FOR ETHYLENE

Adsorption of ethylene at 90 K on oxide coated thermionic emission cathodes was measured (Wooten & Brown, JACS 65 113, 1943). The volume adsorbed is in V ml measured at 1 Torr and 25 C. The vapor pressure is $P_s = 30.6(10^{-3})$ Torr.

The linearized forms of the Langmuir and BET equations are

$$\frac{P}{V} = a + bP$$

$$y = \frac{x}{(1-x)V} = \frac{1}{kV_m} + \frac{k-1}{kV_m}x, \qquad x = P/P_s$$

The (P, V) and derived data are tabulated. From the plots,

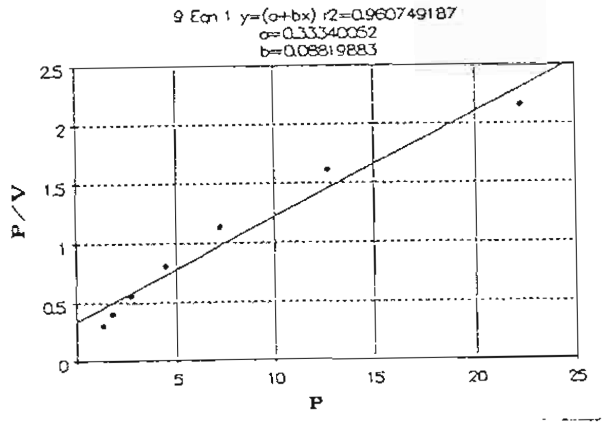
(a) In the first plot it is apparent that the Langmuir does not fit.

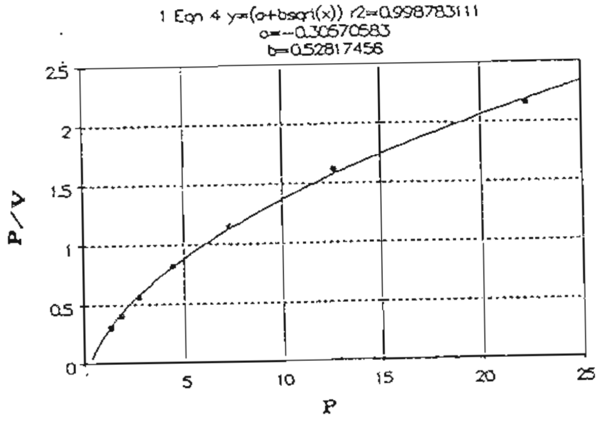
(b). The equation $P/V = 0.306+0.528\sqrt{P}$ does correlate the data but there is no simple mechanism to account for this form.

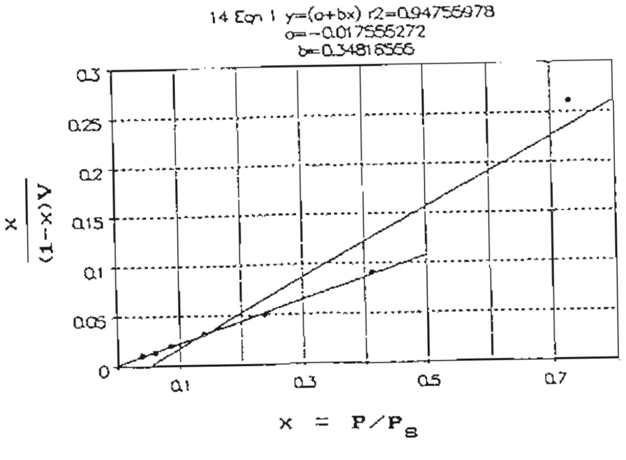
(c) The BET plot of the third graph is a good fit when the highest pressure point is omitted. Then,

$$\frac{x}{(1-x)V} = 0.00067 + 0.213x$$

P	V	x	P/V	y
22.3	10.34	0.729	2.157	0.2602
12.7	7.85	0.415	1.618	0.0904
7.3	6.42	0.239	1.137	0.0489
4.48	5.52	0.146	0.812	0.0310
2.74	4.98	0.0895	0.550	0.0197
1.85	4.60	0.0605	0.402	0.0140
1.32	4.33			







P6.02.10. ADSORPTION AT TWO TEMPERATURES

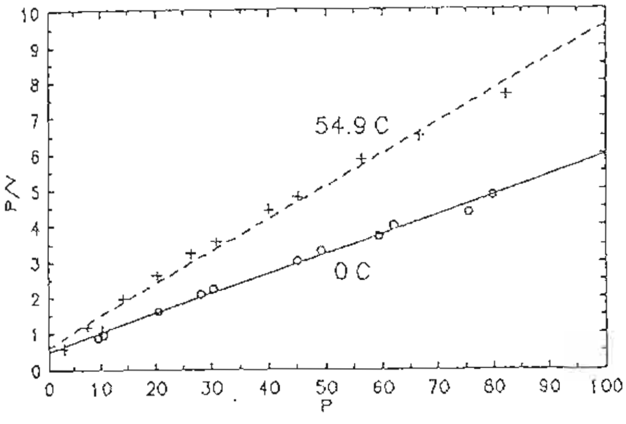
The adsorption of ammonia on barium fluoride has been measured at 0 C and 54.9 C (Crawford & Tompkins, Trans Faraday Soc 44 698, 1948). The pressures are in cm Hg, V is in cc at STP. The vapor pressures ,P_s, at the two temperatures are 4.24 atm and 22.75 atm. Check the Langmuir and BET equations against these data.

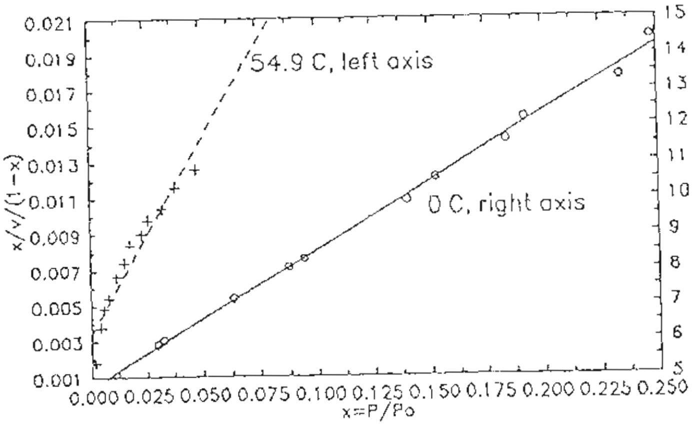
Langmuir, $P/V = k_1 + k_2P$

BET, $y = \dfrac{x}{(1-x)V} = k_1 + k_2x$, $x = P/P_s$

The plots indicate that both equations represent the data well at the lower temperature, but neither as well at the higher one.

0 C			54.9 C	
P	V		P	V
10.5	11.1		10.4	6.9
28.2	13.5		20.3	7.8
49.2	14.9		30.9	8.7
62.0	15.5		14.1	7.2
79.8	16.5		26.4	8.2
9.6	11.0		45.1	9.4
20.5	12.7		66.6	10.3
30.4	13.7		82.2	10.8
45.1	15.0		3.1	5.4
59.4	16.0		7.5	6.4
75.5	17.3		40.0	9.0
			56.3	9.7





P6.02.11. ADSORPTION OF HYDROGEN WITH DISSOCIATION

Under some conditions molecular hydrogen is adsorbed with dissociation. The data are for pure copper powder. Pressures are in Torr and w is in g H_2/g Cu The Langmuir equations for the two cases are,

Without dissociation, $w = k_1P/(1+k_2P)$, or $P/w = a+bP$

With dissociation, $w = k_1\sqrt{P}\,/(1+k_2\sqrt{P}\,)$, or $\sqrt{P}/w = a+b\sqrt{P}$.

When dissociation occurs, the mechanism of the adsorption process is, $H_2 + 2\sigma \Leftrightarrow 2H\sigma$, where σ is an active site on the surface. At adsorptive equilibrium the rates in terms of the fraction ϑ of occupied surface are

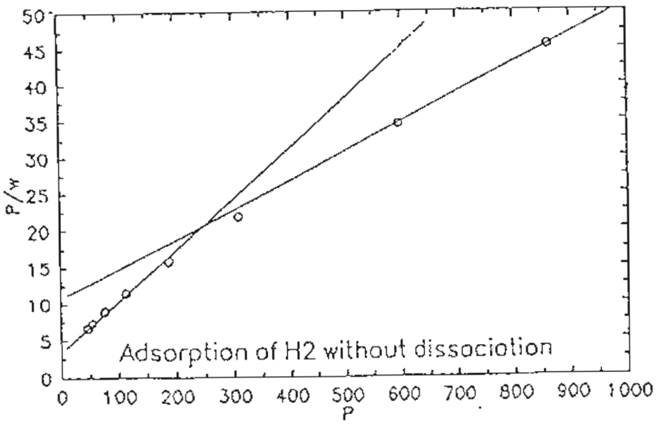
$r = k_1P(1-\vartheta)^2 = k_2\vartheta^2$

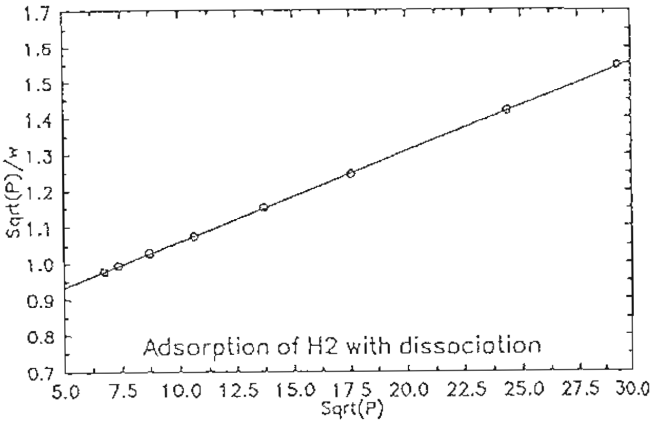
Since the amount of adsorbate, w, is proportional to the fraction of surface occupied,

$w = k_1\sqrt{P}\,/(1+k_2\sqrt{P}\,)$

The plot for dissociation is quite linear, but the one for molecular adsorption begins to deviate from linearity even at the lowest pressures.

P	w
862	19.0
595	17.2
308	14.1
188	11.9
113	9.9
75.6	8.47
54.1	7.41
45.4	6.90



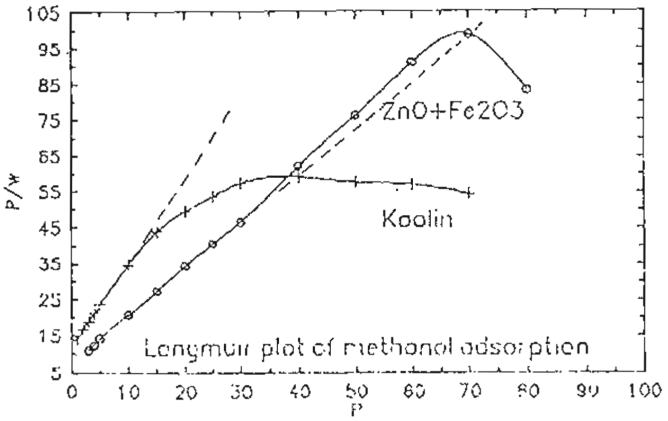


P6.02.12. ADSORPTION OVER A WIDE PRESSURE RANGE

Methanol vapor is adsorbed at 20 C on the oxides $ZnO+Fe_2O_3$ and on kaolin. The pressure is in Torr and the adsorption is in millimoles/g adsorbent.

The Langmuir plots in the linearized form, p/w = a + bP, are linear at the lowest pressures, over a wider range for the oxides, but reach maxima in both cases.

Oxides				Kaolin	
P	w			P	w
3	0.27			1	0.072
4	0.32			2	0.120
5	0.35			3	0.158
10	0.48			4	0.189
15	0.55			5	0.212
20	0.585			10	0.289
25	0.62			15	0.343
30	0.64			20	0.405
40	0.645			25	0.467
50	0.655			30	0.524
60	0.66			40	0.678
70	0.71			50	0.867
80	0.96			60	1.054
				70	1.288



P6.02.13. THE BET EQUATION

Data are available for the adsorption of nitrogen at 77.3 K when the vapor pressure is 759 Torr. Pressures are in Torr and adsorption is ml/g. Find the constants of the BET equation.

The BET equation for adsorption is

$$V = \frac{kV_m x}{(1-x)[1+(k-1)x]} \quad , \ x = P/P_s = P/759$$

and in linearized form, with constants from the plot,

$$1000y = \frac{1000x}{V(1-x)} = \frac{1}{kV_m} + \frac{k-1}{kV_m} = 0.2867 + 50.00x$$

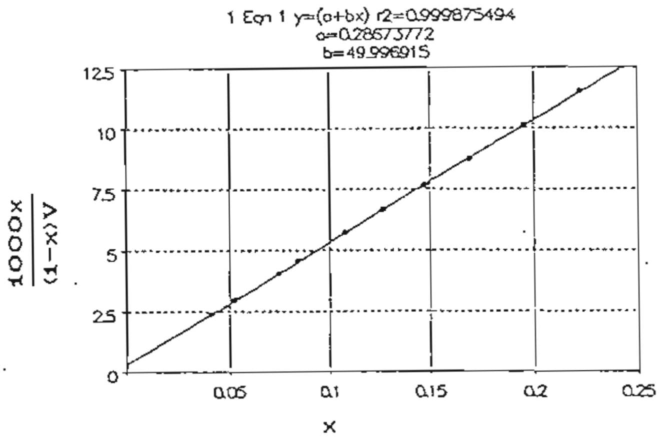
from which

$kV_m = 1000/0.2867 = 3488$

$(k-1)/kV_m = 50/1000,\ k = 175.4,\ V_m = 19.886$

The requirement of linearity is well satisfied.

P	V	y
31.7	18.6	2.33
40.1	19.0	2.95
56.6	19.9	4.10
64.5	20.3	4.55
82.7	21.4	5.68
96.7	22.0	6.70
112.4	23.0	7.51
128.8	23.5	8.72
148.6	24.1	10.00
169.3	24.9	11.60



P6.03.01. INITIAL RATES AS DISCRIMINANTS

For the reactions, A+B ⇒ Products, of Tables 6.1 and 6.2, develop initial rate equations and plots and use them to identify possible valid mechanisms.

Take the partial pressures of A and B the same, and make all the constants of the equations unity. For surface reaction rate controlling,

Cases 5, 6 and 7: $r_0 = 0.25\left(\frac{P}{1+P}\right)^2$, limit ⇒ 0.25

Case 5a: $r_0 = 0.25P^2/(1+P)$, limit ⇒ ∞

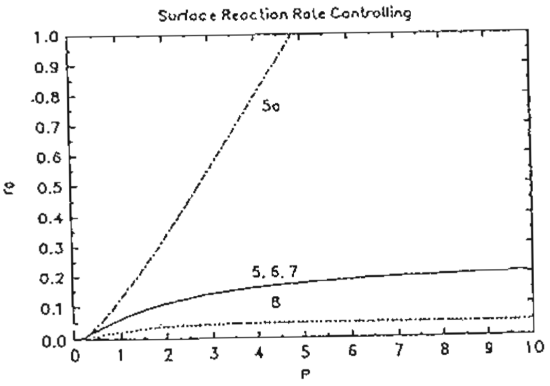
Case 8: $r_0 = 0.25\,\frac{P^2}{(1+\sqrt{P/2}+P/2)^3}$, limit ⇒ 0

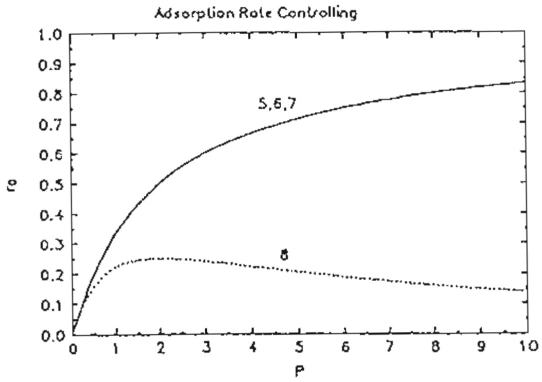
For adsorption rate controlling,

Cases 5, 6 and 7: $r_0 = 0.5P/(1+0.5P)$, limit ⇒ 1.00

Case 8: $r_0 = 0.5P/(1+0.5P)^2$, limit ⇒ 0

Cases 5, 6 or 7 of neither set can be distinguished from each other, although the limiting values do distinguish the two sets.





P6.03.02. RATE OF AMMONIA FORMATION

Develop the rate equation of Temkin & Pyzhev for the rate of the reaction, N_2 (A) + $3H_2$(B) ⇔ $2NH_3$(C), on these assumptions:

1. Ammonia is in surface reaction equilibrium with an equilibrium pressure, $p_a^* = p_c^2/K_b p_b^3$.

2. A logarithmic form of adsorption isotherm is valid so that the rates of adsorption and desorption are

$$r_{ads} = k_a p_a \exp(-g\vartheta)$$
$$r_{desorp} = k_{-a}\exp(h\vartheta)$$

At equilibrium these rates are equal so that the surface coverage becomes,

$$\vartheta = \ln[\ \frac{k_a p_a^*}{k_{-a}}\ )^{1/(g+h)}]$$

Accordingly the net rate of the reaction becomes

$$r = r_{ads} - r_{desorp}$$
$$= k_1 p_a (p_c^2/p_b^3)^{\alpha} - k_2 (p_c^2/p_b^3)^{\beta}$$

where the constants of previous equations have been grouped into new constants.

P5.03.03. OXIDATION OF HYDROCARBONS

A mechanism for the catalytic oxidation of hydrocarbons is due to Mars & Van Krevelen (*Spec Suppl Chem Eng Sci* 3 41, 1954). These assumptions are made:

1. The catalyst is alternately reduced by the hydrocarbon and reoxidized by the molecular oxygen.

2. The two rates are related by the stoichiometry, as $r_r = br_0$.

The reaction rates are of power law form,

$$r_r = k_r p_h^n \vartheta \quad \text{and } r_0 = k_0 p_0^m (1-\vartheta)$$

Equating these rates at equilibrium and solving for the surface coverage gives

$$\vartheta = \frac{bk_0 p_0^m}{k_r p_h^n + bk_0 p_0^m}$$

The rate of oxidation then becomes, in reciprocal form,

$$\frac{1}{r_r} = \frac{1}{k_r p_h^n} + \frac{1}{bk_0 P_o^m}$$

To find the constants from experimental data, hold one of the partial pressures constant while varying the other one. Then interchange the partial pressures to find the other constants. In some cases the exponents m and n have been found to be fractional.

P6.03.04. TWO PARTICIPANTS NOT IN ADSORPTIVE EQUILIBRIUM

For the reaction, A+B ⇔ M+N, neither A nor B is in adsorptive equilibrium. Find the equation for the overall rate in terms of measurable quantities.

Surface reaction equilibrium is assumed to exist, so

$$\vartheta_m \vartheta_n = K_e' \vartheta_a^* \vartheta_b^* \qquad (1)$$

M and N are in adsorptive equilibrium, so their surface coverages are,

$$\vartheta_m = k_m p_m \vartheta_v^* \qquad (2)$$
$$\vartheta_n = k_n p_n \vartheta_v^* \qquad (3)$$

and the uncovered surface is

$$\vartheta_v^* = 1 - \vartheta_a^* - \vartheta_b^* - \vartheta_m - \vartheta_n \qquad (4)$$

In the steady state,

$$r = r_a = r_b$$

and

$$k_{a1}p_a\vartheta_v^* - k_{a2}\vartheta_a^* = k_{b1}p_b\vartheta_v^* - k_{b2}\vartheta_b^* \qquad (5)$$

The five unmeasurable quantities (ϑ_a^*, ϑ_b^*, ϑ_v^*, ϑ_m, ϑ_n) can be solved for from the five numbered equations in terms of the four partial pressures (p_a, p_b, p_m, p_n) and seven constants (K_e', k_{a1}, k_{a2}, k_{b1}, k_{b2}, k_m, k_n). These results are substituted into the steady state rate equation,

$$r = r_a = k_{a1}p_a\vartheta_v^* - k_{a2}\vartheta_a^* \qquad (6)$$

Data of r as a function of the partial pressures then will permit evaluation of the constants by nonlinear regression.

P6.03.05. DISSOCIATION OF A TRIATOMIC MOLECULE

A triatomic molecule undergoes the reaction, $A_3 \Leftrightarrow B + C$, in contact with a catalytic surface. It dissociates completely on adsorption. Write rate equations for the two cases (a) Surface reaction rate controlling, adsorptive equilibrium of all participants maintained; (b) Rate of desorption of substance B controlling, surface reaction equilibrium maintained.

With adsorptive equilibrium, the surface coverages are.

$$\vartheta_a = k_a p_a^{1/3}\vartheta_v$$
$$\vartheta_b = k_b p_b \vartheta_v$$
$$\vartheta_c = k_c p_c \vartheta_v$$
$$\vartheta_v = 1/(1+k_a p_a^{1/3} + k_b p_b + k_c p_c)$$

The surface reaction rate is

$$r = k_1\vartheta_a^3 - k_2\vartheta_b\vartheta_c\vartheta_v = \frac{k_1k_ap_a - k_2k_bk_cp_bp_c}{(1+k_ap_a^{1/3}+k_bp_b+k_cp_c)^3} \qquad (a)$$

With the rate of desorption of controlling and surface reaction at equilibrium ,

$$\vartheta_a = k_a p_a^{1/3}\vartheta_v^*$$
$$\vartheta_b^* = K_e'\vartheta_a^3/\vartheta_v^*$$
$$\vartheta_c = k_c p_c \vartheta_v^*$$
$$\vartheta_v^* = 1-\vartheta_a-\vartheta_b^*-\vartheta_c$$
$$p_b = K_e p_a/p_c$$

The net rate of desorption of B is

$$r = r_a = k_1 p_b \vartheta_v - k_2\vartheta_b^*$$
$$= \frac{k_1p_b - k_2p_a/p_c}{1+k_ap_a^{1/3}+k_bp_a/p_c+k_cp_c} \qquad (b)$$

Various constants are combined along the way into other constants.

P6.03.06. THREE MECHANISMS CONTROLLING

Develop the overall rate equation of the reaction, $A \Leftrightarrow B$, with the three controlling steps,

a. Adsorption rate of A
b. Desorption rate of B
c. Surface reaction rate of A and B.

Note that the rates of these three steps involve the surface coverages ϑ_a, ϑ_b and ϑ_v. After those terms are eliminated from the overall rate equation, there will result a relation between the measurable quantities r, p_a and p_b.

$$r = k_1(p_a\vartheta_v - \vartheta_a/k_2)$$
$$= k_3(\vartheta_b/k_4 - p_b\vartheta_v)$$

$$= k_5(\vartheta_a - \vartheta_b/k_6)$$

Various manipulations give these results.

$$\vartheta_a = r/k_5 + \vartheta_b/k_6$$

$$\vartheta_v = 1-\vartheta_a-\vartheta_b = 1 - r/k_5 - (1+1/k_6)\vartheta_b$$

$$= \frac{1}{p_b}\left(\frac{\vartheta_b}{k_4} - \frac{r}{k_3}\right)$$

$$\vartheta_b = \frac{1-r/k_5+r/k_3p_b}{1+ 1/k_4p_b+1/k_6} \tag{1}$$

$$\vartheta_a = \frac{r}{k_5} + \frac{1-r/k_5+r/k_3p_b}{1+k_6+k_6/k_4p_b} \tag{2}$$

Substitute Eqs (1) and (2) into

$$r = k_5(\vartheta_a-\vartheta_b/k_6) \tag{3}$$

to obtain an implicit equation relating r, p_a and p_b.

P.6.03.07. ALL PARTICIPANTS IN ADSORPTIVE EQUILIBRIUM

All participants of the reaction, $A+B \Leftrightarrow M+N$, and an inert substance I are maintained in adsorptive equilibrium. Find the rate of the surface reaction.

For each participant the net rate of adsorption is

$$r_i = k_{1i}p_i\vartheta_v - k_{2i}\vartheta_i = 0$$

whence

$$\vartheta_i = k_ip_i\vartheta_v$$

The uncovered surface fraction is

$$\vartheta_v = 1-\vartheta_a - \vartheta_b - \vartheta_m - \vartheta_n - \vartheta_I = 1 - \vartheta_v\Sigma k_ip_i$$

$$= \frac{1}{1+k_ap_a+ k_bp_b + k_mp_m + k_np_m + k_Ip_I}$$

The rate of the surface reaction is

$$r = K_1\vartheta_a\vartheta_b - K_2\vartheta_m\vartheta_n = (k_1p_ap_b - k_2p_mp_n)\vartheta_v^2$$

$$= \frac{k_1p_ap_b - k_2p_mp_n}{(1+k_ap_a+k_bp_b+k_mp_m+k_np_n+k_Ip_I)^2}$$

P6.03.08. THE REACTION A+B ⇔ M+N.

Write the stoichiometric equations of the reactions between the active sites, σ, and other participants of the reaction, and the rate equations of the several cases.

1. Adsorptive equilibrium of all participants.

$$A + \sigma \Leftrightarrow A\sigma$$

$$r_a = k_1p_a\vartheta_v - k_2\vartheta_a = 0 \text{ at equilibrium}$$

$$\vartheta_a = k_ap_a\vartheta_v$$

$$\vartheta_v = 1 - \Sigma\vartheta_i = 1/(1+\Sigma k_ip_i)$$

Surface reaction ,

$$A\sigma + B\sigma \Leftrightarrow M\sigma + N\sigma$$

$$r = k_1\vartheta_a\vartheta_b - k_2\vartheta_m\vartheta_n = (k_1p_ap_b - k_2p_mp_n)\vartheta_v^2$$

2. Adsorption of A_2 with dissociation, all substances in adsorptive equilibrium.

$$A_2 + 2\sigma \Leftrightarrow 2A\sigma$$

$$r_a = k_1p_a\vartheta_v^2 - k_2\vartheta_a^2 = 0 \text{ at equilibrium}$$

$$\vartheta_a = k_a\sqrt{p_a}\,\vartheta_v$$

$$\vartheta_v = 1/(1+k_a\sqrt{p_a}+k_bp_b+k_mp_m+k_np_n)$$

Surface reaction,

$$2A\sigma + B\sigma \Leftrightarrow M\sigma + N\sigma + \sigma$$

$$r = k_1\vartheta_a^2\vartheta_b - k_2\vartheta_m\vartheta_n\vartheta_v = (k_1p_ap_b - k_2p_mp_n)\vartheta_v^3$$

3. Reaction of unadsorbed A, directly from the gas phase:

$$A + B\sigma \Rightarrow \text{Products}$$

$$r = k_1p_a\vartheta_b = k_1p_ap_b\vartheta_v = \frac{k_1p_ap_b}{1+k_ap_a+k_bp_b+k_mp_m+k_np_n}$$

4. Surface reaction at equilibrium, only A not in adsorptive equilibrium.

$$\vartheta_m\vartheta_n/\vartheta_a^*\vartheta_b = K_e'$$

$$p_a^* = p_mp_n/K_ep_b$$

Rate of reaction equals rate of adsorption of A,

$$r = k_1p_a\vartheta_v^* - k_2\vartheta_a^* = (k_1p_a - k_2p_a^*)\vartheta_v^*$$

$$= \frac{k_1p_a - k_2p_mp_n/K_ep_b}{1+k_ap_mp_n/K_ep_b+k_bp_b+k_mp_m+k_np_n}$$

P6.03.09. THREE MECHANISMS

The mechanism of the solid catalyzed gas phase reaction, $A+B \Leftrightarrow C$, at constant pressure and temperature is to be investigated. Write the rate equations for these possible controlling mechanisms.

(a) Surface reaction between adsorbed A and adsorbed B.

$$r = k_1\vartheta_a\vartheta_b - k_2\vartheta_c\vartheta_v = \frac{k(p_ap_b - p_c/K_e)}{(1+k_ap_a+k_bp_b+k_cp_c)^2}$$

(b) Reaction between A in the gas phase and adsorbed B.

$$r = k_1p_a\vartheta_b - k_2\vartheta_c = \frac{k(p_ap_b - p_c/K_e)}{1+k_ap_a+k_bp_b+k_cp_c}$$

(c) Desorption of adsorbed C, surface reaction at equilibrium.

$$p_c^* = K_ep_ap_b$$

$$\vartheta_c^* = \frac{k_cp_c^*}{1+k_ap_a+k_bp_b+k_cp_c^*}$$

$$r = k_1\vartheta_c^* - k_2p_c\vartheta_v = \frac{k(p_ap_b - p_c/K_e)}{1+k_ap_a+k_bp_b+k_cp_ap_b}$$

P6.03.10. TEMPERATURE OF MAXIMUM INITIAL RATE

The rate of a surface catalyzed reaction, $A_2+B \Rightarrow C+D+E$, is determined by the reaction between adsorbed A and gas phase B. Substance A_2 dissociates upon adsorption. The Arrhenius equation applies to all constants. Find the temperature at which the initial rate is a maximum.

$$r = k\vartheta_a^2p_b = \frac{kp_ap_b}{(1+\sqrt{k_ap_a}+k_bp_b+k_cp_c+k_dp_d+k_ep_e)^2}$$

$$r_0 = \frac{kp_{a0}p_{b0}}{(1+\sqrt{k_ap_{a0}}+k_b\,p_{b0})^2}$$

$$= \frac{k_1 p_{a0} p_{bo} \exp(-k_2/T)}{[1+k_3\sqrt{p_{a0}} \exp(-k_4/T) + k_5 p_{b0} \exp(-k_6/T)]^2}$$

For the maximum rate set

$$d(\sqrt{1/r_0})/d(1/T) = 0$$

and solve by trial for 1/T.

P6.03.11. ADSORPTION AND SURFACE REACTION CONTROLLING

For the reaction, $A \Leftrightarrow B$, there are two simultaneously controlling mechanisms, namely (1) adsorption of A and (2) unimolecular decomposition of adsorbed A. Given the tabulated data, find the rate equation.

p_a	1.5	1.2	0.8
p_b	0.7	1.0	1.0
r	1.2575	1.0244	0.8235
p_a/r	1.1928	1.1714	0.9715

The two stoichiometric equations are

$$A + \sigma \Rightarrow A\sigma$$

$$A\sigma \Rightarrow B + \sigma$$

At steady state the rate is

$$r = k_1 p_a \vartheta_v^* = k_2 \vartheta_a^*$$

Eliminate ϑ_a^* and ϑ_v^* from this equation.

$$\vartheta_a^* = r/k_2$$

$$\vartheta_v^* = 1 - \vartheta_a^* - \vartheta_b = 1 - r/k_2 - k_b p_b \vartheta_v^* = \frac{1-r/k_2}{1+k_b p_b}$$

Substitute into the equation for r and solve explicitly for r.

$$r = \frac{k_1 p_a (1-r/k_2)}{1+k_b p_b} = \frac{k_1 p_a}{1+(k_1/k_2)p_a+k_b p_b}$$

In linearized form

$$y = p_a/r = a + bp_a + cp_b$$

Substitute from the data table and solve the three linear equations simultaneously with the results

$$a = 0.1435,\ b = 0.4998 \text{ and } c = 0.4281$$

Accordingly the rate equation becomes

$$r = \frac{6.969 p_a}{1+3.483 p_a+2.983 p_b}$$

P6.03.12. OXIDATION OF SO_2 OVER V_2O_5 CATALYST

A mechanism for the oxidation of SO_2 in the presence of V_2O_5 catalyts assumes that the catalyst alternately surrenders its oxygen to the SO_2 and is reoxidized by oxygen from the gas. These reactions are assumed to occur according to Regner & Simecek (*Coll Czech Chem Comm* 33 2540, 1968).

$$SO_2 + 2V^{5+} \Leftrightarrow SO_3 + 2V^{4+} \qquad (1)$$

$$O_2 + 2V^{4+} \Leftrightarrow 2V^{5+} + 2O^- \qquad (2)$$

$$O^- + V^{4+} \Leftrightarrow V^{5+} + O^{2-} \qquad (3)$$

or in simpler notation

$$A + 2B + C \Leftrightarrow D + 2E \qquad (1a)$$

$$F + 2E \Leftrightarrow 2D + 2C \qquad (2a)$$

$$G + E \Leftrightarrow B + C \qquad (3a)$$

Reactions (1) and (3) are assumed to be in equilibrium, and the rate of reaction (2) then is assumed controlling. Accordingly,

$$DE^2 = k_1AB^2C \qquad (4)$$

$$BC = k_3GE \qquad (5)$$

$$r = k(FE^2 - B^2G^2/k_2) \qquad (6)$$

When the unstable intermediates C and G are eliminated with the equilibrium conditions, the rate becomes

$$r = kE^2[F- \frac{1}{k_1^2k_2k_3^2}(D/A)^2] = kE^2[F - (D/A)^2/k_4] \qquad (7)$$

The quantity E is eliminated in favor of the total vanadium concentration which is measurable,

$$V_t = B + E \qquad (8)$$

and also assuming that C remains constant, so that

$$DE^2/AB^2 = k_1C = k_m \qquad (9)$$

Then

$$B/E + 1 = V_t/E = 1 + \sqrt{D/Ak_m} \qquad (10)$$

Solving for E and substituting into Eq (7) gives the result,

$$r_{SO2} = kC_{V_t}\frac{K_MP_{SO2}}{[P_{SO3}^{1/2}+(K_MP_{SO2})^{1/2}]^2}[P_{O2} - (P_{SO3}/KP_{SO2})^2] \qquad (11)$$

which fits data better than some earlier rate equations.

P6.04.01. DIFFERENTIAL REACTOR DATA

Measurements of the rate of a gas phase reaction, A ⇒ 2B, were made in a differential reactor with the tabulated results. The pressure is in atm and the rate in lbmol/(hr)(lb catalyst).

Find if these rate equations are suitable.

$$r_1 = k_1p_a/(1+ k_2p_a)$$

$$r_2 = k_1p_a/(1+ k_2\sqrt{p_a})^2$$

In linearized form,

$$y_1 = p_a/r_1 = 1/k_1 + (k_2/k_1)p_a$$

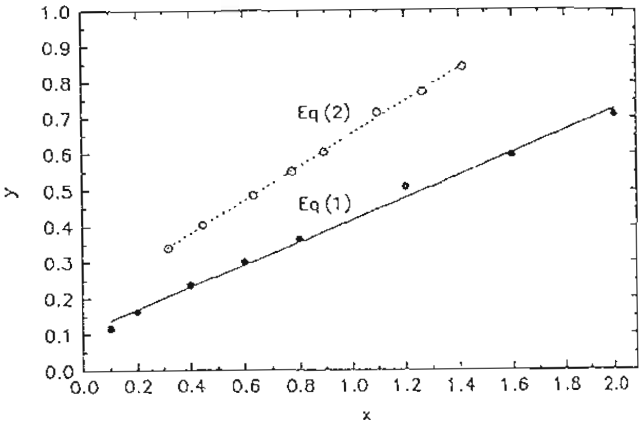
$$y_2 = \sqrt{p_a/r_2} = 1/\sqrt{k_1} + (k_2/\sqrt{k_1})\sqrt{p_a} = 0.2 + 0.45\sqrt{p_a}$$

The second mechanism is a better fit, with

$$k_1 = 25,\ k_2 = 2.25,$$

$$r = \frac{25p_a}{(1+2.25\sqrt{p_a})^2}$$

p_a	2.0	1.6	1.2	0.8	0.6	0.4	0.2	0.1
r	2.834	2.699	2.367	1.198	1.986	1.698	1.230	0.864



P6.04.02. CONSTANTS OF A RATE EQUATION

A rate equation has the form

$$r = \frac{k_1p_a(p_a-r/k_2)}{1+k_3p_b}$$

Given these data, find the constants

p_a	1.5	1.2	0.8
p_b	0.7	1	1
r	1.8863	1.2293	0.6588

The equation can be solved explicitly as

$$r = \frac{k_1p_a^2}{1+(k_1/k_2)p_a+k_3p_b}$$

and linearized

$$p_a^2/r = [1+(k_1/k_2)p_a+k_3p_b]/k_1$$

The known data are substituted and the three linear equations solved simultaneously.

$$1.1928 = a + 1.5b + 0.7c$$
$$1.1714 = a + 1.2b + c$$
$$0.9715 = a + 0.8b + c$$

The results are

$a = 0.1435$, $b = 0.4998$, $c = 0.4281$

$k_1 = 6.9686$, $k_2 = 2.0008$, $k_3 = 2.9832$

P6.04.03. ADSORPTION AND SURFACE REACTION CONTROLLING

For the reaction, $A \Leftrightarrow B$, there are two simultaneously controlling mechanisms, namely (1) adsorption of A and (2) unimoleclular decomposition of adsorbed A. Given the tabulated data, find the rate equation.

p_a	p_b	r	p_a/r
1.5	0.7	1.2575	1.1928
1.2	1.0	1.0244	1.1714
0.8	1.0	0.8235	0.9715

The two stoichiometric equations are

$$A + \sigma \Rightarrow A\sigma$$
$$A\sigma \Rightarrow B + \sigma$$

At steady state the rate is

$$r = k_1p_a\vartheta_v^{\bullet} = k_2\vartheta_a^{\bullet} \quad (1)$$

Eliminate the unobservables from this equation.

$$\vartheta_a^{\bullet} = r/k_2 \quad (2)$$

$$\vartheta_v^{\bullet} = 1-\vartheta_a^{\bullet}-\vartheta_b = 1-r/k_2-k_bp_b\vartheta_v^{\bullet} = \frac{1-r/k_2}{1+k_bp_b} \quad (3)$$

Combine these equations and solve explicitly for r.

$$r = \frac{k_1p_a(1-r/k_2)}{1+k_bp_b} = \frac{k_1p_a}{1+(k_1/k_2)p_a+k_bp_b}$$

In linearized form,

$$y = p_a/r = a + bp_a + cp_b$$

Substitute from the data table and solve the three linear equations simultaneously with the results

$$a = 0.1435,\ b = 0.4998,\ c = 0.4281$$

Accordingly the rate equation is

$$r = \frac{6.969p_a}{1+3.483p_a+2.983p_b}.$$

P6.04.04. DISSOCIATION UPON ADSORPTION

The effect of system pressure on the initial rate of the reaction, $A_2 \Rightarrow B$, was observed with the results tabulated. All experiments started with pure A. It is expected that the controlling step is a surface reaction rate, but it is not known if dissociation occurs on adsorption. Check this point.

Without dissociation,

$$r = \frac{k(p_a-p_b/K_e)}{1+k_ap_a+k_bp_b}$$

$$r_0 = \frac{kp_a}{1+k_ap_a} = \frac{k\pi}{1+k_a\pi}$$

$$\pi/r_0\ 1/k + (k_a/k)\pi \qquad (1)$$

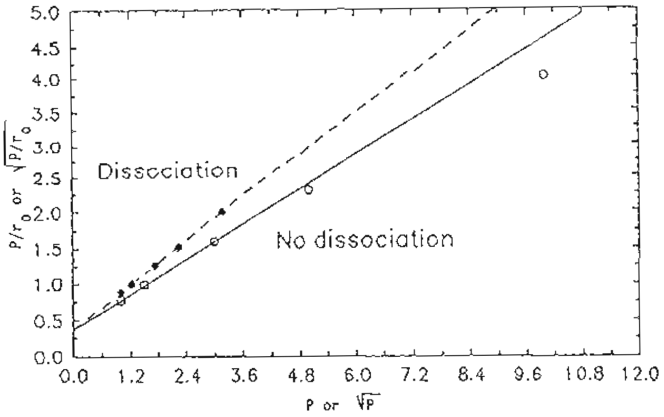
With dissociation,

$$r = \frac{k(p_a-p_b/K_e)}{(1+k_a\sqrt{p_a}+k_bp_b)^2}$$

$$\sqrt{\pi/r_0} = a + b\sqrt{\pi} \qquad (2)$$

Equation (2) is more nearly linear, so dissociation occurs.

π	r_0	$\sqrt{\pi}$	π/r_0	$\sqrt{\pi/r_0}$
1	1.29	1	0.775	0.88
1.5	1.51	1.223	0.993	0.998
3	1.89	1.732	1.588	1.260
5	2.17	2.236	2.30	1.515
10	2.50	3.16	4.00	2.00



P6.04.05. INITIAL RATE DATA FOR THREE MECHANISMS

For the solid catalyzed reaction, $2A \Leftrightarrow B+C$, initial rate data were obtained as tabulated, starting with pure A. Consider these three reaction mechanisms,

1. Surface reaction rate controlling.
2. Net adsorption rate of A controlling

3. Net desorption rate of B controlling.

(1) Surface reaction rate controlling,.

$$r = k_1\vartheta_a^2 - k_2\vartheta_b\vartheta_c = \frac{k_1p_a^2 - k_2p_bp_c}{(1+k_ap_a+ k_bp_b+ k_cp_c)^2}$$

$$p_{ao} = \pi$$

$$r_0 = \frac{k_1\pi^2}{(1+k_a\pi)^2}$$

$$\pi/\sqrt{r_0} = a + b\pi = 0.504 + 0.500$$

The following data are plotted and confirm this mechamnism.

π	1	1.8	2.5	4.0	7.0	10.0
r_0	1.00	1.65	2.07	2.56	3.06	3.31
$\pi/\sqrt{r_0}$	1	1.40	1.74	2.50	4.00	5.50

(2) Adsorption of A controlling,

$$p_a^* = \sqrt{p_bp_c/K_e}$$
$$\vartheta_a^* = k_a\vartheta_v^*\sqrt{p_bp_c/K_e}$$
$$r = k_1p_a\vartheta_v^* - k_2\vartheta_a^* = k_1p_a\vartheta_v^* - k_2k_ap_a^*\vartheta_v^*$$
$$p_{a0}^* = \pi$$
$$r_0 = k_1p_{a0} = k_1\pi \qquad (2)$$

Clearly Eq (2) does not fit the data, so this mechanism is invalid.

(3) Net adsorption of B controlling,

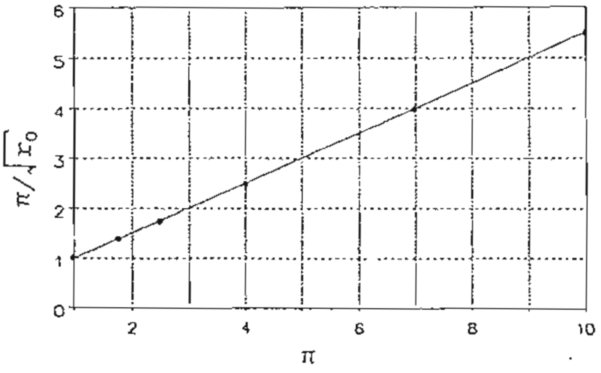
$$p_b^* = K_ep_a^2/p_c$$
$$\vartheta_b^* = k_bp_b^*\vartheta_v^*$$
$$B + \sigma \Leftrightarrow B\sigma$$

$$r = \frac{k_1p_b - k_2k_bK_ep_a{}^2/p_c}{1+k_ap_a+ k_bk_ep_a^2/p_c+ k_cp_c}$$

$$= \frac{k_1p_bp_c - k_2k_bK_ep_a^2}{p_c+ k_ap_ap_c+ k_bK_ep_a^2+ k_cp_c^2}$$

$$r_0 = -k_2 \qquad (3)$$

Clearly the last equation does not fit the data, so this mechanism also is invalid.



P6.04.06. INVALID MECHANISMS

Use the gven data of rate of reaction as a function of partial pressure to check te validity of these rate equations.

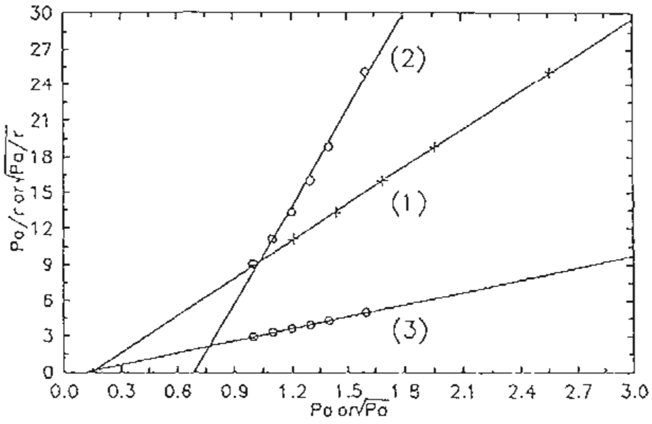
(1). $r = k_1\, p/(1+k_2 p)$ or $y_1 = p/r = a + b\, p$

(2). $r = k_1 p/(1+k_2\sqrt{p})$ or $y_2 = p/r = a + b\sqrt{p}$

(3). $r = k_1 p/(1+k_2\sqrt{p})^2$ or $y_3 = \sqrt{p/r} = a + b\sqrt{p}$

The data are tabulated and plotted. All three lines are good linear fits, but they all have negative intercepts so the mechanisms they represent are not physically realistic.

p	r	p/r	$\sqrt{p}$	$\sqrt{p/r}$
2.56	0.1020	25.00	1.6	5.0
1.96	0.1041	18.80	1.4	4.33
1.69	0.1057	16.00	1.3	4.00
1.44	0.1080	13.33	1.2	3.67
1.21	0.1090	11.10	1.1	3.33
1.00	0.1111	9.00	1.0	3.00



P6.04.07. THREE ALTERNATE MECHANISMS

The reaction, A ⇒ B, occurs at 2.0 atm. With the given rate data, appraise these three mechanisms:

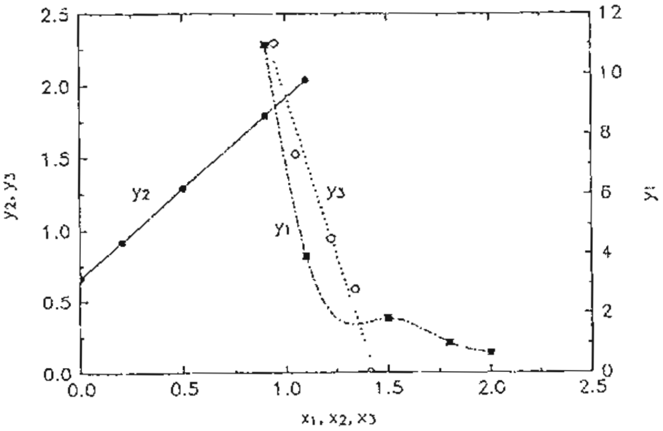
(1). $y_1 = p_a/r = a + b\, p_a$

(2). $y_2 = \dfrac{p_a - 0.67 p_b}{r} = a + b\, p_b$

(3). $y_3 = \left(\dfrac{p_a p_b}{r}\right)^{1/3} = a + b\sqrt{p_a}$

According to the plots, mechanism (1) is out because the plot is nonlinear, mechanism (2) is acceptable because the constants are positive, and mechanism (3) is out because the slope is negative.

p_a	p_b	r	p_a/r	$\frac{p_a-0.67p_b}{r}$	$\left(\frac{p_a p_b}{r}\right)^{1/3}$	$\sqrt{p_a}$
2	0	3.00	0.667	0.667	0	1.414
1.8	0.2	1.821	0.988	0.915	0.583	1.342
1.5	0.5	0.905	1.811	1.289	0.939	1.225
1.1	0.9	0.280	3.93	1.786	1.523	1.049
0.9	1.1	0.082	10.98	2.037	2.294	0.949



P6.04.08. THREE INVALID MECHANISMS

These alternative mechanisms of the controlling rate of the conversion, $A_2 \Rightarrow B$, are to be examined:

(a) $A_2 + 2\sigma \Rightarrow 2A\sigma$

$$r_a = kp_a\vartheta_v^{*2} = k_1p_a/(1+k_2\sqrt{\pi-p_a})^2$$

$$y_a = \sqrt{p_a/r_a} = a + b\sqrt{\pi-p_a}$$

(b) $A_2 + \sigma = A_2\sigma$

$$r_b = kp_a\vartheta_v^* = k_1p_a/[1+k_2(\pi-p_a)]$$

$$y_b = a + b(\pi-p_a)$$

(c) $A_2\sigma \Rightarrow B\sigma$

$$r_c = k\vartheta_a = k_1p_a/(1+k_2p_a)$$

$$y_c = a + b\ p_a$$

Use the tabulated rate data at 5 atm to appraise these three mechanisms.

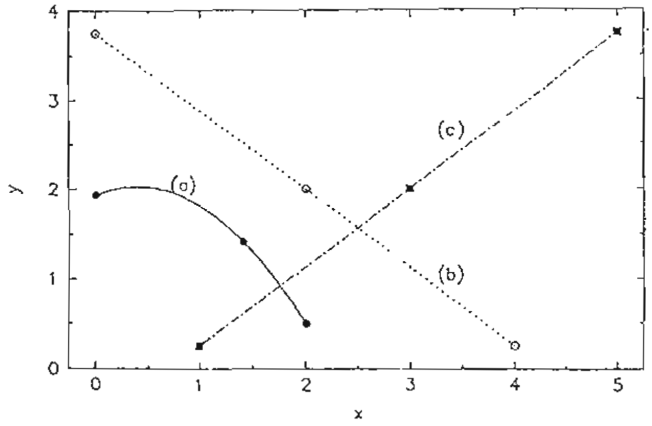
Plot of y_a is curved so that mechanism is ruled out.

Plot of y_b is straight but the slope is negative.

Plot of y_c is straight but the intercept is negative.

These data do not support any of these mechanisms.

π	p_a	r	$\sqrt{\pi-p_a}$	$\pi-p_a$	$\sqrt{p_a/r}$	p_a/r
5	5	1.33	0	0	1.936	3.75
5	3	1.5	1.41	2	1.414	2.0
5	1	4.00	2.00	4	0.5	0.25



P6.04.09. INITIAL RATE DATA EVALUATION OF MECHANISMS

Initial rates were measured at several pressures for the reaction, $2A \Rightarrow B$, starting with pure A. Check these two proposed rate equations:

$$r_1 = k_1[p_a/(1+k_ap_a+k_bp_b)]^2$$

$$r_2 = k_1p_a/(1+k_ap_a+k_bp_b)^2$$

Rearrange the equations and set $p_{a0} = \pi$ and $p_{b0} = 0$.

$$y_1 = p_a/\sqrt{r_1} = a + bp_a + cp_b$$

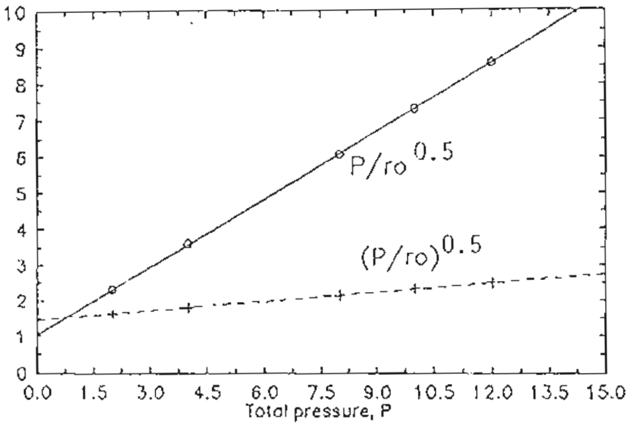
$$y_2 = \sqrt{p_a/r_2} = a + bp_a + cp_b$$

$$y_{10} = \pi/\sqrt{r_1} = a + b\pi \tag{1}$$

$$y_{20} = \sqrt{\pi/r_2} = a + b\pi \tag{2}$$

According to the plots, the constants are all positive, so both equations are acceptable. Data beyond the initial will be needed to discriminate, if possible, between the two mechanisms.

π	r_0	$\pi/\sqrt{r_0}$	$\sqrt{\pi/r_0}$
2	0.75	2.309	1.633
4	1.24	3.592	1.796
8	1.75	6.047	2.138
10	1.87	7.313	2.312
12	1.96	8.57	2.474



P6.04.10. TWO MECHANISMS THAT DO NOT FIT

Data for the solid catalyzed reaction, $A \Leftrightarrow B$, are tabulated. Adsorption of B is small compared with that of A. Check the validity of these mechanisms:

(1) The rate of surface reaction is controlling

(2) The rate of adsorption of A is controlling

The rate equations are

$$r_1 = k\vartheta_a = k_1p_a/(1+k_2p_a)$$

$$r_2 = kp_a\vartheta_v^* = \frac{k_1p_a}{1+k_ap_a^*} = \frac{k_1p_a}{1+k_ap_b/K_e}$$

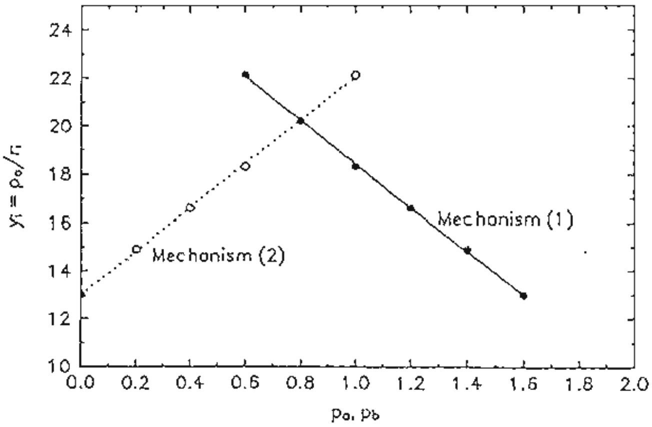
Linearizing,

$$y_1 = p_a/r_1 = a + bp_a$$

$$y_2 = p_a/r_2 = a + bp_b$$

On the plots, Eq (1) has a negative slope so it is ruled out, but Eq (2) is acceptable.

p_a	p_b	r	p_a/r
1.6	0	0.123	13.0
1.4	0.2	0.094	14.9
1.2	0.4	0.0722	16.6
1.0	0.6	0.0547	18.3
0.8	0.8	0.0395	20.2
0.6	1.0	0.0272	22.1



P6.04.11. PHOSGENE FORMATION. SEVEN MECHANISMS

The mechanism of the formation of phosgene according to the reaction, CO (A) + Cl_2(B) ⇒ $COCl_2$(C), is to be checked with given data at 30.6 C (Potter & Baron, CEP 47 473, 1951). Six Langmuir-Hinshelwood equations and a power law model are examined. The rate equations are analyzed in linearized forms. Those that have negative constants are not physically realistic.

(1). Cl_2 adsorbs with dissociation.

$$r = \frac{k_0AB}{(1+k_1A+k_2\sqrt{B}+k_3C)^3} \qquad A\sigma + 2B\sigma \Rightarrow C + 3\sigma$$

$$(AB/r)^{1/3} = (1/k_0)^{1/3}(1+k_1A+k_2\sqrt{B}+k_3C)$$

(2). Cl_2 adsorbs with dissociation, CO adsorbs only slightly but enough to account for a surface reaction.

$$r = \frac{k_0AB}{(1+k_2\sqrt{B}+k_3C)^3} \qquad A\sigma + 2B\sigma \Rightarrow C + 3\sigma$$

$$(AB/r)^{1/3} = (1/k_0)^{1/3}(1+k_2\sqrt{B}+k_3C)$$

(3). Cl_2 adsorbs without dissociation, CO reacts from the gas phase and adsorbs very little.

$$r = \frac{k_0AB}{1k_2B+k_3C} \qquad A + B_2\sigma \Rightarrow C + 2\sigma$$

$$AB/r = (1/k_0)(1+k_2B+k_3C)$$

(4). All participants are adsorbed molecularly, surface reaction controlling.

$$r = \frac{k_0AB}{(1+k_1A+k_2B+k_3C)^2} \qquad A\sigma + B_2\sigma \Rightarrow C + 2\sigma$$

$$(AB/r)^{1/2} = (1/k_0)^{1/2}(1+k_1A+k_2B+k_3C)$$

(5). Cl_2 adsorbs with dissociation, CO is adsorbed very little and reacts from the gas phase.

$$r = \frac{k_0AB}{(1+k_2\sqrt{B}+k_3C)^2} \qquad A + 2B\sigma \Rightarrow C + 2\sigma$$

$$(AB/r)^{1/2} = (1/k_0)^{1/2}(1+k_2\sqrt{B}+k_3C)$$

(6). As in case (4), but CO adsorption is small.

$$r = \frac{k_0AB}{(1+k_2B+k_3C)^2} \qquad A\sigma + B_2\sigma \Rightarrow C + 2\sigma$$

$$(AB/r)^{1/2} = (1/k_0)^{1/2}(1+k_2B+k_3C)$$

(7). Homogeneous reaction, power law rate equation.

$$r = k\ A^aB^bC^c$$

$$\ln(r) = \ln(k) + a\ \ln(A) + b\ \ln(B) + c\ \ln(C)$$

The constants of the seven equations equations are found by POLYMATH Multilinear Regression. They are recorded in the second table. POLYMATH graphs of the regressions are shown.

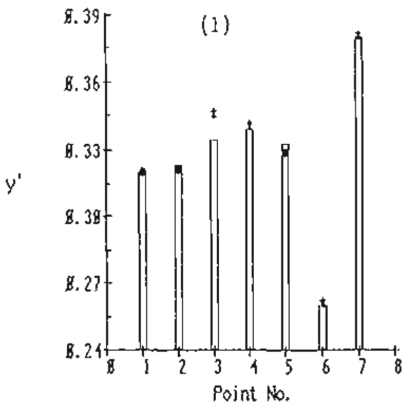
According to the criterion that all constants should be positive, mechanisms (2), (3), (5) and (6) are acceptable, possibly along with the homogeneous mechanism (7). Mechanism (6) is the simplest of the valid mechanisms and is as good a fit as any.

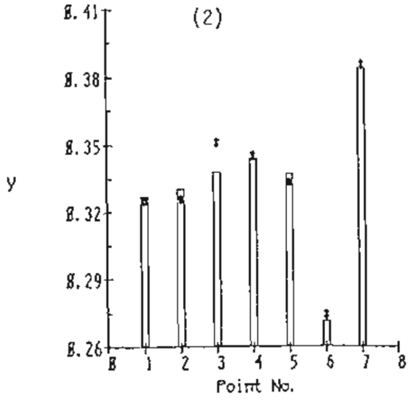
DATA

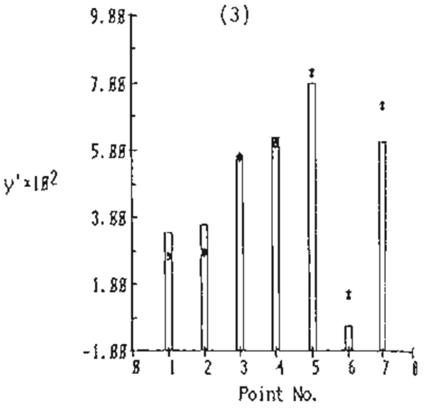
Rate×10^3	p_{CO}	p_{Cl_2}	p_{COCl_2}
4.41	0.406	0.352	0.226
4.4	0.396	0.363	0.231
2.41	0.31	0.32	0.356
2.45	0.287	0.333	0.376
1.57	0.253	0.218	0.522
3.9	0.61	0.113	0.231
2.0	0.179	0.608	0.206

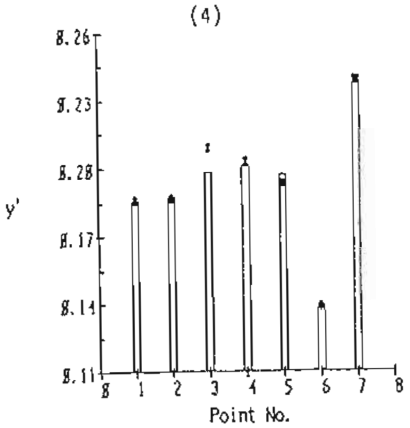
Case	k_0	k_1	k_2	k_3
1	25.20	-0.0614	0.003223	-0.000464
2	4.816	0	0.04864	0.02952
3	15.90	0.	0.007649	0.04223
4	6.602	-0.1230	-0.001728	-0.06819
5	1424.0	0	0.006063	0.002873
6	0.1508	0	0.9798	0.5891

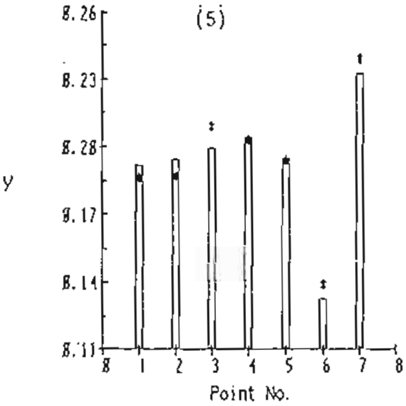
$$r_7 = 0.0195(p_{CO})^{1.3311}(p_{Cl_2})^{0.5771}(p_{COCl_2})^{-0.683}$$

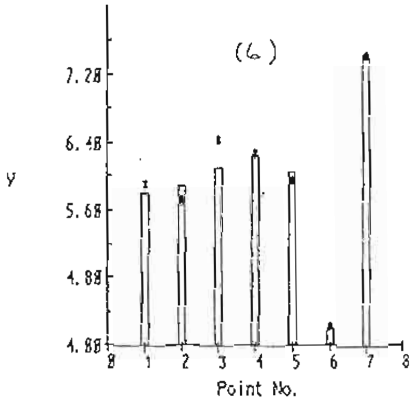












P6.04.12. PHOSGENE SYNTHESIS AT SEVERAL TEMPERATURES

The reaction, $CO + Cl_2 \Rightarrow COCl_2$, in the presence of activated carbon catalyst was studied at several temperatures with the results shown (Potter & Baron, CEP 47, 473, 1951). The controlling mechanism is believed to be reaction between adsorbed CO and Cl_2, but the amount of adsorbed CO is relatively small. Find the Arrhenius constants of all the terms.

$A = CO$, $B = Cl_2$, $C = COCl_2$

$A\sigma + B\sigma \Rightarrow C\sigma + \sigma$

$$r = k\vartheta_a\vartheta_b = \frac{kp_ap_b}{(1+k_bP_b+k_3p_C)^2}$$

$k_a << k_b$ or k_c

The linearized form of the rate equation is

$$y = \sqrt{p_ap_b/r} = (1+k_bp_b+k_cp_c)/\sqrt{k}$$

The constants are found by POLYMATH Multilinear Regression. The effect of temperature on the constants is represented by the Arrhenius equation, $k = \exp(A - B/T°K)$.

The activation energy, $-B/R$, is positive for the specific rate, but negative for the adsorption equilibrium constants, k_a and k_c, as expected since adsorption usually falls off with increasing temperature.

CONSTANTS

T	k	k_b	k_c
30.6	0.1508	0.9798	0.5891
42.7	0.2270	1.0446	0.2182
52.5	0.2587	0.7382	0.1474
64.0	0.3572	0.6996	0.0650

ARRHENIUS

	A	B
k	+6.5124	-25465
k_b	-3.9875	+122
k_c	-22.1362	+6551

T°C	10^3r	p_{CO}	p_{Cl_2}	p_{COCl_2}	y
30.6	4.14	0.406	0.352	0.226	5.875
	4.40	0.396	0.363	0.231	5.715
	2.41	0.310	0.320	0.356	6.416
	2.45	0.287	0.333	0.376	6.247
	1.57	0.253	0.218	0.522	5.930
	3.90	0.610	0.113	0.231	4.204
	2.00	0.179	0.608	0.206	7.376
42.7	4.83	0.206	0.578	0.219	4.97
	10.73	1.569	0.194	0.226	3.21
	1.34	0.128	0.128	0.845	3.50
	9.18	0.397	0.370	0.209	4.00
	9.10	0.394	0.373	0.213	4.02
52.5	14.28	0.380	0.386	0.234	3.20
	15.46	0.410	0.380	0.210	3.17
	6.00	0.139	0.742	0.118	4.15
	3.68	0.218	0.122	0.660	2.69
64.0	25.74	0.412	0.372	0.216	2.44
	24.46	0.392	0.374	0.234	2.45
	13.78	0.185	0.697	0.118	3.06
	8.29	0.264	0.131	0.605	2.04

P6.04.13. FOUR CONSTANTS OF A RATE EQUATION

Find the constants of the rate equation

$$r = \frac{k_1(p_mp_n - p_s/K_e)}{(1+k_2p_m + k_3p_n + k_4p_s)^2}$$

given the tabulated data.

Rearrange the equation into a linear form.

$$y = \sqrt{\frac{p_mp_n - p_s/Ke}{r}} = 1/k_1+(k_2/k_1)p_m+(k_3/k_1)p_n+(k_4/k_1)p_s$$

$$= 0.707 + 0.106p_m + 0.176p_n + 0.0353p_s$$

from which

$$r = \frac{1.414(p_mp_n - p_s/40)}{(1+0.15p_m+ 0.25p_n + 0.05p_s)^2}$$

The equilibrium constant is evaluated from the first entry in the table,

$$K_e = 1.6/(0.2)^2 = 40$$

The values of y are calculated and stored in the table. The other constants are found by setting up four linear equations and solving them by Gaussian elimination.

p_m	p_n	p_s	r	y
0.2	0.2	1.6	0	
0.8	0.8	0.6	0.6859	0.9546
0.5	1.1	0.3	0.5823	0.9642
0.25	1.4	0.45	0.3408	0.9970
0.25	1.75	0	0.4020	1.0430

P6.04.14. RATE EQUATION FOR P6.04.15

Rate data for a solid catalyzed reaction, A ⇒ 2B, in the gas phase at 900 R and 10 atm are tabulated. Examine these possible rate equations,

$$r_1 = kp_a/(1+k_ap_a) \quad \text{or } y_1 = p_a/r_1 = a + bp_a$$

$$r_2 = k\left(\frac{p_a}{1+k_ap_a}\right)^2 \quad \text{or } y_2 = p_a/\sqrt{r_2} = a + bp_a$$

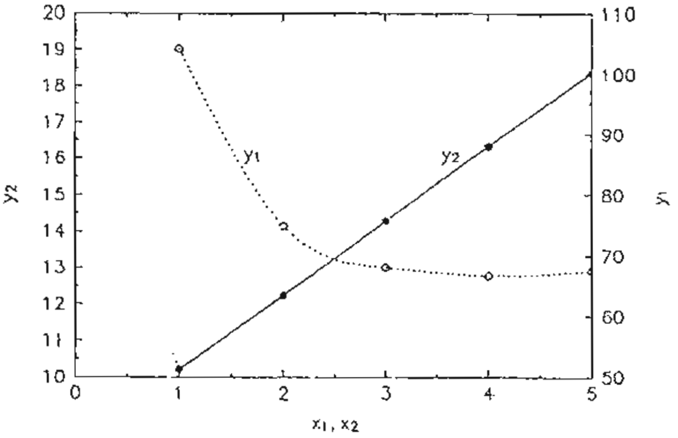
As the plots show, the second mechanism appears to be a valid one, with

$$y_2 = 8.1 \quad 2.054p_a$$

or

$$r = 0.0152\left(\frac{p_a}{1+0.254p_a}\right)^2$$

p_a	r	p_a/r	$p_a/\sqrt{r}$
5	0.0741	67.48	18.37
4	0.0600	66.67	16.33
3	0.0441	68.03	14.29
2	0.0267	74.91	12.24
1	0.0096	104.17	10.21



P6.04.15. INERT AND REACTIVE TRACERS IN A ROTATING BASKET

A reaction is expected to have a rate equation of the form

$$r = k_1\left(\frac{C}{1+k_2C}\right)^2$$

Data for evaluation of the constants are in the table. In another test, an impulse amount of the same reactant was charged to the vessel and solvent flow was continued at a residence time $\bar{t} = 5$.

(a) Find the constants of the rate eqaution

(b) For the unsteady state test, find $f = C/C_0$ as a function of $t/\bar{t}$

(c) Compare the result of part (b) with the behavior of an inert tracer under the same conditions.

In the steady state, the material balance is

$$C_0 = C + \bar{t}r = C + k_1\bar{t}\left(\frac{C}{1+k_2C}\right)^2$$

$$1 = f + k_1C_0\bar{t}\left(\frac{f}{1+k_2C_0f}\right)^2$$

linearized form,

$$y = f\sqrt{\frac{\bar{t}}{1-f}} = (1+k_2C_0f)/\sqrt{k_1C_0}$$

$$= 0.500 + 0.700f$$

which makes the rate equation

$$r = 4C_0\left(\frac{f}{1+f}\right)^2 \tag{a}$$

For the unsteady state with impulse input of reactant, when $t = 0$, $C = C^0 = m/V_r$, $f = C/C^0 = 1$, and the material balance is

$$0 = V'C + V_r\left(r + \frac{dC}{dt}\right)$$

$$0 = f + 4\bar{t}\left(\frac{f}{1+1.4f}\right)^2 + \bar{t}\,\frac{df}{dt}$$

This equation is integrated with $\bar{t} = 5$ and the plot is shown.

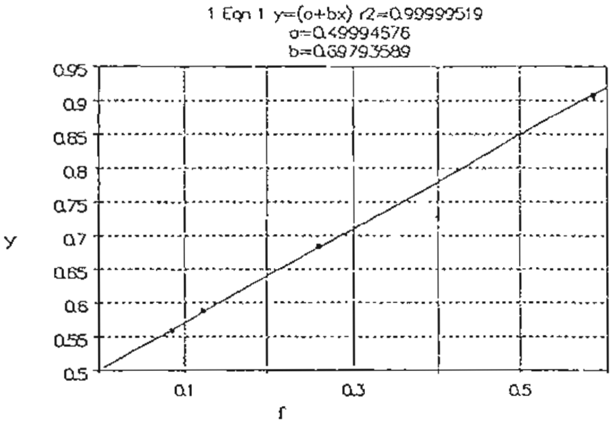
For a non reactive tracer,

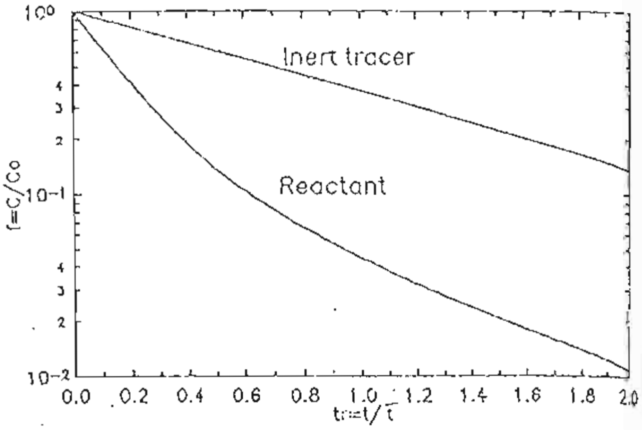
$$\frac{df}{dt_r} = -f,$$ with $f = 1$ when $t_r = t/\bar{t} = 0$. The integral is

$$f_{inert} = \exp(-t_r)$$

This result also is plotted.

$\bar{t}$	f	y
1	0.585	0.9081
5	0.2625	0.6835
20	0.1227	0.5858
40	0.0845	0.5585





P6.04.16. ETHYL CHLORIDE

The synthesis of ethyl chloride from ethylene and hydrogen chloride in the presence of methane (inert) was studied in a differential reactor by Thodos & Stutzman (Ind Eng Chem 50 413, 1958) over zirconium oxychloride deposited on silica gel. The reaction is

$$C_2H_4 + HCl \Leftrightarrow C_2H_5Cl, \quad A + B \Leftrightarrow M$$

Data were taken at 28.3 atm and 350 F. Equilibrium constant was $K_r = 35.5$. Check the mechanisms that lead to these rate equations,

$$r_a = \frac{k(p_a p_b - p_m/K_r)}{(1 + K_a p_a + K_b p_b + K_m p_m + K_I p_I)^2}$$

$$r_a = \frac{k(p_a - p_m/K_r p_b)}{1 + K_a p_m/K_r p_b + K_b p_b + K_m p_m + K_I p_I}$$

The rate equations are linearized and the five linear equations are then solved by Gaussian elimination for the five constants.

$$y_1 = \sqrt{\frac{p_a p_b - p_m/35.5}{r}}$$

$$= -2.895 - 0.429p_I + 36.47p_a + 35.51p_b + 13.48p_m$$

$$y_2 = \frac{p_a - p_m/35.5p_b}{r}$$

$$= -350.1 - 114.2p_I + 5723.4p_a + 1117.2p_b + 854.1p_m$$

Both equations have some negative constants and therefore should be invalidated. For the first mechanism, however, the negative constants are small and possibly could be regarded as substantially zero so that mechanism could be considered valid. In the original article, all positive constants were found for the first equation, but that result could not be confirmed here.

1000r	.262	.260	.252	.216	.263
p_I	7.005	7.090	7.001	9.889	10.169
p_a	.300	.416	.343	.511	.420
p_b	.370	.215	.289	.489	.460
p_m	.149	.102	.181	.334	.175
y_1	20.19	18.25	19.31	33.37	26.76
y_2	1101.7	1548.3	1291.1	2277.0	1556.0

P6.04.17. DEHYDRATION OF BUTANOL-1

Initial rate data of the catalytic dehydration of butanol-1 are believed controlled by the surface reaction rate with this rate equation in terms of the fugacity, f,

$$r_0 = \frac{k_1 f}{(1+k_2 f)^2} \quad \text{lbmols/(h)(lb catalyst)}$$

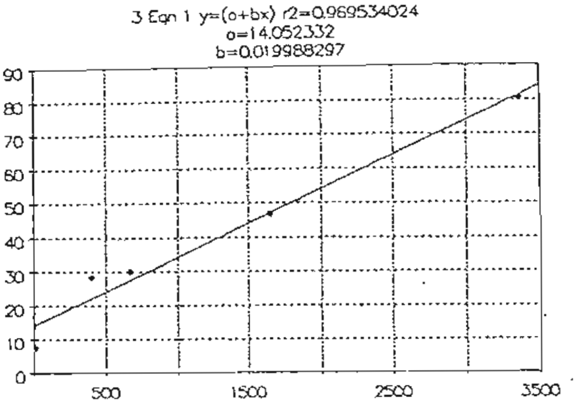
Find the constants with these data of Maurer & Sliepcevich (Chem Eng Prog Symp Series 4 33, 1952),

In linearized form the rate equation is

$$\sqrt{f/r_0} = (1 + k_2 f)/\sqrt{k_1} = 14.052 + 0.0200f$$

$$k_1 = 0.00506, \quad k_2 = 0.00143$$

r_0	f	$\sqrt{f/r_0}$
0.27	15	7.45
0.51	409	28.3
0.76	676	29.8
0.76	1653	46.6
0.52	3370	80.5



P6.04.18. HYDROGENATION OF ETHYLENE

Initial rate data for the hydrogenation of ethylene at 41 C were taken by Sussman & Potter (Ind Eng Chem 46 457, 1954). Check the validity of the following controlling steps and corresponding initial rate equations where p_a = pressure of hydrogen, p_b= pressure of ethylene, in atm, r in gmol/(h)(g catalyst). Hydrogen adsorption is relatively small.

(a) Desorption of product controlling,

$y_a = p_a p_b/r_0 = a + bp_b$

(b) Adsorption of hydrogen controlling,

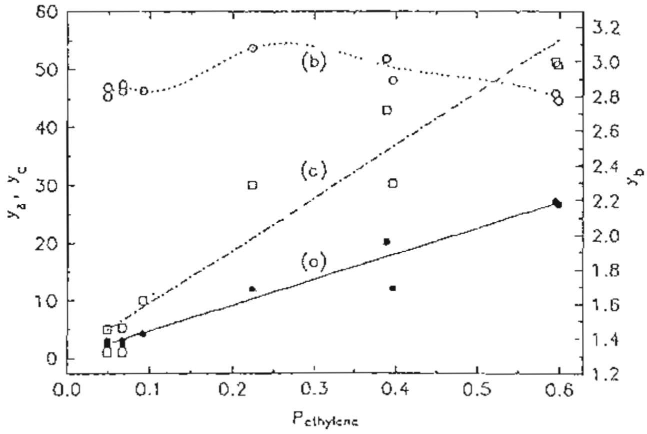
$p_a/r_0 = a+bp_b$

(c) Surface reaction controlling, with dissociation of hydrogen upon adsorption,

$y_c = (p_a p_b/r_0)^{1/3} = a + bp_b$

The graphs show that the plot of mechanism (a) is most nearly linear.

p_a	p_b	r_0	y_a	y_b	y_c
.405	.595	.00882	27.3	3.0	45.9
.401	.599	.009	26.7	2.98	44.6
.611	.389	.01172	20.3	2.72	52.0
.776	.224	.01444	12.0	2.29	53.7
.908	.092	.01964	4.25	1.62	46.3
.933	.067	.02021	2.32	1.32	47.4
.933	.067	.0206	3.09	1.46	46.2
.951	.049	.02008	3.03	1.45	45.3
.951	.049	.0203	2.30	1.32	46.9
.603	.397	.01253	12.1	2.30	48.1
.611	.389	.01183	20.1	2.72	51.7



P6.04.19. OLEIC ACID HYDROGENATION

Oleic acid was hydrogenated at 25-17 C with mild agitation in the presence of a slurried catalyst with 5.3 wt% platinum. These data were obtained,

cat concn, gm/ml	0.025	0.05	0.1	0.2	0.3	0.4
rate, std ml H_2/min	1.6	2.8	5.5	8.7	11.2	12.5

Show that these data are consistent with the view that the catalyst is saturated with hydrogen and that the reaction rate is given in terms of the Langmuir isotherm.

Since the catalyst is saturated with hydrogen, the amount of adsorbed hydrogen is proportional to the concentration of Pt in the slurry, which is called C_{Pt}.

$$r = \frac{k_1 p_{H_2}}{1+k_2 p_{H_2}} = \frac{k_1 C_{Pt}}{1+k_2 C_{Pt}} = \frac{0.053 k_1 C_{cat}}{1+0.053 k_2 C_{cat}}$$

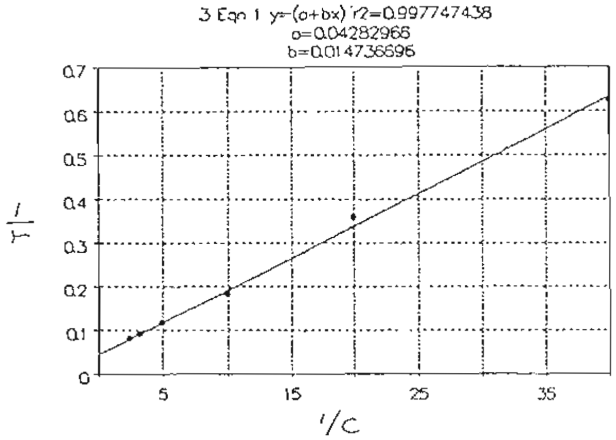
Linearizing,

$$\frac{1}{r} = \frac{1}{0.053 k_1}\left(\frac{1}{C_{cat}}\right) + k_2/k_1 = 0.04283\ \left(\frac{1}{C}\right) + 0.01474$$

or

$$k_1 = 440.5,\ k_2 = 6.49$$

The linear fit is close, confirming the Langmuir mechanism.



P6.04.20. MULTIPLE STATES WITH A L.H. EQUATION?

A reaction with rate equation, $r = k_1C^2/(1+k_2C)$, is to be conducted in an isothermal CSTR. Examine the possibility of the occurrence of more than one steady state conversion.

The material balance is

$$C_0 = C + \bar{t}r = C + \frac{k_1\bar{t}C^2}{1+k_2C}$$

The roots of the quadratic equation are

$$C = \frac{k_2C_0-1 \pm \sqrt{(k_2C_0-1)^2+4(k_1\bar{t}+k_2)C_0}}{2(k_1\bar{t}+k_2)}$$

When $k_2C_0 > 1$, one root is positive and the other negative,
When $k_2C_0 < 1$, the root with the + sign is positive and the other is negative.

Since C must be positive, only one steady state is attainable.

P6.04.21. HYDROGENATION OF BENZENE ON KIESELGUHR

Initial rate data on hydrogenation of benzene over kieselguhr at 173 C and 1 atm were taken by Kehoe & Butt (J appl Chem Biotech, p 23, 1972). Check the rate equation,

$$r_0 = \frac{kp_ap_b}{(1+k_ap_a+k_bp_b)^2}$$

A = benzene, B = hydrogen. Tthe partial pressure of benzene is varied but the total pressure is constant, so

$$p_a + p_b = 1$$

The linearized equation is

$$y = \sqrt{\frac{p_a(1-p_a)}{r_0}} = [1+k_ap_a+k_b(1-p_a)]/\sqrt{k}$$

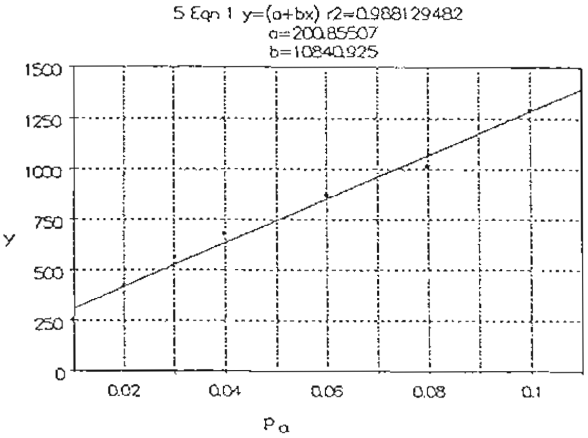
$$= [1+k_b+(k_a-k_b)p_a]/\sqrt{k} = 200.86 + 10840.9\ p_a$$

or

$$r = \frac{24.8(10^{-6})p_ap_b}{(1+53.97p_a)^2}$$

k_a and k_b cannot be found separately from these data.

p_a	10^7r	y
0.01	1.54	253.5
0.02	1.11	420.2
0.03	0.927	560.3
0.04	0.833	679.0
0.06	0.745	870.1
0.08	0.710	1018.1
0.10	0.667	1290.7



P6.04.22. CONSTANTS OF A RATE EQUATION

A rate equation has the form

$$r = \frac{k_1p_a(p_a-r/k_2)}{1+k_3p_b}$$

Given these data, find the constants

p_a	1.5	1.2	0.8
p_b	0.7	1	1
r	1.8863	1.2293	0.6588

The equation can be solved explicitly as

$$r = \frac{k_1p_a^2}{1+(k_1/k_2)p_a+k_3p_b}$$

and linearized

$$p_a^2/r = [1+(k_1/k_2)p_a+k_3p_b]/k_1$$

The known data are substituted and the three linear equations solved simultaneously.

$$1.1928 = a + 1.5b + 0.7c$$

$$1.1714 = a + 1.2b + c$$

$$0.9715 = a + 0.8b + c$$

The results are

$$a = 0.1435,\ b = 0.4998,\ c = 0.4281$$

$$k_1 = 6.9686,\ k_2 = 2.0008,\ k_3 = 2.9832$$

P6.04.23. SURFACE REACTION OR ADSORPTION, WITH OR WITHOUT DISSOCIATION.

For the reaction, $A_2 \Leftrightarrow B$, a rate equation is to be derived with the aid of data relating the initial rate to the total pressure. Four mechanisms are to be examined.

(a) Surface reaction without dissociation of A_2
(b) Surface reaction with dissociation
(c) Adsorption of A_2 without dissociation
(d) Adsorption of A_2 with dissociation.

Case (a),

$$r = k_a\vartheta_a - k_b\vartheta_b = \frac{k_1(p_a-p_b/K_e)}{1+k_2p_a+k_3p_b}$$

$$r_0 = k_1\pi/(1+k_2\pi)$$

$$y = \pi/r_0 = (1+k_2\pi)/k_1$$

Case (b),

$$r = \frac{k_1(p_a-p_b/K_e)}{(1+k_2\sqrt{p_a}+k_3p_b)^2}$$

$$y = \sqrt{\pi/r_0} = (1+k_2\sqrt{\pi})/\sqrt{k_1}$$

Case (c)

$$r = kp_a\vartheta_v^* = \frac{k_1p_a}{1+(k_2/K_e+k_b)p_b}$$

$$r_0 = k_1\pi$$

$$y = \pi/r_0 = k_1$$

Case (d),

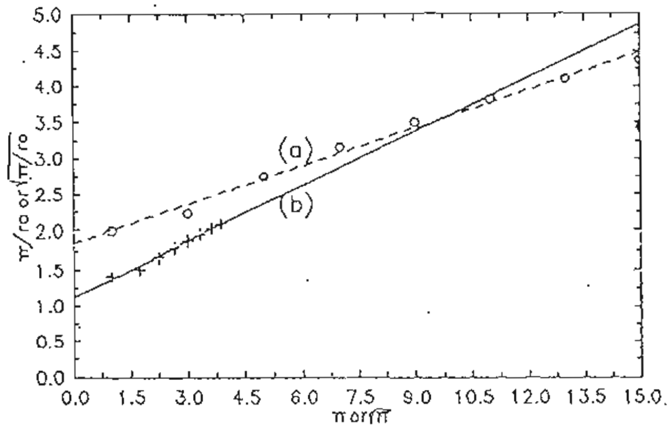
$$r = \frac{k_1p_a}{[1+k_2\sqrt{p_b/K_e}+k_3p_b]^2}$$

$$r_0 = k_1\pi$$

$$y = \pi/r_0 = k_1$$

From the plots, either (a) or (b) is a feasible mechanism since their lines are straight with positive constants. The other cases obviously do not fit since they predict constant values of y.

π	r_0	π/r_0	$\sqrt{\pi/r_0}$	$\sqrt{\pi}$
1	0.5	2	1.414	1
3	1.344	2.232	1.494	1.732
5	1.827	2.737	1.654	2.236
7	2.225	3.146	1.774	2.646
9	2.571	3.501	1.871	3
11	2.862	3.817	1.954	3.317
13	3.166	4.106	2.026	3.606
15	3.430	4.373	2.091	3.873



P6.04.24. DATA OF A PFR

The reaction, A ⇒ 2B, has the rate equation

$$r_a = \frac{k_1 C_a}{(1+k_2\sqrt{C_a}+k_3 C_b)^2}$$

In a plug flow reactor this reaction goes from C_a = 3.0 to 0.6, starting with pure A. Given the tabulated data, find the constants of the equation and the value V_r/V' for the PFR.

In linear form

$$y = \sqrt{C_a/r} = (1+k_2\sqrt{C_a}+k_3 C_b)/\sqrt{k_1}$$

Substituting data and solving the three linear equations simultaneously results in

$$r_a = \frac{1.503 C_a}{[1+1.002\sqrt{C_a}+0.2(2)(3-C_a)]^2}$$

In the PFR, integrating with the trapezoidal rule,

$$V_r/V' = \int_{0.6}^{3} \frac{dC_a}{r_a} = 8.37$$

P6.04.25. NON-LINEARIZABLE EQUATION

For the reaction, A + B ⇒ Products, the reactants adsorb on separate regions of the catalyst surface before reacting. The corresponding rate equation is

$$r_a = \frac{k_1 p_a p_b}{(1+k_2 p_a)(1+k_3 p_b)}$$

The data are,

p_a	1	1.5	2
p_b	1.5	2	1.5
r_a	0.46	0.72	0.75

Substitute the data and solve the resulting three nonlinear eqautions simultaneously, with the result

$$r_a = \frac{0.712 p_a p_b}{(1+0.293 p_a)(1+0.530 p_b)}$$

P6.04.26. ROTATING BASKET DATA

A liquid phase reaction, 2A ⇒ B, is conducted in a rotating basket of granular catalyst. The overall reaction rate is controlled by the rate of surface reaction but substance B is not adsorbed appreciably. The data are of residual concentration, $f = C/C_0$, against residence time, $\bar{t}$. Find the conversion in a two stage CSTR with residence times of 2.5 in each stage, with the same initial concentration as in the test work.

The rate equation will have the form

$$r = k_1\left(\frac{C}{1+k_2C}\right)^2$$

The material balance on the rotating basket is

$$C_0 = C + \bar{t}r = C + k_1\bar{t}\left(\frac{C}{1+k_2C}\right)^2$$

$$1 = f + k_1C_0\bar{t}\left(\frac{f}{1+k_2C_0f}\right)^2$$

In linear form,

$$y = f\sqrt{\frac{\bar{t}}{1-f}} = (1+k_2C_0f)/\sqrt{k_1C_0}$$

$$= 0.7067 + 2.1219\ f$$

The rate equation then becomes

$$r = 2.00\left(\frac{f}{1+3.00f}\right)^2$$

In the two stage CSTR, the material balances are

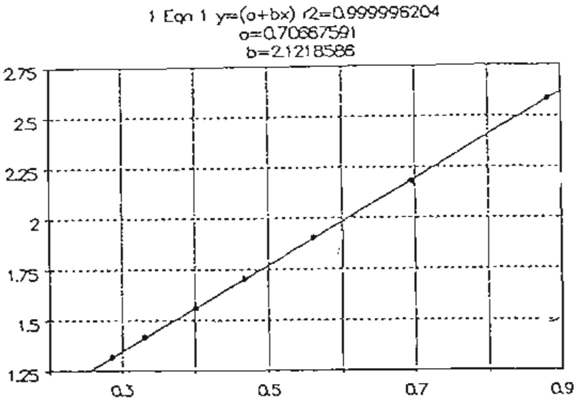
$$1 = f_1 + 2(2.5)\left(\frac{f_1}{1+3f_1}\right)^2$$

$$f_1 = f_2 + 5\left(\frac{f_2}{1+3f_2}\right)^2$$

The solution of this pair is

$f_1 = 0.737,\ f_2 = 0.528$

$\bar{t}$	f	y
1	0.883	2.5815
3	0.695	2.1797
5	0.562	1.8988
7	0.469	1.7013
9	0.402	1.5601
12	0.333	1.4140
15	0.287	1.3158



P6.04.27. HYDROCHLORINATION OF ACETYLENE

It has been proposed (Shankar, PhD Thesis, Monash University, Australia, 1976) that the gas phase catalytic hydrogenation of acetylene occurs by adsorption of HCl, followed by reaction between adsorbed HCl and acetylene from the gas phase. The equilibrium constant is very large. The rate of reaction is measured at varying total pressure but constant composition of reactants. The results show a linear relationship between r and P_{total} all the way down to pressures approaching zero. What conclusions may be drawn from these data regarding the form of the rate equation?

Assume the stoichiometric mechanism to be

$A\sigma + B \Rightarrow C\sigma$, $A = HCl$, $B = C_2H_2$, $C = C_2H_3Cl$

The corresponding rate equation is

$$r = k\vartheta_a p_b = \frac{kp_ap_b}{1+k_ap_a+k_bp_b+k_cp_c}$$

Since the compositions are stated to be constant, the data must be at initial conditions.

$$p_{a0} = (n_{a0}/n_{t0})\pi$$
$$p_{b0} = (n_{bo}/n_{to})\pi$$

Then the initial rate becomes

$$r_0 = \frac{k_1\pi^2}{1+k_2\pi+k_3\pi}$$

Since r_0 is known to vary linearly with the pressure, the adsorption terms must be large in comparison with unity, so that

$$r_0 = \frac{k_1}{k_2+k_3}\pi$$

as found experimentally.

If the reaction had been between both adsorbed components,

$A\sigma + B\sigma \Rightarrow C\sigma + \sigma$

the rate equation would have been

$$r_0 = \left(\frac{k_1\pi}{1+k_2\pi+k_3\pi}\right)^2$$

$$\Rightarrow \left(\frac{k_1}{k_2+k_3}\right)^2,\text{ when unity in the denominator is negligible.}$$

This result is not confirmed experimentally.

P6.04.28. MECHANISM OF REVERSIBLE ISOMERIZATION

An isomerization reaction has the simnple form, $A \Leftrightarrow B$. Consider rate equations for the following cases:

(a) The adsorption of A is controlling

(b) The surface reaction between adsorbed A and an adjacent vacant active site is controlling.

(c) The desorption of B from the surface is controlling

(d) The reaction is homogeneous, in the gas phase.

Show how the initial rates depend on the total pressure.

The partial pressure corresponding to surface reaction equilibrium is $= p_b/K_e$, $\vartheta_v^* = 1/(1+k_ap_a^*+k_bp_b)$. Initial conditions are $p_{a0} = \pi$ and $p_{b0} =. 0$.

(a) The stoichiometric equation is

$A + \sigma \Rightarrow A\sigma$

$$r = kp_a\vartheta_v^* = \frac{kp_a}{1+k_ap_a^*+k_bp_b} = \frac{kp_a}{1+(k_a/K_e+k_b)p_b}$$

$$r_0 = k\pi$$

(b) $A\sigma + \sigma \Rightarrow A\sigma_2$

$$r = k\vartheta_a\vartheta_v = \; = \frac{kp_a}{(1+k_ap_a+k_bp_b)^2}$$

$$r_0 = \frac{k\pi}{(1+k_a\pi)^2}$$

$\Rightarrow k'/\pi$, at high pressure

(c) $B\sigma \Rightarrow B + \sigma$

$$r = k\vartheta_b^* = \frac{kp_b}{1+k_ap_a+k_bp_b^*}$$

$$r_0 = 0$$

(d) Homogeneous reaction,

$$r = k(p_a-p_b/K_e)$$

$$r_0 = k\pi$$

Mechanisms (a) and (d) cannot be distinguished by initial rate mesurements, but the others can be distinguished.

P6.04.29. CHLORINE FROM HCl

The Deacon process for production of chlorine involves the gas phase reaction

$$HCl + 0.25\ O_2 \Leftrightarrow 0.5\ Cl_2 + 0.5\ H_2O;\quad A+B \Leftrightarrow C+D$$

A study of the kinetics (Furusaki, *AIChE Journal* 19 1009, 1973) concluded that the rate of disappearance of HCl could be correlated by the equation,

$$r = \frac{k[C_aC_b^{0.25} - C_c^{0.5}C_d^{0.5}/K_e]}{(1+k_1C_a+k_2C_c)^2} \qquad (1)$$

Initial rate data at 350 C with a feed of HCl and air are tabulated. Units of the rate are 10^{-6} mgmol/(g catalyst)(s), and of HCl concentration, 10^{-6} mgmol/cc. Find the values of as many of the constants as possible.

At 250 C, the concentration of oxygen in air is

$$C_{bo} = \frac{0.21(273.2)(10^6)}{22400(523.2)} = 4110(10^{-6})\ \text{mgmol/cc}$$

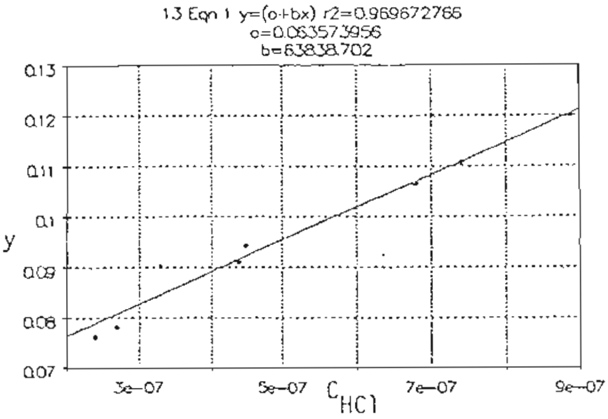
This concentration remains practically the same over the full range of HCl concentrations. Rearrange the initial rate equation into a linear form.

$$y_0 = \sqrt{\frac{C_aC_b^{0.25}}{r_0}} = \frac{1+k_1C_a}{\sqrt{k}} = 0.06357 + 63839(10^{-6})C_{HCl}$$

The plot is roughly linear, confirming the assumed initial rate mechanism.

The numerator of Eq (1) is that of a homogeneous mass action rate law. The denominator seems to have been added to account for adsorption of some of the participants.

r_0	C_{HCl}	C_{O_2}	y_0
10.5	0.24	4110	0.0761
11.2	0.27		0.0781
10.3	0.33		0.0901
13.5	0.44		0.0909
12.8	0.45		0.0944
15.2	0.58		0.1064
18.8	0.74		0.1107
15.7	0.89		0.1198



P6.04.30. THREE POSSIBLE MECHANISMS

The tabulated data are to be used to check the possible validity of these three equations:

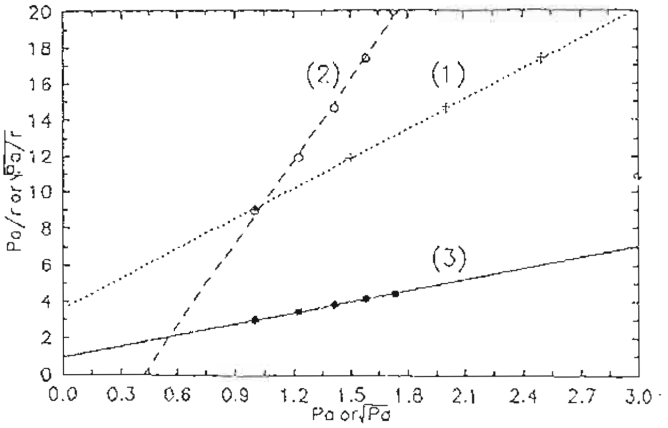
(1) $r_1 = kp_a/(1+k_1p_a)$ or $p_a/r_1 = (1+k_1p_a)/k$

(2) $r_2 = kp_a/(1+k_1\sqrt{p_a})$ or $p_a/r_2 = (1+k_1\sqrt{p_a})/k$

(3) $r_3 = kp_a/(1+k_1\sqrt{p_a})^2$ or $\sqrt{p_a/r_3} = (1+k_1\sqrt{p_a})/\sqrt{k}$

The plot of Eq (2) has a negative intercept so it is ruled out. The other mechanisms are equally valid.

p_a	$\sqrt{p_a}$	r	p_a/r	$\sqrt{p_a/r}$
3.0	1.732	0.1502	19.98	4.47
2.5	1.581	0.1438	17.39	4.17
2.0	1.414	0.1363	14.67	3.83
1.5	1.225	0.1261	11.90	3.45
1.0	1.00	0.1111	9.0	3.00



P6.04.31. A DISSOCIATION MECHANISM

The rate of a solid catalyzed reaction, $A_2 \Leftrightarrow B$, is expected to be surface reaction controlled. With the aid of the given data, determine if it is the dissociated or molecular species that participates in the reaction. The equilibrium constant is $K_e = p_{be}/p_{ae} = 3$.

With dissociation,

$2A\sigma \Leftrightarrow B\sigma + \sigma$

$$r = \frac{k_1(p_a - p_b/3)}{(1+k_2\sqrt{p_a}+k_3p_b)^2}$$

$$y_1 = \sqrt{\frac{p_a - p_b/3}{r}} = (1+k_2\sqrt{p_a}+k_3p_b)/\sqrt{k_1}$$

Without dissociation,

$$A_2\sigma \Leftrightarrow B\sigma$$

$$y_2 = \frac{p_a - p_b/3}{r} = (1+k_2p_a+k_3p_b)/k_1$$

By Gaussian elimination, the solutions of three linear equations for each case are

$$y_1 = 0.7076 + 0.3527\sqrt{p_a} + 0.7075p_b$$
$$y_2 = -1.084 - 0.1763p_a + 4.3862p_b$$

The first equation, for the dissociation mechanism, has all positive constants so that mechanism is feasible.

p_a	p_b	r	y_1	y_2
1	1	0.2133	1.7679	3.1255
2	1.5	0.2917	2.2677	5.1423
3	2.5	0.2273	3.0874	9.3522

P6.04.32. DATA OF A SLURRY REACTOR

A reaction, A + B ⇒ Products, is conducted in a CSTR with a slurried catalyst. The overall rate of reaction is believed to be controlled by the rates of adsorption of A and of the surface reaction between A and B. Given the tabulated data, find the rate equation. The starting condition in every case was $C_{a0} = 2$ and $C_{b0} = 4$.

The stoichiometric equations are

$$A + \sigma \Rightarrow A\sigma$$
$$A\sigma + B\sigma \Rightarrow \text{Products}$$

The corresponding rate equations at steady state are

$$r = k_1C_a\vartheta_v$$
$$= k_2\vartheta_a\vartheta_b = k_3C_aC_b\vartheta_v^2$$

whence

$$\vartheta_v = k_1/k_3C_b$$

and the rate equation becomes

$$r = \frac{k_1^2C_a}{k_3C_b} = \frac{kC_a}{2+C_a}$$

The material balance on the CSTR is

$$C_{a0} = C_a + \bar{t}r = C_a + \frac{k\bar{t}C_a}{2+C_a}$$

The constant becomes

$$k = \frac{4-C_a^2}{\bar{t}C_a}$$

The values of k calculated from the data are fairly constant and have an average value k = 2.398.

$\bar{t}$	C_a	k
0.5	1.49	2.3890
1	1.13	2.4098
5	0.32	2.4360
10	0.17	2.3359
15	0.11	2.4169

P6.04.33. DEHYDRATION OF BUTANOL-1

Initial rate data of the catalytic dehydration of butanol-1 are believed controlled by the surface reaction rate with this rate equation in terms of the fugacity, f,

$$r_0 = \frac{k_1 f}{(1+k_2 f)^2} \quad \text{lbmols/(h)(lb catalyst)}$$

Find the constants with these data of Maurer & Sliepcevich (Chem Eng Prog Symp Series 4 33, 1952),

In linearized form the rate equation is

$\sqrt{f/r_0} = (1 + k_2 f)/\sqrt{k_1} = 14.052 + 0.0200f$

$k_1 = 0.00506, \quad k_2 = 0.00143$

r_0	f	$\sqrt{f/r_0}$
0.27	15	7.45
0.51	409	28.3
0.76	676	29.8
0.76	1653	46.6
0.52	3370	80.5

P6.04.34. HYDROGENATION OF ETHYLENE

Initial rate data for the hydrogenation of ethylene at 41 C were taken by Sussman & Potter (Ind Eng Chem 46 457, 1954). Check the validity of the following controlling steps and corresponding initial rate equations where p_a = pressure of hydrogen, p_b= pressure of ethylene, in atm, r in gmol/(h)(g catalyst). Hydrogen adsorption is relatively small.

(a) Desorption of product controlling,

$y_a = p_a p_b/r_0 = a + bp_b$

(b) Adsorption of hydrogen controlling,

$p_a/r_0 = a+bp_b$

(c) Surface reaction controlling, with dissociation of hydrogen upon adsorption,

$y_c = (p_a p_b/r_0)^{1/3} = a + bp_b$

The graphs show that the plot of mechanism (a) is most nearly linear.

p_a	p_b	r_0	y_a	y_b	y_c
.405	.595	.00882	27.3	3.0	45.9
.401	.599	.009	26.7	2.98	44.6
.611	.389	.01172	20.3	2.72	52.0
.776	.224	.01444	12.0	2.29	53.7
.908	.092	.01964	4.25	1.62	46.3
.933	.067	.02021	2.32	1.32	47.4
.933	.067	.0206	3.09	1.46	46.2
.951	.049	.02008	3.03	1.45	45.3
.951	.049	.0203	2.30	1.32	46.9
.603	.397	.01253	12.1	2.30	48.1
.611	.389	.01183	20.1	2.72	51.7

P6.05.01. AMOUNT OF CATALYST NEEDED

A gas containing 50 mol% of substance A and the balance inerts is charged to a catalyst packed reactor at 50 lbmol/hr.The reaction is, A ⇒ 2B, the temperature is 340 F and the pressure is 5 atm. The rate equation is

$$r_a = \frac{dna}{dt} = \frac{25p_a}{(1+2.25\sqrt{p_a})^2} \qquad (1)$$

Find the amount of catalyst required for 90% conversion of A.

$$p_a = \frac{n_a}{n_t}\pi = \frac{n_a}{n_{to}+n_{a0}-n_a}\pi = \frac{5n_a}{75-n_a} \qquad (2)$$

The flow reactor equation is

$$-dn_a = r_a dW$$

$$W = \int_{2.5}^{25} \frac{(1+2.25\sqrt{p_a})^2}{25p_a}\, dn_a \qquad (3)$$

Substitute p_a from Eq (2) and integrate numerically. Results are,

n_a/n_{a0}	1	0.8	0.6	0.4	0.2	0.1
W	0	1.72	3.60	5.72	8.34	10.12

P6.05.02. CATALYST REQUIREMENT

A gas phase reaction, A ⇒ 2B, has a rate equation

$r_a = 0.2p_a/(1+0.5p_a)$ lbmol/(hr)(cuft of catalyst

The feed rate is 6.0 lbmol/hr of pure A. The pressure is 5 atm. What conversion is obtained with a catalyst volume V_r = 5 cuft?

$$p_a = (n_a/n_t)\pi = \frac{n_a}{2n_{a0}-n_a}\pi = \frac{5f}{2-f}\ ,\ f = n_a/n_{a0}$$

$$V_r = -n_{a0}\int_1^f \frac{df}{r} = 6\int_f^1 \frac{(2-f)}{5f}\, df = 40$$

By numerical integration and trial, V_r = 5.00 when f = 0.0787.

f	0.077	0.0787	0.079
V_r	5.05	5.00	4.99

P6.05.03. REACTION IN PLUG OR SEGREGATED FLOWS

A reaction, A ⇒ 2B, takes place at 900 R and 10 atm with a feed of 80 lbmols/hr A and 20 lbmols/hr inerts. The rate equation is

$$r = 0.0152\left(\frac{p_a}{1+0.254p_a}\right)^2 \text{ lbmol/(h)(cuft catalyst)} \quad (1)$$

Find the catalyst volume per unit of feed, V_r/n_{a0}, over a range of $f = n_a/n_{a0} = n_a/80$,

(a) In plug flow

(b) In segregated flow with $E(t_r)$ as that of a five stage CSTR, for $f = 0.2$ at the same residence time as in the plug flow unit of part (a).

(a). Plug flow,

$$n_t = 2n_{a0}+n_i-n_a = 180-n_a$$

$$p_a = (n_a/n_t)\pi = \frac{10n_a}{180-n_a} = \frac{10f}{2.25-f} \quad (2)$$

Flow reactor equation is

$$-n_{a0}df = r\,dV_r$$

$$V_r/n_{a0} = \int_1^f \frac{df}{r} \quad (3)$$

Substitute Eq (2) into Eq (1) which makes

$$r = 1.52\left(\frac{f}{2.25+1.54f}\right)^2 \quad (4)$$

Then substitute into Eq (3) and integrate. The result is tabulated over a range of f. When $f = 0.2$, $V_r/n_{a0} = 21.91$ and $t = 0.188$.

(b). Segregated flow,

The volumetric flow rate is

$$V' = n_t(RT/\pi) = (180-n_a)(0.73)(900)/10 = 65.7n_{a0}(2.25-f) \quad (5)$$

The residence time is

$$t = n_{a0}\int_f^1 \frac{df}{rV'} \quad (6)$$

Substitute Eqs (4) and (5) into (6). The integrals are tabulated. The residence time distribution is

$$E(t_r) = 130.2(t/\bar{t})^4\exp(-5t/\bar{t}) \quad (7)$$

From the table, the plug flow residence time at $f = 0.2$ is

$$\bar{t} = 0.188 \text{ hrs}$$

Performance in segregated flow is

$$(V_r/n_{a0})_{seg} = \int_0^\infty (V_r/n_{a0})_{plug\ flow}E(t_r)dt/\bar{t}$$
$$= 22.91 \quad (8)$$

compared with 21.91 in plug flow. Integration is with the trapezoidal rule.

f	V_r/n_{a0}	1000t	$E(t_r)$	$(V_r/n_{a0})E(t_r)$
1	0	0	0	0
.9	1.006	11.78	0.0022	0.0022
.8	2.15	24.34	0.0245	0.0528
.7	3.52	38.13	0.0917	0.3229
.6	5.17	53.83	0.1559	0.8059
.5	10.11	72.59	0.4255	3.0931
.4	14.35	96.56	0.6901	6.98
.3	21.91	130.5	0.9357	13.43
.2	28.86	187.9	0.8773	19.22
.15	41.92	238.7	0.5744	16.58
.1	78.83	332.0	0.1576	6.609
.05	127.1	587.7	0.0009	0.068
.03	400	940	0	0.0000
.01				

P6.05.04. INTEGRATION OF A RATE EQUATION

The rate of an deal gas reaction, A ⇒ 2B, is surface reaction controlled. The feed mixture contains 50% A, 10% B and 40% of inert I. All three substances are adsorbed. Find an algebraic expression for the size of reactor, lb catalyst/(lbmol feed/h), needed to reduce the partial pressure of A to half its original value.

With surface reaction controlling,

$$r_a = \frac{kp_a}{1+k_ap_a+k_bp_b+k_ip_i} \tag{1}$$

Stoichiometric relations are,

$$n_t = n_{t0}+n_{a0}-n_a = 2n_{a0}+n_{b0}+n_i-n_a \tag{2}$$

$$p_a = (n_a/n_t)\pi = \frac{n_a}{n_{t0}+n_{a0}-n_a}\pi \tag{3}$$

$$n_a = (n_{t0}+n_{a0})\frac{p_a}{\pi+p_a} \tag{4}$$

$$n_b = n_{b0}+2(n_{a0}-n_a) \tag{5}$$

$$p_b = (n_b/n_a)p_a = \left(\frac{2n_{a0}+n_{b0}}{n_{t0}+n_{a0}}\right)(\pi+p_a)-2p_a \tag{6}$$

$$p_i = (n_{io}/n_a)p_a = \frac{n_{a0}}{n_{t0}+n_a}(\pi+p_a) \tag{7}$$

From Eq (3),

$$dn_a = -\frac{\pi(n_{t0}+n_{a0})}{(\pi+p_a)^2}dp_a \tag{8}$$

The flow reactor equation is

$$-dn_a = r_a dW_c$$

$$W_c = \int_{n_a}^{n_{a0}} \frac{dn_a}{r_a} \tag{9}$$

Substitute Eq (6) and (7) into the rate Eq (1), then that result and Eq (8) into the integral Eq (9). That will then have only p_a as a variable and will be integrable.

P6.05.05. HYDROCHLORINATION OF ETHYLENE

Tests were made on the rate of the reaction, $C_2H_4 + HCl \Leftrightarrow C_2H_5Cl$, in the presence of inert methane and a solid catalyst. The tabulated data are of $10^4 r$ in lbmol/(h)(lb catalyst) and partial pressures of methane (I), C_2H_4 (A), HCl (B) and C_2H_5Cl (C) in atm. Inlet partial pressures were 10 for methane and one each for ethylene and HCl. The rate equation is believed to be

$$r_a = \frac{k_1(p_a p_b - p_c/35)}{(1+k_2p_a+k_3p_b+k_4p_c+k_5p_{C_{H_4}})^2}$$

Find numerical values of the space velocity, (cuft feed @ STP)/(h)(lb catalyst) over a range of conversions of ethylene.

Linearize the equation,

$$y = \sqrt{\frac{p_a p_b - p_c/35}{r}} = (1+k_a p_a+k_b p_b+ k_c p_c+ k_i p_i)/\sqrt{k_1}$$

The values of y are tabulated with the data. There are 5 constants and 5 equations. The solution of the linear equatioons by Gaussian elimination results in the rate equation

$$r_a = \frac{6.079(p_a p_b - p_c/35)}{(1+29.86p_a+36.95p_b+37.54p_c+2.194p_i)^2} \qquad (1)$$

Stoichiometric relations are

$$n_t = 11n_{a0}+n_a$$

$$f = n_a/n_{a0}$$

$$p_a = p_b = (n_a/n_t)p_t = \frac{12f}{11+f} \qquad (2,\ 3)$$

$$p_c = \frac{12(1-f)}{11+f} \qquad (4)$$

$$p_{CH_4} = \frac{120}{11+f} \qquad (5)$$

At equilibrium, $p_a p_b = p_c/35$ or

$$\left[\frac{12f}{11+f}\right]^2 = \frac{12(1-f)}{35(11+f)}$$

$$f = 0.1502$$

The volumetric flow rate is

$$(V'_0)_{STP} = 359.2n_{t0} = = 359.2(12)n_{a0} = 4310n_{a0}$$

The flow reactor equation is

$$W_c/n_{a0} = \int_f^1 \frac{df}{r_a}$$

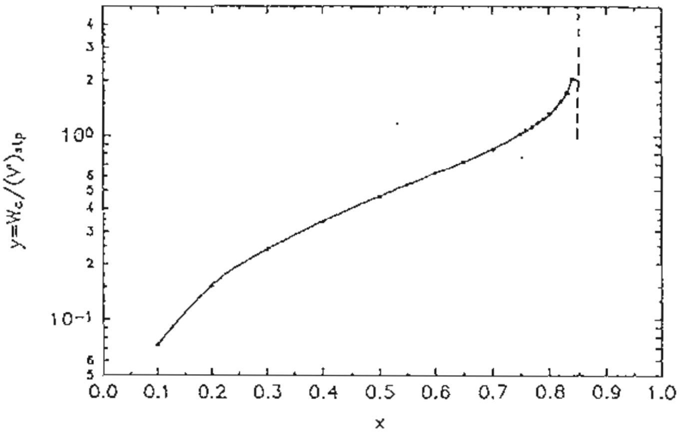
or

$$\text{Space velocity} = \frac{W_c}{(V'_0)_{STP}} = \frac{1}{4310}\int_f^1 \frac{df}{r_a} \qquad (6)$$

Substitute Eqs (2), (3) and (4) into (1), and the result into (6) which will have only f as the variable. Values of the integrand and of the integral are tabulated, and the integral is plotted.

RESULTS

1-f	$1/4310r_a$	Sp Vel
0	0.701	0
.1	0.758	0.073
.2	0.883	0.153
.3	0.939	0.241
.4	1.092	0.343
.5	1.338	0.465
.55	1.526	0.536
.6	1.792	0.619
.65	2.195	0.719
.7	2.877	0.846
.75	4.258	1.024
.8	8.461	1.319
.82	14.13	1.538
.84	42.99	2.036



DATA

r	p_i	p_a	p_b	p_c	y
2.71	7.005	0.300	0.370	0.149	19.85
2.63	7.090	0.416	0.215	0.102	18.14
2.44	7.001	0.343	0.289	0.181	19.62
2.58	9.889	0.511	0.489	0.334	30.52
2.69	10.169	0.420	0.460	0.175	26.45

P6.05.06. RATE AT A PARTICULAR CONVERSION

The rate of the reaction, C_2H_4 (A) + HCl (B) ⇔ C_2H_5Cl (C), is given by the equation

$$r_a = \frac{4.67(10^{-4})(p_a p_b - p_c/35.5)}{(1+27.42p_a+34.54p_b+36.76p_c+2.20p_i)^2}$$

Given a feed at 400 psig and containing 0.8485, 0.1010 and 0.0505 mol fractions of methane, ethylene and hydrogen chloride respectively, find the rate of reaction at a time when 40% conversion of ethylene has occurred. Pressures are in atm. The rate is lbmol/(h)(lb catalyst).

From the stoichiometry, when 40% conversion has happened,

$n_a = 0.6(0.1010) = 0.0606$

$n_b = 0.0505 - 0.4(0.1010) = 0.0101$

$n_c = 0.0404$

$n_{methane} = 0.8485$

$n_t = 0.9596$

$p_i = (n_i/n_t)\pi = (n_i/0.9596)(415/14.7)$

$p_a = 1.78,\ p_b = 0.296,\ p_c = 1.184,\ p_{methane} = 24.94$

Substitution of these partial pressures into the rate equation gives

$r_a = 92.5(10^{-10})$ lbmol/(h)(lb catalyst)

P6.05.07. ETHYLBENZENE IN A FLUIDIZED BED

A fluidized bed reactor is used to accomplish the catalytic dehydrogenation of ethylbenzene in the presence of steam which serves as an inert diluent. The reaction is

$C_6H_5C_2H_5 \Leftrightarrow C_6H_5C_2H_3 + H_2$, $A \Leftrightarrow B + C$

The rate equation is

$$r = k(p_a - p_bp_c/K_e) \qquad (1)$$

and the parameters are functions of T,

$$\ln k = 4.10-4770/T \qquad (2)$$

$$\ln K_e = 15.34-14651/T \qquad (3)$$

Specific heat of steam is 0.52, and the average of the other constituents is 0.41. Heat of reaction is assumed constant at $\Delta H_r = 60{,}000$ Btu/lbmol.

Inlet temperature is 898 K, operating pressure is 1.2 atm, charge rate is 20 lbmol of ethylbenzene and 400 lbmols of steam. Under fluidizing conditions bulk density of the bed is 25 lb/cuft. Conditions are adiabatic.

Find the volume of the catalyst bed needed to effect 30% conversion.

In a shallow fluidized bed, temperature will be substantially uniform and will correspond to the effluent conversion. The absence of a composition gradient in a fluidized bed is less certain. Accordingly, three cases will be solved for comparison,

(a). With both temperature and composition gradients (PFR behavior).
(b). Uniform temperature with composition gradient.
(c). Uniform temperature and composition (CSTR behavior).

x = mols A converted/hr

$n_t = 420+x$ = total mols/hr

$$p_a = \frac{1.2(20-x)}{420+x}$$

$$p_b = p_c = \frac{1.2x}{420+x}$$

Substituting into the rate equation,

$$r = \frac{1.2k}{420+x}\left[20-x - \frac{1.2x^2}{K_e(420+x)}\right] \qquad (4)$$

The heat balance is

$$60000x = [2120(0.41)+7200(0.52)](898-T)$$

$$T = 898 - 13x \qquad (5)$$

(a). In the PFR with temperature gradient, the integration is done with Simpsons Rule.

$$W_c = \int_0^6 \frac{dx}{r} = 3056 \text{ lb catalyst} \qquad (a)$$

x	T	k	K_e	1/r
0	898	0.0616	0.370	284
3	876.4	0.0446	0.245	468
6	854.8	0.0295	0.155	900

(b). In (b) In a

PFR at constant temperature, T = 854.8, k = 0.0295, K_e = 0.155. The integrand is

x	0	3	6
1/r	592	710	900

and the integral is

$W_c = 3332$ lbs (b)

(c) In a CSTR, r = 1/900 and

$W_c = \Delta x/r = 6(900) = 5400$ lbs (c)

P6.05.08. L-H EQUATION WITH VARIABLE PRESSURE

An ideal gas phase reaction, 2A ⇔ B, is surface reaction controlled and has the rate equation

$$r = \frac{p_a^2 - p_b}{(1+p_a+p_b)^2} \qquad (1)$$

Pure A is charged at the rate n_{a0}. The pressure varies linearly from $\pi_0 = 2$ at the inlet to $0.5\pi_0$ at the outlet. Express the conversion in terms of n_{a0} and the total volume of the reactor, V_{rt}.

Applying the stoichiometry,

$n_t = 0.5(n_{a0}+n_a)$

$f = n_a/n_{a0}$

$$p_a = (n_a/n_{a0})\pi = \frac{2f}{1+f}\pi \qquad (2)$$

$$p_b = \frac{1-f}{1+f}\pi \qquad (3$$

$$\pi = \pi_0(1 - 0.5V_r/V_{rt}) = 2 - V_r/V_{rt} \qquad (4)$$

$$d\pi = -(1/V_{rt})dV_r \qquad (5)$$

The flow reactor equation is

$$-dn_a = -n_{a0}df = r\,dV_r = -\frac{r}{V_{rt}}d\pi \qquad (6)$$

Substitute Eqs (2) and (3) into (1). This will result in r as a function of f and π,

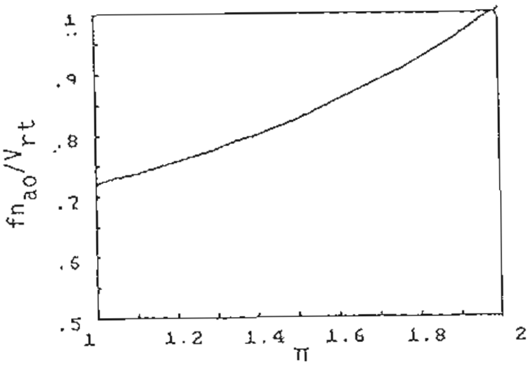
$$r = \phi(f, \pi) \qquad (7)$$

The differential equation then becomes

$$\frac{df}{d\pi} = \frac{V_{rt}}{n_{a0}}\phi(f, \pi),\ f_0 = 1,\ \pi_0 = 2 \qquad (8)$$

The integration of this equation is graphed. At the outlet where $\pi = 1$,

$$f = 0.7231\ V_{rt}/n_{a0} \qquad (9)$$



P6.05.09. L-H EQUATION IN CSTRs

A packed bed reactor has an RTD like that of a five stage CSTR. The rate equation is

$$r = 0.5C/(1+0.2C) \qquad (1)$$

and the inlet concentration is $C_0 = 1.5$. Find the conversion in a segregated flow reactor with mean residence times $\bar{t} = 2$ and $\bar{t} = 5$. Compare with conversions in five stage CSTRs.

The RTD is

$$E(t_r) = 130.2\ t_r^4 \exp(-5t_r) \qquad (2)$$

In a batch reactor,

$$t = \int_{C_b}^{1.5} \frac{dC_b}{r} = 2\ [\ln(1.5/C_b) + 0.2(1.5-C_b)] \qquad (3)$$

Values of $(C_b,\ t)$ are tabulated. In segregated flow,

$$C_{seg} = \int_0^\infty C_b E(t_r)dt/\bar{t} \qquad (4)$$

The integrands are tabulated. Results of integration with the trapezoidal rule are

$$C_{seg} = 0.6966, \text{ with } \bar{t} = 2 \qquad (5)$$

$$0.2466, \text{ with } \bar{t} = 5$$

In a CSTR battery the material balances are

$$C_{n-1} = C_n + \frac{0.5(\bar{t}/5)C_n}{1+0.2C_n}\ ,\ n = 1,\ 2,\ 3,\ 4,\ 5$$

Solution of the five simultaneous equations for the outlet concentration is

$$C_{CSTR} = 0.691, \text{ with } \bar{t} = 2 \qquad (6)$$

$$0.235, \text{ with } \bar{t} = 5$$

Lines (5) and (6) agree closely.

		$\bar{t} = 5$			$\bar{t} = 2$		
C_b	t	t_r	$E(t_r)$	C_bE	t_r	$E(t_r)$	C_bE
1.5	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.45	0.088	0.018	0.000	0.000	0.044	0.000	0.001
1.40	0.178	0.036	0.000	0.000	0.089	0.005	0.007
1.35	0.270	0.054	0.001	0.001	0.135	0.022	0.030
1.30	0.366	0.073	0.003	0.003	0.183	0.059	0.076
1.25	0.465	0.093	0.006	0.008	0.232	0.119	0.148
1.20	0.566	0.113	0.012	0.015	0.283	0.203	0.244
1.15	0.671	0.134	0.022	0.025	0.336	0.309	0.355
1.10	0.780	0.156	0.035	0.039	0.390	0.429	0.472
1.05	0.893	0.179	0.054	0.057	0.447	0.555	0.583
1.00	1.011	0.202	0.079	0.079	0.505	0.679	0.679
0.95	1.134	0.227	0.111	0.105	0.567	0.790	0.750
0.90	1.262	0.252	0.149	0.135	0.631	0.880	0.792
0.85	1.396	0.279	0.196	0.166	0.698	0.943	0.801
0.80	1.537	0.307	0.250	0.200	0.769	0.974	0.779
0.75	1.686	0.337	0.312	0.234	0.843	0.971	0.728
0.70	1.844	0.369	0.381	0.267	0.922	0.936	0.655
0.65	2.012	0.402	0.457	0.297	1.006	0.872	0.567
0.60	2.193	0.439	0.537	0.322	1.096	0.783	0.470
0.55	2.387	0.477	0.621	0.342	1.193	0.677	0.372
0.50	2.597	0.519	0.706	0.353	1.299	0.561	0.280
0.45	2.828	0.566	0.788	0.355	1.414	0.443	0.199
0.40	3.084	0.617	0.863	0.345	1.542	0.330	0.132
0.35	3.371	0.674	0.924	0.323	1.685	0.230	0.081
0.30	3.699	0.740	0.965	0.290	1.849	0.147	0.044
0.25	4.084	0.817	0.976	0.244	2.042	0.083	0.021
0.20	4.550	0.910	0.944	0.189	2.275	0.040	0.008
0.15	5.145	1.029	0.851	0.128	2.573	0.015	0.002
0.10	5.976	1.195	0.675	0.067	2.988	0.003	0.000
0.05	7.382	1.476	0.385	0.019	3.691	0.000	0.000
0.04	7.833	1.567	0.311	0.012			
0.03	8.412	1.682	0.232	0.007			
0.02	9.227	1.845	0.149	0.003			
0.01	10.617	2.123	0.065	0.001			

P6.05.10. METHANE FROM CARBON DIOXIDE

The rate of the catalytic hydrogenation of carbon dioxide to produce methane is

$$r = \frac{7.0p_ap_b^4}{(1+0.3p_a+1.73p_b)^5} \quad \text{kgmol } CH_4\text{/(kg catalyst)(h)(atm)}^{-5}$$

A = CO_2, B = H_2. The pressure is 30 atm and the temperature is 314 C. For a feed rate of 100 kgmol/h of CO_2 and stoichiometric amount of H_2, find the amount of catalyst needed to convert 20% of the carbon dioxide.

$$CO_2 \ + \ 4H_2 \ \Rightarrow \ CH_4 \ + \ 2H_2O$$

$$1-\varepsilon \quad 4(1-\varepsilon) \quad \varepsilon \quad 2\varepsilon \quad \Sigma = 5 - 2\varepsilon$$

The partial pressures as a function of the fraction converted are

$$p_a = \frac{30(1-\varepsilon)}{5-\varepsilon}, \quad p_b = 4p_a$$

The flow reactor equation is

$$-dn_a = rdW_c$$

$$W_c = \int_{80}^{100} \frac{dn_a}{r} = 247.3 \text{ kg catalyst}$$

Integration is with Simpsons rule for which the data are tabulated.

ε	n_a	p_a	$1/r$
0	100	6	12.27
0.1	90	5.510	12.36
0.2	80	5	12.48

P6.05.11. PFR WITH AN L-H RATE EQUAITON

A plug flow reactor is used for a reaction with stoichiometry, $2A \Rightarrow 3B$, in the gas phase. The rate equation is

$$r_a = 0.5\left(\frac{p_a}{1+0.2p_a+0.1p_b}\right)^2 \quad (1)$$

Pressure is 5 atm, n_{t0} = 10 kgmol/h, n_{a0} = 3 kgmol/h, n_{b0} = 0, and the balance inert. Find the amount of catalyst needed for conversion of 80%.

Stoichiometric relations are

$$n_b = n_{b0} + 1.5(n_{a0}-n_a) = 1.5(3-n_a)$$

$$n_t = n_a+n_b+n_i = n_a+1.5(3-n_a)+7 = 11.5-0.5n_a$$

$$p_a = (n_a/n_t)\pi = \frac{5n_a}{11.5-0.5n_a} \quad (2)$$

$$p_b = \frac{7.5(3-n_a)}{11.5-0.5n_a} \quad (3)$$

Substitute Eqs (2) and (3) into (1), and the result into the flow reactor equation which is

$$W_c = \int_{0.6}^{3} \frac{dn_a}{r_a} = 19.6$$

The tabulation for the integration with Simpsons rule is

n_a	p_a	p_b	$1/r_a$
3	1.5	0	1.502
2.6	1.2745	0.2941	2.031
2.2	1.0577	0.5769	2.880
1.8	0.8491	0.8491	4.368
1.4	0.6482	1.1111	7.329
1.0	0.4546	1.3636	14.58
0.6	0.2679	1.6071	41.10

P6.05.12. REACTOR SIZE FOR HYDROGENATION OF OCTENES

Hydrogenation of octenes occurs with surface reaction controlling (Hougen & Watson, Chemical Process Principles, p 943, 1947). The rate equation is

$$r = \frac{p_h p_u}{(a+fp_h+bp_u+cp_s)^2},\quad \text{lbmol octenes/(h)(lb catalyst}$$

u = unsaturates, s = saturates, h = hydrogen. The constants are known at three temperatures.

	200 C	275 C	325 C
a	2.64	3.14	3.43
b	1.53	1.58	1.61
c	1.29	0.203	0.0762
f	1.01	0.774	0.653

An equimolal mixture of octenes and hydrogen is fed to a fluidized bed of catalyst at 2 atm. Find the required weight of catalyst per unit of feed, W_c/F_0, as a function of conversion in (a) plug flow; (b) a completely mixed bed.

x = fractional conversion

$n_t = 2-x$

$$p_u = p_h = (n_u/n_t)\pi = \frac{2(1-x)}{2-x}$$

$$p_s = \frac{2x}{2-x}$$

In plug flow,

$$W_c/F_0 = \int_0^x dx/r$$

In completely mixed,

$$W_c/F_0 = \Delta x/r$$

Substitute for the partial pressures in the rate equation in terms of x. For the plug flow case, values of 1/r are tabulated over a range of x at the three temperatures, as well as some values of the integrals. Some values of W_c/F_0 also are shown for the mixed cases. Note that at high conversions, the completely mixed reactor is much larger than the plug flow.

	1/r				$(W_c/F_0)_{pf}$				$(W_c/F_0)_{mixed}$		
x	200	275	325		200	275	325		200	275	325
0	26.83	30.18	32.41								
0.1	29.92	32.39	34.72								
0.2	34.02	35.25	37.71								
0.3	39.67	39.11	41.74								
0.4	47.89	44.57	47.43								
0.5	60.68	52.81	56.01		19.5	19.3	20.6		30.4	26.4	28.0
0.6	82.72	66.48	70.22		26.7						
0.7	127.0	92.76	97.47		37.8						
0.8	244.0	158.4	165.3		55.7						
0.9	822.0	460.1	475.8		109.0	76.7	80.5		740	414	428

P6.05.13. ETHYL CHLORIDE AT TWO TEMPERATURES

For the synthesis of ethyl chloride from ethylene and HCl in the presence of methane, the rate equation and its constants were found at 300 F and 400 F (Thodos & Stutzman, Ind Eng Chem 50 413, 1958).

$$r = \frac{0.514(p_a p_b - p_m/93.4)}{(1+7.21p_a+7.87p_b+14.4p_m+1.29p_i)^2}\ ,\ \text{at 300 F}$$

$$\frac{32.8(p_a p_b - p_m/14.45)}{(1+86.7p_a+133.5p_b+85.1p_m+3.49p_i)^2}\ ,\ \text{at 400 F}$$

pressures are in atm and r is lbmol/(h)(lb catalyst).

A feed at 400 psig contains 0.8485, 0.1010 and 0.0505 mol fractions of methane, ethylene and HCl respectively. Find the amounts of catalyst at the two temperatures needed for 40% conversion.

The partial pressures are expressed in terms of fractional conversion, x, and pressure π = 28.2 atm:

$p_a = 28.2(0.101-x)/(1-x)$
$p_b = 28.2(0.0505-x)/(1-x)$
$p_m = 28.2x/(1-x)$
$p_i = 28.2(0.8485)/(1-x)$

The flow reactor equation is

$$W_c/n_{a0} = \int_0^{0.0404} \frac{dx}{r} = 21.5,\ \text{at 300 F}$$

$$147,\ \text{at 400 F}$$

The integrands are tabulated at several values of x and the integration is with Simpsons rule.

Conversion proceeds more rapidly at the lower temperatures because of the large effect of temperature on the adsorption constants.

x	$1/r_{300}$	$1/r_{400}$
0	193	2050
0.0101	270	2420
0.0202	398	3120
0.0303	685	4370
0.0404	1580	8200

P6.05.14. DEHYROGENATION OF BENZENE

A rate equation for the dehydrogenation of benzene to cyclohexane in the gas phase for a supported nickel catalyst is reported by Nagata et al (Kagaku Kogaku, Abridged English Edition 2(1), 18, 1964),

$$r = \frac{k_p k_h^3 k_b p_h^3 p_b}{(1+k_h p_h+k_b P_b+k_c p_c)^4}\quad \text{gmol/(h)(g catalyst)}$$

$\ln k_p = (-13300/T+33.5)/R$
$\ln k_h = (15500/T-31.9)/R$
$\ln k_b = (11200/T-23.1)/R$
$\ln k_c = (8900/T-19.4)/R$

The reaction is to be conducted at 500 K and 10 atm with the starting composition: benzene = 100, hydrogen = 400, methane(inert) = 100 and 90% conversion is required. Find the catalyst requirement per unit of benzene feed.

The values of the constants at 500 K are: k_p=3.4726, k_h=0.6358, k_b=0.7031, k_c=0.4470. Let x = fractional conversion of benzene. Then the partial pressures are

$p_h = 10(1-x)/(6-3x)$

$p_b = 10(4-3x)/(6-3x)$
$p_c = 10x/(6-3x)$
$p_{methane} = 10/(6-3x)$

The partial pressures and and the rates will be found at conversions of 0, 45% and 90% and Simpsons rule will be applied for a very rough value of the integration. With the data of the table,

$$W_c/n_{b0} = \int_0^{0.9} \frac{dx}{r} = \frac{0.45}{3}[5.450+4(8.749)+51.02]$$

$$= 13.7 \text{ g catalyst/(gmol benzene charged/hr)}$$

	x=0	x=0.45	x=0.9
p_b	1.667	1.1830	0.3030
p_h	6.667	5.6989	3.9394
p_c	0	0.9677	2.7273
p_m	1.667	2.0150	3.030
1/r	5.450	8.749	51.02

P6.05.15. HYDRATION OF ETHYLENE

Direct catalytic hydration of ethylene in the vapor phase at 136 atm was studied by Mace & Bonilla (Chem Eng Prog 50 385, 1954) who concluded that surface reaction is controlling without appreciable adsorption of ethanol. The reaction is

$C_2H_4 + H_2O \Leftrightarrow C_2H_5OH$, A + B ⇔ C

At 520 F the rate equation is

$$r = \frac{5.26(10^{-7})(p_ap_b-p_c/225)}{[1+0.00889(p_a+p_b)]^2} \text{ (gmols/hr)/g catalyst}$$

For 20% conversion of an equimolal feed, find W_c/n_{a0}, g catalyst/ (gmol ethanol/hr).

x = fractional conversion of ethylene
$p_a = p_b = 136(1-x)/(2-x)$
$p_c = 136x/(2-x)$

In a flow reactor,

$$W_c/n_{a0} = \int_0^{0.2} \frac{dx}{r} = 423$$

Values of the integrand are tabulated. Integration is with the trapezoidal rule.

x	0	0.05	0.10	0.15	0.20
1/r	2006	2054	2109	2170	2240

P6.05.16. OXIDATION OF NO WITH AIR

Oxidation of NO is catalyzed by active carbon,

$NO + 0.5O_2 \Leftrightarrow NO_2$, A + 0.5B ⇔ C

The rate equation at 30 C is given by Rao & Hougen (Chem Eng Prog Symp Series 4 110, 1952) as

$$r = \frac{p_a^2p_b}{0.0001619+4.842p_a^2+0.001352p_c} \text{ (gmol No converted/hr)/g catalyst.}$$

Mol fractions at inlet to a reactor are 0.015 NO, 0.2068 O_2 and 0.7782 N_2. and the pressure is 3 atm. Find the catalyst requirement for converting 90%of the NO.

x = mols NO converted/mol total feed

$p_a = 3(0.015-x)/(1-0.5x)$

$p_b = 3(.2068-0.5x)/(1-0.5x)$

$p_c = 3x/(1-0.5x)$

The flow reactor equation is

$$W_c/n_t = \int_0^{0.0135} \frac{dx}{r} = 0.116 \text{ g catalyst/(gmol total feed/hr)}$$

Some values of the integrand are tabulated. Integration is with the trapezoidal rule.

1000x	0	1.5	3.0	4.5	6.0	7.5	9.0	10.5	12.0	13.5
1/r	7.82	7.85	7.89	7.93	7.99	8.07	8.21	8.49	10.35	13.76

P6.05.17. A LIQUID PHASE L-H REACTION

The reaction, A+B ⇒ C, has a rate equation

$$r = \frac{172.1C_aC_b}{(1+2.16c_a+632.6C_b)^2} \quad \text{mol/(liter)(sec)}$$

Feed at the rate of 100 liters/min contains 0.1 mols/liter of each reactant. How large a flow reactor is needed to make 5 mols/min of C?

With equimolal reactants the rate equation becomes

$$r = 172.1\left(\frac{C}{1+634.8C}\right)^2$$

The flow reactor equation becomes

$$V_r/V' = \frac{V_r}{100/60} = \int_{0.05}^{0.1}\left(\frac{1+634.8C}{C}\right)^2 dC = 122.2$$

$$V_r = 203.5 \text{ liters}$$

P6.06.01. TWO DIFFUSION STEPS AND SURFACE REACTION

The overall rate of conversion of the solid catalyzed gas phase reaction, 2A ⇔ B, is influenced by three mechanisms:

(a) diffusion of A to the surface

(b) diffusion of B away from the surface

(c) surface reaction

In the steady state the three rates are equal.

$$r = k_1(p_{ag}-p_{ai}) = k_2(p_{bi}-p_{bg}) = k_3\vartheta_a^2 - k_4\vartheta_b\vartheta_v$$
$$= (k_3p_{ai}^2 - k_4p_{bi})\vartheta_v^2 \quad (1)$$

Isolate ϑ_v, p_{ai}, and p_{bi} in terms of observable quantities.

$$p_{ai} = p_{ag} - r/k_1 \quad (2)$$

$$p_{bi} = p_{bg} + r/k_2 \quad (3)$$

$$\vartheta_v = 1/(1+k_5p_{ai}+k_6p_{bi}) \quad (4)$$

Substitute Eqs (2) and (3) into Eq (4), then (2), (3) and the resulting (4) into Eq (1.). The final result is a cubic equation in r involving six constants and the two partial pressures in the gas phase, p_{ag} and p_{bg}, of the form

$$r = \frac{a+br+cr^2}{d+er+fr^2}.$$

P6.06.02. DIFFUSION, SURFACE REACTION, DESORPTION

The rate of a solid catalyzed reaction, 2A ⇔ B, is controlled by three simultaneous factors,

(a) rate of diffusion of A to the surface

(b) rate of surface reaction

(c) rate of desorption of B

Express the overall rate of conversion as a single equation in terms of readily measurable parameters of the system and the minimum number of empirical constants.

In the steady state,

$$r = k_1(p_a-p_{ai}) = k_2\vartheta_a^2 - k_3\vartheta_b\vartheta_v = k_4\vartheta_b$$

Solve for the non measurable quantities,

$$p_{ai} = p_a - r/k_1$$

$$\vartheta_b = r/k_4 \tag{1}$$

$$\vartheta_a = k_5 p_{ai}\vartheta_v = k_5(p_a-r/k_1)\vartheta_v \tag{2}$$

$$\vartheta_v = 1 - \vartheta_a - \vartheta_b = 1 - k_5(p_a-r/k_1)\vartheta_v - r/k_4$$

$$= k_1\left[\frac{1-r/k_4}{k_1+k_5(k_1p_a-r)}\right] \tag{3}$$

Substitute Eqs (1), (2) and (3) into

$$r = k_2\vartheta_a^2 - k_3\vartheta_b\vartheta_v \tag{4}$$

$$= k_2[k_5(p_a-r/k_1)]^2\vartheta_v^2 - (k_3/k_4)r\vartheta_v$$

Final substitution of ϑ_v will give the sought for result, which will be a ratio of fourth and third degree polynomials in r.

Non linear regression would be needed to find the five constants.

P6.06.03. DIFFUSION, CHEMISORPTION, SURFACE REACTION

The rate of a reaction, A ⇒ Products, is controlled by three steps in series,

(a) Diffusion to the surface, $r_1 = k_1(p_g - p_s)$

(b) Chemisorption on the surface, $r_2 = k_2p_s(1-\vartheta)$

(c) A second order reaction on the surface, $r_3 = k_3\vartheta^2$.

In the steady state the three rates are equal. Eliminate the non measurable quantities, p_s and ϑ.

$$p_s = p_g - r/k_1$$

$$\vartheta = 1 - r/k_2p_s = 1 - \frac{r}{k_2(p_g-r/k_1)}$$

$$r = k_3\left[1 - \frac{r}{k_2(p_g-r/k_1)}\right]^2$$

This is a cubic equation in r with three constants and the partial pressure of the reactant in the gas phase, p_g, as the variable.

P6.06.04. DIFFUSION AND SURFACE REACTION

Diffusion of A to the surface and surface reaction between adsorbed A and B occur simultaneously. Adsorption of A is relatively small but a component C also is adsorbed.

The free surface fraction is

$$\vartheta_v = \frac{1}{1+k_bp_b+k_cp_c}$$

In the steady state,

$$r = k_1(p_a-p_{as}) = k_2p_{as}p_b\vartheta_v^2$$

$$= k_2(p_a-r/k_1)p_b\vartheta_v^2$$

$$= \frac{k_2p_ap_b}{1/\vartheta_V^2 + (k_2/k_1)p_b} = \frac{k_2p_ap_b}{1/(1+k_bp_b+k_cp_c)^2+(k_2/k_1)p_b}$$

Although r is isolated, the equation cannot be transformed so that the constants could be found by a linear process.

P6.06.05. DIFFUSION AND REACTION WITH DISSOCIATION

The solid catalyzed reaction, $A_2 + B \Rightarrow$ Products, takes place with a large excess of substance B so its partial pressure does not change appreciably. The rate of diffusion is

$$r_{diff} = 0.015(p_{ag}-p_{ai})$$

The reaction products are assumed not to adsorb appreciably. Two possible controlling mechanisms are to be examined, both being surface reactions between adsorbed substances.

(1) between adsorbed B and adsorbed monatomic A

(2) between adsorbed B and adsorbed diatomic A_2.

(a) Given the tabulated data, find which mechanism is a better fit.

(b) Find the magnitude of the quantity RTV_r/V' required to change the partial pressure of A from 5 to 2 in a plug flow reactor. The concentration of A is so low that the volumetric feed rate V' may be taken constant.

(a) The surface concentrations are evaluated from

$$p_{ai} = p_{ag}-r/0.015$$

For mechanism (1)

$$2A\sigma + B\sigma \Rightarrow \text{Products}$$

$$r = k\vartheta_a^2\vartheta_b = \frac{kp_{ai}p_b}{(1+\sqrt{k_ap_{ai}}+k_bp_b)^3}$$

$$\Rightarrow \frac{k_1p_{ai}}{(1+k_2\sqrt{p_{ai}})^2}, \text{ since } p_b \text{ is constant}$$

In linearized form,

$$y_1 = (p_{ai}/r)^{1/3} = (1+k_2\sqrt{p_{ai}})/K_1)^{1/3}$$

$$= 0.487 + 3.212\sqrt{p_{ai}} \qquad (1)$$

The linear plot is good. The rate equation becomes

$$r_1 = \frac{8.637p_{ai}}{(1+6.590\sqrt{p_{ai}})^3}$$

For mechanism (2),

$$A\sigma + B\sigma \Rightarrow \text{Products}$$

$$r = k\vartheta_a\vartheta_b = \frac{k_1p_{ai}}{(1+k_2p_{ai})^2}$$

$$y_2 = \sqrt{p_{ai}/r} = (1+k_2p_{ai})/\sqrt{k_1} \qquad (2)$$

This plot is not quite linear, so mechanism (2) is ruled out.

(b) In the plug flow reactor,

$$-V'dC_{ag} = -\frac{V'}{RT}dp_{ag} = 0.015(p_{ag}-p_{ai})dV_r$$

$$\frac{RTV_r}{V'} = \frac{1}{0.015}\int_2^5 \frac{dp_{ag}}{p_{ag}-p_{ai}} = 3.27 \qquad \text{(Answer)}$$

Integration is with the trapezoidal rule. The relation between p_{ai} and p_{ag} is

$$r = 0.015(p_{ag}-p_{ai}) = \frac{8.637p_{ai}}{(1+6.59\sqrt{p_{ai}})^3}$$

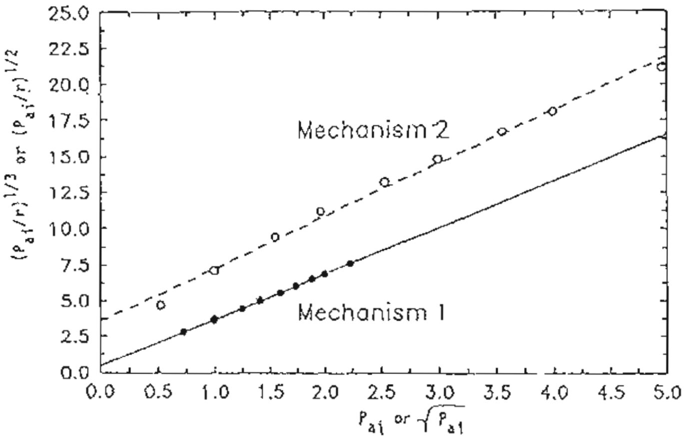
The second table gives some of the results.

Experimental Data

p_{ag}	r	p_{ai}	$(p_{ai}/r)^{1/3}$	$\sqrt{p_{ai}/r}$	$\sqrt{p_{ai}}$
2.1	0.0237	0.52	2.80	4.08	0.72
2.3	0.0197	0.99	3.69	7.09	0.99
2.7	0.0174	1.54	4.46	9.41	1.24
3.0	0.0156	1.96	5.01	11.21	1.40
3.5	0.0145	2.53	5.59	13.21	1.59
3.9	0.0136	2.99	6.04	14.83	1.73
4.4	0.0128	3.55	6.52	16.65	1.88
4.8	0.0122	3.99	6.89	18.08	2.00
5.7	0.0111	4.96	7.65	21.14	2.23

Plug Flow Reactor

p_{ag}	p_{ai}	$1/(p_{ag}-p_{ai})$	Integral
5	4.208	1.263	0
4.5	3.664	1.196	1.62
4	3.109	1.122	1.19
3.5	2.539	1.041	1.74
3	1.941	0.944	2.23
2.5	1.281	0.820	2.67
2	0.619	0.724	3.27



P6.06.06. DIFFUSION AND SURFACE REACTION

In terms of the partial pressure, p_s, at the surface of the catalyst, the rate of a reaction is expressed by

$$r = k_1p_s/(1+k_2p_s)$$

The mass transfer coefficient is k_ga = 0.5 lbmol/(h)(atm)(cuft of bed). Given the tabulated data, find the constants of the rate equation.

At steady state,

$$r = 0.5(p-p_s) = k_1p_s/(1+k_2p_s)$$

$$p_s = p-r/0.5$$

$$y = p_s/r= (1+k_2p_s)/k_1 = 1.4287 + 0.2857p_s$$

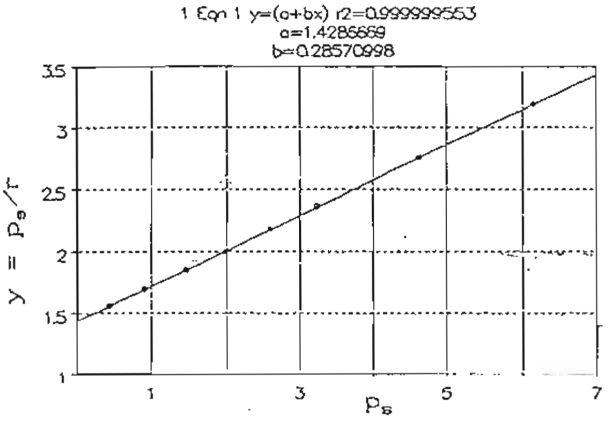
Accordingly,

$$k_1 = 0.700,\ k_2 = 0.200$$

$$r = \frac{0.7(p-2r)}{1+0.2(p-2r)}$$

This quadratic equation could be solved explicitly for r.

p	r	p_s	p_s/r
1	0.2814	0.4372	1.5536
2	0.5420	0.9160	1.69
3	0.7814	1.4372	1.8372
4	1	2	2
5	1.1984	2.6032	2.1723
6	1.3775	3.245	2.3557
8	1.6834	4.6332	2.7523
10	1.9293	6.1414	3.1832



P6.06.07. ROTATING BASKET DATA

The reaction, $A_2 + B \Rightarrow C$, has the rate equation

$$r_a = \frac{k_1C_aC_b}{(1+k_2\sqrt{C_a})^2}$$

Under normal operating conditions the overall conversion rate also is limited by the rate of diffusion of B for which the equation is

$$r_d = 0.9(C_b-C_{bi})$$

Equimolal concentrations of A and B are charged to the reactor and the density remains constant. Laboratory tests were made with a rotating basket reactor in which diffusional resistances were effectively eliminated, with the tabulated results.

(a) Find the constants of the rate equation

(b) With $C_{ao} = C_{bo} = 3$, what reaction time is needed for 80% conversion in a CSTR?

(c) Same as part (b), but in a PFR.

In the absence of diffusional limitations, $C_a = C_b$ and

$$r_a = \frac{k_1C_a^2}{(1+k_2\sqrt{C_a})^2}$$

and

$$y = C_a/\sqrt{r_a} = (1+k_2\sqrt{C_a})/\sqrt{k_1}$$

$$= 1.1955 + 0.5974\sqrt{C_a},\ \text{from the plot}$$

Accordingly $k_1 = 0.6997$, $k_2 = 0.4997$ and the rate equation becomes

$$r_a = \frac{k_1C_aC_{bi}}{(1+\sqrt{C_a})^2} = k_3(C_b-C_{bi})$$

Since $C_a = C_b$,

$$C_{bi} = C_b-r_a/k_3 = C_a-r_a/k_3$$

$$r_a = \frac{k_1C_a(C_a-r_a/k_3)}{(1+k_2\sqrt{C_a})^2} = \frac{k_1C_a^2}{(1+k_2\sqrt{C_a})^2+(k_1/k_2)C_a}$$

$$= \frac{0.7\quad C_a^2}{(1+0.5\sqrt{C_a})^2+0.778C_a} \qquad \text{(a)}$$

In the CSTR,

$$C_a = 0.2(3) = 0.6,\ r_a = 0.1054$$

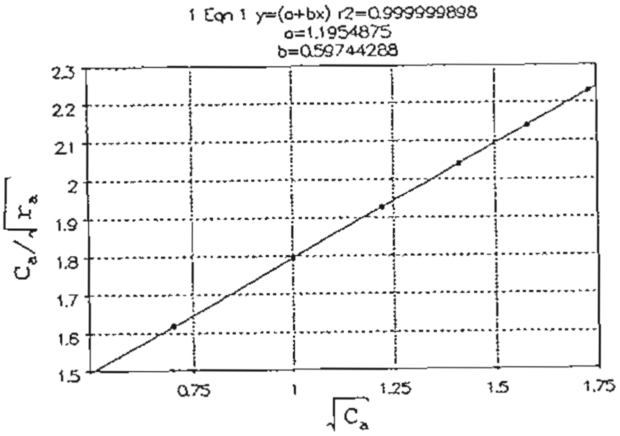
$$\bar{t} = (C_{a0}-C_a)/r_a = 2.4/(0.1054) = 22.77 \qquad \text{(b)}$$

In the PFR,

$$V_r/V' = \int_{0.6}^{3} dC_a/r_a = 0.308 \qquad (3)$$

by the trapezoidal rule.

C_a	r_a	$C_a/\sqrt{r_a}$	$\sqrt{C_a}$
3	1.8093	2.2303	1.7321
2.5	1.3640	2.1401	1.5811
2	0.9608	2.0404	1.4141
1.5	0.6058	1.9272	1.2247
1	0.3111	1.7928	1
0.5	0.0955	1.6180	0.7071



P6.06.08. FLOW REACTOR WITH DIFFUSION AND SURFACE REACTION

A solid catalyzed gas phase reaction, $A_2 \Rightarrow 2B$, normally has a rate equation dependent on the partial pressure of the reactant as follows,

$$r_s = 2p/(1+3\sqrt{p})^2, \quad \text{lbmol/(h)(lb catalyst)}$$

Under the conditions at which the reaction is to be conducted, however, the rate of diffusion to the catalyst surface also is a factor in the overall rate. The rate equation for diffusion is

$$r_d = 0.5(p_a-p_{ai})$$

When the feed is pure A and the pressure is 2 atm, find the ratio, W_c/n_{a0} lb catalyst/(lb feed/hr), needed to reduce the partial pressure from 2.0 to 0.2 in a PFR.

In the steady state,

$$r = 0.5(p_a-p_{ai}) = \frac{2p_{ai}}{(1+3\sqrt{p_{ai}})^2} = \frac{2(p_a-2r)}{(1+3\sqrt{p_a-2r})^2} \qquad (1)$$

Applying the gas law,

$$n_a = n_t(p_a/\pi) = (2n_{a0}-n_a)p_a/2 = \frac{2n_{a0}p_a}{2+p_a}$$

$$f = n_a/n_{a0} = \frac{2p_a}{2+p_a} \qquad (2)$$

Flow reactor equation is

$$-df = \frac{r dW}{n_{a0}}$$

$$W/n_{a0} = \int_f^1 df/r \qquad (3)$$

With p_a as a parameter, values of r are found from Eq (1)and f from Eq (2). Integration is with the trapezoidal rule. Values of W/n_{a0} are in the last column of the table.

p_a	p_{ai}	r	1/r	f	W/n_{a0}
2	1.7176	0.1412	7.0822	1	0
1.8	1.5244	0.1378	7.2559	0.9474	0.3771
1.6	1.3326	0.1337	7.4794	0.8889	0.8081
1.4	1.1417	0.1292	7.7399	0.8235	1.3058
1.2	0.9529	0.1235	8.0972	0.7500	1.8878
1.0	0.7668	0.1166	8.3612	0.6667	2.5733
0.8	0.5846	0.1077	9.2851	0.5714	3.4140
0.6	0.4081	0.0966	10.3520	0.4615	4.4931
0.4	0.2421	0.0790	12.6582	0.3333	5.9681
0.2	0.0966	0.0417	19.3424	0.1818	8.3921

P6.06.09. TEMPERATURE AND FLOW RATE VARIABLE

A gas phase reaction, A ⇒ B, is carried out under conditions where both surface reaction and diffusion to the external surface influence the overall rate of conversion. The feed rate is 200 lbmol/hr of pure A, the pressure is 2 atm and 50% conversion is required.

The surface reaction rate is

$r_s = k_1p_s/(1+k_2p_s)$

$k_1 = 3.0$ at 400 K, 6.0 at 425 K

$k_2 = 0.50$ at 400 K, 0.579 at 425 K

and the diffusion rate is

$r_d = k_3(p-p_s)$

$k_3 = 2.0$ at 5 lbmol/(h)(sqft), 6.06 at 20 lbmol/(h)(sqft)

Compare the amounts of catalyst needed for 50% conversion with these combinations of variables,

(a) 400 K, 20 lbmol/(h)(sqft)

(b) 425 K, 5 lbmol/(h)(sqft)

In the steady state,

$$r = k_3(p-p_s) = \frac{k_1p_s}{1+k_2p_s} = \frac{k_1(p-r/k_3)}{1+k_2(p-r/k_3)} \qquad (1)$$

The flow reactor equation is

$$dW = \int_1^2 \frac{dn_a}{r} = \frac{n_{a0}}{\pi}\int_1^2 \frac{dp_a}{r} = 100 \int_1^2 \frac{dp_a}{r}$$

The tabulation gives the values of r from Eq (1) at spacings designed for integration with Simpsons rule.

$W_{400,\ 20} = 47.27$ lb catalyst

$W_{425,\ 5} = 42.43$ lb catalyst

p_a	$r_{400,20}$	$r_{425,5}$
2	2.634	3.186
1.5	2.179	2.449
1	1.611	1.670

P6.06.10. DIFFUSION AND ADSORPTION IN A BATCH REACTOR

The rate of a liquid phase reaction is governed by diffusion to and adsorption on the surface of the catalyst. The steady state relation is

$$r = 2(C-C_s) = \frac{1.5C_s}{1+0.8C_s}$$

Find the batch time for change of C from 2.0 to 0.6.

The rate can be written

$$r = \frac{1.5(C-0.5r)}{1+0.8(C-0.5r)}$$

In a batch reactor,

$$t = \int_{0.6}^{2} dC/r = 1.946$$

The tabulation of the integrand is for application of Simpsons rule.

C	2	1.3	0.6
1/r	0.9807	1.2690	2.2836

P6.06.11. DIFFUSION AND SURFACE REACTION IN A PFR

Laboratory data were obtained for the gas phase reaction, 2A ⇒ B, starting with pure A, with the tabulated results. Pressure in atm and r in lbmol/(h)(cuft catalyst). The diffusion rate is

$$r_d = 0.2(p_{ag}-p_{as})$$

and the rate of the surface reaction has the form

$$r_s = k_1[p_{as}/(1+k_2p_{as})]^2$$

Find the amount of catalyst needed for 90% conversion at 10 atm, 900 R and a charge rate of 50 lbmol/h of pure A.

At steady state,

$$r = 0.2(p_{ag}-p_{as}) = k_1\left(\frac{p_{as}}{1+k_2p_{as}}\right)^2$$

$$p_{as} = p_{ag}-r/0.2$$

$$y = p_{as}/\sqrt{r} = (1+k_2p_{as})/\sqrt{k_1}$$

$$= 2.4 + 0.708p_{as}, \text{ from the linear plot}$$

$$k_1 = 0.1736,\ k_2 = 0.295$$

and the rate equation becomes

$$r = 0.708\left[\frac{p_{ag}-5r}{1+0.295(p_{ag}-5r)}\right]^2 \tag{1}$$

In the plug flow reactor,

$2A \Rightarrow B$

$$f = n_a/n_{a0}$$

$$p_{ag} = \frac{2f}{1+f}\pi$$

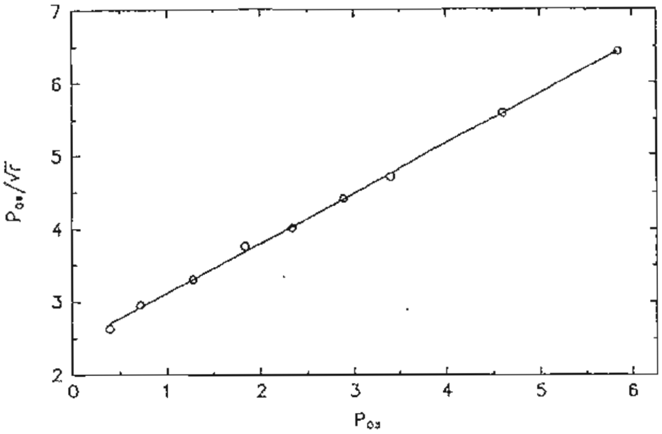
$$f = \frac{p_{ag}}{20-p_{ag}} \tag{2}$$

$$V_r/n_{a0} = V_r/50 = \int_f^1 \frac{df}{r} \tag{3}$$

The integral is shown in the last column of the table. For 90% conversion,

$$V_r = 50(10.982) = 99.1 \text{ Cuft}$$

p_{ag}	r	f	1/r	V_r/n_{ao}
10	0.83	1.00	1.205	0
8	0.68	0.667	1.471	0.446
6	0.52	0.529	1.923	0.849
5	0.425	0.333	2.353	1.055
4	0.335	0.250	2.985	1.276
3	0.235	0.176	4.255	1.544
2	0.147	0.111	6.803	1.903
1.82	0.133	0.100	7.519	1.982



P6.06.12. DIFFUSION AND SURFACE REACTION. EXPLICIT RATE EQUATION

The overall rate of a reaction governed by diffusioon and surface reaction is

$$r = (p-p_s)/k_1 = k_2p_s/(1+k_3p_s)$$

Given the tabulated data and $k_1 = 2$, find the values of the other constants and derive an explicit equation for the rate, r.

In linearized form the rate equation is

$$y = p_s/r = (1+k_3p_s)/k_2$$

$$= 1.4205 + 0.2862\ p_s,$$ from the linear plot

$$p_s = p - k_1r$$

$$k_1 = 2,\ k_2 = 0.704,\ k_3 = 0.2015$$

The rate equation

$$r = \frac{k_2(p-k_1r)}{1+k_3(p-k_1r)}$$

becomes in expanded form

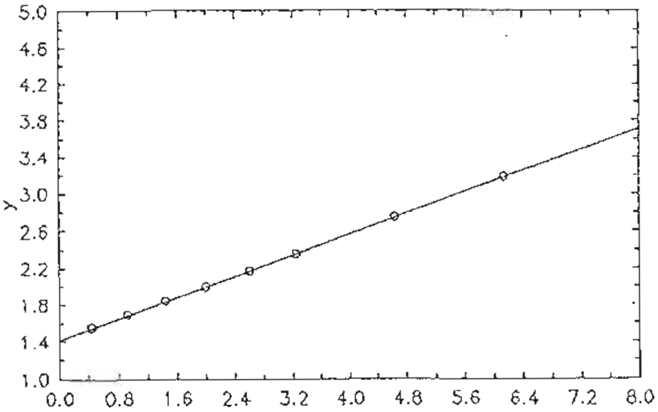
$$k_1k_3r^2 -(1+k_1k_2+k_3p) + k_2p = 0$$

or

$$0.403r^2 -(2.408+0.2015p)r + 0.704p = 0$$

This quadratic in r is readily solvable.

p	r	p_s	p_s/r
1	0.2814	0.4372	1.5536
2	0.5420	0.9160	1.6900
3	0.7814	1.4372	1.8392
4	1	2	2
5	1.1984	2.6032	2.1723
6	1.3775	3.2450	2.3557
8	1.6834	4.6332	2.7523
10	1.9293	6.1414	3.1832



P6.06.13. DIFFUSION AND SECOND ORDER SURFACE REACTION

The rate of a batch slurry reaction is controlled by diffusion from the bulk liquid to the surface of the catalyst and by a second order reaction on the surface. Equations for the two processes are

$$r_d = 0.25(C-C_s)$$

$r_s = 0.1C_s^2$

Integrate the rate equation over a range of conversions when starting with C = 2 lbmol/cuft.

At steady state,

$C_s = C - 4r$

$r = 0.1(C-4r)^2$

$16r^2 - (10+8C)r + C^2 = 0$

$t = \int_C^2 \frac{dC}{r}$

Integrands and integrals are tabulated.

C	1/r	t
2	5.81	0
1.8	6.80	
1.6	8.13	
1.4	10.0	
1.2	12.74	
1	17.06	9.82
0.8	24.61	13.99
0.6	40.0	20.45
0.4	81.27	32.58
0.2	288.6	69.56

P6.06.14. NET DESORPTION

The overall rate of the reaction, $A \Leftrightarrow B + C$, is controlled by the net rate of desorption of B from the surface and by the rate of diffusion of A to the surface. The data available are of the rate against fractional conversion of A at constant pressure and temperature. Find an expression for the rate in terms of the minimum number of constants to be evaluated.

At steady state,

$$r = k_1(p_a - p_{ai})$$

$$= k_2\vartheta_b^* - k_3p_b\vartheta_v$$

$$\vartheta_b^* = \frac{k_4p_{ai}}{p_c}\vartheta_v \quad \text{(surface reaction equilibrium)}$$

$$\vartheta_v = 1/[1+(k_5+k_4/p_c)p_{ai}+k_6p_c]$$

$$r = \frac{k_2k_4p_{ai}/p_c - k_3p_c}{1+(k_5+k_4/p_c)p_{ai}+k_6p_c} \qquad (1)$$

Replace

$$p_{ai} = p_a - r/k_1 \qquad (2)$$

The partial pressures are related to the fractional conversion of x when starting with pure A by

$$p_a = \frac{1-x}{1+x}\pi, \quad p_b = p_c = \frac{x}{1+x}\pi \qquad (3)$$

Six constants are involved in these non linear equations, which calls for either a nonlinear regression or the solution of six nonlinear equations at selected data points.

P6.06.15. DIFFUSION AND ADSORPTION

A reaction, A ⇒ B, is rate controlled by diffusion of A to the catalyst surface and by its adsorption. The diffusion coefficient is $k_1 = 1/3$ and these data are known: $r = 0.1538$ when $p_a = 1$ and $p_b = 0.5$; $r = 0.0625$ when $p_a = 0.5$ and $p_b = 1$. Find the overall rate equation.

The rates of the individual processes are equal in the steady state.

$$r_{diff} = k_1(p_a - p_{ai}),\quad k_1 = 1/3$$

$$r_{ads} = k_2 p_{ai}\vartheta_v = \frac{k_2 p_{ai}}{1+k_a p^*_{ai}+k_b p_b} = \frac{k_2 p_{ai}}{1+(k_a/K_e+k_b)p_b}$$

Combining and simplifying the constants,

$$r = \frac{k_2(p_a - r/k_1)}{1+k_3 p_b} = \frac{k_2 p_a}{1+k_2/k_1+k_3 p_b} = \frac{k_2 p_a}{1+3k_2+k_3 p_b}$$

Substituting the known data and solving the two simultaneous equations gives

$$k_2 = 0.5\ ,\quad k_3 = 1.5$$

$$r = \frac{0.5p_a}{2.5+1.5p_b}$$

P6.06.16. SECOND ORDER SURFACE REACTION

The rate of the reaction, 2A ⇒ Products, is limited by diffusion to the catalyst surface and the rate of the second order surface reaction. Only A is adsorbed appreciably. Given these data, find the rate equation.

p_a	1.0	1.5	2.0
r	0.3100	0.4935	0.6667

At steady state,

$$r = k_1(p_a - p_{ai}) = k\vartheta_a^2 = k_2\left(\frac{p_{ai}}{1+k_3 p_{ai}}\right)^2 = k_2\left[\frac{p_a - r/k_1}{1+k_3(p_a - r/k_1)}\right]^2$$

Substitute the three known sets of data, solve simultaneously and find

$$k_1 = 1.0,\ k_2 = 1.5,\ k_3 = 0.75$$

P6.06.17. A LIQUID PHASE L-H REACTION

The reaction, A+B ⇒ C, has a rate equation

$$r = \frac{172.1C_a C_b}{(1+2.16c_a+632.6C_b)^2}\quad \text{mol/(liter)(sec)}$$

Feed at the rate of 100 liters/min contains 0.1 mols/liter of each reactant. How large a flow reactor is needed to make 5 mols/min of C?

With equimolal reactants the rate equation becomes

$$r = 172.1\left(\frac{C}{1+634.8C}\right)^2$$

The flow reactor equation becomes

$$V_r/V' = \frac{V_r}{100/60} = \int_{0.05}^{0.1}\left(\frac{1+634.8C}{C}\right)^2 dC = 122.2$$

$$V_r = 203.5 \text{ liters}$$

P6.06.18. DIFFUSIONAL RESISTANCE OR NOT?

Experimental data are shown for the rate of a surface catalyzed reaction, 2A ⇒ B. It is expected that the rates of surface reaction and diffsion to the surface both are factors. The diffusional coefficient is $k_d = 137.5$.

At steady state,

$$r = 137.5(p_{ag}-p_{ai}) \qquad (1)$$

$$= k_1p_{ai}^2/(1+k_2p_{ai})^2 \qquad (2)$$

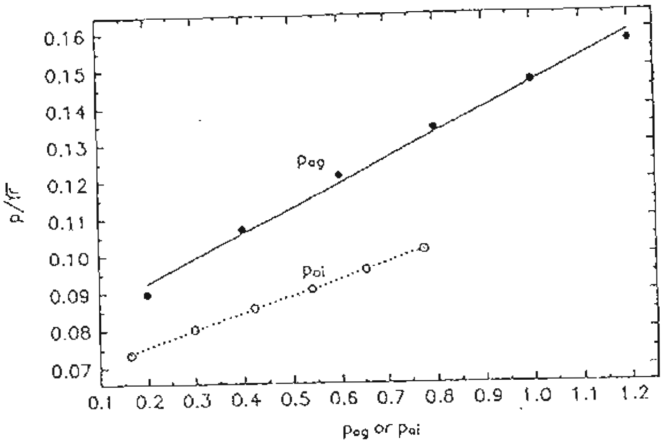
Values of p_{ai} are calculated from the first equation and substituted into the second. In linearized form,

$$p_{ai}/\sqrt{r} = (1 + k_2p_{ai})/\sqrt{k_1} \qquad (3)$$

The plot of Eq (3) is a good fit of the data. For comparison a plot also is shown of $p_{ag}/\sqrt{r}$ against p_{ag} which is not straight.

p_{ai} can be eliminated from the rate equation in favor of p_{ag}. Then a cubic equation results.

p_{ag}	r	p_{ai}	$p_{ai}/\sqrt{r}$	$p_{ag}/\sqrt{r}$
1.2	58.5	0.775	0.1013	0.1570
1.0	47.5	0.655	0.0961	0.1465
0.8	35.5	0.540	0.0909	0.1340
0.6	24.35	0.423	0.0857	0.1213
0.4	13.9	0.299	0.0802	0.1071
0.2	4.96	0.164	0.0735	0.0897



P6.06.19. MASS TRANSFER COEFFICIENT

Find the mass transfer coefficient by the method of Dwivedi & Upadhyay, Eq 6.23, for these conditions at 400 K and 2 atm:

viscosity, μ = 0.0003 g/(cm)(sec)
density, ρ = 0.002 g/cc
kinematic viscosity, k7n = υ/ρ = 0.15 $\mathrm{cm^2/sec}$
diffusivity, D = 0.12 $\mathrm{cm^2/sec}$
Schmidt number, Sc = ν/D = 1.25
superficial velocity, u = 100 cm/sec
porosity, ε = 0.4
particle diameter, d_p = 0.5 cm
Reynolds number, d_pu/ν = 333

Mass transfer coefficient,

$$k_c = \frac{u}{\varepsilon\ Sc^{2/3}}\left[\frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}\right]$$

$$= \frac{100}{0.4(1.16)}(0.00654 + 0.0378) = 9.76 \text{ cm/sec}$$

Rate of mass transfer,

$$r_d = k_c\Delta C \text{ gmol/(cm}^2\text{)(sec), with } \Delta C \text{ in gmol/cm}^3$$

$$\frac{k_c}{RT}\Delta P, \text{ w;ith } \Delta P \text{ in atm and } R = 82.05\ \frac{\text{atm(cm}^3\text{)}}{\text{gmol(}^0\text{K)}}$$

P6.06.20. FIVE STEPS CONTROLLING

For the reaction, A ⇒ B, external diffusional resistances are present and the substances are not in adsorptive equilibrium. Find the rate relation in terms of the following five steps:

$$r = k_1(p_{ag} - p_{ai}) \qquad \text{diffusion of } A \text{ to the surface} \tag{1}$$

$$r = k_2\left(p_{ai}\theta_v - \frac{\theta_a}{k_3}\right) \qquad \text{adsorption of } A \tag{2}$$

$$r = k_4\theta_a \qquad \text{surface reaction} \tag{3}$$

$$r = k_5\left(p_{bi}\theta_v - \frac{\theta_b}{k_6}\right) \qquad \text{desorption of } B \tag{4}$$

$$r = k_7(p_{bi} - p_{bg}) \qquad \text{diffusion of } B \text{ from the surface} \tag{5}$$

$$\theta_v = 1 - \theta_a - \theta_b \tag{6}$$

Under steady-state conditions, the rates of all five steps must be equal when they are correctly defined in terms of interfacial surface conditions.

The six equations contain five quantities which cannot be measured directly, namely, p_{ai}, p_{bi}, θ_a, θ_b, and θ_v. However, these unknowns can be eliminated by algebraic manipulation of the six equations, as follows:

$$p_{ai} = p_{ag} - \frac{r}{k_1} \tag{7}$$

$$p_{bi} = p_{bg} + \frac{r}{k_7} \tag{8}$$

$$\theta_a = \frac{r}{k_4} \tag{9}$$

$$\theta_b = 1 - \theta_a - \frac{1}{p_{ai}}\left(\frac{r}{k_2} + \frac{\theta_a}{k_3}\right) = 1 - \frac{r}{k_4} - \frac{k_1 r}{k_1 p_{ag} - r}\left(\frac{1}{k_2} + \frac{1}{k_3 k_4}\right) \tag{10}$$

$$\begin{aligned} r = {} & \frac{k_5(k_7 p_{bo} + r)}{k_7}\left(1 - \frac{r}{k_4}\right) \\ & - k_5\left(p_{bo} + \frac{r}{k_7} + \frac{1}{k_6}\right)\left[1 - \frac{r}{k_4} - \frac{k_1 r}{k_1 p_{ag} - r}\left(\frac{1}{k_2} + \frac{1}{k_3 k_4}\right)\right] \end{aligned} \tag{11}$$

The last equation contains only constants which can be evaluated from empirical data of r as a function of p_{ag} and p_{bg}, though the practical handling of this cubic equation presents some problems.

More tractable equations arise from fewer steps. Thus, consider only diffusion and surface reaction, that is, steps 1, 3, and 5. The partial pressures in the vicinity of the surface are p_{ai} and p_{bi}, so

$$\theta_a = \frac{k_1 p_{ai}}{1 + k_1 p_{ai} + k_2 p_{bi}} \tag{12}$$

$$p_{ai} = p_{ag} - \frac{r}{k_3} \tag{13}$$

$$p_{bi} = p_{bg} + \frac{r}{k_4} \tag{14}$$

Consequently,

$$r = k_5\theta_a = \frac{k_1 k_5 p_{ai}}{1 + k_1 p_{ai} + k_2 p_{bi}} = \frac{k_1 k_6 (p_{ag} - r/k_3)}{1 + k_1(p_{ag} - r/k_3) + k_2(p_{bg} + r/k_4)} \tag{15}$$

Rearranging,

$$\left(\frac{k_2}{k_4} - \frac{k_1}{k_3}\right)r^2 + \left(1 + \frac{k_1 k_6}{k_3} + k_1 p_{ag} + k_2 p_{bo}\right)r = k_1 k_6 p_{ag} \tag{16}$$

CHAPTER 7
REACTIONS WITH POROUS SOLID CATALYSTS

THEORY

PROBLEMS

INTRODUCTION

Catalysis by solids depends on the amount of surface exposed to the fluid. Large specific surface is obtained with small particles, but primarily with highly porous structures. For instance, to achieve 1 m^2/cc the diameter of a sphere must be reduced to $6(10^{-4})$ cm, but porous catalysts may have several hundred m^2/cc. Practical limitations exist to the smallness of particles that can be used, such as pressure drop and entrainment. In fixed or moving beds, particle diameters are several millimeters, in fluidized beds they may be less than 0.1 mm.

Internal surface of porous particles also has limitations. Diffusional resistances of participants may be such that only a fraction of the pore surfaces is accessed, resulting in a waste of expensive catalyst, or undersizing of equipment that is designed for full utilization of the catalytic surface. Appraising the effectiveness of internal surface is the main thesis of this chapter.

7.1. PARTICLES AND PORES.

Catalyst manufacturing processes usually make particles in a distribution of sizes, although special shapes such as Raschig rings or cylinders made by extrusion and other shapes made by stamping may be quite uniform. Size distribution is measured by sieving or elutriation. A mean diameter is a convenient quantity. The kind of mean value that is applicable when surface is the main property of interest is the volume-surface mean that is applied in P7.01.09.

Measurement of other properties also is treated in Chapter 6. Pore volume is measured with helium and mercury pososimeters that together measure the empty space between particles and within particles. P6.01.05 is an example of this type. Porosities of commercial catalytic particles are 0.1-0.3 cc/cc. Measurement of pore diameters is described in P6.01.01. A mean diameter may be figured on the assumption that the pores are parallel uniform cylinders as

$$\bar{d}_p = 2V_p/S_p \qquad (7.1)$$

where V_p is the volume of the pores and S_p is their specific suface; such a calculation is made in P6.01.06. The range of practical pore diameters is 10-100 Angstroms (1 A = 10^{-8} cm). Specific surface is measured through nitrogen adsorption; several cases are treated in Section P6.01.

Shapes of pores have a great effect on diffusion through them. They are greatly varied and usually cannot be observed directly for commercial materials. For theoretical comparisons they may be assumed parallel cylinders of some mean diameter. Diffusion experments also have been performed with parallel small capillaries.

Theoretical considerations lead to the conclusion that the travel path through a bed of particles is $\sqrt{2}$ times the nominal thickness of the bed. When uniform cylindrical pores are distributed randomly, Peng & Stewart (IEC Fund 12 143, 1973) find that $\tau = 3$. Other factors such as distribution of sizes and variable diameters along single pores lead to the concept of a generalized tortuosity, τ. This is a factor by which a theoretical diffusivity must be divided to find the effective diffusivity.

$$D_{\text{effective}} = D_{\text{theoretical}}/\tau \qquad (7.2)$$

There are no correlations for τ but the range can be from less than 1.0 to more than 10.

7.2. DIFFUSION AND DIFFUSIVITY.

The statement that rate of diffusion is proportional to the concentration gradient is known as Fick's law (1855),

$$r_d = -D\frac{\partial C}{\partial z} \qquad (7.3)$$

where D is the diffusivity, cm^2/s in typical units. A one dimensional extension is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}(D\frac{\partial C}{\partial z}) \qquad (7.4)$$

and

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \qquad (7.5)$$

when D is independent of position. There are books full of solutions of these and related equations. A digest with emphasis on chemical reactions is by Walas (*Modelling with Differential Equations in Chemical Engineering,* 1991) Two examples are presented in this chapter in abbreviated fashion as P7.02.06 and P7.02.07

In a bed of particles with concentrations C_g in the fluid and C_s on the surface of the particle, the rate of mass transfer is

$$r_d = k_g a(C_g-C_s), \text{ mols/(s)(cc)} \qquad (7.6)$$

where a is surface per unit volume, cm^2/cc in typical units; for spheres, a = $6/d_p$. Many empirical correlations have been developed for the mass transfer coefficient (Sherwood et al, Mass Transfer, 1975). One is cited in Section 6.12 and applied in P7.06.19 and P7.07.14.

7.2.1. Molecular diffusivity

Resistance to transfer of material by diffusion is caused by collisions with other molecules and with the walls of narrow passages. The corresponding diffusion coefficients are termed molecular diffusivity D_m and Knudsen diffusivity D_k. A fundamental equation for D_m was developed by Stefan and Maxwell (about 1871); it is cited in P7.01.06. In terms of mol fraction driving force, the rate of molecular diffusion is

$$r_d = -D\frac{\partial C}{\partial z} = \frac{DP}{RT}\frac{\partial y}{\partial z} = kT^{0.5}\frac{\partial y}{\partial z} \qquad (7.7)$$

Thus the rate of diffusion varies as the square root of the temperature and independently of pressure. This is different from Knudsen diffusion which is proportional to pressure and inversely to $\sqrt{T}$.

7.2.2. Knudsen diffusivity

Collisions of molecules with the walls of the passage provide the resistance to diffusion when the mean free path, λ, is appreciably greater than the diameter, d, of the passage. In experimental work the ratio, λ/d, is taken as 10 or more to isolate the Knudsen effect. That investigator did experiments with small capillaries and deduced the equation

$$D_k = \frac{2}{3} r_e \left(\frac{8RT}{\pi M}\right)^{1/2} = 9700\ r_e\sqrt{T/M}\quad \text{cm}^2/\text{s} \qquad (7.8)$$

where r_e , in cm, is the radius of the pore and M is the molecular weight of the gas.

Assuming uniform cylindrical pores, the radius is expressed in terms of the pellet density ρ_p, the specific surface S_p and porosity ε. This converts the equation to

$$D_k = \frac{19400\ \varepsilon}{S_p\rho_p}\sqrt{\frac{T}{M}} \qquad (7.9)$$

With driving force expressed in mol fractions, the rate of Knudsen diffusion is

$$r_d = -D_k\frac{\partial C}{\partial z} = -\frac{D_k}{RT}\frac{\partial P}{\partial z} = -\frac{D_k}{RT}\frac{\partial y}{\partial z}$$

$$= \frac{9700 r_e}{R\sqrt{MT}}\frac{\partial P}{\partial z} = \frac{9700\ r_e P}{R\sqrt{MT}}\frac{\partial y}{\partial z} \qquad (7.10)$$

which may be compared with Eq 7.7 for molecular diffusion.

The two kinds of diffusivities are calculated in P7.01.07.

As a rough rule, Knudsen diffusion predominates when the ratio of mean free path to pore radius, $\lambda/r_e \geq 10$ or so, and molecular when $\lambda/r_e \leq 0.1$. For common gases at atmospheric conditions these values correspond to pore radii of 50 to 5000 Å.

This makes for two not entirely consistent rules for the transitional range,

$$0.1 \leq \lambda/r_e \leq 10 \qquad (7.11)$$

$$10\lambda \geq r_e \geq 0.1\lambda \qquad (7.12)$$

Data of mean free paths may be found in CRC Handbook of Chemistry and Physics. Since these ranges include many porous catalysts, the intermediate diffusional range is of practical interest. The subject is treated by Scott & Dullien (AIChE J 8 113, 1962). A simpler rule than theirs is that of Pollard & Present (Phys Rev 73 762, 1948)

$$\frac{1}{D} = \frac{1}{D_m} + \frac{1}{D_k} \qquad (7.13)$$

7.2.3. Effective diffusivity.

In working with porous materials it is convenient to express the mass transfer per unit superficial cross section and per unit length of the particle. The fractional open cross section is the same as the porosity, ε. A correction for the length of path is incorporated with factors for dead ends, a distribution of pore diameters and variations in shapes of passages into a term called the tortuosity, τ. An effective diffusivity accordingly is defined as

$$D_{eff} = D\varepsilon/\tau \tag{7.14}$$

Then Knudsen diffusivity becomes

$$D_{k,eff} = \frac{19400\ \varepsilon^2}{\tau S_p \rho_p}\sqrt{\frac{T}{M}} \tag{7.15}$$

There are no correlations for tortuosity. Sometimes a value of $\tau = 4$ is mentioned or a rule such as

$$\tau\sqrt{\varepsilon} = 2.46 \tag{7.16}$$

where ε is the fractional porosity. To a collection of data on 24 commercial catalysts by Satterfield and Cadle (IECPDD 7 256, 1968) for instance, this rule applies overall, but the range is from 0.21 to 5.75 which does not inspire confidence in 2.46. Apparently τ covers too many particle properties for a simple correlation to be adequate. The effects of distribution of pore diameters and of pore shape are touched on in P7.01.01 and P7.01.02. It is found that the tortuosity of parallel pores of different diameters is less than one, and that of a pore with variable cross section is greater than one. It may perhaps be concluded that small values of tortuosity are due to the presence of some relatively wide pores, and large values to the presence of constricted or dead end pores. At present, apparently, only experiment really can find effective diffusivity.

7.3. EQUATIONS OF DIFFUSION AND REACTION

In reacting systems, transfer of matter and heat occurs by bulk flow and diffusion or conduction. Usually transfer in an axial direction is appreciable by bulk flow only. In a rectangular region the various elements of a material balance in one dimensional flow are,

$$\text{Output} - \text{Input} = -d(A\ D\frac{\partial C}{\partial x}) + d(uAC)$$

$$\text{Sink} = kC^n dV = kC^n A dx \text{ or } = r_c dV \text{ in general}$$

$$\text{Accumulation} = \frac{\partial C}{\partial t}\, dV$$

Putting it together with constant diffusivity,

$$-D\frac{\partial^2 C}{\partial x^2} + u\frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + r_c = 0 \tag{7.17}$$

Similarly a heat balance equation is

$$-\lambda\frac{\partial^2 T}{\partial x^2} + u\rho C_p\frac{\partial T}{\partial x} + \rho C_p\frac{\partial T}{\partial t} + \Delta H_r r_c = 0 \tag{7.18}$$

Similar equations may be developed for other geometries such as spheres and cylinders. To complete the mathematical representation of a problem, initial and boundary conditions are specified.

Dimensionless variables. Equations may be more convenient to handle in terms of the dimensionless variables,

$y = C/C_r$

$z = x/L$, in rectangular coordinates

$\rho = r/R$, in a sphere or cylinder

$t_r = t/\tau$

where C_r is a reference concentration, such as an initial or inlet or boundary concentration and τ is a reference time such as mean residence time or other time interval typical of the system. Substitution into the first equation makes it, after rearrangement,

$$-\frac{\partial^2 y}{\partial z^2} + \frac{1}{Pe}\frac{\partial y}{\partial z} + \frac{\partial y}{\partial t_r} + \phi_L^2\, y^n = 0 \qquad (7.19)$$

The two dimensionless groups are

Peclet number, $Pe = D/uL$ (7.20)

Thiele modulus for a slab, $\phi_L = L\sqrt{k_v C_r^{n-1}/D}$ (7.21)

A large number of analytical solutions of these equations appear in the literature. Mostly, however, they deal only with first order reactions. All others require solution by numerical or other approximate means. In this book, solutions of two examples are carried along analytically part way in P7.02.06 and P7.02.07. Section 7.4 considers flow through an external film, while Section 7.5 deals with diffusion and reaction in catalyst pores under steady state conditions.

7.4 DIFFUSION AND REACTION ON NONPERMEABLE SOLID CATALYSTS

In the steady state, the rate of diffusion to the surface equals the rate of reaction on the catalytic surface,

$r = k_g a(C_g - C_s) = k_v C_s^n$ (7.22)

for a power law rate equation on the surface. In normalized form,

$1 - y = Da\ y^n$ (7.23)

$y = C_s/C_g$

$Da = k_v C_g^{n-1}/k_g a$, Damkohler number (7.24)

A relation of special interest is the ratio of the rate of reaction under external diffusional conditions to the rate in the absence of diffusional resistance. This is called the external effectiveness, η_e, and may be written

$$\eta_e = \frac{k_v C_s^n}{k_v C_g^n} = (C_s/C_g)^n = y^n \qquad (7.25)$$

Then the rate of reaction in terms of the bulk fluid concentration may be written

$r = k_v \eta_e C_g^n$ (7.26)

Solutions for η_e with several power law equations are developed in P7.03.14 and for an L-H rate equation in P7.03.15.

7.5. DIFFUSION AND REACTION IN PORES. EFFECTIVENESS

For diffusion with reaction in uniform pores in a sphere, the steady material balance is

$$\frac{d^2 f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho} = \phi_s^2\, f^n \qquad (7.27)$$

in terms of normalized variables and a Thiele modulus,

$f = C/C_s$, $\rho = r/R$, $\phi_s = R\sqrt{k_v C_s^{n-1}/D_{eff}}$ (7.28)

At the inlet of the pore, $\rho = 1$, $f = f_s$ (7.29)

At the center of the sphere, $\rho = 0$, $df/d\rho = 0$ (7.30)

In P7.03.01 these equations are written for other geometries.

Integration. When a numerical solution is required, the second order equation is solved as the linear pair,

$$\frac{df}{d\rho} = f', \quad \frac{df'}{d\rho} = \phi_s^2 f^n - \frac{2}{\rho}f'$$

Because the boundary conditions are at two points, the shooting method is applicable:

(i) Start at the center where $f' = df/d\rho = 0$. Assume a trial value of $f = f_0$.

(ii) Integrate backwards to the surface where $\rho = 1$ and note if the requirement $f = f_s$ is met. If not, re[peat with other trial values of f_0.

(iii) When the requirement is met, the value of the derivative $(df/d\rho)_{r=R}$ also will be known.

Effectiveness. As the reactant diffuses through a pore it reacts with the wall and a concentration gradient develops. A concept of catalyst effectiveness, η, however, enables the rate of reaction to be expressed in terms of the constant concentration C_s at the inlet to the pore, as

$$r_c = k\eta f(C_s) \qquad (7.31)$$

The effectiveness is the ratio of the real rate and an ideal rate on the assumption that all of the pore surface is exposed to C_s. The real rate equals the rate of diffusion into the pore at steady state,

$$r_{real} = k_v A\left(\frac{dC}{dr}\right)_{r=R} \qquad (7.32)$$

$$r_{ideal} = k_v V_r f(C_s) \qquad (7.33)$$

The gradient at the pore mouth is found after integration of Eq 7.27.

For simple power law rate equations the effectiveness can be expressed in terms of the Thiele modulus, Eq 7.28. In those cases restriction is to irreversible, isothermal reactions without volume change. Other cases can be solved, but then the Thiele modulus alone is not sufficient for a correlation.

The chief cases that are the subject of the problems here are zero, first and second order in spheres, slabs and cylinders with sealed flat ends, problems P7.03.03 to P7.03.11. A summary of calculations of effectiveness is in P7.03.02. The correlations are expressed graphically and either analytically or as empirical curve fits for convenience of use with calculator or computer. A few other cases are touched on: L-H type rate equation, conical pores and changes in volume. Nonisothermal reactions are in another section.

Generalization. It has been observed that all plots of effectiveness against Thiele modulus are similar and that a single plot can represent the nine main cases fairly adequately by defining a generalized modulus as

$$\phi_m = 3\left(\frac{V_p}{A_p}\right)\left(\frac{3}{n+1}\right)^{1/2}\left(\frac{k_v C_s^{n-1}}{D_{eff}}\right)^{1/2} \qquad (7.34)$$

V_p/A_p = (volume of particle)/(external surface of particle)

R/3 for spheres

L for a slab with one permeable face

R/2 for a cylinder with sealed flat ends

n = order of reaction

This value of the modulus is to be used in the result for second order in a sphere, namely,

$$\eta = \frac{1.0357+0.3173\phi_m+0.000427\phi_m^2}{1+0.4172\phi_m+0.139\phi_m^2} \qquad (7.35)$$

Figure 4 of P7.03.02 of this generalized correlation reveals that only zero order deviates much, in the range from about $\phi = 1$ to 5. Since effective diffusivities are rarely known other than roughly such an error may not be significant.

An effectiveness of a given size of pellet can be determined experimentally by running tests of reaction conversion with a series of diminishing sizes of pellets until a limiting rate is found. Then η will be the ratio of the rate with the pellet size in question to the limiting value. Application of such a result is in P7.03.20.

Since theoretical calculation of effectiveness is uncertain and is moreover sensitive to operating conditions, for industrially important cases it is determined by such reaction tests. Common types of curve fits may be used. For ammonia synthesis catalyst, for instance, an equation is provided by Dyson & Simon (IEC Fundam <u>7</u> 605, 1968) in terms of temperature and fractional conversion,

$$\eta = a_0+a_1T+a_2x+a_3T^2+a_4x^2+a_5T^3+a_6x^3 \qquad (7.36)$$

The pellets were 6-10 mm, and different constants are provided at 150, 225 and 300 atm.

7.6. EXTERNAL AND INTERNAL DIFFUSION

In many situations of practical interest, an appreciable drop in concentration arises between a fluid phase and the external surface of the catalyst because of diffusional resistance. In the steady state, the rate of diffusion to the external surface equals the rate of input to the pore mouth,

$$r_d = k_g a(C_g-C_s) = D(dC/dr)_{r=R,C=C_s} \qquad (7.37)$$

When the rate of reaction is known as a function of the concentration,

$$r_c = f(C) \qquad (7.38)$$

the value of the derivative in Eq 7.37 is found by solution of the pore equation

$$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = \frac{1}{D} f(C) \qquad (7.39)$$

An overall effectiveness, η_t, then can be defined as

$$\eta_t = \frac{A_pD(dC/dr)_{r=R}}{V_pf(C_g)} \qquad (7.40)$$

For first order reaction in a porous slab this problem is solved in P7.03.16. Three dimensionless groups are involved in the representation of behavior when both external and internal diffusion are present, namely, the Thiele number, a Damkohler nunmber and a Biot number. Problem P7.03.16 also relates η_t to the common effectiveness based on the surface concentration,

$$\eta = \frac{A_pD(dC/dr)_{r=R}}{V_pf(C_s)} \qquad (7.41)$$

For a second order reaction in a slab or a sphere, analytical solutions proceed in terms of elliptic functions beyond the solution of P7.03.11, although a numerical solution throughout may be preferable. Such a numerical procedure is adopted in P7.03.19 for a second order reversible reaction.

In those cases where the internal effectiveness is known in equation form, the steady state rate relation may be written

$$r_d = k_g a(C_g-C_s) = k_v\eta C_s^n \qquad (7.42)$$

When the various constants are known, the Thiele modulus is used in the form

$$\phi = k_\phi\sqrt{C_s^{n-1}} \qquad (7.43)$$

and the effectiveness is taken from P7.01.01, for instance,

$$\eta = \frac{1.0357+0.3179\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (7.44)$$

When a value of C_g is specified, corresponding values of ϕ, η and C_s can be found by simultaneous solution of the last three equations. Then a plug flow reactor, for instance, can be sized as

$$V_r/V' = \int_g^{C_{g0}} \frac{dC_g}{k_g a(C_g-C_s)} \qquad (7.45)$$

Problems P7.05.06, P7.05.09, P7.05.12, P7.05.14 and others of the same Section use this method of solution.

7.7. VARIABLE TEMPERATURE

Porous solids are not good conductors of heat, so reactions with appreciable heats of reaction can develop significant gradients of temperature and reaction rate along the pore, as well as over an external film. Enhancement of a rate by temperature can counteract the effect of falling concentration. Exothermic reaction rates in pores, as a consequence, can be much greater than at the surface condition. Another peculiarity that can arise with adiabatic reactions is multiple steady states.

For slab geometry as an example, the material and energy balances over a pore are

$$D\frac{d^2C}{dx^2} = r_c \qquad (7.46)$$

$$\lambda\frac{d^2T}{dx^2} = -\Delta H_r r_c \qquad (7.47)$$

Elimination of r_c followed by integration gives the linear relation between temperature and concentration in the pore,

$$T-T_0 = \frac{-\Delta H_r D}{\lambda}(C_0-C) \qquad (7.48)$$

The maximum temperature difference will develop when C = 0, that is,

$$(T-T_0)_{max} = \frac{-\Delta H_r D C_0}{\lambda} \qquad (7.49)$$

Problems P7.06.03 and P7.06.04 are numerical examples. Usually a temperature drop through an external film is much greater than over a pore.

An effectiveness parameter can be developed with simultaneous solution of the material and heat balances. A numerical solution is necessary. Besides the Thiele modulus, two other parameters are involved,

$$\beta = \frac{(\Delta T)_{max}}{T_0} = \frac{-\Delta H_r D}{\lambda T_0}C_0 \text{ , Heat of reaction parameter} \qquad (7.50)$$

$$\gamma = \frac{E}{RT_0}, \text{ Activation energy parameter} \qquad (7.51)$$

Problem P7.06.02 reproduces one result from the literature. There it is apparent that in some ranges of the parameters, effectiveness can be much greater than unity, and also that at low values of Thiele modulus several steady states are possible. When both external and internal adiabatic diffusion occur, moreover, other studies find that half a dozen or more steady states can exist. Those kinds of findings involve much computer work. A book by Aris (Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, Vol II, 1975) deals with such problems.

7.8. DEACTIVATION OF CATALYSTS

Causes of decline in catalyst activity can be physical or chemical. The surface may sinter because of hot spots or the surface crystals can grow. Chlorine for instance causes crystal growth of copper and iron catalysts. Sulfur and arsenic form stable nonvolatile compounds with ammonia synthesis catalysts. Metallic catalysts - Ni, Fe, Pt and others - are poisoned by sulfur. Oxygen compounds are temporary poisons in ammonia synthesis since activity can be restored by operating for a time with a stream free of the culprit impurity. Other cases of this kind also occur. Trace metal deposition on cracking catalyst eventually requires replacement of the catalyst. Traces of acetylene and nitric oxide in shift catalysis cause gum deposits. Coke deposits from petroleum feed stocks can be burned off in suitably designed plant. Some platinum reformers operate with several reactors simultaneously on stream, one being always regenerated.

Testing of catalyst poisoning is best done in CSTRs since then all of the catalyst is exposed to the same concentration of impurity and the temperature is uniform.

7.8.1. DEPENDENCE ON TIME

Activity may depend on time on stream. One index of activity is the ratio of the rate at time t to the rate with fresh catalyst,

$$\alpha = \frac{r_c \text{ @ } t}{r_c \text{ @ } t=0} \tag{7.52}$$

The rate of gradual destruction of active sites and pore structure can be expressed as a mass action relation, for instance a second order reaction,

$$-\frac{d\alpha}{dt} = k_d\alpha^2 \tag{7.53}$$

and the integral

$$\alpha = \frac{1}{1+k_d t} \tag{7.54}$$

The constant is expected to have an Arrhenius dependence on temperature. Deactivation by coke deposition in cracking operations apparently has this kind of correlation.

Assumption of a first order rate law gives rise to

$$\alpha = \exp(k_1-k_2t) \tag{7.55}$$

Another relation sometimes successful is

$$\alpha = \frac{1}{1+k_1t^{k_2}} \tag{7.56}$$

When the feed stock contains constant proportions of reactive impurities, the rate of decline also may depend on the concentration of the main reactant, thus

$$-\frac{d\alpha}{dt} = k_d\alpha^pC^q \tag{7.57}$$

Such a differential equation together with a rate equation for the main reactant constitute a pair that must be solved simultaneously. Take the example of a CSTR for which the unsteady material balance is

$$C_0 = C + k\bar{t}\alpha C^q + \bar{t}\frac{dC}{dt} \tag{7.58}$$

Problem P7.06.16 solves the last two equations simultaneously.

The constants of the various time dependencies of activity are found by methods like those for finding constants of any rate equation, given suitable data.

7.8.2. UNIFORM DEACTIVATION

Two limiting cases of the behavior of catalyst poisons have been recognized. In one, the poison is distributed uniformly throughout the pellet and degrades it gradually. In the other, the poison is so effective that it kills completely as it enters the pore and is simultaneously removed from the stream. Complete deactivation begins at the mouth and moves gradually inward.

When uniform poisoning occurs the specific rate declines by a factor $(1-\beta)$ where β is the fractional poisoning. Then a power law rate equation becomes

$$r_c = k_v(1-\beta)\eta C_s^n \tag{7.59}$$

The effectiveness also depends on β through the Thiele modulus,

$$\phi = L\sqrt{\frac{k_v(1-\beta)C_s^{n-1}}{D_{eff}}} \tag{7.60}$$

To find the effectiveness under poisoned conditions this form of the modulus is substituted into the various equations for effectiveness summarized in problem P7.03.02 and given elsewhere in the same Section. For first order reaction in slab geometry, for instance,

$$\eta = \frac{1}{L}\sqrt{\frac{D}{k_v(1-\beta)}}\ \tanh[L\sqrt{\frac{k_v(1-\beta)}{D}}] \tag{7.61}$$

For a first order reaction in a slab the rate of reaction thus becomes,

$$r_c = k_v(1-\beta)\eta C_s = k_v(1-\beta)\ \frac{\tanh(\phi)}{\phi}\ C_s$$

$$= \frac{\sqrt{k_v(1-\beta)D}}{L}\ \tanh[L\sqrt{\frac{k_v(1-\beta)}{D}}]\ C_s \tag{7.62}$$

7.8.3. PORE MOUTH (OR SHELL) POISONING

When the complete poisoning of a pore surface begins at the mouth and moves gradually inward, the reactant must diffuse through the dead zone before it starts to react. A sketch of such a pore state is in P7.06.97. β is the fraction of the pore that is deactivated, C_1 is the concentration at the end of the inactive region, and $x = (1-\beta)L$ is the coordinate there.

The rate of diffusion into the pore equals the rate of diffusion through the dead zone,

$$D(\frac{dC}{dx})_{x=(1-\beta)L} = D\ \frac{\Delta C}{\Delta x} = D\ \frac{C_s-C_1}{\beta L} \tag{7.63}$$

The pore equation for a slab is

$$\frac{d^2C}{dx^2} = \frac{k}{D}\ C^n \tag{7.64}$$

At a sealed face or at the center of a slab with two permeable faces,

$$(\frac{dC}{dx})_{x=0} = 0 \tag{7.65}$$

The usual shooting method can be applied to the solution of the last three equations. This is done in problem P7.06.07 for first order reaction.

A comparison of uniform and pore mouth poisoning appears in P7.06.08 as a function of fractional poisoning. At a given fraction, effectiveness is reduced much more by pore mouth poisoning.

P7.01.01. PARALLEL PORES OF TWO DIAMETERS

Compare Knudsen flow through two parallel pores of different diameters with that through two equal pores of the same total cross section.

Knudsen flow rate with a specified pressure gradient is

$$N = k' r_e A \, dP/dz = kd^3$$

One pore has a diameter d and the other a diameter nd. The uniform pore size is given by

$$2d_m^2 = d^2+(nd)^2$$

and

$$d_m = d\sqrt{\frac{n^2+1}{2}}$$

The ratio of the flows is

$$\tau = N_m/N = \frac{kd^3{}_m}{k[d^3+(nd)3\,]} = \frac{2}{n^3+1}\left(\frac{n^2+1}{2}\right)^{3/2}$$

Values are tabulated. Flow rate is greater through the two sizes of pores.

n	1	2	3	5	10	∞
τ	1	0.878	0.799	0.744	0.717	0.707

P7.01.02. FLOW THROUGH A TRUNCATED CONE

Compare Knudsen flows through a truncated cone of radii d_0 and d_1 with that through a uniform pore of the same length and volume and pressure difference.

At a fractional distance, z/L, from the small end the diameter is

$$D = d_0+\frac{d_1-d_0}{L}z$$

Knudsen flow is

$$N = -kD^3\frac{dP}{dz}$$

The integral is

$$k\Delta P/N = \int_L^0 dz/D^3 = \frac{L}{2}\frac{d_0+d_1}{(d_0d_1)^2}$$

and the flow rate is

$$N = \frac{2k\Delta P}{L}\frac{(d_0d_1)^2}{d_0+d_1} \qquad (1)$$

The diameter of a cylinder of the same length and volume is

$$d_m = \sqrt{\frac{d_o^2+d_1^2+d_0d_1}{3}}$$

The flow through the cylinder is

$$N_m = k\frac{\Delta P}{L}d_m^3 \qquad (2)$$

In terms of $m = d_1/d_0$ the ratio of flow rates is

$$\tau = N_m/N = \frac{m+1}{2m^2}\left(\frac{m^2+m+1}{3}\right)^{3/2}$$

Values are tabulated. The uniform pore (m = 1) accomodates the greater flow rate.

$m = d_1/d_0$	1	2	3	5	10	∞
$\tau = N_m/N$	1	1.337	2.005	3.986	12.378	∞

P7.01.03. PORES WITH NORMAL DISTRIBUTION OF SIZES

The distribution of pore radii of a catalyst is statistically normal with

$$y = \frac{1}{\sigma\sqrt{2\pi}}\exp(-z^2/2), \quad z = (r-\bar{r})/\sigma, \quad \bar{r} = 10, \quad \sigma = 4$$

Compare Knudsen flow through these pores with that through an assembly of uniform pores with r = 10 and the same total cross section.

Knudsen flow varies as r^3 and the cross section as r^2. Take a total of 200 pores. On the plot, divide the area under the curve into 20 equal parts and label each part with the average value $\bar{z}$ in that part. The curve is symmetrical. The corresponding radii in each part are tabulated. Find

$\Sigma nr^3 = 10(29145) = 291450$

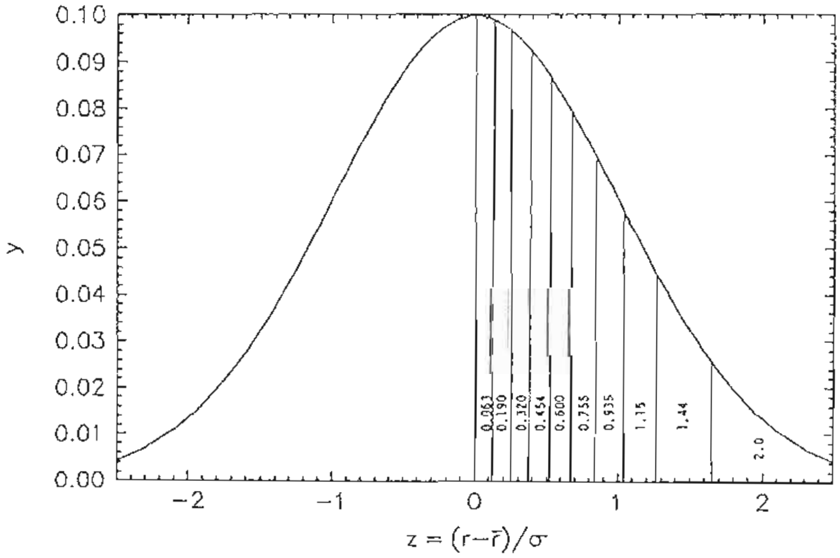
$\Sigma nr^2 = 10(2305) = 23050$

Number of uniform pores = $23050/(10^2) = 230.5$

$$\text{Ratio} = \frac{\text{Flow through uniform pores}}{\text{Flow through distributed pore sizes}}$$

$$= \frac{230.5(10^3)}{291450} = 0.7908$$

Area	$\bar{z}$	r
1	2.00	2.0
2	1.44	4.24
3	1.15	5.44
4	0.935	6.26
5	0.755	6.98
6	0.600	7.60
7	0.454	8.18
8	0.320	8.72
9	0.190	9.24
10	0.063	9.75
11	0.063	10.25
12	0.190	10.76
13	0.320	11.28
14	0.454	11.82
15	0.600	12.40
16	0.755	13.02
17	0.935	13.74
18	1.15	14.56
19	1.44	15.76
20	2.00	18.00



P7.01.04. PORE TORTUOSITY

A naphtha is desulfurized by reducing its thiophene content with hydrogen at 660 K and 30 atm. The reaction is apparently first order with k = 0.3 cc thiophene/(g catalyst)(sec). The catalyst particle diameter is 0.35 cm, true density 2.65 g/cc, specific surface 180 m^2/g, porosity 40%. In an experiment with very fine particles, conversion was 90%, but with the particles in question it was 70%. Find the effectiveness of the catalyst and the tortuosity of the pores.

Particle density = 0.6(2.65) = 1.59 g/cc

Specific rate, $k_v = 0.3(1.59)$

$= 0.477$ cc thiophene/(cc cat)(sec)

Assuning uniform cylindrical pores, the pore radius is

$$r = 2V_p/S_p = \frac{2(0.4)}{1.59(180(10^4)} = 28(10^{-8})\text{ cm}$$

Knudsen diffusivity,

$$D = 9700\, r\sqrt{T/M} = 9700(28)(10^{-8})\sqrt{660/84.1} = 0.0076\text{ cm}^2/\text{s}$$

Effective diffusivity

$$D_e = D\vartheta/\tau = 0.0076(0.4)/\tau = 0.00304\tau \qquad (1)$$

With fine particles the effectives is $\eta = 1$ and

$$k\bar{t} = \ln(1/0.1) = 2.303$$

With the large particles,

$$k\eta\bar{t} = \ln(1/0.3) = 1.0987$$

Effectiveness is

$$\eta = 1.0987/2.303 = 0.477 \qquad (2)$$

Thiele modulus is

$$\phi = R_p\sqrt{k_v/D_e} = 0.175\sqrt{0.477\tau/(0.00304)} = 2.19\sqrt{\tau} \qquad (3)$$

For first order reaction in spherical particles,

$$\eta = \frac{1}{\phi}\left(\frac{\phi}{\tanh(\phi)} - \frac{1}{\phi}\right) = 0.477$$

$$\phi = 3.9 \qquad (4)$$

and the tortuosity is

$$\tau = (3.9/2.19)^2 = 3.73 \qquad (5)$$

P7.01.05. DIFFUSION THROUGH A POROUS PLATE

Permeability tests were made on a porous plate 25 cm^2 across and 0.5 cm thick at a pressure difference of 0.5 atm. The measured diffusion rate was 0.3 gmol/hr. Upstream pressure was 1.5 atm and the temperature was 573.2 K. The plate had these additional properties: $\rho_p = 1.5$ g/cc, $S_p = 200$ m^2/g., porosity 0.75 cc/cc. Find the tortuosity of the plate.

The pore radius is

$$r = \frac{2\vartheta}{S_p\rho_p} = \frac{2(0.75)}{200(10^4)(1.5)} = 50(10^{-8})\text{ cm}$$

This barely in the Knudsen range. The diffusivity is

$$D = 9700(50)(10^{-8})\sqrt{573.2/28} = 0.0219\text{ cm}^2/\text{s},\ 78.84\text{ cm}^2/\text{h}$$

The rate of diffusion is

$$N = D_e\frac{\Delta C}{\Delta L} = \frac{D\vartheta}{RT\tau}\frac{\Delta P}{\Delta L} = \frac{0.3}{25} = 0.012\text{ gmol/(h)(cm}^2)$$

Solve for the tortuosity.

$$\tau = \frac{78.84(0.75)(0.5)}{0.012(82.06)(573.2)(0.5)} = 3.76$$

P7.01.06. MOLECULAR DIFFUSIVITY

Molecular diffusivity of gas A in gas B is represented by

$$D_{ab} = \frac{\sqrt{2}}{P}\left(\frac{RT}{\pi N}\right)^{1.5}\left(\frac{1}{r_a+r_b}\right)^2\left(\frac{1}{M_a}+\frac{1}{M_b}\right)^{0.5}$$

where N is the Avogadro number, r_a and r_b are molecular radii and M_a and M_b are molecular weights.

A more modern and improved equation is

$$D_{12} = \frac{0.001858\ T^{1.5}}{P\sigma_{12}^2\Omega}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^{0.5}\ \text{cm}^2/\text{s},\quad P\ \text{atm},\ T^\circ\text{K}$$

The collision integral is given by the empirical curve fit,

$$\Omega \cong 0.6702 + 0.8459/x - 0.0745/x^2, \quad 0.3 \le x \le 10$$

$$x = kT/\varepsilon_{12} \cong 1.30T/\sqrt{T_{c1}T_{c2}}$$

Other empirical relations are

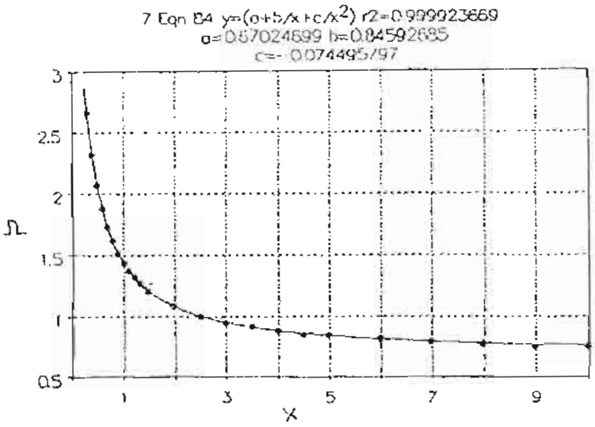
$$\sigma_{12} = 0.5(\sigma_1+\sigma_2)$$

$$\sigma \cong 1.18V_b^{1/3}$$

T_c = critical temperature

V_b = liquid molar volume at the normal boiling point, can be found from molecular contributions.

Values of k/ε, σ and V_b for several substances are tabulated, for instance, by Satterfield (*Mass Transfer in Heterogeneous Catalysis*, 1970).



P7.01.07. MOLECULAR AND KNUDSEN DIFFUSIVITIES

For SO_2 in propane at 5 atm and 873 K find (a) the molecular diffusivity; (b) the Knudsen diffusivity in a pore whose radius is 2 times the mean free path.

(a) Use the material of P7.01.06. These data are known,

	M	σ	T_c
SO_2	64	4.290	430.8

C_3H_8	44	5.061	369.8

These calculations are made,

$$x = kT/\varepsilon_{12} = 1.3(873)/\sqrt{430.8(369.8)} = 2.84$$

$$\Omega = 0.6702+0.8459/x-0.0745/x^2 = 0.959$$

$$D_{12} = \frac{0.001858(873)^{1.5}}{5(0.959)}\left(\frac{2}{4.290+5.061}\right)^2(1/64+1/44)^{0.5.}$$

$$= 0.0895\ \mathrm{cm^2/s}$$

(b) From Glasstone (*Textbook of Physical Chemistry*, p 268, 1940) the mean free path is

$$\lambda = \frac{0.305(10^{-6})T}{P\,\sigma^2}\ \text{cm, with } \sigma \text{ in } 10^{-8} \text{ cm or } \mathring{A}$$

$$= \frac{0.305(10^{-6})(873)}{5(4.29)^2} = 2.89(10^{-6})\ \text{cm}$$

With $r_e = 2\lambda$ the Knudsen diffusivity is

$$D = 9700(2)(2.89)(10^{-6})\sqrt{873/64} = 0.207\ \mathrm{cm^2/s}$$

P7.01.08. DIFFUSION THROUGH A SLAB

These data are known for a porous plate 25 cm square and 0.2 cm thick: $\rho_p = 1.5$ g/cc, $\vartheta = 0.75$ cc/cc, $S_p = 400\ \mathrm{m^2/g}$, $\tau\sqrt{\vartheta} = 2.46$. Find the rate of diffusion of sulfur dioxide, gmol/hr, when the temperature is 200 C and the pressure difference is 0.1 atm.

The mean pore radius is

$$r_e = \frac{2\vartheta}{S_p\rho_p} = \frac{2(0.75)}{400(10^4)1.5} = 0.25(10^{-6})\ \text{cm, } 25\ \mathring{A}$$

Therefore diffusion is in the Knudsen range.

$$D = 9700r_e\sqrt{T/M} = 9700(0.25)(10^{-6})\sqrt{473/64} = 0.0066\ \mathrm{cm^2/s}$$

The tortuosity is

$$\tau = 2.46/\sqrt{0.75} = 2.84$$

and the effective diffusivity is

$$D_e = D\vartheta/\tau = 0.00174\ \mathrm{cm^2/s}$$

The rate of mass transfer is

$$N = \frac{D_eA}{RT}\frac{\Delta P}{\Delta L} = \frac{0.00174(25)(0.1)3600}{82.06(473)(0.2)} = 0.00202\ \text{gmol/h}$$

P7.01.09. MEAN PARTICLE DIAMETER

For a mixture of particles of several sizes, one evaluation of a mean diameter is the volume surface mean, or Sauter mean. When w_i is the weight or volume fraction of particles of diameter d_i the mean is

$$\bar{d} = \frac{\Sigma w_i d_i^3}{\Sigma w_i d_i^2}$$

This kind of mean diameter is pertinent in connection with diffusion phenomena since surface is the major factor then.

Calculations for the mean diameter are given in the table for a mixture whose screen analysis is listed in the first two columns.

$\bar{d} = 11/36.4 = 0.302$ cm

d_i, cm	w_i	$10^3w_id_i^3$	$10^3w_id_i^2$
0.555	0.02	3.42	6.16
0.394	0.05	3.06	7.76
0.280	0.10	2.20	7.84
0.198	0.18	1.40	7.06
0.140	0.25	0.686	4.91
0.099	0.25	0.243	2.45
0.041	0.15	0.0103	0.252
Sum	1.00	11.00	36.4

P7.02.01. ESCAPE FROM A POROUS SPHERE

A sphere of radius R, porosity ϑ, with initial concentration in pores of C_{10} is immersed in a vessel of volume V_2 with initial concentration $C_{20} = 0$. Both regions are kept separately at uniform concentrations. Mass transfer coefficient at the surface is k. Find C_1 as a function of time.

The depletion rate equals the transfer rate, or

$$-V_1\vartheta \frac{dC_1}{dt} = kA\vartheta(C_1-C_2)$$

The overall material balance is

$$V_1\vartheta(C_{10}-C_1) = V_2(C_2-C_{20}) = V_2C_2$$

Combining,

$$-\frac{dC_1}{dt} = \frac{kA}{V_1}[C_1-\frac{V_1\vartheta}{V_2}(C_{10}-C_1)] = (\frac{kA}{V_1}+\frac{kA\vartheta}{V_2})C_1 - \frac{kA\vartheta}{V_2}C_{10}$$

$$= k_1C_1 - k_2C_{10}$$

The integral is

$$k_1t = \ln\frac{(k_1-k_2)C_{10}}{k_1C_1-k_2C_{10}}$$

Substitute $A = \pi R^2$ and $V_1 = (4/3)\pi R^3$. When V_2 is large, $k_2 \Rightarrow 0$ and

$$C_1 = C_{10}\exp(-3kt/R)$$

The time can be found when

$$C_1= C_2 = \frac{C_{10}}{1+V_2\vartheta/V_1}$$

P7.02.02. DIFFUSIONAL RESISTANCE AT THE SURFACE

A second order reaction is catalyzed by a nonporous solid when diffusional resistance at the surface exists. Find the governing equations when the reaction is carried out (a) in plug flow; (b) in a CSTR.

Let C_s be the surface concentration and C that of the fluid phase. At steady state,

$$r = k_1C_s^2 = k_2(C-C_s) = k_1(C-r/k_2)^{2\,2}$$

$$r^2- (2k_2C+k_2^2/k_1)r + k_2C^2 = 0$$

Solve this quadratic equation for r and substitute into

(a) for plug flow, $V_r/V' = \int_C^{C_0} dC/r$

(b) for CSTR, $C = C_0 - \bar{t}r$

P7.02.03. REACTION ON GRANULES IN AN ANNULAR SPACE

A reaction is conducted in an annular vessel with catalyst whose bulk density is ρ_c. Porosity of the bed is ε. The reaction is first order with specific rates k_c per unit mass on the catalyst and k_h per unit volume in the space not occupied by the granules. The two walls are maintained at temperatures T_1 and T_2 The reaction also proceeds on the walls with corresponding specific rates k_{w1} and k_{w2} per unit area. Only radial diffusion occurs. Write equations of the material balances and the boundary conditions.

$$\text{Output} - \text{Input} = u(2\pi r\ dr)dC - D(2\pi\ dz)\ d(r\ \frac{\partial C}{\partial r})$$

$$\text{Sink} = 2\pi r\ dr\ dz\ \rho_c k_c C + 2\pi r\ dr\ dz\ \varepsilon\ k_h C$$

$$\text{Accumulation} = 2\pi r\ dr\ dz\ \frac{\partial C}{\partial t}$$

On combining these elements of the material balance,

$$\frac{\partial C}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}(r\ \frac{\partial C}{\partial r}) - u\ \frac{\partial C}{\partial z} - (\rho_c k_c + \varepsilon k_h)C$$

At $z = 0$, $C = f_1(r,0,t)$
At $t = 0$, $C = f_2(r,z,0)$

At $r = R_1$, $-D\ \frac{\partial C}{\partial r} = k_{w1}C$

At $r = R_2$, $-D\ \frac{\partial C}{\partial r} = k_{w2}C$

The solution of this linear partial differential equation could be started by taking

$$C(r,z,t) = f(r)g(z)h(t)$$

solving the resulting set of three ordinary differential equations and finally fitting the boundary conditions.

P7.02.04 A CYLINDRICAL REACTOR

A plug flow reactor is packed with catalyst granules where the rate equation is $r = k_c C^n$ per unit volume. The wall also is catalytic with rate equation $r_w = k_w C^n$ per unit area. Diffusion is appreciable only in the radial direction. Explain how to find the concentration axially and radially.

Make the material balance over an elemental hollow cylinder with length dz and wall dr. In the axial direction change will accompany bulk flow, u, and in the radial direction change will accompany diffusion.

$$\text{Output} - \text{Input} = u(2\pi r dr)dC - D(2\pi dz)d(r\frac{\partial C}{\partial r})$$

$$\text{Sink} = 2\pi r\ dr\ dz\ kC^n$$

In the steady state there is no accumulation. Together,

$$u\frac{\partial C}{\partial z} - \frac{D}{r}\frac{\partial}{\partial r}(r\frac{\partial C}{\partial r}) + kC^n = 0 \tag{1}$$

Boundary conditions are,

At the inlet, $C(0,r) = C_0$ (2)
At the center by reason of symmetry, $\partial C/\partial r = 0$, $r = 0$ (3)
At the wall, $C = C(R,z)$, $-D\frac{\partial C}{\partial r} = k_w C^n$ (4)

Analytical solution is possible only for first or zero order. Otherwise a numerical solution by finite differences, method of lines or finite elements is required. The analytical solution proceeds by the method of separation of variables which converts the PDE into one ODE with variables separable and the other a Bessel equation. The final solution is an infinite series whose development is quite elaborate and should be sought in books on Fourier series or partial differential equations.

P7.02.05. TWO CATALYTIC PLATES

A reactor is made up of two parallel catalytic plates of unit width and a distance 2W apart. The side plates are inert. The packing is a granular catalyst on which the rate equation is $r = k_1C/(1+k_2C)$ per unit volume. The rate on the wall is $r = k_wC$ per unit area. Discuss how to find the variation of concentration laterally and axially as a function of time.

Make the material balance on a volume element of unit width, length dz and height dy. Neglect diffusion in the axial direction.

$$\text{Output} - \text{Input} = u\,dy\,dC - D(dz)\frac{\partial C}{\partial y}$$

$$\text{Sink} = r\,dV = \frac{k_1C\,dy\,dz}{1+k_2C}$$

$$\text{Accumulation} = dV\,\frac{\partial C}{\partial t} = dy\,dz\,\frac{\partial C}{\partial t}$$

Together,

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} - D\,\frac{\partial^2 C}{\partial y^2} + \frac{k_1C}{1+k_2C} = 0 \qquad (1)$$

Boundary conditions on $C(y,z,t)$,

At $t = 0$, $C = C(y,z,0)$ (2)

At the inlet, $C = C(y,0,t)$ (3)

At the wall, $C = C(w,z,t)$, $-D\,\dfrac{\partial C}{\partial y} = k_wC$ (4)

Analytical solution is possible only when the reaction in the body of the reactor is first or zero order, otherwise a numerical solution will be required by finite differences, method of lines or finite elements. The analytical solution proceeds by separation of variables whereby the PDE is converted into ODEs whose solutions are in terms of trigonometric functions. Satisfying all of the boundary condtions makes the solution of the PDE an infinite series whose development is quite elaborate and should be sought in books on Fourier series or partial differential equations.

P7.02.06. ONE DIMENSIONAL UNSTEADY DIFFUSION

A block of concentration C_0 is placed in contact with a block of zero concentration at time zero. The material balance is represented by this differential equation and associated boundary conditions,

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2}$$

$C(\infty,0) = 0$

$C(0,t) = C_0/2$

$C(\infty,t) = C_0$

Boltzmann (1894) made the inspired substitution

$$z = x/\sqrt{4Dt}$$

which converts the partial differential equation into an ordinary one,

$$\frac{d^2C}{dz^2} + 2z\,\frac{dC}{dz} = 0,\ C(0) = C_0,\ C(\infty) = 0$$

The solution of this linear equation is

$$C/C_0 = 0.5[1 + \mathrm{erf}(x/\sqrt{4Dt})]$$

where $\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2)dt$

Tabulations of this function are available (Abramowitz & Stegun, 1964), or it can be found by numerical integration.

P7.02.07. DIFFUSION IN A RADIAL DIRECTION

Take the unsteady condition of diffusion in a radial direction with reaction in the fluid at rate k_vC per unit volume and reaction at the wall at rate k_vC per unit surface. The material balance is made over a ring shaped zone between z and z+dz in the axial direction and between r and r+dr in the radial direction. The material balance is

Output - Input + Sink + Accumulation = 0

$$-d[2\pi rdz(D\frac{\partial C}{\partial r})] + 2\pi rdrdz(k_vC) + \frac{\partial}{\partial t}(2\pi rdrdzC) = 0$$

which is rearranged to

$$-\frac{D}{r}\frac{\partial}{\partial r}(r\frac{\partial C}{\partial r}) + \frac{\partial C}{\partial t} + k_vC = 0$$

The boundary conditions are

$$-D\frac{\partial C}{\partial r} = k_vC, \text{ at } r = R \text{ (the wall)}$$

$$C(r,0) = C_0 \quad \text{(uniform initial concentration)}$$

$$\frac{\partial C}{\partial r} = 0, \text{ at } r = 0 \text{ (the center)}$$

The steady state equation is

$$\frac{d^2C}{dr^2} + \frac{1}{r}\frac{dC}{dr} = \frac{k_v}{D}C$$

It is a Bessel equation whose general solution is

$$C + AJ_0(\sqrt{k_v}\,r) + BY_0(\sqrt{k_v}\,r)$$

The integration constants A and B are evaluated to fit the boundary conditions. A trick is required that leads ultimately to a solution in infinite series. This is explained in books on Fourier series or partial differential equations.

The unsteady state equation is solvable by separation of variables. Make the substitution

$$C(r,t) = f(r)g(t)$$

which converts the equation into

$$Dg(f''+f'/r) = f(g'+k_vg)$$

or

$$\frac{D}{f}(f''+f'/r) = \frac{g'}{g} + k_v = -\lambda^2$$

Note that two functions of independent variables can be equal only when they are constant. Later developments show that the constant must be negative. Accordingly, the solution of the partial differential equation is reduced to that of the pair of ordinary ones,

$$\frac{d^2C}{dr^2} + \frac{1}{r}\frac{df}{dr} + (\lambda^2/d)f = 0$$

$$\frac{dg}{dt} + (k_v+\lambda^2)g = 0$$

Fitting of the boundary conditions requires the complete solution to be an infinite series. Numerical solutions may be preferable, and are always required for other than first order reactions.

P7.03.01. DIFFERENTIAL EQUATIONS OF REACTION IN PORES

Fick's law states that the rate of diffusion is proportional to the concentration gradient,

$$\text{Rate} = -DA\frac{\partial C}{\partial x}$$

Material balances for a reaction of order n at steady state are applied over differential elements of volume in the form,

Input = Output + Sink

a. Pores in a sphere of radius R. The material balance over a shell with radii r and r+dr is

$$-D(4\pi r^2)\frac{dC}{dr} = -D(4\pi)[r^2\frac{dC}{dr} + d(r^2\frac{dC}{dr})] + 4\pi r^2\ dr\ kC^n$$

which becomes

$$\frac{1}{r^2}d(r^2\frac{dC}{dr}) = \frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = \frac{k}{D}C^n \qquad (1)$$

At the inlet, $r = R$, $C = C_s$ (2)

At the center, $r = 0$, $dC/dr = 0$ (3)

In terms of the normalized variables,

$\rho = r/R$, $f = C/C_s$ (4)

$$\frac{d^2f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho} = \frac{R^2kC_s^{n-1}}{D}f^n = \phi_s^2\ f^n \qquad (5)$$

$\phi_s = R\sqrt{kC_s^{n-1}/D}$, Thiele modulus of a sphere (6)

At the inlet, $\rho = 1$, $f = f_s$ (7)

At the center, $\rho = 0$, $df/d\rho = 0$ (8)

B. Pore in a wide slab of thickness 2L, both faces permeable. The material balance over an element extending from x to x+dx,

$$-DA\frac{dC}{dx} = -DA[\frac{dC}{dx} + d(\frac{dC}{dx})] + kA\ dx\ C^n$$

which reduces to

$$\frac{d^2C}{dx^2} = \frac{k}{D}C^n \qquad (1)$$

At the faces, $x = L$, $C = C_s$ (2)

At the center, $x = 0$, $dC/dx = 0$ (3)

In terms of normalized variables,

$z = x/L,\ f = C/C_s$ (4)

$$\frac{d^2f}{dz^2} = \frac{L^2kC_s^{n-1}}{D} f^n = \phi_L^2 f^n \tag{5}$$

$\phi_L = L\sqrt{kC_s^{n-1}/D}$, Thiele modulus of a slab (6)

At the surface, $z = 1,\ f = f_s$ (7)

At the center, $z = 0,\ df/dz = 0$ (8)

C. Pore in a cylinder of radius R and with impermeable flat faces. Material balance over an element between r and r+dr,

$$-D(2\pi rL)\frac{dC}{dr} = -D(2\pi L)[r\frac{dC}{dr} + d(r\frac{dC}{dr})] + 2\pi rLkC^n$$

which becomes

$$\frac{1}{r}\frac{d}{dr}(r\frac{dC}{dr}) = \frac{d^2C}{dr^2} + \frac{1}{r}\frac{dC}{dr} = \frac{k}{D} C^n \tag{1}$$

At the curved face, $r = R,\ C = C_s$ (2)

At the center, $r = 0,\ dC/dr = 0$ (3)

In terms of normalized variables,

$\rho = r/R,\ f = C/C_s$ (4)

$$\frac{1}{\rho}\frac{d}{d\rho}(\rho\frac{df}{d\rho}) = \frac{d^2f}{d\rho^2} + \frac{1}{\rho}\frac{df}{d\rho} = \frac{R^2kC_s^{n-1}}{D} f^n = \phi_c^2 f^n \tag{5}$$

$\phi_c = R\sqrt{kC_s^{n-1}/D}$, Thiele modulus of a cylinder (6)

At the curved surface, $\rho = 1,\ f = f_s$ (7)

At the center, $\rho = 0$

$df/d\rho = 0$

P7.03.02. EFFECTIVENESS (INTERNAL) OF A POROUS CATALYST

Effectiveness, η, is a measure of the utilization of internal surface of a porous catalyst.

$$\eta = \frac{\text{Rate of flow into the pore at steady state}}{\text{Rate of reaction if all of internal surface were at } C_s}$$

$$= \frac{\text{D(external surface)(gradient at the inlet to the pore)}}{\text{k(volume of the particle)}C_s^n}$$

$$= \frac{D(A_p/V_p)(dC/dz)_s}{kC_s^n} \tag{1}$$

The gradient $(dC/dx)_s$ or $(dC/dr)_s$ is found after integration of the differential equations of P7.03.01.

The rate of reaction in the pore then is expressed in terms of the surface concentration as

$r = k\eta C_s^n$ (2)

The result of integration of second order reaction in a porous sphere is correlated by the curve fit,

$$\eta = \frac{1.0357+0.3173\phi+0.000437\phi^2}{1+0.4172\phi+0.1390\phi^2} \tag{3}$$

This equation is approximately valid for other orders and other geometries by substituting the modified Thiele modulus,

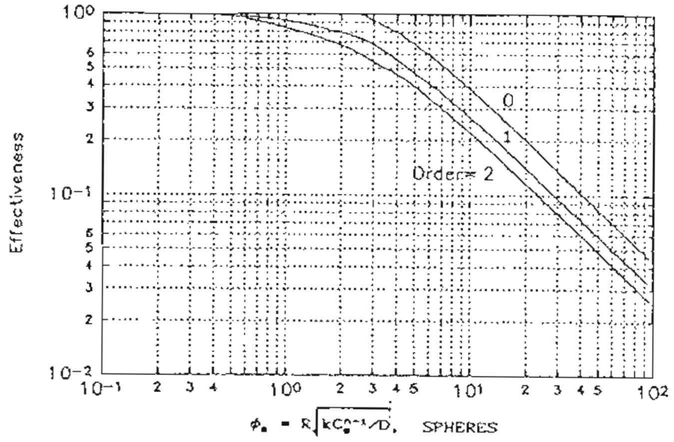
$$\phi_m = 3\left(\frac{V_p}{A_p}\right)\left(\frac{3}{n+1}\right)^{0.5}\left(\frac{kC_s^{n-1}}{D}\right)^{0.5} \tag{4}$$

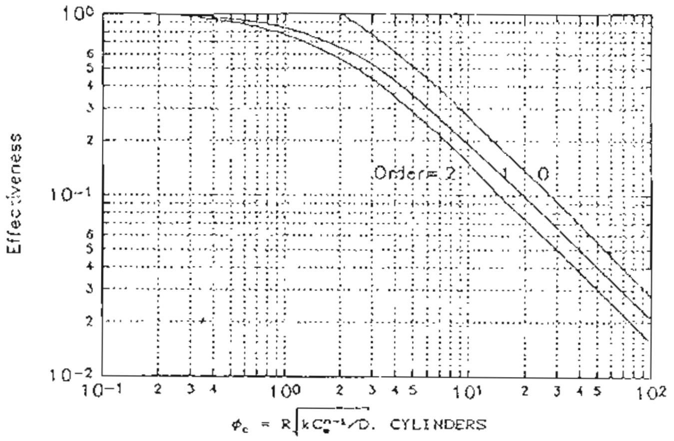
V_p/A_p =(volume of particle)/(external surface of particle)
= R/3 for spheres
L for a slab with one permeable surface
R/2 for a cylinder with sealed ends
n = order of the reaction

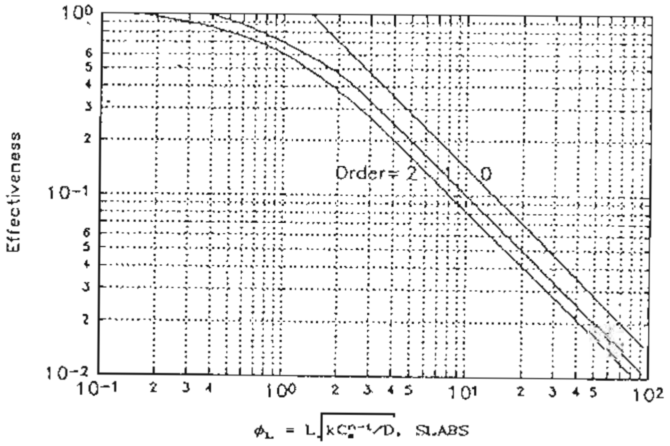
Example: When $\eta = 0.4$, the various values of ϕ_m are tabulated,

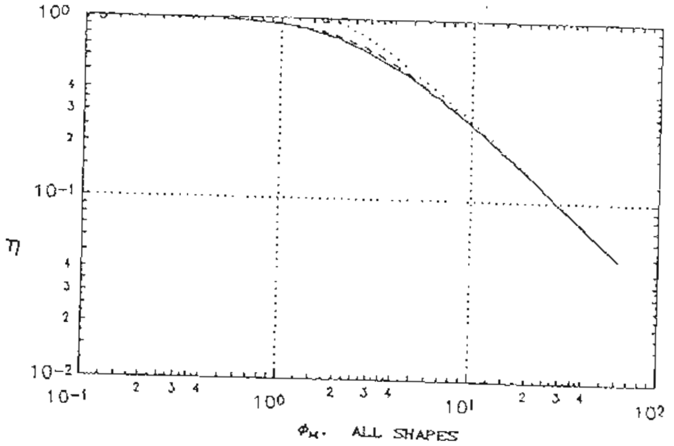
Shape	n=0	n=1	n=2
Sphere	8.69	6.15	5.02
Slab	3.90	2.05	1.67
Cylinder	5.80	4.10	3.34

Graphs are shown for spheres and slabs separately, and with the modified Thiele modulus for all geometries and orders.









P7.03.03. ZERO ORDER REACTION IN A SPHERE

With a zero order reaction, the concentration becomes zero at some location, r_m, which is to be found. The differential equation is

$$\frac{d^2f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho} = \frac{R^2k}{DC_s} = \phi_s^2 \qquad (1)$$

with the conditions

$f = 1$ when $\rho = 1$ (2)

$f = 0$ and $df/d\rho = 0$ when $\rho = \rho_m$, ρ_m to be found (3)

Substituting $M = df/d\rho$ into Eq (1),

$$\frac{dM}{d\rho} + \frac{2}{\rho}M = \phi_s^2 \qquad (4)$$

This is a first order linear equation whose solution is

$$M = \frac{df}{d\rho} = \frac{1}{\rho^2}[\int\phi_s^2\rho^2 d\rho + I] = \frac{1}{\rho^2}(\frac{\phi_s^2\rho^3}{3} + I) \qquad (5)$$

Applying (3) makes the integration constant

$I = \phi_s^2\rho_m^3/3$

and making (5)

$$\frac{df}{d\rho} = \frac{\phi_s^2}{3}(\rho - \rho_m^3/\rho^2) \qquad (6)$$

The integral is

$$f = \frac{\phi_s^2}{3}(\rho^2/2 + \rho_m^3/\rho - 1.5\rho_m^2) \qquad (7)$$

Place $f = 1$ when $\rho = 1$ and solve for ρ_m as a function of ϕ_s. The values are tabulated.

$3 = \phi_s^2(0.5 + \rho_m^3 - 1.5\rho_m^2)$ (8)

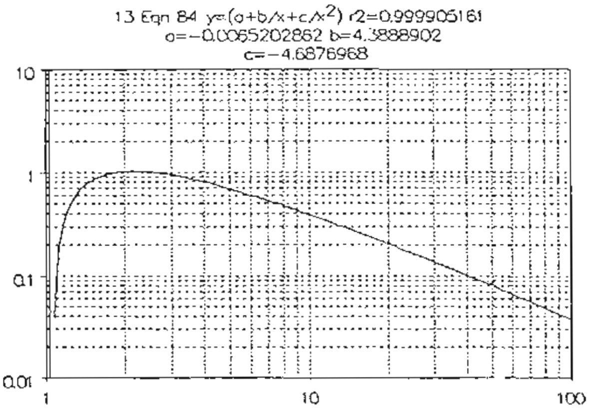
The effectiveness is the ratio of the volume in which the concentration is nonzero to the total volume.

$$\eta = \frac{R^3 - r_m^3}{R^3} = 1 - \rho_m^3 \qquad (9)$$

This is tabulated and plotted. The data also are curve fitted as

$$\eta = -0.00652 + .3889/\phi - 4.6877/\phi^2, \quad \phi \geq \sqrt{6} \qquad (10)$$

ϕ_s	ρ_m	η
2.45	0	1
2.5	0.1204	0.9883
3	0.3869	0.9421
4	0.5841	0.8007
5	0.6813	0.6838
6	0.7409	0.5933
7	0.7813	0.5230
8	0.8109	0.4669
9	0.8334	0.4211
10	0.8510	0.3837
20	0.9275	0.2021
50	0.9716	0.0827
100	0.9864	0.0402



P7.03.04. ZERO ORDER REACTION IN A SLAB

With a zero order reaction, the concentration can become zero at some distance x_m from the face. The thickness of the slab is L and diffusion is from one face only. The differential equation and the conditions are

$$\frac{d^2C}{dx^2} = k/D = k/D \tag{1}$$

At the surface, $x = 0$, $C = C_s$ (2)
When $x = x_m$, $C = 0$ (3)
When $x = x_m$, $dC/dx = 0$ (4)

The integral is

$$C = \frac{k}{2D} x^2 + I_1 x + I_2 \tag{5}$$

In view of conditions (2) and (3), the integration constants are

$$I_2 = C_s \ , \ I_1 = \frac{1}{x_m}(\frac{kx_m^2}{2D} + C_s) \tag{6}$$

Change the variables to

$z = x/L$
$z_m = x_m/L$
$\phi_L^2 = L^2k/DC_s$
$f = C/C_s$

Then Eq (5) becomes

$$f = 0.5\phi_L^2 z(z-z_m)+1-z/z_m \tag{7}$$

Apply condition (4) to evaluate z_m,

$df/dz = 0$

$$[0.5\phi_L^2(2z-z_m)-1/z_m]_{z=z_m} = 0$$

Therefore,

$$z_m = x_m/L = \sqrt{2}/\phi_L \tag{8}$$

Since the rate of reaction is either constant or zero depending on the presence or absence of reactant, the effectiveness is

$$\eta = \sqrt{2}/\phi_L \ , \ \phi_L \geq \sqrt{2} \tag{9}$$

$$1 \ , \ \phi_L \leq \sqrt{2} \tag{10}$$

P7.03.05. ZERO ORDER REACTION IN A CYLINDER WITH SEALED ENDS

With a zero order reaction, the concentration can fall to zero at some position r_m or ρ_m in the pore. The differential equation is developed in P7.03.01,

$$\frac{d}{d\rho}(\rho \frac{df}{d\rho}) = \frac{R^2k}{DC_s} \rho = \phi_c^2 \rho \tag{1}$$

At the surface, $\rho = 1$, $f = 1$ (2)
When $\rho = \rho_m$, $f = 0$ (3)
$df/d\rho = 0$ (4)

Integrating once,

$$\rho\, df/d\rho = 0.5\phi_c^2\rho^2 + I = 0.5\phi_c^2(\rho^2-\rho_m^2) \tag{5}$$

Integrating again,

$$f = 0.5\phi_s^2(\rho^2/2 - \rho_m^2 \ln \rho) + I \tag{6}$$

When $\rho = 1$, $f = 1$ and $I = 1-0.25\phi_c^2$ (7)

$$f = 1 + 0.25\phi_c^2(\rho^2-1-2\rho_m \ln \rho) \tag{8}$$

To find ρ_m, put f = 0 and $\rho = \rho_m$ in Eq (8),

$$0 = 1 + 0.25\phi_c^2(\rho_m^2-1-2\rho_m^2 \ln \rho_m) \qquad (9)$$

The effectiveness is the ratio of the volume in which the concentration is nonzero to the total volume,

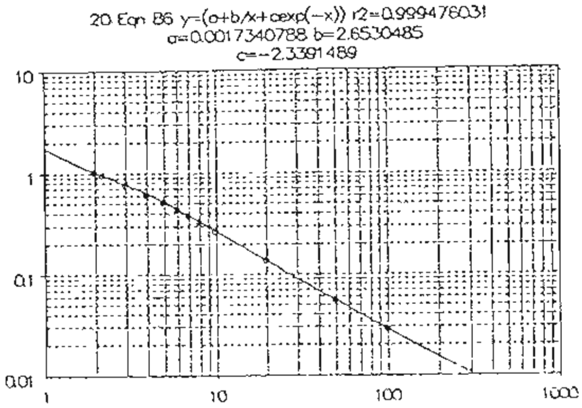
$$\eta = \frac{R^2-r_m^2}{R^2} = 1-\rho_m^2, \quad \phi_c \ge 2 \qquad (10)$$

$$1 \quad , \quad \phi_c \le 2 \qquad (11)$$

The values are tabulated, plotted and curve fitted.

$$\eta = 0.0001734+2.6353\phi_c-2.339 \exp(-\phi_c), \quad \phi_c \ge \sqrt{2}$$

ϕ_c	ρ_m	η
2	0	1
2.5	.3366	.8867
3	.4708	.7784
4	.6184	.6176
5	.7005	.5093
6	.7532	.4327
7	.7900	.3759
8	.8173	.3320
9	.8382	.2974
10	.8548	.2693
20	.9284	.1382
50	.9716	.0560
100	.9862	.0274



P7.03.06. FIRST ORDER REACTION IN A POROUS SPHERE

The differential equation and the boundary conditions are derived in P7.03.01.

$$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = \frac{k}{D} C = \alpha^2 C \qquad (1)$$

At the surface, r = R, $C = C_s$ (2)

At the center, r = 0, dC/dr = 0 (3)

Make the substitution,

$$u = Cr \qquad (4)$$

$$\left[\frac{1}{r}\frac{d^2u}{dr^2} - \frac{2}{r^2}\frac{du}{dr} + \frac{2}{r^3}u\right] + \frac{2}{r}\left[\frac{1}{r}\frac{du}{dr} - \frac{u}{r^2}\right] = \alpha^2(u/r)$$

which reduces to an equation with constant coefficients,

$$\frac{d^2u}{dr^2} = \alpha^2 u \qquad (5)$$

The integral is

$$C = \frac{u}{r} = \frac{1}{r}\,[I_1\exp(\alpha r) + I_2\exp(-\alpha r)] \qquad (6)$$

$$\frac{dC}{dr} = -\frac{1}{r}[I_1\exp(\alpha r)+I_2\exp(-\alpha r)] + \frac{\alpha}{r}[I_1\exp(\alpha r) - I_2\exp(-\alpha r)]$$

Applying condition (3) shows that $I_1 = -I_2 = I$ so that

$$C = \frac{2I}{r}\sinh(\alpha r)$$

Application of condition (2) leads to the result

$$C = \frac{C_sR}{r}\,\frac{\sinh(\alpha r)}{\sinh(\alpha R)}$$

$$= \frac{C_s}{\rho}\,\frac{\sinh(\phi_s\rho)}{\sinh(\phi_s)} \tag{7}$$

where $\rho = r/R$, $\phi_s = R\sqrt{k/D}$ (8)

The gradient at the inlet to the pore is

$$\left(\frac{dC}{d\rho}\right)_{\rho=1} = \frac{C_s}{\sinh(\phi_s)}\left[-\frac{1}{\rho^2}\sinh(\phi_s\rho) + \frac{\phi_s}{\rho}\cosh(\phi_s\rho)\right]_{\rho=1}$$

$$= C_s[\phi_s\coth(\phi_s) - 1] \tag{9}$$

The rate of flow into the pore

$= 4\pi R^2D(dC/dr)_{r=R} = 4\pi RD(dC/d\rho)_{\rho=1}$ (10)

Ideal reaction rate with all surface at C_s,

$= (4/3)\pi R^3kC_s$ (11)

The ratio of (10) and (11) is the effectiveness,

$$\eta = \frac{3D}{kR^2}[\phi_s\coth(\phi_s) - 1] = \frac{3}{\phi_s^2}\left[\frac{\phi_s}{\tanh(\phi_s)} - 1\right] \tag{12}$$

$$\simeq \frac{3(\phi_s-1)}{\phi_s^2}\quad,\ \phi_s \geq 5 \tag{13}$$

Eq (13) is numerically correct to about four decimals. Numerical values are tabulated here and plotted in problem P7.03.02.

ϕ_s	η
0.1	0.9933
0.5	0.9836
1	0.9391
2	0.8060
3	0.6716
4	0.5626
5	0.4800
7.5	0.3467
10	0.2700
15	0.1867
20	0.1425
50	0.0588

P7.03.07. FIRST ORDER REACTION IN A SLAB

The material balance on an element of volume in P7.03.02 leads to this differential equation for first order reaction in a porous slab,

$$\frac{d^2C}{dx^2} = (k/D)C = \alpha^2C,\quad \alpha = \sqrt{k/D} \tag{1}$$

The thickness of the slab is 2L and diffusion is into both faces.

At each face, $x = L$, $C = C_s$ (2)

At the center, $x = 0$, $dC/dx = 0$ (3)

The integral is

$C = I_1\exp(\alpha x) + I_2\exp(-\alpha x)$ (4)

In view of condition (3), $I_1 = I_2 = I$ so that

$C = 2I\cosh(\alpha x)$

Application of condition (2) leads to evaluation of I and the concentration becomes

$$C/C_s = \frac{\cosh(\alpha x)}{\cosh(\alpha L)} = \frac{\cosh(\phi_L z)}{\cosh(\phi_L)} \tag{5}$$

$z = x/L$, $\phi_L = L\sqrt{k/D}$ (6)

At the surface the gradient is

$$\left(\frac{dC}{dx}\right)_{x=L} = C_s\alpha\tanh(\alpha L) = C_s\alpha\tanh(\phi_L) \tag{7}$$

Rate of diffusion into the pore at steady state

$$= DA(dC/dx)_{x=L} \tag{8}$$

Ideal rate of reaction

$$= kVC_s = kALC_s \tag{9}$$

The ratio of (8) and (9) is the effectiveness,

$$\eta = \frac{D\alpha\ \tanh(\sigma L)}{kL} = \frac{\tanh(\phi_L)}{\phi_L} \tag{10}$$

Some values are tabulated here and plotted in problem P7.03.02.

ϕ_L	η
0.1	0.9967
0.5	0.9242
1	0.7616
2	0.4820
2.5	0.3946
3	0.3317
4	0.2498
5	0.1998
7.5	0.1333
10	0.1000
20	0.0500
50	0.0200

P7.03.08. FIRST ORDER REACTION IN A CYLINDER WITH SEALED ENDS

The differential equation of the material balance is developed in problem P7.03.01,

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dC}{dr}\right) - \frac{k}{D}C = 0 \tag{1}$$

At the surface, $r = R$, $C = C_s$ (2)

At the center, $r = 0$, $dC/dr = 0$ (3)

This is a Bessel equation (Jahnke & Emde, p 146, Eq 6). Their parameters are

$$p = 0,\ \beta = \sqrt{-k/D} = i\sqrt{k/D}$$

so the solution is

$$C = Z_0(i\sqrt{k/D}\ r) = AJ_0(i\sqrt{k/D}\ r) + BY_0(i\sqrt{k/D}\ r) \tag{4}$$

The derivative is

$$\frac{dC}{dr} = -i\sqrt{k/D}\ [AJ_1(i\sqrt{k/D}\ r) + BY_1(i\sqrt{k/D}\ r)] \tag{5}$$

Application of condition (3) leads to $B = 0$ since $Y_1(0) \Rightarrow -\infty$.
Application of condition (2) leads to evaluation of A, making

$$C/C_s = \frac{J_0(i\sqrt{k/D}\ r)}{J_0(i\sqrt{k/D}\ R)} \tag{6}$$

Rate of flow into the pore at the surface

$$= 2\pi RhD(dC/dr)_{r=R} = 2\pi RhD(-i\sqrt{k/D})J_1(i\sqrt{k/D}\ R) \tag{7}$$

The ideal rate

$$= kVC_s = \pi R^2h\ kC_s \tag{8}$$

The effectiveness is the ratio of (7) and (8),

$$\eta = \frac{2}{\phi_c}\frac{[-iJ_1(i\phi_c)]}{J_0(i\phi_c)} = \frac{2}{\phi_c}\frac{I_1}{I_0} \tag{9}$$

$$\phi_c = R\sqrt{kC_s^{n-1}/D} \tag{10}$$

Values of the modified Bessel functions I_0 and I_1 are given by Abramowitz & Stegun (p 416, 1964). Those functions and the effectiveness are tabulated here.

ϕ_c	I_1	I_0	η
0.1	0.0501	1.0025	0.9995
0.5	0.2579	1.0635	0.970
1	0.5652	1.2661	0.893
2	1.5906	2.280	0.698
3	3.953	4.881	0.540
4	9.759	11.302	0.432
5	14.24	27.24	0.357
7.5	249.6	268.2	0.248
10	2671	2816	0.190
15			≃0.133
20			≃0.100
50			≃0.040

P7.03.09. SECOND ORDER REACTION IN A POROUS SPHERE

The differential equation is derived in problem P7.03.01,

$$\frac{d^2f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho} = \phi_s^2 f^2 \tag{1}$$

$$f = C/C_s,\ \rho = r/R.,\ \phi_s = R\sqrt{kC_s/D} \tag{2}$$

At the surface, $\rho = 1,\ f = 1$ (3)

At the center, $\rho = 0,\ df/d\rho = 0,\ f_0 = ?$ (4)

This differential equation is analytically solvable in terms of elliptic functions, but here it is solved numerically. Represent the second order equation by the first order pair,

$$\frac{df}{d\rho} = f' \tag{5}$$

$$\frac{df'}{d\rho} = -\frac{2}{\rho}f' + \phi_s^2 f^2 \tag{6}$$

This is a two-point boundary value problem to which the "shooting method" is applicable, according to this procedure:

(i) Start at $\rho = 0$ where $df/d\rho = 0$

(ii) Assume a value of f_0 at $\rho = 0$

(iii) Integrate the differential equations

(iv) Compare the integrated value f_1 at $\rho = 1$ with the requirement that $f_1 = 1$

(v) Repeat as often as needed with other estimates of f_0 until condition (iv) is satisfied.

Complete profiles of f and f' are plotted for $\phi_s = 1$ and $\phi_s = 5$, although these are not necessary for evaluation of the effectiveness. The output of the numerical solution includes the values of the derivative at the surface. The tabulation gives those values and the effectiveness.

$$\eta = \frac{\text{Rate of penetration of the pore}}{\text{Rate of reaction with } C_s \text{ throughout the pore}}$$

$$= \frac{4\pi R^2 D(dC/dr)_{r=R}}{(4/3)\pi R^3 k C_s^2} = \frac{3}{\phi_s^2}(\frac{df}{d\rho})_{\rho=1} \tag{7}$$

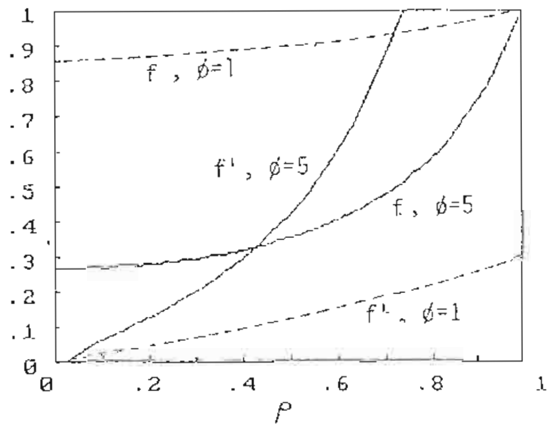
The results are tabulated and plotted, and curve fitted by the equation

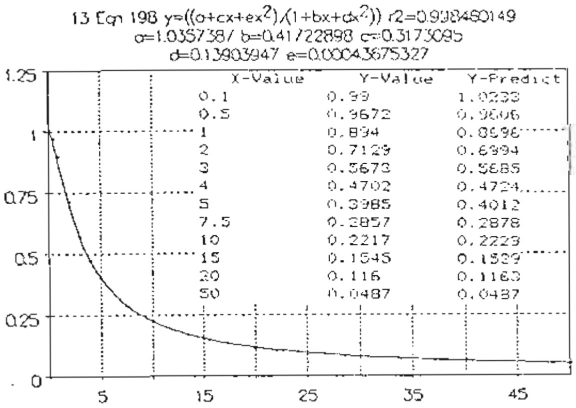
$$\eta = \frac{1.0357+0.3173\phi + 0.000437\phi^2}{1+0.4172\phi + 0.1390\phi^2}, \qquad 0.1 \le \phi \le 50 \tag{8}$$

and also by

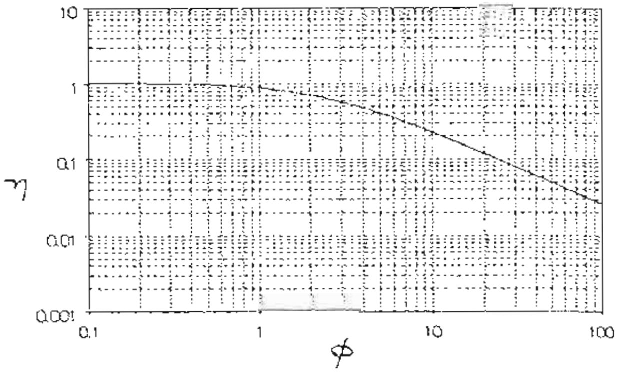
$$\eta = 1.939\ \phi^{-0.942}, \qquad \phi \ge 10 \tag{9}$$

ϕ_s	f_0	$(df/d\rho)_1$	η
0.1	0.998	0.0033	0.9900
0.5	0.960	0.0808	0.9672
1	0.865	0.2980	0.8940
2	0.639	0.9505	0.7129
3	0.464	1.7020	0.5673
4	0.3471	2.5078	0.4702
5	0.2666	3.3206	0.3985
7.5	0.1540	5.3562	0.2857
10	0.0994	7.3884	0.2217
15	0.0512	11.587	0.1545
20	0.0310	15.44	0.1160
50	0.0057	40.66	0.0487




13 Eqn 198 y=((a+cx+ex^2)/(1+bx+dx^2)) r2=0.998480149
a=1.0357387 b=0.41722898 c=0.3173095
d=0.13903947 e=0.00043675327

X-Value	Y-Value	Y-Predict
0.1	0.99	1.0233
0.5	0.9672	0.9606
1	0.894	0.8698
2	0.7129	0.6994
3	0.5673	0.5685
4	0.4702	0.4724
5	0.3985	0.4012
7.5	0.2857	0.2878
10	0.2217	0.2229
15	0.1545	0.1529
20	0.116	0.1163
50	0.0487	0.0487



P7.03.10. SECOND ORDER REACTION IN A SLAB. NUMERICAL INTEGRATION

The differential equation is derived in problem P7.03.01,

$$\frac{d^2f}{dz^2} = \phi_L^2 f^2 \tag{1}$$

$$f = C/C_s,\ z = x/L,\ \phi_L = L\sqrt{kC_s/D} \tag{2}$$

At the surface, $z = 1$, $f = 1$ (3)

At the center, $z = 0$, $df/dz = 0$ (4)

The second order ODE is solved as the first order pair by the "shooting method",

$$\frac{df}{dz} = f' \tag{5}$$

$$\frac{df'}{dz} = \phi_L^2\, f^2 \tag{6}$$

The procedure is,

(i) Assume a value of f_0 at $z = 0$ where $f' = df/dz = 0$

(ii) Integrate the equation from $z = 0$ to $z = 1$

(iii) Compare the integrated value f_1 at $z = 1$ with the requirement that $f_1 = 1$.

(iv) Repeat with other values of f_0 until condition 3 is satisfied. Record the value $y_1' = (df/dz)_1$.

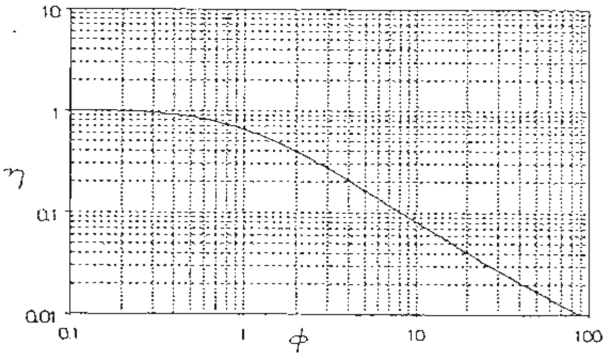
The effectiveness is

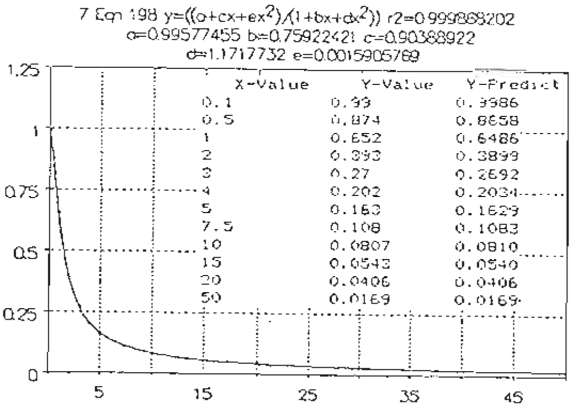
$$\eta = \frac{DA(dC/dx)_{x=L}}{ALkC^2} = \frac{D(C_s/L)(df/dz)_1}{LkC_s^2f^2} = \frac{1}{\phi_L^2}\left(\frac{df}{dz}\right)_1 \tag{7}$$

The results are tabulated and plotted. For convenience a curve fit is

$$\eta = \frac{0.9958 + 0.9039\phi + 0.00159\phi^2}{1 + 0.7592\phi + 1.1781\phi^2} \tag{8}$$

ϕ_L	f_0	$(df/dz)_1$	η
0.1	0.995	0.0099	0.990
0.5	0.900	0.2186	0.874
1	0.712	0.6520	0.652
2	0.445	1.5726	0.393
3	0.298	2.4330	0.270
4	0.2125	3.2300	0.202
5	0.1594	4.0743	0.163
7.5	0.0893	6.0910	0.108
10	0.0570	8.0728	0.0807
15	0.0291	12.2134	0.0543
20	0.0176	16.259	0.0406
50	0.0032	42.16	0.0169





X-Value	Y-Value	Y-Predict
0.1	0.99	0.9986
0.5	0.874	0.8658
1	0.652	0.6486
2	0.393	0.3899
3	0.27	0.2692
4	0.202	0.2034
5	0.163	0.1629
7.5	0.108	0.1083
10	0.0807	0.0810
15	0.0543	0.0540
20	0.0406	0.0406
50	0.0169	0.0169

P7.03.11. SECOND ORDER REACTION IN A SLAB. ANALYTICAL SOLUTION

The differential equation is derived in problem P7.03.01,

$$\frac{d^2C}{dx^2} = (k/D)f^2 = \alpha^2 f^2 \qquad (1)$$

At the surface, $x = L$, $C = C_s$ (2)
At the center, $x = 0$, $dC/dx = 0$ (3)
Also at the center, $C = C_0$, to be found (4)

Let

$$p = dC/dx,\ d^2C/dx^2 = p(dp/dC) \qquad (5)$$

then the integral of (1) is

$$p^2 = (2/3)\alpha^2C^3 + I = (2/3)\alpha^2(C^3 - C_0^3) \qquad (6)$$

$$\frac{dC}{dx} = \sqrt{2/3}\ \alpha\ (C^3 - C_0^3)^{0.5} \qquad (7)$$

Substitute,

$$y = C/C_0,\ y_s = C_s/C_0,\ z = x/L,\ \phi_L = L\sqrt{kC_s/D} \qquad (8)$$

making the equation,

$$\frac{dy}{dz} = \sqrt{2/3y_s}\ \phi_L\ \sqrt{y^3-1} \qquad (9)$$

Indicating the integral from z = 0 to z = 1

$$\sqrt{2/3y_s}\ \phi_L = \int_1^{y_s} \frac{dy}{\sqrt{y^3-1}} = 3^{-0.25}F(\phi_s \backslash 15^\circ) \qquad (10)$$

where ϕ_s is the argument of the elliptic function F and

$$y_s = \frac{2.73203 - 0.73205\cos(\phi_s)}{1 + \cos(\phi_s)} \qquad (11)$$

Properties of the elliptic function of the first kind, $F(\phi\backslash\alpha)$, are given by Abramowitz & Stegun (1964). Equations (10) and (11) determine corresponding values of y_s and ϕ_L.

Flow rate into the pore $= D(dC/dx)_{x=L} = D\sqrt{2k/3D}\ \sqrt{C_s^3 - C_0^3}$ (12)
Ideal reaction rate $= kLC_s^2$ (13)

The ratio of (12) and (13) is the effectiveness,

$$\eta = \frac{1}{\phi_L}\sqrt{2/3}\ \sqrt{[1-(C_0/C_s)^3} \qquad (14)$$

The numerical values are developed perhaps more simply in problem P7.03.10.

P7.03.12. L-H RATE IN A POROUS SPHERE

Following the development of problem P7.03.01, the differential equation with the rate equation,

$$\text{Rate} = kC/(1+k_aC) = kC_sf/(1+k_aC_sf) = kC_sf/(1+k'f) \qquad (1)$$

becomes

$$\frac{d^2f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho} = \frac{R^2}{DC_s}\frac{kC_sf}{1+k'f} = \phi^2\ \frac{f}{1+k'f} \qquad (2)$$

$$\phi = R\sqrt{k/D}\ ,\quad k' = k_aC_s \qquad (3)$$

The effectiveness is

$$\eta = \frac{\text{Rate of input to the pore}}{\text{Rate of reaction with } C_S \text{ throughout}}$$

$$= \frac{4\pi R^2 D(dC/dr)_{r=R}}{(4/3)\pi R^3 kC_s/(1+k_aC_S)}$$

$$= \frac{3(1+k')}{\phi^2}\left(\frac{df}{d\rho}\right)_{\rho=1} \qquad (4)$$

Equation (2) is integrated as the first order pair,

$$\frac{df}{d\rho} = f' \qquad (5)$$

$$\frac{df'}{d\rho} = -\frac{2f'}{\rho} + \frac{\phi^2 f}{1+k'f} \qquad (6)$$

by the shooting method described in problem P7.03.10. Results are tabulated for two values, k' = 1 and k' = 2, and for several values of ϕ.

		$k_aC_S=1$				$k_aC_s=2$		
ϕ		f_0	f_1'	η		f_0	f_1'	η
0.5		0.980	0.0415	0.996		0.985	0.0277	0.997
1		0.920	0.1640	0.984		0.945	0.1103	0.993
2		0.706	0.6227	0.934		0.790	0.4307	0.969
3		0.445	1.2958	0.864		0.566	0.9275	0.928
5		0.107	2.824	0.678		0.164	2.2094	0.795
10		0.00126	6.819	0.409		0.00183	5.585	0.503

P7.03.13. A CONICAL PORE

A first order catalytic reaction takes place in a conical pore of radius R and depth L. Find the concentration profile and the effectiveness.

The radius at a distance x from the face is

$$r = R(1-x/L) = Ru, \quad u - 1-x/L \qquad (1)$$

The material balance on a length dx of the cone is

Input - Output = Sink

$$\pi D\, d(r^2\frac{dC}{dx}) = \pi r^2 dr\, kC$$

$$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = (k/D)C \qquad (2)$$

$$\frac{d^2C}{du^2} + \frac{2}{u}\frac{dC}{du} = \phi^2 C \qquad (3)$$

$$\phi^2 = R^2k/D \qquad (4)$$

At the inlet, $x = 0$, $u = 1$, $C = C_s$ (5)

At the end, $x = L$, $u = 0$, $dC/dx = -LdC/du = 0$ (6)

The substitution

$$w = uC \qquad (7)$$

changes Eq (3) into the linear form,

$$\frac{d^2w}{du^2} = \phi^2 w \qquad (8)$$

whose solution is

$$C = w/u = [I_1\exp(\phi u) + I_2\exp(-\phi u)]/u \qquad (9)$$

Also,

$$\frac{dC}{du} = \frac{\phi}{u}\,[I_1\exp(\phi u) - I_2\exp(-\phi u)]$$

$$- \frac{1}{u^2}\,[I_1\exp(\phi u) + I_2\exp(-\phi u)] \qquad (10)$$

In view of (6),

$I = I_1 = -I_2$

Therefore

$$C = \frac{2I}{u}\sinh(\phi u)$$

In view of (5), $I = C_s/2\sinh(\phi)$, so that

$$C/C_s = \frac{\sinh[\phi(1-x/L)]}{(1-x/L)\sinh(\phi)} \qquad (10)$$

which is the desired concentration profile.

At the inlet, u = 1, x = 0,

$$\frac{dC}{du} = -L\,\frac{dC}{dx} = C_s\left[\frac{u\phi\cosh(\phi u)-\sinh(\phi u)}{u^2\sinh(\phi)}\right]_{u=1}$$

$$\frac{dC}{dx} = \frac{C_s\phi}{L}[\coth(\phi) - 1] \qquad (11)$$

Rate of input to the pore

$$= \frac{\pi R^2 D\phi C_s}{L}[\coth(\phi) - 1] \qquad (12)$$

The ideal rate of reaction in the pore is

$$= \frac{\pi R^2 L}{3}\,kC_s \qquad (13)$$

The effectiveness is the ratio of (12) and (13),

$$\eta = \frac{3D\phi}{kL^2}[\coth(\phi) - 1] \qquad (14)$$

which could be written

$$\eta = \frac{3\phi}{\phi_L^2}[\coth(\phi) - 1] \qquad (15)$$

with

$$\phi_L = L\sqrt{k/D} \qquad (16)$$

P7.03.14. EXTERNAL EFFECTIVENESS OF POWER LAW REACTIONS

When diffusional resistance occurs at the external surface of nonporous catalyst, the rate relations at steady state are

$$r = k_g a(C_g - C_s) = k_s C_s^n \qquad (1)$$

This is rearranged as

$$1 - C_s/C_g = \frac{k_s C_s^{n-1}}{k_g a}\left(\frac{C_s}{C_g}\right)^n$$

or

$$1 - y = D_a y^n \qquad (2)$$

where

$$y = C_s/C_g \qquad (3)$$

$$D_a = (k_s/k_g a)C_s^{n-1}, \quad \text{Damkohler number} \tag{4}$$

The rate at the surface is formally expressible in terms of the fluid phase concentration C_g and an external effectiveness η as

$$r = k_s \eta C_g^n \tag{5}$$

The external effectiveness is defined as the ratio of the actual rate with C_s at the surface to the hypothetical rate with concentration C_g at the surface, thus

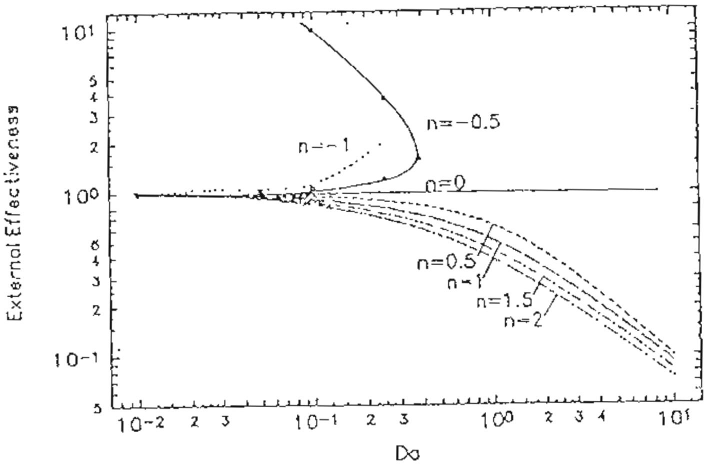
$$\eta = \frac{k_s C_s^n}{k_s C_g^n} = (C_s/C_g)^n = y^n \tag{6}$$

The relation between η and D_a becomes, from Eq (2),

$$1 - \eta^{1/n} = \eta D_a \tag{7}$$

This is solvable for η analytically for some half-integral values of n as tabulated, and numerically in general as shown on the graph. The plots show that multiple values are obtained for n = -0.5 and that a limiting value $\vartheta = 2$ is reached when n = -1.

Order, n	Effectiveness, η
-1	$2/(1+\sqrt{1-4D_a})$
-0.5	$D_a = 1/\eta - 1/\eta^3$, numerical
0	1
0.5	$(-D_a+\sqrt{D_a^2+4})/2$
1.0	$1/(D_a+1)$
1.5	$D_a = 1/\eta - 1/\eta^{1/3}$, numerical
2.0	$[(-1+\sqrt{4D_a+1})/2D_a]^2$



P7.03.15. EXTERNAL EFFECTIVENESS WITH AN L-H RATE EQUATION

At steady state the diffusional and surface reaction rates are equal,

$$r = k_g a(C_g - C_s) = \frac{k_s C_s}{1+k_a C_s} \tag{1}$$

which may be rearranged to

$$1-y = \frac{k_s}{k_g a}\,\frac{y}{1+k_a C_g y} = \frac{D_a y}{1+k_a C_g y} \tag{2}$$

$$y = C_s/C_g \tag{3}$$

$$D_a = k_s/k_g a \tag{4}$$

Eq (2) is rearranged to

$$k_a C_g y^2 + (D_a+1-k_a C_g)y - 1 = 0 \tag{5}$$

which is readily solvable for y. The effectiveness is the ratio of rates with C_s on the surface and with C_g on the surface,

$$\eta_{ext} = \left(\frac{C_s}{1+k_a C_s}\right)/\left(\frac{C_g}{1+k_a C_g}\right) = y\left(\frac{1+k_a C_g}{1+k_a C_g y}\right) \tag{6}$$

Since y depends on D_a from Eq (5), there are two parameters in Eq (6). Some numerical values for η_{ext} are tabulated.

k_aC_g D_a	0	0.1	1	5	10
0.01	0.9901	0.9918	0.9975	0.9997	0.9999
0.05	0.9524	0.9602	0.9875	0.9986	0.9996
0.1	0.9091	0.9231	0.9750	0.9972	0.9992
0.5	0.6667	0.7015	0.8769	0.9853	0.9957
1	0.5000	0.5363	0.7639	0.9689	0.9911
5	0.1667	0.1828	0.3230	0.7701	0.9368
10	0.0909	0.0999	0.1802	0.5110	0.8028

P7.03.16. EXTERNAL AND INTERNAL DIFFUSION IN A SLAB

A first order reaction occurs in a porous slab when both external and internal diffusional resistances are present. An equation for the overall effectiveness will be devekoped.

The differential equation for the concentration inside the pore is obtained in P7.03.01. The rate of reaction is per unit volume.

$$\frac{d^2C}{dx^2} = \frac{k}{D}C = \alpha^2 C \tag{1}$$

At the surface, $x = L$, $k_g(C_g-C_s) = D(\frac{dC}{dx})_{x=L}$ (2)

At the center, $x = 0$, $dC/dx = 0$ (3)

In Eq (2), the rate is per unit area. The integral is

$$C = I_1\exp(\alpha x) + I_2\exp(-\alpha x) \tag{4}$$

$$dC/dx = \alpha[I_1\exp(\alpha x) - I_2\exp(-\alpha x)] \tag{5}$$

Application of condition (3) shows that $I_1 = I_2 = I$ so that

$$C = 2I\cosh(\alpha x) \tag{6}$$

At $x = L$,

$$k_g(C_g-C_s) = 2D\alpha\ I\sinh(\alpha L) \tag{7}$$

from which

$$2I = \frac{k_g(C_g-C_s)}{D\alpha\sinh(\alpha L)} \tag{8}$$

and Eq (7) becomes after rearrangement,

$$\frac{C}{C_g} = \frac{k_g(C_g-C_s)}{D\alpha}\frac{\cosh(\alpha x)}{\sinh(\alpha L)} \tag{9}$$

At $x = L$, $C = C_s$ and Eq (9) becomes,

$$\frac{C_s}{C_g} = \frac{k_g(1-C_s/C_g)\coth(\alpha L)}{D\alpha} = \frac{1}{(D\alpha/k_g)\tanh(\alpha L)+1} \tag{10}$$

Substituting into Eq (9),

$$\frac{C}{C_g} = \frac{k_g\cosh(\alpha x)}{D\alpha\sinh(\alpha L)}[1 - \frac{1}{(D\alpha/k_g)\tanh(\alpha L)+1}]$$

$$= \frac{\cosh(\phi z)}{(\phi/Bi)\sinh(\phi) + \cosh(\phi)} \tag{11}$$

$$z = x/L \tag{12}$$

$\phi = \alpha L = L\sqrt{k/D}$, Thiele modulus (13)

$Bi = k_gL/D$, Biot number (14)

At x=L,

$$\left(\frac{dC}{dx}\right)_{x=L} = \frac{(\phi C_g/L)\sinh(\phi)}{(\phi/Bi)\sinh(\phi)+\cosh(\phi)} = \frac{\phi C_g/L}{\phi/Bi + \coth(\phi)} \qquad (15)$$

The overall effectiveness is

$$\eta_t = \frac{DA(dC/dx)_{x=L}}{kALC_g} = \frac{D\phi}{kL^2[\phi/Bi + \coth(\phi)]}$$

$$= \frac{1}{\phi[\phi/Bi + \coth(\phi)]} \qquad (16)$$

A relation exists between the several groups, thus

$$\frac{\phi^2}{Bi} = \frac{L^2k}{D}\frac{D}{k_gL} = Lk/k_g = aL(k/k_ga) = \frac{aL}{D_a} \qquad (17)$$

where a = transfer surface per unit volume and D_a is the Damkohler number. For a first order reaction, the external effectiveness from P7.03.14 is

$$\eta_{ext} = 1/(1+D_a) \qquad (18)$$

The internal effectiveness from P7.03.07 is

$$1/\eta_{int} = \phi\coth(\phi) \qquad (19)$$

Combining the last four equations gives this relation between the several kinds of effectiveness,

$$\frac{1}{\eta_t} = \frac{aL\eta_{ext}}{1-\eta_{ext}} + \frac{1}{\eta_{int}} \qquad (20)$$

for whatever it is worth.

P7.03.17. VARIABLE VOLUME REACTION, 2A ⇒ B AT CONSTANT PRESSURE

Derivations will be made of the differential equation of the pore and the expression for the rate of diffusion into the pore or the rate of reaction in the pore. The reaction is 2A ⇒ B at constant pressure.

$$f = n_a/n_{a0}$$

$$n_t = n_a + n_b = 0.5(n_{a0}+n_a)$$

$$C_a = \frac{n_a}{V} = \frac{2P}{RT}\left(\frac{n_a}{n_{a0}+n_a}\right) = \frac{2P}{RT}\left(\frac{f}{1+f}\right) = \beta\left(\frac{f}{1+f}\right), \qquad (1)$$

$$\beta = 2P/RT$$

$$r = kC_a^2 = k\beta^2\left(\frac{f}{1+f}\right)^2 \qquad (2)$$

For Fick's Law,

$$dC_a = \beta\left(\frac{1}{1+f}\right)^2 df \qquad (3)$$

Material balance on a slab geometry,

Input - Output = Sink

$$D\, d\frac{dC_a}{dx} = r\, dx$$

$$\beta\frac{d}{dx}\left[\left(\frac{1}{1+f}\right)^2\frac{df}{dx}\right] = \beta^2\left(\frac{k}{D}\right)\left(\frac{f}{1+f}\right)^2$$

Finally,

$$\frac{d^2f}{dx^2} - \frac{2}{1+f}\frac{df}{dx} = \frac{\beta k}{D}f^2 \qquad (4)$$

At the face, $x = L$, $f = f_s$ (5)

At the center, $x = 0$, $df/dx = 0$ (6)

After integration the derivative can be evaluated at the mouth of the pore where $f = f_s$ and the rate will be,

$$r_{pore} = D\left(\frac{dCa}{dx}\right)_{x=L} = \frac{\beta D}{(1+f_s)2}\left(\frac{df}{dx}\right)_{x=L} \qquad (7)$$

The effectiveness depends strongly on the stoichiometry of the reaction, and the single Thiele parameter alone is not sufficient to represent its behavior. But evaluation is feasible for specific cases by integration of equations like Eq (4). The ideal rate is obtained from Eq (2) by replacing f by f_s.

P7.03.18. L-H RATE EQUATION. EFFECTIVENESS AND REACTOR SIZE

A catalyst bed is made up of porous spheres of 0.2 cm radius and with diffusivity $D = 0.02\ \text{cm}^2/\text{s}$. A stream with $C_0 = 1.0$ and rate equation

$$r_c = 1.5C/(1+0.2C) \qquad (1)$$

is to be taken to 80% conversion. Find V_r/V' for this operation, and also the variation of catalyst effectivenes along the reactor.

The material balance on the pores is

$$\frac{d^2f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho} = \frac{R^2}{D}\frac{1.5f}{1+0.2f} = \frac{3.0f}{1+0.2f} \qquad (2)$$

$f = C/C_0 = C$

$\rho = r/R = r/0.2$

At the external surface, $\rho = 1$, $f = f_s$, $df/d\rho = (df/d\rho)_s$ (3)

At the center, $\rho = 0$, $f = f_0$, $df/d\rho = 0$ (4)

Integrate the differential equation by the shooting method. Start at the center at $\rho = 0$, assume a value of f_0, integrate to $\rho = 1$ and find f_s and $(df/d\rho)_s$ at that point. Do this for a range of values of f_s from 1 to 0.2. The results are tabulated. The plots (f_0, f_s) and (f_0, f_s') are nearly linear.

At each value of f_s along the reactor, the rate of reaction per unit volume is

$$r_c = aD\left(\frac{dC}{dr}\right)_s = \frac{3D}{R}\frac{C_0}{R}\left(\frac{df}{d\rho}\right)_s = 1.5\left(\frac{df}{d\rho}\right)_s \qquad (5)$$

The reactor size is given by

$$V_r/V' = \int_{0.2}^{1}\frac{df}{r_c} = 1.428 \qquad (6)$$

The integrand is tabulated and integration is with the trapezoidal rule. The ideal rate of reaction per unit volume is

$$r_{ideal} = \frac{k_1C_s}{1+k_2C_s} = \frac{1.5f_s}{1+0.2f_s} \qquad (7)$$

and the effectiveness is the ratio of (5) and (7)

$$\eta = \frac{1+0.2f_s}{f_s}\left(\frac{df}{d\rho}\right)_s \qquad (8)$$

Values of η are tabulated.

f_0	f_s	$(df/d\rho)_s$	r_c	$1/r_c$	r_{ideal}	η
0.6666	1.0	0.7309	1.0964	0.9121	1.2498	0.8773
0.5313	0.8	0.6043	0.9065	1.1031	1.0344	0.8764
0.3960	0.6	0.4678	0.7017	1.4251	0.8034	0.8734
0.2607	0.4	0.3204	0.4806	2.0807	0.5616	0.8358
0.1254	0.2	0.1605	0.2409	4.1511	0.2886	0.8347

P7.03.19. REVERSIBLE REACTION WITH EXTERNAL AND INTERNAL DIFFUSION.

A reversible reaction, $2A \Rightarrow B$, has the rate equation

$$r_c = 0.5[C^2-(1-C)/15] \qquad (1)$$

It is to be carried out with a porous catalyst with external diffusional resistance with the rate relation

$$\text{Rate} = 0.25(C_g-C_s) = D\left(\frac{dC}{dr}\right)_{r=R} \qquad (2)$$

The quantity V_r/V' is to be found for 90% of equilibrium conversion. These data are known,

$C_0 = 1$

$D = 0.02\ \text{cm}^2/\text{s}$

$R = 0.5\ \text{cm}$

The equilibrium value is $C_e = 0.227$ so the required final value is

$C = 1-0.9(1-0.227) = 0.3043$

The pore equation is

$$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = \frac{r_c}{D} = 25[C^2-(1-C)/15)] \tag{3}$$

To solve this equation, follow this procedure:

(i) Start at the center where $dC/dr = 0$ and assume a series of values at the center, C_{center}. The corresponding values found at $r = R = 0.5$ will be C_s and $(dC/dr)_{r=R} = (dC/dr)_s$.

(ii) Find Rate $= D(dC/dr)_s = 0.02(dC/dr)_s$

(iii) Find C_g from Eq (2). Linear interpolation is used to find the other values at $C_g = 1.000$ and 0.3043. Those values are identified by * in the table.

Then V_r/V' is found by integration,

$$V_r/V' = \int_{3043}^{1.0} \frac{dC_g}{\text{Rate}} = 61.45, \text{ by trapezoidal rule} \tag{4}$$

The ideal rates in terms of C_s or C_g are calclulated from Eq (1) and are tabulated as r_s and r_g. The corresponding values of effectiveness are

internal $\eta_s = \text{Rate}/r_s$, external $\eta_g = \text{Rate}/r_g$

C_{cent}	C_s	$(dC/dr)_s$	Rate	C_g	1/Rate	r_s	r_g	η_s	η_g
0.55	0.9782	2.5130	0.0503	1.792					
	0.8457*		0.0386	1.000*	25.91	0.353	0.500	0.143	0.077
0.50	0.8266	1.8452	0.0369	0.9742	27.10	.0336	0.474	0.110	0.078
0.45	0.6901	1.3068	0.0261	0.7946	38.31	0.228	0.309	0.115	0.085
0.40	0.5670	0.8765	0.0175	0.6371	57.14	0.146	0.197	0.120	0.092
0.35	0.4561	0.5369	0.0107	0.4991	93.11	0.086	0.108	0.125	0.100
0.30	0.3559	0.2733	0.0055	0.3778	182.8	0.042	0.051	0.131	0.108
	0.2955*		0.0027	0.3043*	369.0	0.020	0.023	0.139	0.117
0.25	0.2656	0.0734	0.0015	0.2714					

P7.03.20. EFFECTIVENESS EXPERIMENTALLY.

A series of tests of a second order reaction were made in a rotating basket CSTR with several sizes of catalyst pellets. All runs were made with the same residence time and with inlet $C_0 = 4$. Effluent concentrations were measured. Beyond R = 0.1 cm, there were no differences in conversion.

R	C_{out}	ΔC
0.75	2.8	1.2
0.1	1.05	2.95.
0.05	1.05	2.95

From these data the effectiveness is

$$\eta = \frac{r_{0.75}}{r_{0.1}} = \frac{\Delta C_{0.75}}{\Delta C_{0.1}} = \frac{1.2}{2.95} = 0.407$$

For second order spheres, the corresponding modulus is

$$\phi = 4.9 = R\sqrt{k_vC/D_{eff}} = 0.75\sqrt{2.8k_v/D_{eff}}$$

$$k_v/D_{eff} = 15.24$$

In general,

$$\phi = R\sqrt{15.24C}$$

When R = 0.5 and C = 0.5, for instance,

$$\phi = 0.5\sqrt{15.24(0.5)} = 1.38$$

$\eta = 0.81$, from the chart or equation.

P7.04.01. EFFECTIVE DIFFUSIVITY. PARTICLES OF SEVERAL SIZES.

A series of experiments were performed using various sizes of catalyst spheres. The reaction was first order irreversible. The first two columns of the table record the diameter d_p in cm and the rate in mol/(h)(cc). The surface concentration was $C_s = 0.0002$ mol/cc. Find the true specific rate and the effective diffusivity.

The rate of reaction is

$$r = k\eta C_s$$

Assume that $\eta = 1$ with the smallest particles. Then

$$k = r/C_s = 2.4/0.0002 = 12000/\text{hr}$$

and the effectiveness is

$$\eta = r/2.40 \tag{1}$$

For first order reaction in a porous sphere,

$$\eta = \frac{3}{\phi^2}\left[\frac{\phi}{\tanh(\phi)} - 1\right] \tag{2}$$

The Thiele modulus is

$$\phi = r_p\sqrt{k/D} \tag{3}$$

and the effective diffusivity is

$$D = \frac{kd_p}{4\phi^2} = \frac{3000d_p}{\phi^2} \tag{4}$$

The calculations are summarized in the table. The calculated values of D are nearly constant at 0.2 cm²/hr, thus confirming the various assumptions.

d_p	r	η	ϕ	D
0.25	0.22	0.0917	31.7	0.1866
0.075	0.70	0.2917	9.13	0.2024
0.025	1.60	0.6667	3.05	0.2016
0.0075	2.40	1		

P7.04.02. EFFECTIVENESS OF GAS OIL CRACKING CATALYST

A gas oil is cracked at 630 C and 1 atm by passing vaporized feed through a bed of silica-alumina catalyst spheres with radius 0.088 cm. At a feed rate of 0.2 mol/(h)(cc catalyst bed) conversion was 50%. The reaction is pseudo first order. The effective diffusivity is 0.0008 cm²/s. As an approximation, assume a constant volumetric flow rate. Find the effectiveness of the catalyst.

The volumetric feed rate per unit reactor volume is

$$V'/V_r = \frac{0.2(22400)(903)}{3600(273)} = 4.12 \text{ cc/(s)(cc bed)}$$

The flow reactor equation is

$$-V'dC = k\eta CdV_r$$

With the given data,

$$k\eta = \frac{V'}{V_r}\ln(2) = 4.12(0.693) = 2.85 \qquad (1)$$

The Thiele modulus is

$$\phi = R\sqrt{k/D} = R\sqrt{\frac{2.85}{\eta D}} = 0.088\sqrt{\frac{2.85}{0.0008\eta}} = 5.25/\sqrt{\eta} \qquad (2)$$

For a first order reaction,

$$\eta = \frac{3}{\phi^2}\left[\frac{\phi}{\tanh(\phi)} - 1\right] \qquad (3)$$

Substitute Eq (2) into Eq (3) and solve for η the only variable. In this particular case $\tanh(\phi) \cong 1$ so the equation to solve is

$$\eta = 0.1088\eta(5.25/\sqrt{\eta} - 1)$$

The result is

$$\eta = 0.265 \qquad (4)$$

The Thiele modulus is $\phi = 10.19$; at this value the assumption that $\tanh(\phi) = 0.9999+$ is valid.

P7.04.03. SPECIFIC RATE OF A SLURRY REACTION

A reaction was performed with 20% conversion in a continuous stirred tank containing a slurried porous catalyst for which these data are known: diffusivity $D = 0.002\ \text{cm}^2/\text{s}$, porosity $\varepsilon = 0.4$, incoming concentration $C_0 = 0.05$ mol/cc, particle diameter $d = 0.5$ cm. The superficial residence time, the ratio of the reactor volume to the volumetric flow rate, is $\bar{t} = 15$ sec. Find the specific rate k in the units

$$\frac{\text{mol}}{(\text{sec})(\text{cc catalyst})}\left(\frac{\text{cc fluid}}{\text{mol}}\right)^2$$

The units of the specific rate identify the reaction as second order. The material balance on the reactor is

$$V'C_0 = V'C + k\eta V_r C^2$$

Rearranging,

$$k\eta = \frac{C_0 - C}{(1-\varepsilon)\bar{t}C^2} = \frac{0.05-0.04}{0.6(15)(0.04)^2} = 0.6944 \qquad (1)$$

The Thiele modulus is

$$\phi = R\sqrt{kC/D} = 0.25\sqrt{0.04k/0.002} = 1.117\sqrt{k} \qquad (2)$$

Also,

$$\phi = \frac{1.0357+0.3173\phi+0.000487\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (3)$$

Solving the numbered equations together results in

$$\phi = 0.998,\ \eta = 0.870,\ k = 0.798 \qquad (4)$$

P7.04.04. PFR AND CSTR REACTORS

A reaction with rate equation

$$r = k\eta C_s^{1.5}\ \text{kgmol/(h)(m}^3)$$

is conducted in the presence of spherical catalyst particles. Inlet concentration is 2.5 kgmol/m^3. At this concentration the Thiele modulus is $\phi_0 = 8$ and 80% conversion is required.

(a) Find kV_r/V' of a PFR

(b) Find the residence time, as $k\bar{t}$, in each vessel of a two stage CSTR.

(a) The modulus at other concentrations is

$$\phi = 8(C_s/C_{s0})^{0.25} = 6.36C_s^{0.25} \tag{1}$$

The PFR equation is

$$kV_r/V' = \int_{0.5}^{2.5} \frac{dC_s}{\eta C_s^{1.5}} \tag{2}$$

The integrand is tabulated. Using Simpsons rule,

$$kV_r/V' = 2.42 \tag{3}$$

C_s	ϕ	η	Integrand
2.5	8	0.29	0.9195
2.0	7.57	0.31	1.1405
1.5	7.04	0.33	1.6495
1.0	6.36	0.37	2.7027
0.5	5.35	0.43	9.1927

(b) The material balances on the two CSTR stages are

$$2.5 = C_{s1} + k\bar{t}\eta_1 C_{s1}^{1.5} \tag{4}$$

$$C_{s1} = 0.5 + k\bar{t}(0.43)(0.5)^{1.5} = 0.5 + 0.1520k\bar{t} \tag{5}$$

The value $\eta_2 = 0.43$ is from part (a).
Solve (4) and (5) together,

$$k\bar{t} = \frac{2.5-C_{s1}}{\eta_1 C_{s1}^{1.5}} = \frac{C_{s1}-0.5}{0.1520} \tag{6}$$

The solution procedure is

(i) Assume a value of C_{s1}

(ii) Find ϕ from (1) and the corresponding η_1 from the correlation.

(iii) Check if (6) is satisfied.

Several trial values are tabulated. The correct value is $k\bar{t} = 3.63$.

C_{s1}	ϕ	η_1	$(k\bar{t})_1$	$(k\bar{t})_2$
1.0	6.36	0.37	4.054	3.290
1.05	6.44	0.37	3.755	3.618
1.052	6.44	0.37	3.627	3.632

P7.04.05. A MULTILAYER CATALYST BED

A reactor is packed with four equal layers of porous spheres of diameters 1.0, 0.3m 0.09 and 0.027 cm. The reaction is second order. Additional data are:

$D = 8(10^{-6})$ cm^2/s, diffusivity

$k = 150$ cc catalyst/(gmol reactant)(s)

$C_0 = 1.2(10^{-5})$ mol/cc, inlet concentration

$\varepsilon = 0.6$, porosity

$V' = 0.02$ cc/(s)(cm^2 vessel cross section)

$V_r = 50$ cc/cm^2, reactor volume per unit cross section

(a) Find the conversion in a 50 cm depth of this composite bed.

(b) Find the conversion in a 50 cm depth containing only particles of 0.32 cm diameter.

$$f = C/C_0$$

$$\phi = R\sqrt{kfC_0/D} = R\sqrt{150(1.2(10^{-5})f/8(10^{-6})} = 15R\sqrt{f} \tag{1}$$

$$\eta = \frac{1.0357+0.3173\phi+0.00437\phi^2}{1+0.4172\phi+0.139\phi^2} \tag{2}$$

$$r = k(1-\varepsilon)\eta C_0^2 f^2 = 150(0.4)(1.2)(10^{-10})\eta f^2$$

$$= 86.4(10^{-10})\eta f^2 \tag{3}$$

The flow reactor equation is

$$\frac{V_r}{V'} = C_0 \int_{f_1}^{f_2} \frac{df}{\eta f^2} = 1388 \int_{f_1}^{f_2} \frac{df}{\eta f^2}$$

Each layer has

$$V_r/V' = 12.5/0.02 = 625$$

so the integral over each layer is

$$\int_{f_1}^{f_2} \frac{df}{\eta f^2} = 625/1388 = 0.45 \tag{4}$$

In the first layer,

$$\phi_1 = 15(0.5)(0.027)\sqrt{f} = 0.203\sqrt{f}$$

$$\phi_{10} = 0.203,\ \eta_0 = 1.00$$

Accordingly $\eta = 1$ throughout the smallest layer. With $f_1 = 1$, integration of Eq (4) gives

$$f_2 = \frac{1}{1+0.45} = 0.690$$

In the second layer,

$$\phi_2 = 15(0.5)(0.09)\sqrt{f} = 0.675\sqrt{f}$$

At the inlet to this layer,

$$\phi_{20} = 0.675\sqrt{0.690} = 0.561,\ \eta_{20} = 0.950$$

The variation of the integrand is expected to be small, so the integral is approximated as

$$\int_{f_a}^{f_b} \frac{df}{\eta f^2} \cong 0.5\left(\frac{1}{\eta_a} + \frac{1}{\eta_b}\right)\left(\frac{1}{f_b} - \frac{1}{f_a}\right) = 0.450$$

With the known values,

$$\left(\frac{1}{0.950} + \frac{1}{\eta_2}\right)\left(\frac{1}{f_2} - \frac{1}{0.690}\right) = 2(0.450) = 0.9$$

Some trial values are tabulated:

Trial f_2	ϕ_2	η_2	calc f_2
0.530	0.491	0.962	0.520
0.520	0.487	0.963	0.527
0.524		0.9626	0.524

In the third layer,

$$\phi_3 = 15(0.15)(0.3)\sqrt{f_3} = 2.25\sqrt{f_3}$$

$$\phi_{30} = 2.25\sqrt{0.524} = 1.629,\quad \eta_{30} = 0.759$$

The approximate integration is

$$\left(\frac{1}{0.759} + \frac{1}{\eta_3}\right)\left(\frac{1}{f_3} - \frac{1}{0.524}\right) = 0.9$$

Trial f_3	ϕ_3	η_3	Calc f_3
0.45	1.509	0.779	0.414
0.44	1.492	0.782	0.443
		0.781	0.443

interpolated

In the fourth layer,

$\phi_4 = 15(0.5)\sqrt{f_4}$

$\phi_{40} = 7.5\sqrt{0.443} = 4.995,\ \eta_{40} = 0.402$

$(\frac{1}{0.402} + \frac{1}{\eta_4})(\frac{1}{f_4} - \frac{1}{0.443}) = 0.9$

Trial f_4	ϕ_4	η_4	Calc f_4
0.3	4.108	0.464	0.408
0.4	4.743	0.418	0.410
0.410	4.800	0.414	0.410

interpolated

A summary of the multilayer operation is tabulated.

Layer	η	f
1	1.00	1
1	1.00	0.690
2	0.95	0.690
2	0.9626	0.524
3	0.759	0.524
3	0.781	0.443
4	0.402	0.443
4	0.410	0.410

With uniform spheres, R = 0.15 cm,

$\int_f^1 \frac{df}{\eta f^2} = 1.80$

$\phi = 15(0.15)\sqrt{f} = 2.25\sqrt{f}$

The integrands and the trapezoidal integrals are tabulated. Interpolating to 1.8 as the value of the integral,

$f = 0.432$

f	ϕ	η	$1/\eta f^2$	Integral
1	2.25	0.663	1.508	0
0.9	2.135	0.680	1.817	0.166
0.8	2.012	0.698	2.240	0.369
0.7	1.882	0.72	2.835	0.623
0.6	1.743	0.74	3.754	0.952
0.5	1.591	0.79	5.063	1.393
0.45	1.509	0.80	6.172	1.674
0.432				1.8
0.4	1.423	0.80	7.813	2.024

P7.04.06. SEGREGATED CONVERSION WITH POROUS CATALYST

A reaction of order 1.5 is carried out in contact with porous spherical catalyst. The RTD is

$$E(t) = 2.079\, t^{0.5} \exp(-1.5t),\ t \text{ in minutes} \qquad (1)$$

Inlet concentration is $C_o = 0.5$ mol/liter, specific rate is $k = 2.38$ mol(liter/mol)$^{1.5}$/(min)(liter catalyst). The Thiele modulus at the inlet is $\phi = 20$. Find the conversion in segregated flow.

The modified modulus is

$$\phi = 20\left(\frac{3}{n+1}\right)^{0.5}(0.5f)^{0.25} = 18.42f^{0.25} \qquad 2)$$

$$f = C/C_0$$

$$\eta = \frac{1.0357+0.3173\phi+0.000487\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (3)$$

The rate equation is

$$r = -C_0\frac{df}{dt} = k\eta(C_0f)^{1.5}$$

$$-\frac{df}{dt} = 2.38\eta(0.5)^{0.5}f^{1.5} = 1.6818\eta f^{1.5}\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

In a batch reactor,

$$t = 0.5946\int_f^1 \frac{df_b}{\eta f_b^{1.5}} = \int_1^f Idt \qquad (5)$$

The integrand and the integral are tabulated. In segregated flow,

$$\bar{f} = \int_0^\infty f_{batch}E(t)dt = 0.680 \qquad (6)$$

The integrand is tabulated. Both integrations are with the trapezoidal rule.

For comparison, in plug flow with $\bar{t} = 1.00$ and a mean value $\bar{\eta} = 0.13$,

$$k\bar{t} = 2.38(1) = \int_C^{C_0} \frac{dC}{0.13C^{1.5}} \qquad (7)$$

Although analytical integration is possible, the result is found numerically,

$$f = C/C_0 = 0.556 \qquad (8)$$

f_b	ϕ	η	I	t	E(t)	$f_bE(t)$
1	18.42	0.126	5.61	0	0	0
0.9	17.94	0.129	6.42	0.602	0.6539	0.5885
0.8	17.42	0.133	7.43	1.294	0.3395	0.2716
0.7	16.85	0.137	8.81	1.606	0.2369	0.1658
0.6	16.21	0.142	10.71	2.582	0.0695	0.0417
0.5	15.49	0.148	13.51	3.793	0.0137	0.0069
0.4	14.65	0.156	17.92	5.37	0.0015	0.0006
0.3	13.63	0.167	25.77	7.55	0.0001	0
0.2	12.32	0.184	42.95	11.0		
0.1	10.36	0.216	103.5	18.31		

P7.04.07. SLURRY REACTORS

A second order reaction is carried out in a two stage CSTR battery. The catalyst is in the form of small spheres slurried with the liquid but they do not leave the vessel. Specific rate of the reaction is 5.5 cuft/(lbmol)(min). Inlet concentration is 1.2 lbmol/cuft. At this concentration the Thiele modulus is $\phi_0 = 16$. Find the residence time in each vessel for a conversion of 90%.

$$r = k\eta C^2$$

$$C_2 = 0.1C_0 = 0.12$$

$$\phi = 16\sqrt{C/1.2} = 14.6\sqrt{C} \qquad (1)$$

$$\phi_2 = 5.05$$

$$\eta = \frac{1.0357+0.31737\phi+0.000487\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (2)$$

$$\eta_2 = 0.4$$

In the second stage,

$$C_1 = C_2 + k\bar{t}\eta_2 C_2^2 = 0.12 + 5.5(0.4)(0.12)^2\bar{t}$$

$$= 0.12 + 0.0317\bar{t} \qquad (3)$$

In the first stage,

$$1.2 = C_1 + 5.5\bar{t}\eta_1 C_1^2$$

or

$$\eta_1 = \frac{1.2-C_1}{5.5\bar{t}C_1^2} \qquad (4)$$

The solution procedure is

(i) Assume a value of $\bar{t}$
(ii) Find C_1 from Eq (3)
(iii) Find ϕ from Eq (1)
(iv) Find η_1 from Eq (4) and compare with that from Eq (2).

Two trial values are shown. The interpolated value is $\bar{t} = 6.1$.

Trial $\bar{t}$	6.0	6.5	6.1
C_1	0.3102	0.3261	
ϕ	8.13	8.34	
η_1	0.2802	0.23	0.264
η [Eq (2)	0.265	0.260	0.264

P7.04.08. CONVERSION IN A TWO STA2E SLURRY REACTOR

A two stage CSTR with slurried catalyst conducts a reaction with rate equation

$$r = 1.307\eta C^{1.64} \text{ mol/(min)(liter)}$$

Residence time in each stage is $\bar{t} = 15$ min, inlet concentration is $C_0 = 0.81$ mol/liter. At the inlet conditions the Thiele modulus is $\phi_0 = 10$. Find the concentrations of the effluents from each stage.

For this order of reaction, the modified Thiele modulus is

$$\phi = 10(C/0.81)^{0.32} = 10.70C^{0.32} \qquad (1)$$

Also,

$$\eta = \frac{1.0357+0.3173\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (2)$$

In the first stage,

$$0.81 = C_1 + 15(1.307)\eta_1 C_1^{1.64} \qquad (3)$$

Solving Eq (1), (2) and (3) simultaneously,

$$\phi_1 = 6.73,\ \eta_1 = 0.315,\ C_1 = 0.2348 \qquad (4)$$

In the second stage,

$$0.2348 = C_2 + 15(1.307)\eta_2 C_2^{1.64} \qquad (5)$$

Solving Eq (1), (2) and (5) simultaneously,

$$\phi_2 = 4.91,\ \eta_2 = 0.407,\ C_2 = 0.0876 \qquad (6)$$

P7.04.09. RESIDENCE TIME IN A CSTR BATTERY

A slurry battery of two equal stages is used to obtain 90% conversion of a second order reaction. Find the residence time in each stage, given these data:

$$kC_o = 4$$

$$\phi = 10\sqrt{C/C_0} \qquad (1)$$

$$\eta = \frac{1.0357+0.3173\phi+0.00437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (2)$$

Material balances on the two stages are

$$1 = f_1 + \bar{t}_1 kC_0\eta_1 f_1^2 = f_1 + 4\eta_1 f_1^2\bar{t}_1 \qquad (3)$$

$$f_1 = f_2 + 4\eta_2 f_2^2\bar{t}_2 \qquad (4)$$

$$f_2 = 0.1,\ \phi_2 = 3.162,\ \eta_2 = 0.550 \qquad (5)$$

$$\bar{t}_1 = \frac{1-f_1}{4\eta_1 f_1^2} \qquad (6)$$

$$\bar{t}_2 = \frac{f_1-f_2}{4\eta_2 f_2^2} = \frac{f_1-0.1}{4(0.55)(0.01)} = 45.45(f_1-0.1) \qquad (7)$$

Make $\bar{t}_1 = \bar{t}_2$ and solve Eqs (1), (2), (6) and (7) together with the results

$$f_1 = 0.2565,\ \phi_1 = 5.06,\ \eta_1 = 0.397,$$

$$\bar{t}_1 = \bar{t}_2 = 7.113 \qquad (8)$$

P7.04.10. SPECIFIC RATE OF A SLURRY REACTION

A reaction in a slurried catalyst CSTR has the rate equation

$$r = k\eta C_s^{1.5} = 12.5(C-C_s) \qquad (1)$$

The residence time is $\bar{t} = 5$, the inlet is $C_0 = 1.2$ and the outlet is $C = 0.24$. The modified Thiele modulus for this order of reaction is

$$\phi = 4.382\sqrt{kC_s^{0.5}} \qquad (2)$$

Find the specific rate.

$$\eta = \frac{1.0357+0.3173\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (3)$$

In the CSTR,

$$r = \frac{C_0-C_1}{\bar{t}_1} = \frac{1.2-0.24}{5} = 0.192$$

From Eq (1),

$$C_s = C - r/12.5 = 0.24 - 0.192/12.5 = 0.2246$$

Then

$$k\eta = r/C_s^{1.5} = 0.192/(0.2246)^{1.5} = 1.804 \qquad (4)$$

$$\phi = 4.382(0.2246)^{0.25}\sqrt{k} = 3.0166\sqrt{k}$$

$$= 3.0166\sqrt{1.804}/\sqrt{\eta} = 4.0518/\sqrt{\eta} \qquad (5)$$

Solving Eqs (3) and (5),

$$\phi = 7.590,\ \eta = 0.2850 \qquad (6)$$

and from Eq (4),

$$k = 6.33 \qquad (7)$$

P7.04.11. SIZE OF PACKED BED FLOW REACTOR

A second order reaction takes place in a flow reactor with catalyst particles in the shape of lamellae. At the inlet the concentration is 2 lbmol/cuft and the Thiele modulus is $\phi = 4$. Find the value of kV_r/V' for obtaining 90% conversion.

From P7.03.10,

$$\eta = \frac{0.9958+0.9039\phi+0.00159\phi^2}{1+0.7592\phi+1.1718\phi^2}$$

Also,

$$\phi = 4\sqrt{C/C_0} = 2.828\sqrt{C}$$

The flow reactor equation is

$$kV_r/V' = \int_{0.2}^{2} \frac{dC}{\eta C^2} = 12.33$$

The integrand and the integral are tabulated.

C	ϕ	η	$1/\eta C^2$	Integral
2	4	0.2035	1.2285	
1.8	3.79	0.2146	1.4382	
1.6	3.58	0.2269	1.7212	
1.4	3.35	0.2421	2.1073	
1.2	3.10	0.2609	2.6617	
1	2.83	0.2846	3.5141	2.060
0.8	2.53	0.3160	4.9451	2.906
0.6	2.19	0.3601	7.7130	4.172
0.4	1.79	0.4284	14.59	6.402
0.2	1.26	0.5600	44.65	12.33

P7.04.12. MIXTURE OF CATALYST SIZES

A catalyst mass is made up of a mixture of porous spheres with a range of diameters. The average diameters of 10% cuts are shown. A second order reaction with $k = 2.5$ and $C_0 = 1.2$ is performed in a PFR. The Thiele modulus is $\phi = 2.0R\sqrt{C_s}$. Find V_r/V' for 80% conversion.

$$\eta = \frac{1.0357+0.3179\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (1)$$

The volumetric average effectiveness at the inlet is evaluated in the first table,

$$\eta_0 = 0.420$$

and the corresponding value of the Thiele modulus is $\phi_0 = 4.71$. At other concentrations,

$$\phi = 4.71\sqrt{C_s/1.2} = 4.30\sqrt{C_s} \qquad (2)$$

In the PFR,

$$V_r/V' = \int_{1.2}^{0.24} \frac{dC_s}{2.5\eta C_s^2} = 2.37 \qquad (3)$$

d, mm	ϕ	η_0
0.05	0.110	1.00
0.5	1.095	0.852
1.3	2.848	0.886
2.1	4.601	0.427
2.9	6.354	0.331
3.7	8.106	0.269
4.5	9.859	0.226
5.3	11.612	0.194
6.1	13.364	0.171
7.3	15.993	0.144
Sum		0.420

C_s	ϕ	η	$1/\eta C_s^2$
1.2	4.71	0.420	1.653
1.1	4.510	0.434	2.199
1	4.300	0.449	2.227
0.9	4.079	0.466	2.649
0.8	3.846	0.485	3.219
0.7	3.598	0.508	4.020
0.6	3.331	0.533	5.207
0.5	3.041	0.564	7.091
0.4	2.720	0.601	10.393
0.3	2.355	0.648	17.136
0.24	2.107	0.684	25.397

P7.04.13. MIXTURE OF CATALYST SHAPES

A catalyst bed contains a uniform mixture of equivolume porous spheres and cubes with two pairs of opposite faces sealed to diffusion. Accordingly the cubes may be regarded as slabs with diffusion through two faces. The spheres have a diameter of 0.02 ft, so cubes of the same volume have edges of 0.01614 ft.

A gas phase reaction has a zero order rate equation in the concentration range of interest. Given the additional data following, find the space velocity, cuft of feed/(hr)(cuft of catalyst bed), needed for 95% conversion.

$C_0 = 0.005$ lbmol/cuft, inlet concentration

$k = 5$ lbmol/(hr)(cuft of catalyst), specific rate

$D = 0.1$ ft^2/hr, diffusivity

$\varepsilon = 0.40$, fractional free volume

The rate equation is $r = k(1-\varepsilon)\eta$ lbmol/(hr)(cuft of bed)

The flow reactor equation is

$$V_r/V' = \frac{C_{s0}}{k(1-\varepsilon)} \int_0^{0.95} \frac{dx}{\eta} = \frac{0.005}{5(0.6)} \int_0^{0.95} \frac{dx}{\eta} \qquad (1)$$

For the spheres,

$$\phi_s = R\sqrt{k/DC_{s0}(1-x)} = 0.01\sqrt{\frac{5}{0.1(0.005)(1-x)}} = \frac{1}{\sqrt{1-x}} \qquad (2)$$

$$\eta_s = 1, \text{ when } \phi_s \le \sqrt{6}$$

$$-0.0065+4.389/\phi_s-4.688/\phi_s^2, \text{ when } \phi_s \ge \sqrt{6} \qquad (3)$$

The last result is from P7.03.03.

For the cubes, for the same volume as the sphere, the edge is 0.01612 ft.

$$\phi_L = 0.0807\phi_s = 0.0807/\sqrt{1-x} \qquad (4)$$

$$\eta_L = 1, \text{ when } \phi_L \le \sqrt{2}$$

$$\sqrt{2}/\phi_L, \text{ when } \phi_L \ge \sqrt{2} \qquad (5)$$

For the equivolume mixture,

$$\eta = 0.5(\phi_s+\phi_L) \qquad (6)$$

With the data of the table, the integral of Eq (1) is

$$V_r/V' = 0.0017 \text{ duft catalyst/(cfh of feed)} \qquad (7)$$

Space velocity = V'/V_r = 589 cfh/(cf catalyst)

x	ϕ_s	ϕ_L	η_s	η_L	η	$1/\eta$
0	1	0.807	1	1	1	1
0.2	1.12	0.90	1	1	1	1
0.4	1.29	1.04	1	1	1	1
0.6	1.58	1.28	1	1	1	1
0.8	2.24	1.80	1	0.785	0.893	1.120
0.9	3.16	2.55	0.913	0.555	0.734	1.362
0.95	4.70	3.78	0.715	0.374	0.545	1.837

P7.04.14. VARIABLE EFFECTIVENESS

A second order reaction is catalyzed in a PFR by a porous catalyst made up of small spheres. At the inlet the Thiele modulus is ϕ_0 = 10. Integrate the rate equation up to 90% conversion.

$$\phi = \phi_0\sqrt{1-x} = 10\sqrt{1-x}$$

$$\eta = \frac{1.0357+0.3172\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2}$$

The flow reactor equation is

$$-V'C_0dx = k\eta C_0^2(1-x)^2dW_c$$

$$\frac{W_cC_0}{kV'} = \int_0^x \frac{dx}{\eta(1-x)^2} = \int_0^x I\,dx$$

Integrands and integrals are tabulated.

x	ϕ	η	I	Integral
0	10	0.223	4.484	
0.1	9.487	0.234	5.276	
0.2	8.944	0.247	6.236	
0.3	8.367	0.262	7.790	
0.4	7.746	0.280	9.922	
0.5	7.071	0.303	13.207	3.807
0.6	6.325	0.333	18.788	5.407
0.7	5.477	0.374	29.92	7.832
0.8	4.472	0.436	57.3	12.18
0.9	3.162	0.551	181.5	24.12

P7.04.15. EFFECTIVENESS OF DESULFURIZATION CATALYST

The effectiveness of a naphtha desulfurization catalyst is tested by reducing thiophene with hydrogen at 660 K and 30 atm. Particle diameter is

0.35 cm, true density is 2.65 g/cc, surface area is 180 m^2/g and porosity ε =0.40. The reaction is apparent first order with k = 0.3 cc thiophene/(s)(g catalyst). The tortuosity τ is related to the porosity by the empirical relation, $\tau\sqrt{\varepsilon} = 1$. The molecular diffusivity is D = 0.052 cm^2/s.

The effective diffusivity is

$$D_e = D\varepsilon/\tau = D\varepsilon^{1.5} = 0.052(0.4)^{1.5} = 0.0132$$

1 gm of catalyst = 1/(0.4)(2.65) = 0.943 cc

Specific rate per unit volume is,

$$k_v = 0.3\ \frac{\text{cc thiophene}}{\text{g cat/s}}\ \frac{\text{g cat}}{0.943\ \text{cc cat}} = 0.318\ \frac{\text{cc thiopene}}{\text{cc cat/s}}$$

$$\phi_s = R\sqrt{k_v/D_e} = 0.175\sqrt{0.318/0.0132} = 0.859$$

$$\eta = \frac{3}{\phi_s}\left(\frac{1}{\tanh(\phi_s)} - \frac{1}{\phi_s}\right) = 0.95$$

P7.05.01. EXTERNAL DIFFUSION LIMITED AT TWO TEMPERATURES

The rate of a diffusion limited second order reaction is represented by the equations

$$r = k_d(C-C_s) = k_cC_s^2$$

with

$$k_d = \exp(1.55 - 300/T)$$

$$k_c = \exp(k_1 - k_2/T)$$

The measurements of the first three columns of the table have been made. The reaction is to be conducted at 375 K with $C_0 = 2$ in a CSTR with residence time $\bar{t} = 2$. Find the constants k_1 and k_2 and the outlet C and C_s.

$$C_s = C - r/k_d$$

$$k_1 - k_2/T = \ln(r/C_s^2)$$

Various intermediate numbers are tabulated.

$$k_2\left(\frac{1}{350} - \frac{1}{400}\right) = 2.0089 - 0.7137$$

$$k_2\ 3626$$

$$k_1 = 0.7137 + 3626/350 = 11.075$$

Therefore,

$$k_c = \exp(11.075\text{-}3626/T) \qquad (1)$$

At 375 K, $k_c = 4.0782$, $k_d = 2.1170$. The material balance on the CSTR is

$$2 = C + \bar{t}r = C + 2(4.0782)C_s^2 \qquad (2)$$

The rate equation is

$$2.117(C-C_s) = 4.0782C_s^2 \qquad (3)$$

Solving (2) and (3) together,

$$C_s = 0.3985$$

$$C = 0.7045$$

C	T	r	k_d	C_s	$\ln(r/C_s^2)$	k_c
2.5	350	2.7	2.00	1.1500	0.7137	
2.2	400	3.4	2.23	0.6753	2.0089	
	375		2.117			4.0782

P7.05.02. FLUIDIZED TWO STAGE

A fluidized bed reactor with two equal stages is used for a reaction with external diffusional resistance. The rate equation is

$$r = 0.15\eta p_s^2 \approx 0.5(p_g - p_s) \quad \text{lbmol/(hr)(lb cat)} \qquad (1)$$

Pressure is 5 atm, temperature is 1200 R and the Thiele modulus at the entrance to the first stage is $\phi_0 = 10$. Find the residence time in each stage for a 90% overall conversion.

Eq (1) can be written

$$r = 0.15\eta(p_g - 2r)^2 \qquad (2)$$

The material balances on the two stages are,

$$C_0 = C_1 + \bar{t}_1 r_1$$

$$C_1 = C_2 + \bar{t}_2 r_2$$

and in terms of partial pressures

$$p = RTC$$

$$p_{g0} = p_{g1} + RT\,\bar{t}_1 r_1$$

$$p_{g1} = p_{g2} + RT\,\bar{t}_2 r_2$$

from which the residence times are

$$RT\bar{t}_1 = (p_{g0} - p_{g1})/r_1 = (5 - p_{g1})/r_1 \qquad (3)$$

$$RT\bar{t}_2 = (p_{g1} - p_{g2})/r_2 \qquad (4)$$

These residence times are equal, so for 90% conversion,

$$\frac{5-p_{g1}}{r_1} = \frac{p_{g1}-0.5}{r_2} \qquad (5)$$

Other relations are

$$\Phi = 10\sqrt{p_s/p_{s0}} \qquad (6)$$

$$\eta = \frac{1.0357+0.3173\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (7)$$

At the inlet conditions,

$p_{g0} = 5$, $\phi_0 = 10$, $\eta_0 = 0.225$

$r_0 = 0.5260$, from Eq (2)

$p_{s0} = p_{g0} - 2r_0 = 3.948$

$$\phi = 10\sqrt{p_s/p_{s0}} = 10\sqrt{p_s/3.948} = 5.0328 \qquad (8)$$

In the second stage, $p_{g2} = 0.1p_{g0} = 0.5$. The calculation procedure for the second stage is

(i) Assume p_{s2}

(ii) Find ϕ_2 from (8) and η_2 from (7)

(iii) Find r_2 from (2)

(iv) Find $p_{s2} = p_{g2} - 2r_0$ and compare with the assumption. Two trials are

p_{s2}	ϕ_2	η_2	r_2	p_{s2}	
0.40	3.183	0.55	0.03577	0.4296	
0.43	3.300	0.54	0.0352	0.4296	check

The calculation procedure for the first stage is

(v) Assume p_{g1}

(vi) Assume p_{s1}

(vii) Find ϕ_1 from (8) and η_1 from (7)

(viii) Find r_1 from (2)

(ix) Find $p_{s1} = p_{g1}-2r_1$ and compare with the assumption

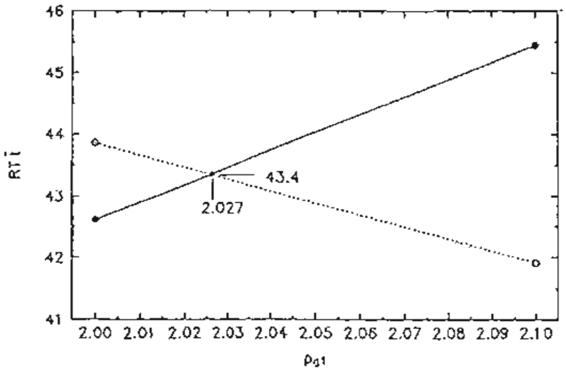
(x) If (5) is not satisfied, repeat with another value of p_{g1}.

Several trials are made. A double linear interpolation is made on the sketch with the results

$p_{g1} = 2.027$

$RT\bar{t} = 43.4$

p_{g1} q (5)	p_{s1}	ϕ_1	η_1	r_1	p_{s1}	$RT\bar{t}$, Eq (5)
2.0	1.6	6.37	0.32	0.07004	1.86	
2.0	1.86	6.86	0.31	0.0684	1.86	$43.86 \not\equiv 42.61$
2.1	1.9	7.05	0.30	0.0692	1.962	$41.91 \not\equiv 45.45$
2.027						43.4



P7.05.03. DIFFUSION AND L-H TYPE SURFACE REACTION

The rate of a gas phase reaction, $2A \Rightarrow B$, is believed controlled by external diffusion and second order surface reaction with only substance A adsorbed to a substantial extent. The rate of diffusion is

$r_d = 0.9(p_g - p_s)$, mol/(h)(kg catalyst)

Experimental data are (p_g atm, r mph/kg) = (5.00, 1.424) and (3.00, 0.823).

(a) Find r as a function of p_g, the partial pressure of the reactant.

(b) A PFR is charged with 10 kgmol/h of a mixture at 10 atm and 500 K with 80% A and 20% inert. What catalyst mass is needed for 60% conversion with unit effectiveness?

(c) The effectivenes of the catalyst is represented by

$$\eta = 1 - 0.95\phi - 0.6\phi^2 \quad (1)$$

$$\phi = 0.5\sqrt{C_a} \quad (2)$$

where C_a is in gmol/liter. The constants of the rate equation found in part (a) apply. What amount of catalyst is needed for 60% conversion?

At steady state,

$$r = 0.9(p_g - p_s) = k_1\left(\frac{p_s}{1+k_2p_s}\right)^2$$

$$= k_1[\frac{p_g-r/0.9}{1+k_2(p_g-r/0.9)}]^2 \qquad (3)$$

Use the two sets of data, (p_g, r), to find

$k_1 = 0.50$, $k_2 = 0.30$

$$r = 0.5[\frac{p_g-r/0.9}{1+0.3(p_g-r/0.9)}] \qquad (a) \quad (4)$$

For the reaction $2A \Rightarrow B$,

$$n_t = n_a+n_b+n_I = 0.5(8+n_a)+2 = 6+0.5n_a$$

$$p_g = (n_a/n_t)\pi = \frac{10n_a}{6+0.5n_a}$$

The flow reactor equation is

$$W_c = \int_{3.2}^{8} \frac{dn_a}{r} = 2.825 \qquad (b) \quad (5)$$

with Simpsons rule using these data

n_a	p_g	$1/r$
8	8	0.4593
5.6	6.3636	0.5588
3.2	4.2105	0.8369

With the given effectiveness equation,

$$C_a = \frac{n_a}{n_t}\frac{\pi}{RT} = \frac{n_a}{6+0.5n_a}\,\frac{10}{0.08205(500)} = \frac{0.2438}{6+0.5n_a} \qquad (6)$$

Substitute into Eq (1) to find η.

The rate equation is

$$r = 0.5\eta[\frac{p_g-r/0.9}{1+0.3(p_g-r/0.9)}]^2 \qquad (7)$$

The integral is

$$W_C = \int_{3.2}^{8} \frac{dn_a}{r} = 3.606 \text{ kg} \qquad (c) \quad (8)$$

using the data of the following table and Simpsons rule.

n_a	p_g	η	$1/r$
8	8	0.7610	0.5691
5.6	6.3636	0.7897	0.7471
3.2	4.2105	0.8324	0.9501

P7.05.04. DATA AT SEVERAL FLOW RATES

The rate of a reaction, $A \Rightarrow B$, has the equations

$$r = k_1(V')^{0.8}(C_g-C_s) = k_2C_s^2 \qquad (1)$$

where V' is the volumetric flow rate, liters/h. Tests were made with inlet concentration 20 mols/liter, and initial rates were measured at two flow rates,

V', liters/hr	10	20
r_0, mol/(h)(kg catalyst)	10	14

Find (a) the constants of the rate equations; (b) the amount of catalyst needed to convert 80% at a feed rate of 20 liters/hr.

Rearrange the rate equation,

$$C_{s0} = C_{g0} - r_0/k_1(V')^{0.8} = \sqrt{r_0/k_2} \qquad (2)$$

Substituting the data,

$$20 - \frac{10}{(10)^{0.8}k_1} = \sqrt{10/k_2}$$

$$20 - \frac{14}{(20)^{0.8}k_1} = \sqrt{14/k_2}$$

from which

$k_1 = 0.1641$

$k_2 = 0.0935$

and

$$r = 0.0685[C_g - \frac{r}{0.1641(V')^{0.8}}]^2 \qquad (3)$$

The flow reactor equation is

$$W_c = \int_{20}^{4} \frac{V' dC_g}{r} = 83.1 \text{ kg}$$

At V' = 20 liters/h, $C_{g0} = 20$ and $r_0 = 14$. The integrand is evaluated with Eq (3) and is tabulated. The integration is done trapezoidally.

C_g	20	16	12	8	4
1/r	0.0714	0.0990	0.1527	0.2892	0.9251

P7.05.05. PFR SIZE WITH POROUS CATALYST

The reaction, 2A ⇒ B + C, has the rate equation

$$r = 8\eta C^2 \qquad (1)$$

Feed rate is 100 cfh, inlet concentration is 0.5 lbmol/cuft and the Thiele modulus at the inlet of the reactor is 15. Find V_r/V' for 90% conversion.

$$\phi = 15\sqrt{C/0.5} = 21.21\sqrt{C} \qquad (2)$$

For second order with spheres,

$$\eta = \frac{1.0357+0.3173\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (3)$$

For a flow reactor,

$$V_r/V' = \int_{0.05}^{0.5} \frac{dC}{8\eta C^2} = 0.125\int IdC$$

$$= 0.125(71.55) = 8.94 \text{ cuft/cfh at } 90\%. \qquad (4)$$

The integrand is found with the aid of Eqs (2), (3) and is tabulated. The integration is with the trapezoidal rule.

C	ϕ	η	$1/\eta C^2$	$\int$
0.5	15	0.15	26.678	0
0.4	13.4	0.17	36.76	3.02
0.3	11.6	0.19	69.44	8.33
0.2	9.5	0.20	125.0	18.05
0.1	6.7	0.32	312.5	39.93
0.05	4.7	0.42	952.3	71.55

P7.05.06. PFR WITH DIFFUSIONAL LIMITATION

The rate of the reaction, 2a ⇒ B + C, is limited by external diffusion and has the equation

$$r = 1.3(C_g-C_s) = 8\eta C \qquad (1)$$

The feed rate is 100 cfh, the inlet concentration is 0.5 lmol/cuft and the Thiele modulus is 15 when the concentration is 0.5. Find V_r/V' for 90%

conversion. Compare with the result of P7.05.05 which ignores external diffusional resistance.

$$\phi = 15\sqrt{C_s/0.5} = 21.21\sqrt{C_s} \qquad (2)$$

$$\eta = \frac{1.0357+0.3173\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (3)$$

For the flow reactor,

$$V_r/V' = \int_{C_g}^{0.5} \frac{dC_g}{1.3\eta(C_g-C_s)} \qquad (4)$$

$$= 6.14 \text{ cuft/cfh for 80\% conversion}$$
$$11.04 \text{ cuft/cfh for 90\% conversion.}$$

The integrand is evaluated in the table by solving Eqs (1), (2) and (3) together.

C_g	ϕ	η	C_s	$1/(C_g-C_s)$
0.5	12.69	0.179	0.3585	7.0671
0.45	12.12	0.186	0.3271	8.1367
0.4	11.52	0.196	0.2951	9.5329
0.35	10.85	0.207	0.2624	11.4155
0.3	10.14	0.221	0.2290	14.0845
0.25	9.36	0.237	0.1947	18.0832
0.2	8.47	0.259	0.1595	24.6914
0.15	7.43	0.291	0.1230	37.037
0.10	6.18	0.339	0.0849	66.225
0.05	4.48	0.436	0.0447	188.68

P7.05.07. DIFFUSION AND AN L-H MECHANISM IN A FLUIDIZED BED

A reaction, A ⇒ 2B, has a rate equation

$$r = 0.2(p_{ag}-p_{as}) = 0.5\left(\frac{p_{as}}{1+0.2p_{as}+0.1p_{bg}}\right)^2$$

in the units kgmol/(h)(kg catalyst). The pressure is 10 atm, inlet partial pressure is $p_{ag0} = 5$, the feed rate is $n_{a0} = 4$ kgmol/h and the feed rate of inert is the same. Find the amount of catalyst needed in a fluidized bed (CSTR) for 80% conversion.

At the outlet of the CSTR at steady state,

$$n_a = 0.2(4) = 0.8$$
$$n_b = n_{b0}+2(n_{a0}-n_a) = 6.4$$
$$n_t = n_a+n_b+n_i = 0.8+6.4+4 = 11.2$$
$$p_{ag} = (n_a/n_t)\pi = (0.8/11.2)10 = 0.714$$
$$p_{bg} = (n_b/n_t)\pi = (6.4/11.2)10 = 5.714$$
$$p_{as} = p_{ag}-r/0.2 = 0.714-5r$$

$$r = 0.5\left[\frac{0.714-5r}{1+0.2(0.714-5r)+0.1(5.714)}\right]^2$$

$$= 0.2973, \text{ by trial}$$

The catalyst requirement in a CSTR is

$$W_c = \frac{n_{a0}-n_a}{r} = \frac{4-0.8}{0.2973} = 10.76 \text{ kg}$$

P7.05.08. CONSTANTS OF AN L-H EQUATION WITH DIFFUSION

The rate of solid catalyzed reaction is controlled by external diffusion and surface reaction, with equation

$$r = 0.2(p_g-p_i) = k_1\left(\frac{p_i}{1+k_2p_i}\right)^2 \qquad (1)$$

Given the rate data of the first two columns of the table, find the constants of the rate equation.

The pressure at the surface is

$$p_i = p_g - r/0.2 \qquad (2)$$

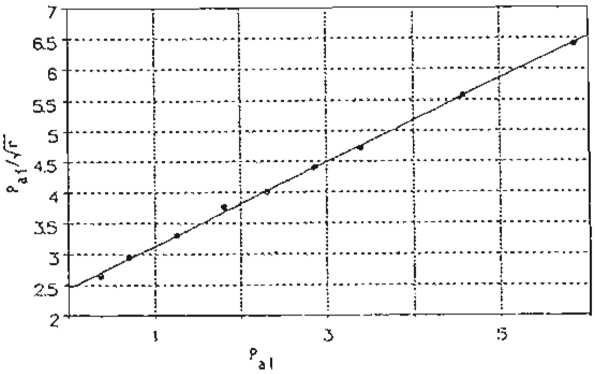
Eq (1) linearized is

$$y = p_i/\sqrt{r} = (1+k_2p_i)/\sqrt{k_1} \qquad (3)$$

$$= 2.436 + 0.682p_i \qquad (4)$$

The plot shows Eq (3) to be a good linear fit of the data.

p_g	r	p_i	$p_i/\sqrt{r}$
10	0.83	5.85	6.421
8	0.68	1.60	5.578
6	0.52	3.40	4.715
5	0.425	2.875	4.410
4	0.335	2.325	4.017
3	0.235	1.825	3.765
2	0.147	1.265	3.299
1	0.058	0.710	2.950
0.5	0.022	0.390	2.629



P7.05.09. PFR WITH EXTERNAL AND INTERNAL DIFFUSION

A second order gas phase reaction, 2A ⇒ 2B, is conducted under flow conditions with a porous catalyst. Diffusional resistance is present both externally and within the pores. Inlet partial pressure of the reactant is 2 atm and the temperature is 2k73 K. Conversion is to be 80%. Other data are,

particle radius R = 0.1 cm

$k_v/D_{eff} = 4.48(10^8)$ cc/mol

At steady state,

$$k_ga(C_g-C_s) = k_v\eta C_s^2 \qquad (1)$$

$$k_ga(p_g-p_s) = \frac{k_v\eta}{RT}\,p_s^2 \qquad (2)$$

$$p_s = p_g - \frac{4.48(10^4)}{82.05(273)}\,\eta p_s^2$$

$$= \frac{-1+\sqrt{1+8\eta p_g}}{4\eta} \qquad (3)$$

$$\phi = R\sqrt{k_vC_s/D} = R\sqrt{k_vp_s/RTD} = 0.1\sqrt{\frac{1.5(10^8)p_s}{22400}}$$

$$= 8.18\sqrt{p_s} \qquad (4)$$

For second order in a sphere the effectiveness is

$$\eta = \frac{1.0357+0.3173\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \tag{5}$$

In plug flow,

$$-dn = -V'dC_g = k_ga(C_g-C_s)dV_r$$

$$\frac{V_r}{V'k_ga} = \int \frac{dC_g}{C_g-C_s} = \int_{0.4}^{2} \frac{dp_g}{p_g-p_s} = 5.787 \tag{6}$$

The table summarizes the data and the calculations with Eqs (3), (4) and (5). Trapezoidal integration is used.

p_g	p_s	ϕ	η	$1/(p_g-p_s)$	$\int$
2	1.247	9.14	0.242	0.328	0
1.8	1.143	8.74	0.252	1.522	0.285
1.6	1.036	8.33	0.263	1.773	0.615
1.4	0.926	7.87	0.275	2.111	1.003
1.2	0.813	7.38	0.292	2.587	1.473
1	0.697	6.83	0.312	3.300	2.061
0.8	0.576	6.21	0.338	4.452	2.838
0.6	0.449	5.48	0.374	6.633	3.947
0.4	0.315	4.59	0.428	11.77	5.787

P7.05.10. RATE OF REACTION AND REACTOR SIZE

The rate of a reaction, A ⇒ B, in steady state is

$$r = 2(p_g-p_s) = \frac{1.2p_s}{1+2.4p_s} \tag{1}$$

Pressure is 2 atm and the feed is pure reactant at 10 lbmol/h. Find the amount of catalyst for 90% conversion.

The rate equation is rearranged to

$$r = \frac{1/2(p_{ag}-0.5r)}{1+2.4(p_a-0.5r)} \tag{2}$$

For the flow reactor,

$$n_a = n_t(p_a/\pi) = 10(p_a/2) = 5p_a$$

$$-dn_a = -5dp_a = rdW_c$$

$$W_c = 5\int_{0.2}^{2} \frac{dp_a}{r} = 5(9/3)[2.50+3(2.94)+9.53] = 31.3 \text{ lb.}$$

The integrand is tabulated. Integration is with Simpsons Rule.

p_a	2.0	1.1	0.2
$1/r$	2.50	2.94	9.53

P7.05.11. PARTIAL PRESSURE AT THE SURFACE AND THE RATE

The overall rate of the gas phase reaction, A+B ⇒ C, is governed by the equations

$$r = 0.25(p_{ag}-p_{ai}) = \frac{0.04p_{ai}p_{bg}}{(1+0.2p_{ai}+0.1p_{bg})^2} \tag{1}$$

For the case of equimolal proportions of the reactants and a total pressure of 10 atm, find the rate of reaction when 50% of A has been converted.

$$n_{a0} = n_{b0}$$

$$p_{ag} = p_{bg}$$

$$n_t = n_a+n_b+(n_{a0}-n_a) = n_{a0}+n_a$$

When $n_a = 0.5n_{a0}$

$$p_{bg} = p_{ag} = (n_a/n_t)\pi = 10/3$$

and Eq (1) becomes

$$0.25(3.333-p_{ai}) = \frac{0.04(3.333)p_{ai}}{[1+0.2p_{ai}+0.1(3.333)]^2} \quad (2)$$

from which

$$p_{ai} = 2.91 \quad (3)$$

At this condition the rate is

$$r = 0.25(3.333-2.91) = 0.1058$$

P7.05.12. ZERO ORDER REACTION

A gas phase isomerization is catalyzed by porous spherical grains. In the absence of complicating factors the rate of chemical reaction is approximately zero order, that is,

$$r = k = 0.16 \text{ lbmol/(h)(cuft of catalyst)}$$

The overall conversion is affected also by the rate of diffusion of the reactant to the external surface and by the accessibility of the internal surface. The rate of diffusion is

$$r_d = 0.25(C_g-C_s)$$

At the inlet to the reactor, $C_{g0} = 1.2$ and the Thiele modulus is $\phi_0 = 10$. Find V_r/V', cuft of catalyst/(cuft of feed/hr), as a function of remaining C_g.

In the steady state,

$$r = 0.16\eta = 0.25(C_g-C_s)$$

$$C_s = C_g - 0.64\eta \quad (1)$$

$$\phi = 10/\sqrt{C_s} = 10/\sqrt{C_g-0.64\eta} \quad (2)$$

From problem P7.03.03 the effectiveness of zero order in a sphere is

$$\eta = -0.00652+4.3889/\phi -4.6877/\phi^2 \quad (3)$$

For the flow reactor,

$$V_r/V' = \int \frac{dC_g}{r} = \int_{C_g}^{1.2} \frac{dC_g}{0.64\eta} \quad (4)$$

Solve Eqs (2) and (3) together, substitute into (1) and integrate. The calculations are summarized in the table.

C_g	ϕ	$1/\eta$	V_r/V'
1.2	10.22	.646	0
1.1	10.73	2.770	1.693
1	11.30	2.907	3.469
0.9	12.03	3.067	5.331
0.8	12.87	3.268	7.313
0.7	13.90	3.509	9.431
0.6	15.21	3.817	11.719
0.5	16.93	4.237	14.238
0.4	19.35	4.808	17.063
0.3	23.06	5.714	20.350
0.2	29.73	7.353	24.438

P7.05.13. EXTERNAL DIFFUSION AND SURFACE REACTION

The rate of a solid catalyzed reaction, A ⇒ B, is determined by the rate of diffusion to the surface, r_d, and the rate of a first order surface reaction, r_s. At steady state,

$$r = r_d = r_s$$

$$= \frac{k_1(p_a-p_{ai})}{\ln \frac{\pi-p_a}{\pi-p_{ai}}} = k_2p_{ai} \qquad (1)$$

At a total pressure of 5, two measurements of the partial pressure and the rate are

p_a	1.00	2.00
r	0.50	0.75

Find the constants of Eq (1).

The interfacial partial pressure is

$$p_{ai} = r/k_2 \qquad (2)$$

Substitute (2) into (1), then the given data into (1) and solve the resulting two equations for the two constants.

$$r \ln \frac{5-p_a}{5-r/k_2} = k_1(p_a-r/k_1) \qquad (3)$$

$k_1 = 0.239$, $k_2 = 1.512$.

P7.05.14. MASS TRANSFER AND SURFACE REACTION

The rate of a second order solid catalyzed reaction is controlled by diffusion to the external surface, by diffusion into the pores and by reaction on the pore surface. The rate relations are

$$r = k_ga(C-C_s) = 1500\eta C_s^2, \text{ mol/(s)(cc catalyst bed)}$$

The coefficient k_g is to be figured by the correlation of Dwivedi and Upadhyay (*IECPDD* 16 157, 1977). The feed rate is 10 mol/h at a concentration of C_0 = 0.01 mol/cc. Find the volume of catalyst needed to convert 90%. Other data are,

$d_p = 0.6$ cm

$a = 6$ cm^2/cc of bed [0.6 cm spheres, 40% porosity]

$D_e = 0.013$ cm^2/s, effective diffusivity

u = 100 cm/sec, superficial velocity

Sc = 2.5, Schmidt number

Re = 10, Reynolds number

The mass transfer coefficient is given by

$$j_d = k_gSc^{2/3}/u = \frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}$$

Substitute Sc = 2.5, Re = 10 and u = 100, making

$k_g = 14.43$ cm/s

$k_ga = 86.6$ /s

The rate equation becomes

$$86.6(C_g-C_s) = 1500\eta C_s^2$$

or

$$86.6(f-f_s) = 1500\eta C_0f_s^2 = 15\eta f_s^2 \qquad (1)$$

$$f = C/C_0,\quad f_s = C_s/C_o,\quad C_0 = 0.01 \qquad (2)$$

The Thiele modulus is

$$\phi = R\sqrt{k_vC_s/D} = 0.3\sqrt{1500C_s/0.013} = 10.19\sqrt{f_s} \qquad (3)$$

For second order reaction in spheres,

$$\eta = \frac{1.0357+0.3179\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \tag{4}$$

In the plug flow reactor,

$$V_r/V' = \int_1^{0.1} \frac{df}{15\eta f_s^2} = \frac{1}{15}\int I\,df \tag{5}$$

The integrand is evaluated with Eqs (1), (3) and (4) and is tabulated along with the integral.

f	f_s	ϕ	η	$1/\eta f_s^2$	Integral
1	0.964	10.01	0.223	4.8255	0
0.9	0.869	9.50	0.234	5.6591	0.524
0.8	0.774	8.97	0.246	6.7855	1.146
0.7	0.679	8.40	0.261	8.3104	1.901
0.6	0.584	7.78	0.279	10.509	2.840
0.5	0.488	7.12	0.302	13.904	4.063
0.4	0.391	6.37	0.331	19.761	5.746
0.3	0.294	5.53	0.371	31.184	8.290
0.2	0.197	4.52	0.433	59.448	12.83
0.1	0.099	3.21	0.547	186.26	25.11

P7.05.15. DIFFUSION AND SURFACE REACTION WITH DISSOCIATION

A solid catalyzed reaction, $A_2 \Rightarrow 2B$, has the rate equations,

$$r = 0.5(p_a-p_{ai}) = \frac{2p_{ai}}{(1+3\sqrt{p_{ai}})^2}, \text{ lbmol/(h)(lb catalyst)} \tag{1}$$

The operating pressure is 2 atm and the feed is pure A_2. Find the ratio, W/n_{a0} lb catalyst/(lbmol feed/h), needed to reduce the partial pressure to 1.0 atm.

$$p_{ai} = p_a - 2r \tag{2}$$

$$n_t = n_a+2(n_{a0}-n_a) = 2n_{a0}-n_a$$

$$p_a = \frac{n_a\pi}{2n_{a0}-n_a} = \frac{2n_a}{2n_{a0}-n_a}$$

$$n_a/n_{a0} = \frac{2p_a}{2+p_a}$$

When $p_a = 1$, $n_a/n_{a0} = 2/3$. For the flow reactor,

$$W/n_{a0} = \int_{2/3}^{1} \frac{d(n_a/n_{a0})}{r} = 2.580 \tag{3}$$

Substitute Eq (2) into (1) and the result into (3). The calculations are tabulated. The trapezoidal rule was used.

p_a	p_{ai}	n_a/n_{a0}	$1/r$
2	1.718	1	7.080
1.8	1.524	0.947	7.258
1.6	1.332	0.889	7.474
1.4	1.142	0.824	7.745
1.2	0.953	0.750	8.098
1.0	0.767	0.667	8.578

P7.06.01. ADIABATIC REACTION ON NONPOROUS CATALYST

Under adiabatic conditions with external diffusion, temperature and concentration differences will develop between the bulk of the fluid and the surface of the catalyst. The rate of reaction is the rate of diffusion,

$$r = k_g a(C_g - C_s)$$

and the heat balance is

$$ha(T_s - T_g) = -\Delta H_r r_c = -\Delta H_r k_g a(C_g - C_s)$$

Solve for the surface temperature.

$$T_s = T_g - \frac{k_g \Delta H_r}{h}(C_g - C_s)$$

$$= T_g[1+\beta_g(1-y)] \qquad (1)$$

$$\beta_g = \frac{-\Delta H_r k_g C_g}{hT_g}$$

$$y = C_s/C_g$$

The specific rate, k_{Ts}, at the surface temperature is expressed in terms of the specific rate, k_{Tg}, at the bulk temperature by

$$k_{Ts} = k_{Tg}\ \exp[-\frac{E}{R}(\frac{1}{T_s} - \frac{1}{T_g})]$$

$$= k_{Tg}\ \exp[\frac{\beta_g \gamma(1-y)}{1+\beta_g(1-y)}]$$

$$\gamma = E/RT_g$$

Under steady state conditions, the rate of diffusion equals the rate of surface reaction.

$$k_g a(C_g - C_s) = k_{Ts} C_s^n$$

or

$$1-y = \frac{k_{Ts} C_g^{n-1}}{k_g a}\ y^n$$

$$= \mathrm{Da}\ y^n\ \exp[\ \frac{\beta_g \gamma(1-y)}{1+\beta_g(1-y)}] \qquad (2)$$

$$\mathrm{Da} = \frac{k_{Tg} C_g^{n-1}}{k_g a}\ ,\ \text{Damkohler number}$$

Eq (2) can be solved for y in terms of the three parameters β_g, γ and Da, as well as C_g and T_g. After that has been done, the temperature difference, $T_g - T_s$, the surface concentration C_s and the effectiveness can be found.

The effectiveness is the ratio of the rate at (C_s, T_s) to the rate with the conditions (C_g, T_g), that is,

$$\eta = \frac{k_{Ts}}{k_{Tg}}(\frac{C_s}{C_g})^n = y^n\ \exp[\frac{\beta_g \gamma(1-y)}{1+\beta_g(1-y)}] \qquad (3)$$

The solution cannot be represented compactly because of the number of parameters.

Numerical example. Take a second order reaction with $\beta_g = 0.8$ and $\gamma = 5.0$, and find the other variables as functions of Da.

Eq (2) becomes

$$y = 1 - \mathrm{Da}\ y^2 \exp[\frac{4(1-y)}{1+0.8(1-y)}]$$

and Eq (3) becomes

$$\eta = y^2 \exp[\frac{4(1-y)}{1+0.8(1-y)}]$$

and Eq (1) becomes

$$\frac{T_s-T_g}{T_g} = \beta_g(1-y) = 0.8(1-y)$$

The solutions are tabulated in terms of Da. For exothermic reactions the effectiveness can exceed unity.

Da	$y=C_s/C_g$	η	$\frac{T_s-T_g}{T_g}$
0.1	0.8800	1.200	0.10
0.5	0.4894	1.021	0.41
1	0.3425	0.658	0.53
5	0.1499	0.172	0.68
10	0.1054	0.091	0.72
∞	0	0	0.80

P7.06.02. ADIABATIC REACTION IN A SPHERICAL POROUS CATALYST

Under steady adiabatic conditions in the absence of phase change the rate of enthalpy change of reaction equals the rate of heat transfer by conduction, that is,

$$\Delta H_r D\frac{\partial C}{\partial r} = \lambda\frac{\partial T}{\partial r}$$

which integrates to

$$T = T_s+\frac{\Delta H_r D}{\lambda}(C-C_s) = T_s[1+\beta(1-y)] \tag{1}$$

$$\beta = -\frac{\Delta H_r D C_s}{\lambda T_s} \tag{2}$$

$$y = C/C_s \tag{3}$$

The specific rate can be expressed in terms of the surface condition as

$$k = k_{Ts} \exp[-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_s})] = k_{Ts} \exp[\frac{\beta\gamma(1-y)}{1+\beta(1-y)}] \tag{4}$$

$$\gamma = E/RT_s \tag{5}$$

For a n-th order reaction the power law rate equation is

$$r_c = kC^n = k_{Ts}C_s^n y^n \exp[\frac{\beta\gamma(1-y)}{1+\beta(1-y)}] \tag{6}$$

For a sphere of radius R, the material balance over a pore is

$$\frac{d^2y}{d\rho^2} + \frac{2}{\rho}\frac{dy}{d\rho} = \phi^2 y^n \exp[\frac{\beta\gamma(1-y)}{1+\beta(1-y)}] \tag{7}$$

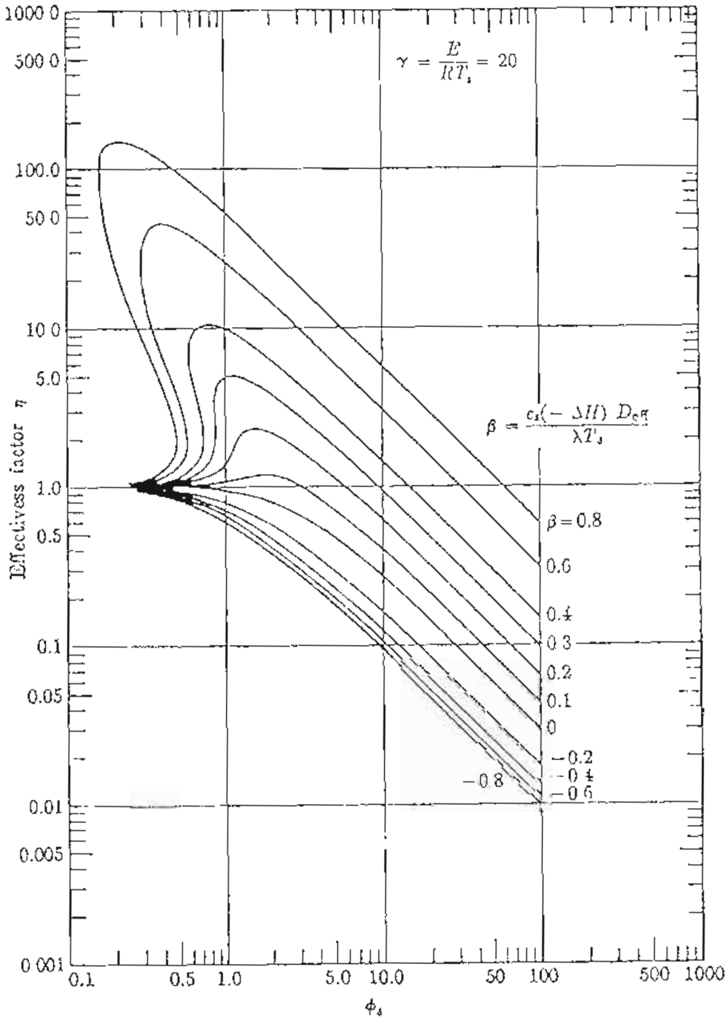
$$\phi^2 = \frac{R^2 k_{Ts} C_s^{n-1}}{D} \tag{8}$$

At the surface, $\rho = r/R = 1$, $y = C/C_s = 1$, $dy/d\rho = (dy/d\rho)_1$; at the center, $\rho = 0$, $y = y_0$, $dy/d\rho = 0$.

After Eq (7) is integrated, the value of the derivative $(dy/d\rho)_1$ becomes known and the effectiveness can be found as

$$\eta = \frac{3}{a\phi^2}\left(\frac{dy}{d\rho}\right)_1 \tag{3}$$

Numerical solutions of several cases appear in the literature. The accompanying figure is of first order reaction in a sphere (Weisz & Hicks, *Chem Eng Sci* 17 265, 1962).



P7.06.03. MAXIMUM SURFACE TEMPERATURE

For diffusion to the external surface, the heat balance is represented by Eq (1) of P7.06.01,

$$T_s - T_g = -\Delta H_r (k_c/h)(C_g - C_s) \tag{1}$$

This can be written in terms of correlations for the coefficients of heat and mass transfer. The Chilton-Colburn factors are

$$j_d = \frac{k_c\rho}{G}(\mu/\rho D)^{2/3} = (k_c\rho/G)Sc^{2/3} \tag{2}$$

$$j_h = \frac{k}{C_pG}(C_p\mu/\lambda)^{2/3} = (h/C_pG)Pr^{2/3} \tag{3}$$

Substituting into Eq (1),

$$T_s - T_g = \frac{j_d}{j_h}\left(\frac{Pr}{Sc}\right)^{2/3} \frac{(-\Delta H_r)}{\rho C_p}(C_g - C_s) \tag{4}$$

The factors j_d and j_h are commonly correlated in terms of Reynolds numbers (as in P7.06.19 for instance). Their ratio often is near unity, and the ratio Pr/Sc also is near unity for simple gases. The maximum difference of temperature between gas phase and the surface of the catalyst is obtained when $C_s \Rightarrow 0$. Then,

$$T_{max} - T_g \simeq \frac{-\Delta H_r C_g}{\rho C_p} \qquad (5)$$

Numerical example. Ethylene is being hydrogenated with equimolar hydrogen at 300 K and 1 atm. The physical properties are

$\Delta H_r = -32.7$ kcal/mol
$\rho = 0.04$ mol/liter
$C_p = 8.5$ cal/(mol)(K)

$$C_g = \frac{0.5(273)}{22400(300)} = 2.03(10^{-5}) \text{ mol/cc}$$

$$T_{max} - 300 = \frac{32700(2.03(10^{-5})(1000)}{0.04(8.5)} = 1952$$

In laboratory work on this process, the ethylene is greatly diluted to moderate the temperature effect.

P7.06.04. MINIMAX OF INTERIOR TEMPERATURES

The temperature in the pore is related to that at the surface by the heat balance, Eq (1) of P7.06.02,

$$T - T_s = -\frac{\Delta H_r D}{\lambda}(C_s - C) \qquad (1)$$

When $C \Rightarrow 0$,

$T - T_s$ = maximum for exothermal reactions
minimum for endothermal reactions

Numerical example. Data are provided (Prater, *Chem Eng Sci* 8 284, 1958) for the dehydrogenation of 20% cyclohexane at 25 atm and 450 C.

$\Delta H_r = +220$ kJ/mol
$D = 0.016\ \text{cm}^2/\text{s}$
$\lambda = 0.22$ J/(s)(m)(K)

$$C_g = \frac{0.2(25)(273)}{22400(723)} = 8.43(10^{-5}) \text{ mol/cc}$$

$$T_{min} - 723 = -\frac{2.2(10^5)(0.016)(8.43)(10^{-5})}{0.0022} = -134.9 \text{ K}$$

P7.06.05. TEMPERATURE AND CON/CENTRATION AT THE SURFACE.

A reacting gas enters a catalyst bed with a concentration $C_f = 5(10^{-5})$ mol/cc and temperature $T_f = 700$ K. The particles have high thermal conductivity so their temperature throughout is the same as at the surface, T_s. In the steady state, all of the heat of reaction goes to heating up the gas. Given the data following, find the temperature, concentration and the rate of reaction on the surface at the point where $C_g/C_f = 0.8$.

$a = 1.5$ cm/cc, catalyst surface
$D_{eff} = 0.01\ \text{cm}^2/\text{s}$
$\rho_g = 0.0009$ mol/cc
$C_p = 7.5$ cal/(mol)(K), gas heat capacity
$h = 0.01\ \text{cal}/(\text{cm}^2)(\text{s})(\text{K})$
$k_g = 1.5$ cm/s

$$k = \exp(20.7-10500/T_s),\ (\mathrm{cc})^2/(\mathrm{mol})(\mathrm{s})(\mathrm{cc\ catalyst}) \qquad (1)$$

$\Delta H_r = -50,000$ cal/mol

$R = 2$ cm, radius of particles

The rate equations are

$$r = k_g a(C_g-C_s) = k\eta C_s^2$$

or in reduced terms,

$$k\eta f_s^2 = \frac{k_g a}{C_f}(0.8-f_s) = \frac{1.5(1.5)(0.8-f_s)}{5(10^{-5})} = 45,000(0.8-f_s) \qquad (2)$$

Heat balance on the gas,

$$-\Delta H_r(C_f-C_g) = \rho C_p(T_g-T_f)$$

$$T_g = T_f + \frac{-\Delta H_r(C_f-C_g)}{\rho C_p} = 700 + \frac{50000(0.2)(0.00005)}{0.0009(7.5)}$$

$$= 774.1 \qquad (3)$$

Heat transfer between surface and gas,

$$ha(T_s-T_g) = k\eta(-\Delta H_r)C_f^2 f_s^2$$

$$k\eta f_s^2 = \frac{0.01(1.5)(T_s-774.1)}{50000[5(10^{-5})]^2} = 120(T_s-774.1) \qquad (4)$$

The Thiele modulus is

$$\phi = R\sqrt{\frac{kC_f f_s}{D}} = 2\sqrt{\frac{5(10^{-5})kf_s}{0.01}} = 0.141\sqrt{kf_s} \qquad (5)$$

and the effectiveness of a second order reaction in spheres is

$$\eta = \frac{1.0357+0.3179\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (6)$$

The numbered equations are solved simultaneously with the results,

$f_s = 0.792$

$T_s = 777.1$

$\phi = 4.565$

$\eta = 0.4303$

and the rate is

$$r = k_g a(f_g-f_s)C_f = 1.5(1.5)(0.8-0.792)(5)(10^{-5})$$

$$= 0.09(10^{-5}),\ \mathrm{mol/s)(cc\ catalyst)}$$

P7.06.06. CSTR WITH UNIFORMLY POISONED CATALYST

For a second order reaction carried out in a slurry CSTR these data are known,

$$k_{clean} = 2.45\ \frac{\mathrm{mol}}{\mathrm{sec(cc\ reactor)}}\left(\frac{\mathrm{cc\ fluid}}{\mathrm{mol}}\right)^2$$

$D_{eff} = 0.0002\ \mathrm{cm^2/s}$

$R = 0.2$ cm

$C_0 = 0.02$ mol/cc

Find the residence time for 50% conversion, (a) with fresh catalyst, (b) with catalyst that is 50% uniformly poisoned.

With a fraction α of uniform poisoning the specific rate is

$k_p = k_c(1-\alpha)$

and the Thiele modulus is

$$\phi = R\sqrt{\frac{k_c(1-\alpha)C}{D_{eff}}} = 0.2\sqrt{\frac{2.45(0.01)(1-\alpha)}{0.0002}} = 2.21\sqrt{1-\alpha}$$

The material balance on the CSTR is

$$C_0 = C + \bar{t}k\eta C^2$$

so that

$$\bar{t} = \frac{0.02-0.01}{(0.01)^2(2.45)(1-\alpha)\eta}$$

When $\alpha = 0$, $\phi = 2.21$, $\eta = 0.68$ and $\bar{t} = 60$ sec.

When $\alpha = 0.5$, $\phi = 1.56$, $\eta = 0.79$ and $\bar{t} = 103$ sec.

P7.06.07. PORE MOUTH POISONING OF FIRST ORDER REACTION IN A SLAB

In pore mouth poisoning, the catalytic activity is completely destroyed in a fraction β of the pore from its mouth. At the mouth of the pore,

$x = L$, $C = C_s$

At the entrance to the active section of the pore,

$x = (1-\beta)L$, $C = C_1$

Rate of diffusion into t=he pore = rate of diffusion through the inactive region at steady state, or

$$D\left(\frac{dC}{dx}\right)_{x=(1-\beta)L} = D\frac{\Delta C}{\Delta x} = D\frac{C_s-C_1}{\beta L} \qquad (1)$$

For first order reaction in slab geometry, the pore equation is

$$\frac{d^2C}{dx^2} = \frac{k}{D}C = \alpha^2 C \qquad (2)$$

As in p7.03.07, the partial solution is

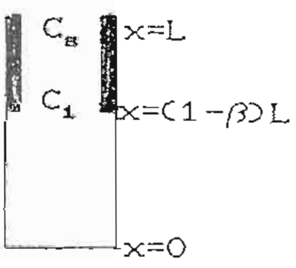
$$C = I\cosh(\alpha x) \qquad (3)$$

The derivative is

$$dC/dx = I\alpha\sinh(\alpha x)$$

Applying Eq (1),

$$I\alpha\sinh[\alpha(1-\beta)L] = \frac{C_s-C_1}{\beta L}$$



from which the integration constant is

$$I = \frac{C_s-C_1}{\alpha\beta L\sinh[\alpha(1-\beta)L]}$$

and the concentration becomes

$$C = \frac{C_s-C_1}{\beta\phi}\frac{\cosh(\alpha x)}{\text{sainh}[\alpha(1-\beta)L]}$$

where

$$\phi = L\sqrt{k/D}$$

When $x = (1-\beta)L$, $C = C_1$ and

$$C_1 = \frac{C_s-C_1}{\beta\phi}\coth[\phi(1-\beta)]$$

$$= \frac{C_s\coth[\phi(1-\beta)]}{\beta\phi+\coth[\phi(1-\beta)]} \qquad (5)$$

Then

$$C_s - C_1 = \frac{C_s\beta\phi}{\beta\phi + \coth[\phi(1-\beta)]} \qquad (6)$$

The rate of reaction equals the rate of diffusion through the dead region of the pore, or

$$r_{actual} = \frac{D(C_s - C_1)}{\beta L} = \frac{D}{L}\,\frac{C_s\phi}{\beta\phi + \coth[\phi(1-\beta)]} \qquad (7)$$

$$r_{ideal} = kLC_s \qquad (8)$$

The effectiveness is the ratio of (7) and (8)

$$\eta_{poisoned} = \frac{1}{\phi\{\beta\phi + \coth[\phi(1-\beta)]\}} \qquad (9)$$

compared with

$$\eta_{clean} = \frac{\tanh\phi}{\phi} \qquad (10)$$

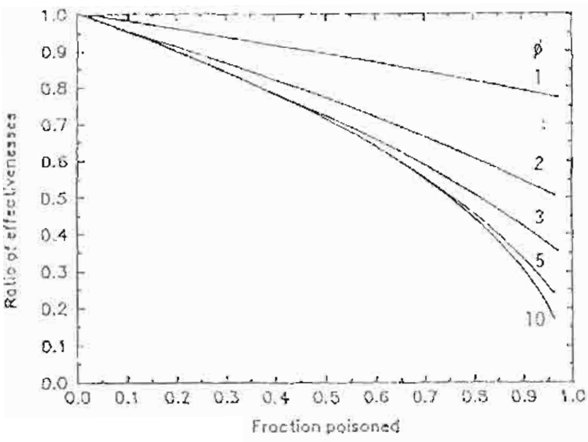
P7.06.08. RATIOS OF EFFECTIVENESS WITH POISONING AND WITHOUT

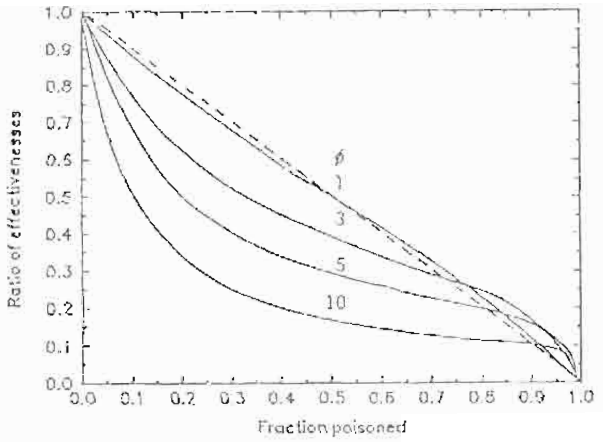
For uniform poisoning, the effectiveness is obtained by simply replacing k_v with $k_v(1-\beta)$ in the definition of ϕ. For pore mouth poisoning the equation for η is in P7.06.07. These results are for first order reaction in slab geometry.

Uniform poisoning: $$\frac{\eta_{poisoned}}{\eta_{clean}} = \frac{\sqrt{1-\beta}\,\tanh(\phi_L)}{\tanh[\phi_L(1-\beta)]}$$

Pore mouth: $$\frac{\eta_{poisoned}}{\eta_{clean}} = \frac{1}{\tanh(\phi_L)\{\beta\phi_L + \coth[\phi_L(1-\beta)]\}}$$

These ratios are plotted against β, the fraction poisoned, with the Thiele modulus as parameter. Pore mouth effectiveness is much more sensitive to the fraction poisoned.





P7.06.09. BATCH REACTION WITH DEACTIVATING CATALYST

A batch reaction is carried out with a slurried catalyst that deactivates gradually. The rate equation is

$$-\frac{dC}{dt} = \frac{k_1C}{1+k_{2t}} = \frac{0.05C}{1+0.005t}, \text{ with t in minutes}$$

Conversion is required to be 95%. How many batches can be processed before batch time becomes 8 hrs?

The integral is

$$\ln(95/5) = \frac{k_1}{k_2} \ln \frac{1+k_2t_2}{1+k_2t_1} = 10 \ln \frac{1+0.005t_2}{1+0.005t_1}$$

$$t_2 = \frac{19^{0.1}\ (1+0.005t_1)-1}{0.005} = 268.4(1+0.005t_1)-200$$

The tabulation shows that the reaction time of 480 minutes is reached between batch numbers 7 and 8.

Batch	t_1	t_2	Δt
1	0	68.5	
2	88.5	160.5	
3	160.5	283.9	
4	283.9	449.6	
5	449.6	672.0	
6	672.0	970.6	
7	970.6	1371.4	400.8
8	1371.4	1909.5	538.1

P7.06.10. GAS OIL CRACKING IN A TRANSFER LINE

Catalytic cracking of a gas oil has the rate equation

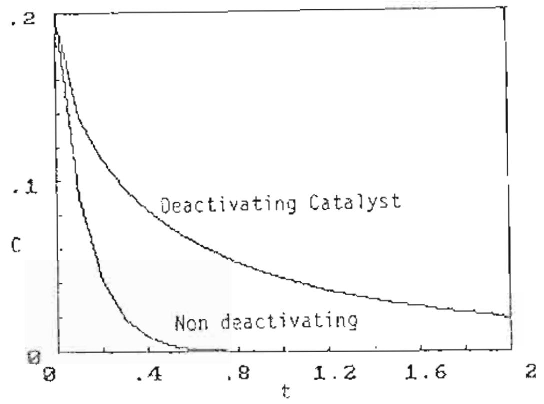
$$-\frac{dC}{dt} = \frac{8C}{(1+7.6t^{0.5})(1+0.01C)} \qquad (1)$$

with the time in seconds. Inlet concentration is $C_0 = 0.2$. The operation is plug flow, with the fluid and catalyst particles both moving at 5 m/s. Find the concentration along a reactor 10 m long, and compare with the performance when the catalyst activity does not deteriorate.

A partial integration of the equation is

$$\ln(C_0/C) + C_0-C = 8 \int_0^t \frac{dt}{1+7.6t^{0.5}} \qquad (2)$$

This could be solved by trial, using a numerical integration, to find C as a function of t. However, the graph is of a direct numerical solution of Eq (1). The degradation of the catalyst is very rapid. In practice the catalyst will proceed from the transfer line to a reactivation zone and will be recycled.



P7.06.11. CSTR WITH DEACTIVATING POROUS CATALYST

A second order reaction is conducted in a CSTR with a slurried porous catalyst whose specific rate depends on time on stream according to

$$k = 5/(1+0.02t) \tag{1}$$

Inlet concentration is $C_0 = 0.5$, residence time is $\bar{t} = 80$ and the Thiele modulus is

$$\phi = 25.8\sqrt{kC} \tag{2}$$

Find the variation of the outlet concentration with time on stream.

For second order reaction on spheres the effectiveness is

$$\eta = \frac{1.0357+0.3179\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \tag{3}$$

The material balance on the reactor is

$$C_0 = C + k\eta\bar{t}C^2$$

$$0.5 = C + 80k\eta C^2 \tag{4}$$

The four numbered equations are solved simultaneously at specified times, as tabulated. The first and last columns supply the desired information.

t	k	ϕ	η	C
0	5.00	17.03	0.136	0.0871
10	4.07	15.98	0.144	0.0921
50	2.50	13.36	0.171	0.1072
75	2.00	12.34	0.184	0.1144
100	1.67	11.57	0.195	0.1207
200	1.00	9.64	0.231	0.1397
500	0.455	7.25	0.297	0.1739
1000	0.238	5.72	0.362	0.2065

P7.06.12. RELATIVE MAGNITUDES OF TWO KINDS OF DEACTIVATION

For first order reaction in slab geometry, evaluate the ratio of effectiveness with uniform poisoning, η_{un}, and pore mouth poisoning, η_{pm}, in terms of fractional poisoning and the Thiele modulus.

The formulas for the two kinds of effectiveness are stated in problem P7.06.08. β is the fraction poisoned. The ratio, η_{un}/η_{pm}, is tabulated, along with the clean effectiveness, η_c. For a given fractional deactivation, pore mouth deactivation is more serious than uniform.

ϕ	η_c	β=0.25	β=0.50	β=0.75
0.5	0.90	2.67	1.50	7.22
1	0.75	1.44	2.36	5.72
5	0.20	1.95	2.51	2.90
10	0.10	3.03	4.24	4.31
30	0.033			11.8
50	0.020	11.69	18.4	19.3

P7.06.13. EFFECT OF THERMAL CONDUCTIVITY

Thermal conductivities of two porous catalytic particles are: nickel-tungsten, 0.47 W/(m)(K), platinum-alumina, 0.22 (Satterfield, *Heterogeneous Catalysis in Practice,* 1980).

(a) Refer to the results of problem P7.06.02. In one case, $\beta = 0.4$ with the first of these catalysts. For each of them, what are the values of η when $\phi = 1$ and when $\phi = 10$? Reading off the figure,

With $\lambda = 0.47$, $\eta = 10$ when $\phi = 1$; $\eta = 1.4$ when $\phi = 10$.

With $\lambda = 0.22$, $\eta = 1.2$ when $\phi = 1$; $\eta = 0.7$ when $\phi = 10$.

(b) Referring to the results of problem P7.06.04, what are the minimum interior temperatures with the two kinds of particles?

With $\lambda = 0.22$, $T_{min} - 723 = -134.9$

With $\lambda = 0.47$, $T_{min} - 723 = -134.9(0.22/0.47) = -63.4$.

P7.06.14. EXPONENTIAL DEACTIVATION

The rate of reaction with a catalyst subject to degradation with time on stream is,

$$-\frac{df}{dt} = 6.0f^2 \exp(-0.365t)$$

Initially $f = C/C_0 = 1$. Find (a) How much time is needed for 90% conversion; (b) the maximum possible conversion.

The integral is

$$1/f - 1 = \frac{6}{0.365}[1-\exp(-0.365t)] = 16.44[1-\exp(-0.365t)]$$

$$f = \frac{1}{1+16.44[1-\exp(-0.365t)]}$$

When $f = 0.1$, $t = 2.74 \ln(1-9/16.44) = 2.17$

When $t \Rightarrow \infty$, $f = 0.0573$, or 94.27 % conversion.

P7.06.15. SLURRY REACTOR WITH DECLINING CATALYST ACTIVITY

A CSTR with slurried catalyst processes a reaction with rate equation

$$r = 3.0 \exp(-0.2t)C^2$$

The inlet concentration is $C_0 = 1$ and the residence time is $\bar{t} = 0.5$. Find the effluent $f = C/C_0$ as a function of time.

The unsteady material balance is

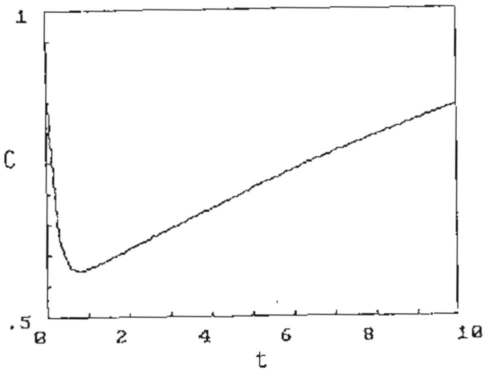
$$C_0 = C + k\bar{t}C^2 + \bar{t}\frac{dC}{dt}$$

or

$$1 = f + 1.5 \exp(-0.2t)f^2 + 0.5\frac{df}{dt}$$

The numerical solution of the

differential equation is straightforward. The plot shows that a minimum value of C occurs at about $t = 2\bar{t} = 1$.



P7.06.16. ACTIVITY DEPENDENT ON TIME AND REACTANT CONCENTRATION

The decline of activity of a catalyst sometimes is exponential with time, that is,

$$-\frac{d\alpha}{dt} = k\alpha,$$

or

$$\alpha = \alpha_0\exp(-kt)$$

Also it may depend on the concentration of the reactant, for instance,

$$-\frac{d\alpha}{dt} = k\alpha C^{\beta}$$

A particular batch reaction is represented by the rate equations,

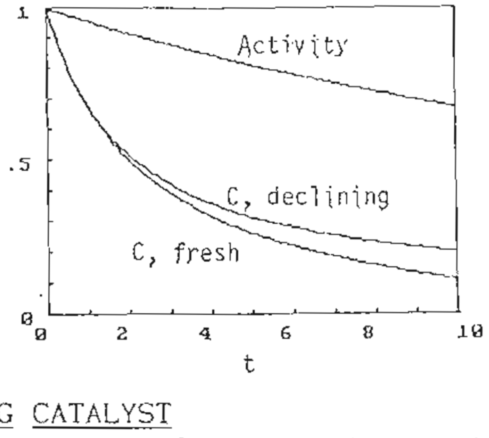
$$-\frac{dC}{dt} = 0.5\alpha C^2 \qquad (1)$$

$$-\frac{d\alpha}{dt} = 0.05\alpha C^{0.2} \qquad (2)$$

At constant activity,

$$-\frac{dC}{dt} = 0.5C^2 \qquad (3)$$

The three equations are solved w;ith $C_0 = 1$ and $\alpha_0 = 1$ and the numerical solutions are plotted. At t = 10, for instance, the residuum is about twice as great with declining activity.



P7.06.17. CUMENE CRACKING CATALYST

The activity of zeolite catalyst for the cracking of cumene was measured at several onstream periods at cumene flow rates of u = 0.01 mol/s and 0.32 mol/s (*IECPDD* 22 609, 1983). The results are tabulated. Taking the relation to be

$$-\frac{d\alpha}{dt} = k\alpha u^{\beta}$$

find the constants k and β.

At constant values of u, the integral is

$$\ln(\alpha) = -ktu^{\beta}$$

The semilog plots are drawn through $(t,\alpha) = (0,1)$ and are approximately linear, with

$$ku^{\beta} = \begin{cases} -0.001423, & \text{when } u = 0.01 \\ -0.004165, & \text{when } u = 0.32 \end{cases}$$

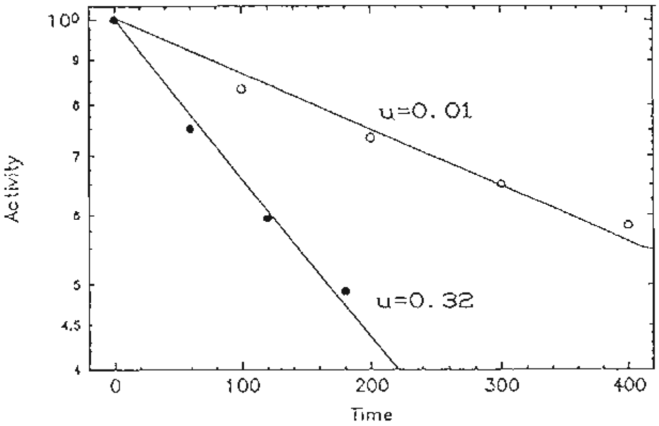
Accordingly

$$\beta = \ln\frac{0.001423}{0.004165} \Big/ \ln\frac{0.01}{0.32} = 0.3098$$

and the activity relation becomes

$$\ln(\alpha) = -0.005928tu^{0.3098}$$

u=0.01		u=0.32	
t	α	t	α
0	1	0	1
100	0.833	60	0.750
200	0.733	120	0.594
300	0.650	180	0.491
400	0.583		



P7.06.18. CUMENE CRACKING IN A BATCH REACTOR

Benzene and propylene are made by cracking of cumene over a silica-alumina catalyst at constant volume in a batch reactor. Initial content of cumene is 9.9%, the remainder inert. The pressure is 20 atm. The tabulated data are of t in sec against x fraction converted (Fogler, 331, 1992). The catalyst is subject to exponential degradation so the rate equation is

$$\frac{dx}{dt} = k\exp(-at)(1-x)^n \tag{1}$$

The constants k, a and n are to be found.

As a first trial, assume first order. The integral is

$$-\ln(1-x) = \frac{k}{a}[1-\exp(-at)] \tag{2}$$

Utilizing all of the data to find the constants a and k calls for a nonlinear regression. An approximate result, however, is obtained by taking pairs of data spaced widely apart and solving the two Eqs (2) simultaneously.

With the points $t = 30$, $x = 0.102$ and $t = 100$, $x = 0.259$ the result is $a = 0.00544$ and $k = 0.00389$.

With the points $t = 100$, $x = 0.259$ and $t = 500$, $x = 0.493$, the result is $a = 0.00527$ and $k = 0.00386$.

These results are nearly enough the same, and also confirm the first order assumption.

t	x
0	0
10	0.037
20	0.071
30	0.102
40	0.130
60	0.180
80	0.223
100	0.259
150	0.330
200	0.379
300	0.441
500	0.493
700	0.512
1000	0.517

P7.06.19. CRACKING OF CYCLOPENTANE

Cyclopentane was cracked over a palladium-alumina catalyst at 200 C in a differential reactor (*J Catal* 54 397, 1978). Data of time against fractional conversion are tabulated. Find the relation between time and catalyst effectiveness.

In a differential flow reactor,

$$r = n_{a0}\frac{dx}{dW_c} \cong n_{a0}\frac{\Delta x}{\Delta W_c}$$

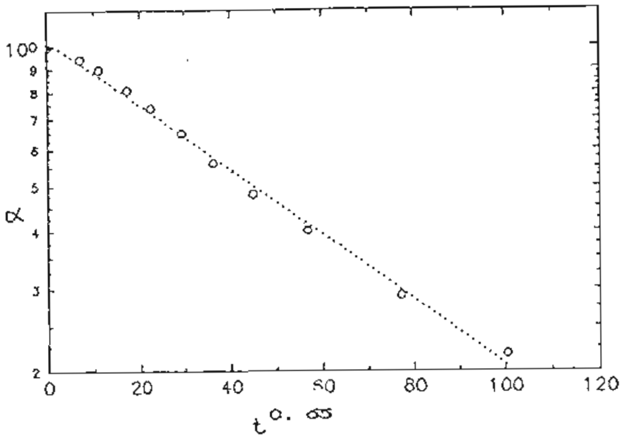
The effectiveness is

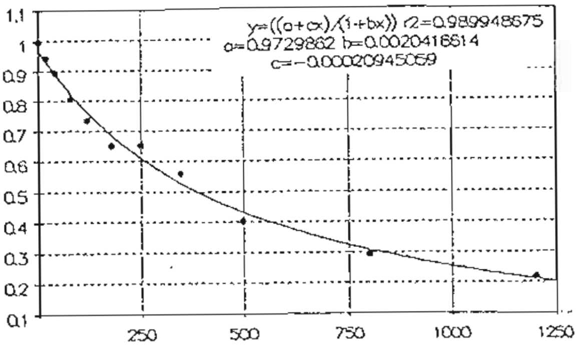
$$\alpha = \frac{(\Delta x)_t}{(\Delta x)_{t=0}} = \frac{(\Delta x)_t}{0.75} \qquad (1)$$

The results are tabulated. Plots of α against t were made several ways, two of which are drawn. The most successful plot has the equation

$$\ln(\alpha) = -0.0159t^{0.65}$$

t	x	α
0	0.75	1
20	0.707	0.9427
40	0.670	0.8933
80	0.605	0.8067
120	0.552	0.7360
180	0.487	0.6493
250	0.420	0.5600
350	0.360	0.4800
500	0.300	0.4000
800	0.220	0.2933
1200	0.163	0.2173





P7.06.20. SPECIFIC RATE OF CYCLOPENTANE CRACKING

The cyclopentane reaction of P7.06.19 was conducted at constant volume in a batch reactor. Initial concentration was 0.03 kmol/m^3 and the catalyst concentration was 0.01 kg/m^3. Data of time against fraction converted are in the first two columns of the table. The activity of the catalyst declines exponentially. Find the order and the specific rate of the reaction.

The equations are

$$n_{a0}\frac{dx}{dt} = k\alpha(1-x)^q \qquad (1)$$

$$\alpha = \exp(-0.0159t^{0.6}) \qquad (2)$$

$$\beta = \int_0^t \alpha dt$$

Integrals of Eq (1) for several orders are:

$q = 0,\ kn_{a0} = \beta/x$
$q = 1,\ kn_{a0} = \beta/\ln(1-x)$
$q = 2,\ kn_{a0} = \beta(1-x)/x$

The tabulation shows that kn_{a0} is most nearly constant for zero order, with

$kn_{a0} \cong 550$

			kn_{a0}		
t	x	$\int\alpha dt$	q=0	q=1	q=2
0	0	0			
10	0.017	9.58	563.5	558.7	553.9
20	0.034	18.7	550.0	540.6	
40	0.066	36.0	545.6	527.4	
70	0.110	60.2	547.5	516.8	
100	0.150	82.8	552.0	509.4	
150	0.215	117.5	546.4	485.3	428.9
200	0.272	149.2	548.5	469.9	
300	0.371	205.5	554.0	443.2	
500	0.539	297.5	552.0	384.2	
800	0.746	401.0	537.5	292.6	
1200	0.883	498.8	564.9	232.5	66.1

P7.06.21. TIME VARYING ACTIVITY AND EFFECTIVENESS

A second order reaction is conducted in a slurry CSTR. The catalyst activity falls off with time on stream according to

$$k = 0.75\exp(-0.006t) \qquad (1)$$

Feed concentration is $C_0 = 2$ and mean residence time is $\bar{t} = 0.5$. At the start the tank is full and $f = C/C_0 = 1$. The Thiele modulus is

$$\phi = \phi_0\sqrt{kC} = 10\ \exp(-0.003t)\sqrt{f} \qquad (2)$$

$$f = C/C_0$$

For second order reactions, the catalyst effectiveness is

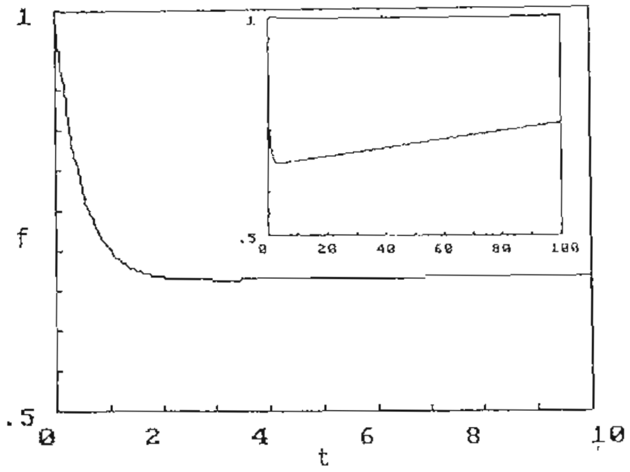
$$\eta = \frac{1.0357+0.3179\phi+0.000437\phi^2}{1+0.4172\phi+0.139\phi^2} \qquad (3)$$

The unsteady material balance on the CSTR is

$$1 = f + kC_0\bar{t}\eta f^2 + \bar{t}C_0\frac{df}{dt}$$

$$1 = f + k\eta f^2 + \frac{df}{dt} \qquad (4)$$

The numbered equations are solved simultaneously with f = 1 when t = 0, using CONSTANTINIDES or POLYMATH. The plots show that a minimum value f = 0.664 is attained when t = 3. The outlet f subsequently keeps increasing, reaching 0.756 at t = 100 and 0.964 when t = 500.



P7.06.22. ACTIVITY DECLINE AND TEMPERATURE

The activity decline of a catalyst with time was found at two temperatures,

α = 1/(1+0.020t), at 500 K (1)

1/(1+0.130t), at 550 K (2)

The specific rate depends on temperature according to

$k = \exp(41.6 - 20000/T)$ (3)

The performance of a CSTR is to be maintained at the condition of 480 K and fresh catalyst. Find how the temperature must be adjusted as time goes on to maintain constant performance.

The constants, 0.02 and 0.13, in Eq (1) and (2) are assumed to have an Arrhenius dependence.

$$\ln k_\alpha + A + B/T$$

$$B = \ln\left(\frac{0.13}{0.02}\right)/\left(\frac{1}{550} - \frac{1}{500}\right) = -\ 10295$$

$$A = \ln(0.13) + 10295/550 = 16.68$$

Therefore

$$\alpha = \frac{1}{1+\exp(16.68 - 10295/T)_t} \qquad (4)$$

At 480 K with fresh catalyst, with Eqs (3) and (4),

$$\alpha k = 0.9355$$

This product is required to be kept constant.

$$0.9355 = \frac{\exp(41.6-20000/T)}{1+\exp(16.68-10295/T)t} \qquad (5)$$

Corresponding values of T and t from Eq (5) are tabulated.

t	T	α
0	480	1
10	481.0	0.918
50	484.9	
100	489.8	
200	498.8	0.2077
300	506.5	
400	512.9	
500	518.3	0.0460
750	529.0	
1000	537.2	0.0118

P7.06.23. SLURRY CSTR WITH DECLINING ACTIVITY

A first order reaction is done in a slurry CSTR. The activity falls off with time accordig to

$$\alpha = \frac{1}{1+0.5\sqrt{t}}$$

Other data are,

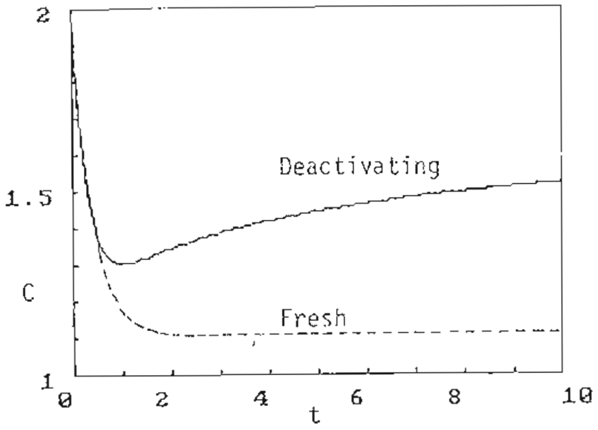
$$C_0 = 2,\ k = 1.6,\ \bar{t} = 0.5$$

The unsteady material balance is

$$C_0 = C + k\bar{t}\alpha C + \bar{t}\frac{dC}{dt}$$

$$2 = (1+\frac{1.6(0.5)}{1+0.5\sqrt{t}})C + 0.5\frac{dC}{dt}$$

The result of numerical integration of the differential equation is shown by graphs for both fresh and deactivating catalysts.



P7.06.24. SPECIFIC RATE DEPENDS ON TIME AND TEMPERATURE

The specific rate of a catalytic reaction depends on time and temperature as in the rate equation,

$$r = \frac{dx}{dt} = \frac{k}{1+0.5t}\exp(-1000/T)(1-x)^2$$

Initially, $T_0 = 300$ and $r_0 = 2$. Find the relation between time, conversion and temperature when the rate is kept constant up to 90% conversion.

At constant rate $r = r_0 = 2$

$t = x/r_0 = 0.5x$

and the rate equation becomes

$$r_0 = k\exp(-12000/300)$$

$$= \frac{k}{1+0.5t}\exp(-12000/T)(1-2t)^2$$

The factor k drops out. The result is a relation between T and t and x = 2t.

$$\exp[12000(\frac{1}{T} - \frac{1}{300})] = \frac{(1-2t^2}{1+0.5t}$$

The solution is tabulated.

x	t	T
0	0	300
0.2	0.1	303.8
0.4	0.2	308.6
0.6	0.3	315.6
0.8	0.4	327.8
0.9	0.45	341.0

CHAPTER 8

MULTIPLE PHASE REACTIONS

THEORY

PROBLEMS

When several phases are in contact, reaction may occur predominantly in one of the phases, or throughout, or at the interface. The rate of reaction will depend on the interfacial area and on the rates of mass and heat transfer between phases. Equipment that is used primarily for effecting mass transfer is adaptable to mass transfer with reaction, including stirred tanks, mixers of all kinds, tray towers, packed vessels, spray towers. Reaction usually enhances the rate of mass transfer by reducing the backward driving force of concentration and by raising the mass transfer coefficient. Numerous studies of such reaction mechanisms have been made and a body of knowledge exists for important industrial processes, but general design correlations are not plentiful.

Solids in contact with fluids may be catalysts or they may be reactants as in combustion or calcination or coal liquefaction or uranium chlorination, etc.

8.1. AXIAL AND RADIAL GRADIENTS IN PACKED BEDS

The situation is that of a reacting fluid usually in contact with a bed of particles, with some temperature control by means of heat transfer at the wall of the vessel. As a consequence, gradients of composition and temperature develop in lateral and axial directions, as well as of pressure axially. The particles may be catalytic or they may be inert to provide mixing or to serve as heat carriers.

Since they vary with time and several position coordinates, material, energy and pressure balances are formulated as partial differential equations.

In the common case of cylindrical vessels with radial symmetry, the coordinates are the radius of the vessel and the axial position. Major pertinent physical properties are thermal conductivity and mass diffusivity or dispersivity. Certain approximations for simplifying the PDEs may be justifiable. When the steady state is of primary interest, time is ruled out. In the axial direction, transfer by conduction and diffusion may be negligible in comparison with that by bulk flow. In tubes of only a few centimeters in diameter, radial variations may be small. Such a reactor may consist of an assembly of tubes surrounded by a heat transfer fluid in a shell. Conditions then will change only axially (and with time if unsteady). The dispersion model of Section P5.8 is of this type.

Boundary conditions are part of the mathematical description of a process. For the energy balance, the condition at the vessel wall is that the rate of heat transfer by conduction equals the rate of transfer to the heat transfer medium. Similarly the rate of mass transfer at the wall equals the rate of reaction on the wall if that is catalytic, or equals zero when the wall is inert and impermeable. Clearly, the temperature , composition and pressure of the inlet to the reactor are part of the problem specification.

Fixed beds are the main interest of this Section. Usually it is adequate to assume that the fluid and solid are at the same temperature at a point. There are cyclic processes, however, where the solid is first heated with flue gases or by burning off carbon before contacting the reacting fluid for a time. A moving bed of heated pebbles (Phillips pebble heater) has been used for the production of olefins from butane and for the fixation of atmospheric nitrogen. A fluidized sand cracker for the production of olefins functions similarly, with burning in a separate zone.

In fluidized beds, the temperature is uniform within a few degrees even in the largest vessels, but variation of composition is appreciable in large vessels, and is not well correlated for design purposes. One currently successful moving bed process is the UOP "Stacked Reactor" platforming where the catalyst is transported and regenerated in a separate zone. When the activity of the catalyst declines fairly rapidly, its variation with time and position must be taken into account by the mathematical formulation.

Porous catalyst particles are complex devices with appreciable internal gradients of temperature and composition, but these factors can be taken account of by the concept of catalyst effectiveness which is sometimes calculable.

Practical design problems may need to take into account many additional factors, including the recycle of some reactants (such as hydrogen), residence time distribution, inhomogeneity of the packing, multiple reactions, approach to equilibria, and so on. All of these problems have been encountered before, and professional simulator routines for solving them are versatile, effective and as reliable as the data provided to them. At least half a dozen such computer packages are commercially available.

The partial differential equations representing material and energy balances of a reaction in a packed bed are rarely solvable by analytical means, except perhaps when the reaction is of zero or first order. Two examples of derivation of the equations and their analytical solutions are P8.0.1.01 and P8.01.02. In more complex cases analytical approximations can be made (by "Collocation" or "Perturbation", for instance), but these usually are quite sophisticated to apply. Numerical solutions, on the other hand, are simple in concept and are readily implemented on a computer. Two such methods that are suited to nonlinear kinetics problems will be described.

8.1.1. FINITE DIFFERENCES

This method is applicable to equations with more than two independent variables, but only two will be considered here. A region over which a solution is sought is divided into a grid with m divisions of variable x and n divisions of variable y, spaced at distances Δx and Δy. A first derivative is approximated by

$$\left(\frac{\partial z}{\partial x}\right)_{mn} = \frac{f(x+\Delta x,y)-f(x,y)}{\Delta x} = \frac{z_{m+1,n}-z_{m,n}}{\Delta x} \qquad (8.1)$$

and

$$\left(\frac{\partial z}{\partial y}\right)_{mn} = \frac{f(x,y+\Delta y)-f(x,y)}{\Delta y} = \frac{z_{m,n+1}-z_{m,n}}{\Delta y} \qquad (8.2)$$

Alternately,

$$\left(\frac{\partial z}{\partial x}\right)_{mn} = \frac{f(x+\Delta x,y)-f(x-\Delta x,y)}{2\Delta x} = \frac{z_{m+1,n}-z_{m-1,n}}{2\Delta x} \qquad (8.3)$$

Problem P8.01.08 uses Eq 8.1 and P8.01.09 uses Eq 8.3.

For the second derivative,

$$\left(\frac{\partial^2 z}{\partial x^2}\right)_{mn} = \frac{f(x+\Delta x,y)-2f(x,y)+f(x-\Delta x,y)}{(\Delta x)^2}$$

$$= \frac{z_{m+1,n}-2z_{m,n}+z_{m-1,n}}{(\Delta x)^2} \qquad (8.4)$$

Problem 8.01.03 converts a differential equation with these equivalents.

When starting at one edge of the boundary, these equations allow the solution to be made one step at a time, but some restrictions on the sizes of the increments must be made for convergence to be obtained. Approximations involving more than three grid points also are in use and are stable regardless of the sizes of the increments. They may permit use of larger spacings or fewer intervals, and may consequently speed up the calculations and reduce the roundoff error of the repeated calculations. The drawback to the use of more than three grid points at a time is that all the grid values must be found by simultaneous solution of the equations for all the variables. This virtually eliminates the feasibility of hand calculations.

8.1.2. THE METHOD OF LINES

The method of lines reduces a partial differential equation to a system of ordinary differential equations which can be solved by readily available software. It is applicable to PDEs that have only the first derivative of one of the variables, for example,

$$\frac{\partial z}{\partial x} = f\left(x,\ y,\ z,\ \frac{\partial z}{\partial y},\ \frac{\partial^2 z}{\partial y^2},\ \text{parameters}\right) \qquad (8.5)$$

The values of z must be known at x = 0 or at some other constant value of x. By this method, the derivatives on the right are replaced by their finite difference equivalents, resulting in a set of equations

$$\frac{dz_m}{dx} = f(\text{grid values}) \qquad (8.6)$$

This procedure is applied in problem P8.01.05. Note that complexity of the rate equation does not complicate the solution because the ODEs remain first order.

8.2 GAS-LIQUID REACTIONS

Reaction between an absorbed solute and a reagent lowers the equilibrium partial pressure of the solute and thus increases the rate of mass transfer. The mass transfer coefficient likewise may be enhanced which contributes further to increased absorption rate. Three modes of contacting gas and liquid phases are possible: The gas is dispersed as bubbles in the liquid, the liquid is dispersed as droplets, the two phases are contacted on a thin liquid film deposited over a packing or wall. The choice between these modes is an important practical problem.

The mathematical relations of gas-liquid reactions are like those for physical absorption but the equilibria and mass transfer coefficients are much more complex because they depend on the chemical nature of the reactant and its remaining concentration at each location in the reactor. Such data are not plentiful or well correlated in print, and the main reliance for particular reactions is on laboratory or pilot plant testing.

8.2.1. MASS TRANSFER COEFFICIENTS

Resistance to transfer of mass between phases is assumed to be confined to that of fluid films between the phases. Let

D = diffusivity
$p_i = f(C_i)$ or $p_i = HC_i$, equilibrium at the interface
a = interfacial area per unit volume
z_g and z_L, film thicknesses

The steady rates of solute transfer across the films are

$$r = k_g a(p_g - p_i)$$
$$= k_L a(C_i - C_L)$$

where

$$k_g = D/z_g$$
$$k_L = D/z_L$$

are the mass transfer coefficients of the individual films. Overall coefficients are defined by

$$r = K_g a(p_g - p_L) = K_L a(C_g - C_L)$$

Upon introducing the equilibrium relation, $p = HC$, the relation between the various coefficients is seen to be

$$\frac{1}{K_g} = \frac{H}{K_L} = \frac{1}{k_g} + \frac{H}{k_L} \tag{8.7}$$

When the solubility is low, H is large and $k_L \Rightarrow K_L$; when the solubility is high, H is small and $k_g \Rightarrow K_g$.

For purely physical absorption, the mass transfer coefficients depend on the hydrodynamics and the physical properties of the phases. Many correlations exist, for example that of Dwivedi & Upadhyay (IEC Proc Des & Dev 16 157, 1977) for packed towers,

$$k = \frac{u'}{Sc^{2/3}}\left(\frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}\right) \tag{8.8}$$

where $Re = \rho u' d_p/\mu$.

With a reactive solvent, the mass transfer coefficient may be enhanced by a factor E so that, for instance, K_g is replaced by EK_g. Like specific rates of ordinary chemical reactions, such enhancements must be found experimentally, although some theoretical relations for idealized situations have been found. Tables 8.1 and 8.2 show a few spot data. A particular correlation of mass transfer coefficients is utilized in problem P8.02.07. The same rather complex correlation for equilibrium is used in P8.02.07 and P8.02.09.

8.2.2. COUNTERCURRENT ABSORPTION TOWERS

Consider mass transfer between gas and liquid in a countercurrent tower, packed or spray or bubble. Let

G_m = mols of inert gas/(unit time)(unit cross section)

L_m = mols of solute-free liquid/(unit tiem)(unit cross section).

$Y = y/(1-y)$ = mols of solute in the gas phase/(mol of inert gas in the vapor phase)

$X = x/(1-x)$ = mols of solute in the liquid/(mol of inert solvent in the liquid).

Z = height of active tower section.

The material balance over a differential height is

$$G_m dY = L_m dX \tag{8.9}$$

In terms of gas film conditions,

$$G_m dY = k_g a(p_g - p_i)dZ \tag{8.10}$$

The partial pressure is related to the total pressure π by

$$p_g = y\pi = \frac{Y}{1+Y}\pi, \quad p_i = \frac{Y_i}{1+Y_i}\pi \tag{8.11}$$

Substitution of (23) into (22) and rearrangement gives the result for the tower height,

$$Z = \frac{G_m}{\pi}\int_{Y_2}^{Y_1} \frac{(1+Y)(1+Y_i)}{k_g a(Y-Y_i)}\,dY \tag{8.12}$$

A similar result applies in terms of the liquid phase condition,

$$C = \frac{X}{1+X} C_t$$

C_t = (mols of solute + solvent)/(volume of liquid)

$$L_m dX = k_L a(C_i - C)dZ$$

$$Z = \frac{L_m}{C_t}\int_{X_2}^{X_1} \frac{(1+X)(1+X_i)}{X-X_i}\,dX \tag{8.13}$$

Making a material balance around one end of the tower where the composition is (X_1, Y_1) and rearranging gives

$$X = X_1 + \frac{G_m}{L_m}(Y - Y_1) \tag{8.14}$$

The interfacial equilibrium relation, $y_i = mx$, can be written

$$\frac{Y_i}{1+Y_i} = m\frac{X}{1+X} \tag{8.15}$$

Eqs (24), (26) and (27) are combined and integrated in P8.02.04.

When the material balance is written

$$G dy = \frac{G}{\pi} dp = k_g a(p-p_i)dZ = [k_g a(p-p_i)]_{lm}\,dZ$$

and G can be taken as approximately constant and the constant log mean driving force is taken applicable, the tower height becomes

$$\frac{\pi}{G_m} Z \cong \frac{p_1 - p_2}{[k_g a(p-p_i)]_{lm}} \tag{8.16}$$

8.2.3. ENHANCEMENT OF MASS TRANSFER COEFFICIENTS

A reagent in solution can enhance a mass transfer coefficient in comparison with that of purely physical absorption. The data of Tables 8.1 and 8.2 have been cited. One of the simpler cases that can be analyzed mathematically is that of a pseudo-first order reaction that goes to completion in a liquid film, problem P8.02.01. It appears that the enhancement depends on the specific rate of reaction, the diffusivity, the concentration of the reagent and physical mass transfer coefficient (MTC). These quantities occur in a group called the Hatta number,

$$\beta = \frac{\sqrt{k_c D C_{bo}}}{k_L} \tag{8.17}$$

The enhancement E is the factor by which the physical MTC is to be multiplied to obtain the reactive MTC. For pseuco-first order reaction,

$$E = \beta \coth \beta \tag{8.18}$$

Fairly closely,

$$E \cong \beta, \text{ when } \beta \geq 2 \tag{8.19}$$

In this upper range the enhancement varies with the square root of the reagent concentration. This result sometimes is applied as an approximation for other reaction types. In problem P8.02.09, for instance, enhancement data are known for one concentration and are extended by the square root of the amount remaining unconverted.

Results for enhanced absorption with reversible and higher order reactions have been obtained numerically. Some of them are quoted in problems P8.02.02 and P8.02.08.

8.2.4. EQUIPMENT

Equipment for reactive absorption is of the same types as for physical absorption, towers of various kinds and stirred tanks. Packed or tray towers are the most common, but spray or bubble towers are used for their mechanical simplicity and when there is a likelihood of clogging. Thus SO_2 is scrubbed from air with a spray of lime slurry in a tower. Fluorine waste gases form solids on contact with water, so they are scrubbed by bubbling the gas through water in an empty tower.

Stirred tanks are operated on a semi-batch basis, with the liquid charged first. Because of its limited solubility the gas then is charged gradually over a period of time. Problem P8.02.03 deals with hydrogenation of oil in a stirred vessel. Another major application of such equipment is to aerobic fermentation like that of the production of penicillin where air and nutrient are charged to a batch of mold over a period of 5 or 6 days. Sometimes agitation by the air is sufficient, but usually mechanical agitation is required.Mass and heat transfer are improved by agitation, the transfer coefficients seeming to vary as the 0.7 exponent of the power input/volume. As a rough guide to common practice these data apply:

Operation	HP/1000 gal	Impeller tip speed ft/sec
Homogeneous reaction	0.5-1.5	7.5-10
With heat transfer	1.5-5	10-15
Liquid-liquid mixing	5	15-20
Gas-liquid mixing	5-10	15-20

8.3 LIQUID-LIQUID REACTIONS

Liquid-liquid reactions of industrial importance are fairly numerous. A list of 26 classes of reactions with 61 references has been compiled by Doraiswamy & Sharma (Heterogeneous Reactions, 1984). They also indicate the kind of reactor normally used in each case. The reactions range from prosaic examples such as making of soap with alkali, nitration of aromatics to make explosives and alkylations with sulfuric acid to make improved gasoline, to some much less familiar operations.

Almost invariably one of the phases is aqueous with reactants distributed between phases, for instance NaOH in water at the start and an ester in the organic phase. Such reactions can be carried out in any kind of equipment that is suitable for physical extraction including mixer-settlers and towers of various kinds: empty or packed, still or agitated, either phase dispersed, provided adequate heat transfer can be incorporated. Mechanically agitated tanks are favored because they can have large interfacial areas, for instance as much as 100 times those of spray towers. Power requirements for L-L mixing normally are about 5 HP/1000 gal and tip speeds of turbine-type impellers are 15-20 ft/sec.

Table 9.3 gives data of common types of L-L contactors. Since the given range of k_La is more than 100/1, this information is not of direct value for sizing equipment. The efficiencies of various kinds of small liquid-liquid contactors for physical extraction are summarized on Figure 8.1. Larger units may have efficiencies less than half of these values. In some cases, however, enhancement of the L-L mass transfer coefficient by reaction may be as appreciable as in some gas-liquid cases.

The mechanisms of few liquid-liquid reactions have been determined although some fundamental work on droplet size and power input has been done. The presence of small contents of surface active and other impurities in reactants of commercial qualities can distort a reactor performance. Diffusivities in liquids are comparatively low, a factor of 10^5 lower than in gases, so it is probable in most industrial examples that they are diffusion rate controlled. One consequence is that L-L reactions are not as temperature sensitive as ordinary chemical reactions, although the effect of temperature rise on viscosity and droplet size sometimes can result in substantial rate increase. On the whole, in the presnt state of the art, the design of L-L reactors must depend on scale-up from laboratory or pilot plant work.

Reactions can occur in one phase or the other, or in both, or at the interface. Nitration of aromatics with aqueous HNO_3-H_2SO_4 occurs in the aqueous phase. An industrial example of reaction in both phases is the oximation of cyclohexanone, a step in the manufacture of caprolactam for nylon. The reaction between butene and isobutane to form isooctane in the presence of sulfuric acid is judged to occur at the interface, although side reactions to form higher hydrocarbons may occur primarily in the hydrocarbon phase. The formation of dioxane from isobutene in a hydrocarbon phase and aqueous formaldehyde occurs predominantly in the aqueous phase where the rate equation is first order in formaldehyde, and the specific rate is proportional to the concentration of isobutene in the organic phase. Reactions involving ions can be favored to occur in the organic phase by the use of phase transfer catalysis. Thus the conversion of 1-chlorooctance to 1-cyanooctane with aqueous NaCN is vastly accelerated in the organic phase by 1.3% tributyl (hexadecyl) phosphonium bromide in the aqueous phase. Hydrolyis of fats by water occurs in the fat phase followed by migration of the glycerine into the water phase. There are instances where an extractive solvent is employed to force completion of a reversible homogeneous reaction by removing the reaction product. In the production of KNO_3 from KCl and HNO_3, for instance, the HCl can be removed continuously from the aqueous phase by contacting with amyl alcohol, thus forcing completion.

Choice of dispersed phase. It is difficult to disperse a liquid when it occupies more than 75% of the volume. Otherwise either liquid can be made continuous in a stirred tank by charging that liquid first, starting the agitator and introducing the liquid to be dispersed. Customarily the phase with the higher volumetric rate is dispersed since a larger interfacial area results in this way with a given drop size. When a reactant diffuses away from a phase, that phase should be dispersed since the travel path then will be lower. In equipment that is subject to backmixing, such as spray or packed towers but not tray towers, the disperse phase is made the one with the smaller volumetric rate. When a substantial difference is known to exist between the phases, the high phase resistance should be compensated for with increased surface by dispersion. The continuous phase should be the one that wets the material of construction. Usually is best to disperse a highly viscous phase. Since the holdup of continuous phase usually is greater, the phase that is less hazardous or less expensive should be continuous.

Experimentally, both dispersed-continous modes should be tried. In the alkylation of C_4's with sulfuric acid, for instance, the continuous emulsion of acid produces a much better product and less consumption of acid.

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Rase, HF, *Chemical Reactor Design for Process Plants,* vol 1, 715-733, Wiley, 1977.

8.4. GAS-LIQUID-SOLID REACTIONS

In many important cases of reactions involving gas, liquid and solid phases, the solid phase is a porous catalyst. It may be in a fixed bed or it may be suspended in the fluid mixture. In general the reaction occurs either in the liquid phase or at the liquid-solid interface. In fixed bed reactors the particles have diameters of about 3 mm and occupy about 50% of the vessel volume. Diameters of suspended particles are limited to 0.1-0.2 mm minimum by requirements of filterability and occupy 1-10% of the volume in stirred vessels.

A list of 74 GLS reactions with literature references has been compiled by Shah (1979), classified into groups where the solid is a reactant, or a catalyst, or inert. A list of 75 reactions made by Ramachandran & Chaudhari (1983) identifies reactor types, catalysts, temperature and pressure. They classify the processes according to hydrogenation of fatty oils, hydrodesulfurization, Fischer-Tropsch reactions, miscellaneons hydrogenations and oxidations.

Some contrasting characteristics of the main kinds of three- phase reactors are summarized in Table 8.3. In trickle bed reactors both phases usually flow down, the liquid as a film over the packing. In flooded reactors the gas and liquid flow upward through a fixed bed. Slurry reactors keep the solids in suspension mechanically; the overflow may be a clear liquid or a slurry, and the gas disengages from the vessel. The fluidized three-phase mixture is pumped through an entrained solids reactor and the effluent is separated into its phases in downstream equipment. In petroleum cracking technology this kind of equipment is called a transfer line reactor. In fluidized bed reactors a stable bed of solids is maintained in the vessel and only the fluid phases flow through, except for entrained very fine particles. Most of the concern in this Section is with trickle bed reactors, but some superior features of the other types are cited.

8.4.1. OVERALL RATE EQUATIONS WITH DIFFUSIONAL RESISTANCES

Say the concentration of dissolved gas A is A^*. The series rates involved are from the gas to the interface where the concentration is A_i and from the interface to the surface of catalyst where the concentration is A_s and where the reaction rate is $\eta w k_m A_s^m$. At steady state,

$$r_A = k_L a_B (A^* - A_i) = k_s a_p (A_i - A_s) = \eta w k_m A_s^m$$

For a first order reaction, m = 1, the catalyst effectiveness η is independent of A_s, so that after elimination of A_i and A_s the explicit solution for the rate is

$$r_A = A^* \left[\frac{1}{k_L a_B} + \frac{1}{k_s a_p} + \frac{1}{\eta w k_1}\right]^{-1}$$

Solutions with other chemical rate equations are in P8.03.03, and some numerical cases in P8.03.04-P8.03.06. Such rate equations can be applied to the sizing of plug flow, CSTR and dispersion reactor models.

8.4.2. TRICKLE BEDS

The catalyst is a fixed bed. Flows of gas and liquid are cocurrent downwards. Liquid feed is at a such a low rate that it is distributed over the packing as a thin film and flows by gravity, helped along by the drag of the gas. This mode is suited to reactions that need only short reaction times, measured in seconds, short enough to forestall undesirable side reactions such as carbon formation. In the simplest arrangement the liquid distributor is a perforated plate with about 10 openings/dm^2, and the gas enters through several risers about 15 cm high. More elaborate distributor caps also are used. Thicknesses of liquid films have been estimated to vary between 0.01 and 0.2 mm. Problem P8.03.01 makes such a calculation.

Liquid holdup is made up of a dynamic fraction, 0.03-0.25, and a stagnant fraction, 0.01-0.05. The high end of the stagnant fraction includes the liquid that partially fills the pores of the catalyst. The effective gas-liquid interface is 20-50% of the geometric surface of the particles, but it can approach 100% at high liquid loads with a consequent increase of reaction rate as the amount of wetted surface changes.

Both phases are substantially in plug flow. Dispersion measurements of the liquid phase usually report Peclet numbers, $u_L d_p/D$, less than 0.2. With the usual small particles, the wall effect is negligible in commercial vessels of a meter or so in diameter, but may be appreciable in lab units of 50 mm dia. Laboratory and commercial units usually are operated at the same space velocity, LHSV, but for practical reasons the lengths of lab units may be only 0.1 those of commercial units.

Countercurrent gas flow is preferred in polution control when removal of gaseous impurities is desired.

8.4.3. TRICKLE BED HYDRODESULFURIZATION

The first large scale application of trickle bed reactors was to the hydrodesulfurization of petroleum oils in 1955. The temperature is elevated to enhance the specific rate and the pressure is elevated to improve the solubility of the hydrogen. A large commercial reactor may have 20-25 m total depth of catalyst, up to 3 m dia, in several beds of 3-6 m, limited by the crushing strength of the catalyst and the need for cold shots. Each bed is adiabatic, but the rise in temperature usually is limited to 30 C by injection of cold hydrogen between beds. Conditions depend on the boiling range of the oil. Pressures are 34-102 atm, temperatures 345-425 C. Catalyst granules are 1.5-3.0 mm, sometimes a little more. Catalysts are 10-20% Co and Mo on alumina.

Limiting flow rates are in Table 8.4. The residence times of the combined fluids are figured for 50 atm, 400 C and a fraction free volume between particles of 0.4. In a 20 m depth, accordingly, the contact times range from 6.9 to 960 sec in commercial units. In pilot units the packing depth is reduced to make the contact times about the same.

An apparent first order specific rate increases with liquid rate as the fraction of wetted surface improves. Catalyst effectiveness of particles 3-5 mm dia has been found about 40-60%.

A case study has been made (Rase, Chemical Reactor Design for Process Plants, 2 179-182, 1977) for removing 50% of the 1.9% sulfur from a 0.92 SG oil at the rate of 24,000 B/D with 2300 SCF H_2/Bbl at 375 C and 50 atm. For a particular catalyst, the bed height was 8.75 m and the diameter 2.77 m.

Figure 8.2 s a sketch of a unit to handle 20,000 B/D of a light cracker oil with a gas stream containing 75% H_2. Liquid rate was 115,000 kg/hr, gas rate 12,700 kg/hr, catalyst charge 40,000 kg or 45 m^3, LHSV ≅ 3. Operating conditions were 370 C and 27 atm. Vessel dimensions were not revealed, but with an H/D = 5, the catalyst bed will have the dimensions 2.25 x 11.25 m.

8.4.4. FLOODED FIXED BED REACTORS

When the gas and liquid flows are cocurrent upward a screen is needed at the top to retain the catalyst particles. Such a unit has been used for the hydrogenation of nitro and double bond compounds and nitriles (Ovcinnikov et al, Brit Chem Eng 13 1367, 1968). High gas rates can cause movement and attrition of the particles. Accordingly such equipment is restricted to low gas flow rates, where for instance a hydrogen atmosphere is necessary but the consumption of hydrogen is slight. Backmixing is substantial in commercial size columns, but less than in bubble columns. Liquid distribution is not a problem, and heat transfer is much better than in the trickle vessel. Liquid holdup and residence times are greater under flooding conditions which may encourage side reactions.

Downward flow of both fluids imposes no restriction on the gas rate, except that the pressure drop will be high. On the whole, the trickle bed is preferred to the flooded bed.

8.4.5. SUSPENDED CATALYST BEDS

There are three main types of three-phase reactors in which the catalyst particles move about in the fluid.

1. Slurry reactors with mechanical agitation. The catalyst may be retained in the vessel or it may flow out with the fluid and be separated from the fluid downstream. In comparison with trickle beds, high heat transfer is feasible, and the residence time can be made very great. Pressure drop is due to sparger friction and hydrostatic head. Filtering cost is a major item.

2. Entrained solids bubble columns with the solid fluidized by bubble action. The three-phase mixture flows through the vessel and is separated downstream. Used in preference to fluidized beds when catalyst particles are

very fine or subject to disintegration in process.

3. GLS fluidized with a stable level of catalyst. Only the fluid mixture leaves the vessel. Gas and liquid enter at the bottom. Liquid is continuous, gas is dispersed. Particles are larger than in bubble columns, 0.2-1.0 mm. Bed expansion is small. Bed temperatures are uniform within 2 C in medium size beds, and heat transfer to embedded surfaces is excellent. Catalyst may be bled off and replenished continuously, or reactivated continuously.

In the reactor of Figure 8.3, a stable fluidized bed is maintained by recirculation of the mixed fluid through the bed and a draft tube. An external pump sometimes is used instead of the built-in impeller shown. Such units were developed for the liquefaction of coal and are called ebullating beds..

Three-phase fluidized bed reactors are used for the treatment of heavy petroleum fractions at 350-600 C and 200 atm. A biological treatment process (Dorr-Oliver Hy-Flo) employs a vertical column filled with sand on which bacterial growth takes place while waste liquid and air are charged. A large interfacial area for reaction is provided, about 33 cm^2/cm^3, so that an 85-90% BOD removal in 15 minutes is claimed compared with 6-8 hr in conventional units.

8.4.6. TRICKLE BED PARAMETERS

Numerous studies have been made of the hydrodynamics and other aspects of the behavior of gas-liquid-solid systems, in particular of trickle beds, and including absorption and extraction in packed beds. A selection of correlations of these parameters is presented in problem P8.03.02. They tell something of what is going on in three-phase reactors.

Review references

Ramachandran, P A, and R V Chaudhari, *Three Phase Chemical Reactors*, Gordon & Breach, 1983

Satterfield, C N, *Trickle Bed Reactors*, AIChE Journal 21 209-228, 1975

Shah, Y T, *Gas-Liquid-Solid Reactor Design*, McGraw-Hill, 1979.

8.5. BIOCHEMICAL REACTIONS

Biochemical industries are based on the growth of microbes such as bacteria, fungi, molds, yeasts and others. Although some microbes are grown as food, interest here is in the production of chemicals with their aid. A distinction is drawn between steps that involve cells and those that employ isolated catalytic enzymes which are metabolic products of cells. Major characteristics of microbial processes that may be contrasted with those of ordinary chemical processing include the following:

..The reaction medium is invariably aqueous

..The products are made in low concentrations, rarely more than 5-10% for chemicals and much less for particular enzymes.

..Reaction temperatures are low, usually in the range of 10-60 C, but the optimum range in individual cases may be 5 C or less.

..The processes require a mild and narrow range of pH.

..With the exception of a very few instances, such as potable ethanol or glucose isomerate, the scale of commercial processes is modest, and for enzymes it is very low, only a few kilograms/day.

..The mass of microbes increases simultaneously with the production of chemicals.

..Batch reactors are used preponderantly, although there are a few large scale continuous processes.

..Avoidance of contamination is a major operating factor, for instance the air must be sterilized.

8.5.1. GLOSSARY

A number of concepts that parallel those of ordinary chemical processing have bioprocessing names.

A substrate is a reactant. It may be a nutrient for the growth of cells, or its main function may be to transform into some desired chemical.

Enzymes are metabolic products of cells that have highly specific catalytic action. They are proteins with molecular weights in the range of 15,000-1,000,000 or so.

Immobilized enzymes are attached to a solid support by adsorption or chemical binding or mechanical entrapment in the pores of a gel structure but retain their catalytic power. Their merit is ease of separation from the finished reaction product.

Microbes are living cells of simple biological organization. Their metabolic products may be chemicals of simple or complex structure.

Fermentation is a process in which chemical changes are brought about in an organic substrate through the action of enzymes whether or not these enzymes occur within the cell or are cell free. Air is needed for metabolism, so the process is aerobic..

Anaerobic fermentation (in the absence of air) is less common, for instance anaerobic digestion of organic wastes is practiced to make methane.

8.5.2. RATE EQUATIONS

The simplest mechanism of enzyme action is formation of a temporary compound ES of enzyme E and substrate S followed by decomposition of ES into E and a product P. When ES is assumed to attain equilibrium, the corresponding rate equation is named after Michaelis and Menten. It is derived in problem P8.04.02.

$$r_s = -\frac{dC_s}{dt} = \frac{kE_0C_s}{K_m+C_s}$$

Problem P8.04.01 takes the case where ES is not in equilibrium. Extensions of the M-M equation take into account the presence of additional substrates and inhibitors, and even other mechanisms. Some of these alternates are treated in the Problems. Clearly the M-M equation is a special case of the Langmuir-Hinshelwood equations of Chapter 6.

A rate equation for the growth of microbe cells proposed by Monod assumes the M-M form of dependence on the concentration of the substrate but includes a proportionality to the concentration C_x of the cells, that is

$$r_x = r_p = \frac{dC_x}{dt} = \frac{kC_xC_s}{K_m+C_s}$$

Before this equation can be applied, some relation must be known between C_x and C_s. Most often, the change in cell content is assumed proportional to the change in substrate content. That is,

$$dC_x = -y_{xs}dC_s$$

or

$$\Delta C_x = -y_{xs}\Delta C_s$$

or

$$C_x = C_{x0} + y_{xs}(C_{s0}-C_s)$$

where y_{xs} is called the yield coefficient. With this assumption the Monod equation is integrated in problems P8.04.04 and P8.04.20.

Microbes tend to form flocks as they grow, into which nutrients and dissolved oxygen must diffuse. The rate of growth thus depends on the diffusional effectiveness. This topic is developed by Atkinson (1974). Similarly enzymes immobilized in gel beads, for instance, have a reduced catalytic effectiveness analogous to that of porous granular catalysts that are studied in Chapter 7. For the M-M equation this topic is touched on in problems P8.04.15 and P8.04.16.

8.5.3. CONSTANTS OF THE RATE EQUATIONS.

The M-M equation is readily analyzed by a choice of several linearized forms when the data are of (r,C). Such analyses are made in problem group P3.08 and in problems P8.04.02 and P8.04.05. When the data are of (C,t), the derivative is first found by numerical differentiation, as in problem P3.08.07. Also in that problem, the integrated form of the M-M equation is used in linearized form. In problem P8.04.05 the three linearized forms give different values of the constants and consequently give somewhat different fits to the original (r, C) data, and with different statistical variances. When the scatter of the data is large and the extra labor is acceptable, non-linear regression should be used to find the constants, that is, after making

$$\Sigma(r_i - \frac{k_1C_i}{k_2+C_i})^2 \Rightarrow \text{minimum}, \quad \frac{\partial\Sigma}{\partial k_1} = \frac{\partial\Sigma}{\partial k_2} = 0$$

When the yield coefficient y_{xs} can be found by inspection of the data, the Monod equation can be put in the linearized form,

$$y = \frac{C_s[C_{x0}+y_{xs}(C_{s0}-C_s)]}{r} = \frac{k_2}{k_1} + (\frac{1}{k_1})(\frac{1}{C_s})$$

The integrated forms developed in problems P8.04.04 and P8.04.20 cannot be linearized. The latter problem, however, takes two representative data points and solves simultaneously for the two constants.

8.5.4. REACTORS

Reactions of cell growth or those using immobilized enzymes are instances of gas-liquid-solid reactions. In principle, accordingly, any of the types of reactors described in Section 8.3 could be employed as fermentors. Mostly, however, mechanically agitated tanks are the type adopted. Aeration supplies additional agitation as well as metabolic need, and moreover sweeps away CO_2 and noxious byproducts.

There are a few other kinds of industrial plants. An air-lift tower fermenter was developed by ICI for the production of single-cell protein from methanol which employs an external loop for heat removal. Trickle beds for the treatment of waste waters employ packing structures or packing elements of 4-6 cm dia and porosities above 50%. Microbial films are formed on the packing that react with the organic substrate and the air as the liquid flows down and the air up.

Reaction times of fermentation range from a few hours to several days. Batch processes are common, but continuous stirred tanks also are used either singly or in stages. A continuous stirred tank reactor (CSTR) also is called a chemostat. Figure 8.4 is a schematic of a fermentor with representative dimensions from the literature.

Exothermicity is a feature of fermentation and strict control of temperature is necessary to keep the cells growing and the enzymes functioning. Reactors up to 500 liters are equipped with jackets, larger units with coils. A vessel of 55,000 liters may have 50-70 m^2 cooling surface. The operating conditions of a large scale penicillin plant may supply perspective on these processes:

Reactor volume	150-200 m^3
Substrate	glucose-lactose (8% in water)
Reaction time	180-220 hrs
Power input	3-4 kW/m^3
Air flow rate	(0.5-1.0 vol/min)/vol
Temperature	25 C
pH	5.5-7.4 (depending on the strain)
Gage pressure	0.3-0.7 atm
Carbon utilization	6-10%

REFERENCES

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Stanbury, P F, & A Whitaker, *Principles of Fermentation Technology*, Pergamon 1984.

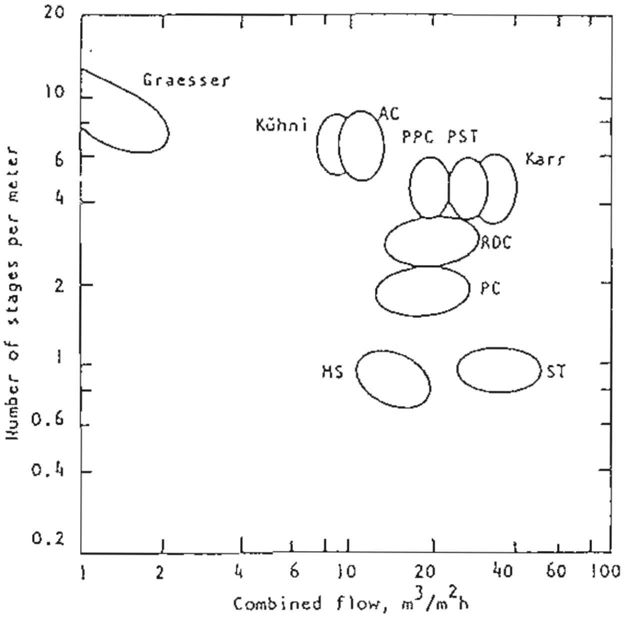


Figure 8.1. Efficiency and capacity range of small diameter extractors, 50–150 mm dia. Acetone extracted from water with toluene as the disperse phase, $V_d/V_c = 1.5$. Code: AC = agitated cell; PPC = pulsed packed column; PST = pulsed sieve tray; RDC = rotating disk contactor; PC = packed column; MS = mixer-settler; ST = sieve tray [*Stichlmair*, Chem. Ing. Tech. 52(*3*), *253–255* (*1980*)].

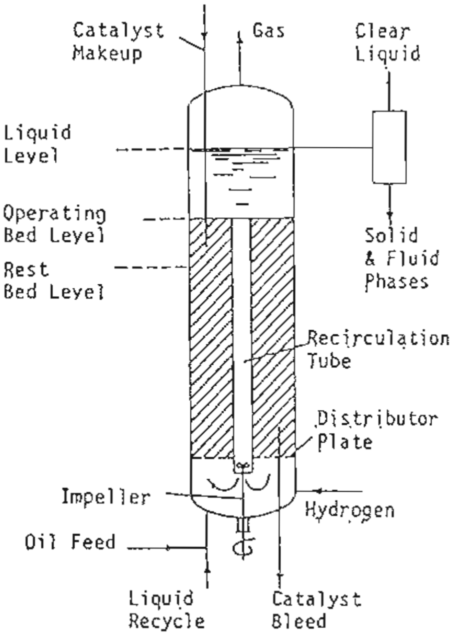


Figure 8.3. Gas-Liquid Fluidized Bed ("Ebullating") Reactor for Hydroliquefaction of Coal (Kampiner, in Winnacker-Kuehler, *Chemische Technologie* 3 252, 1972).

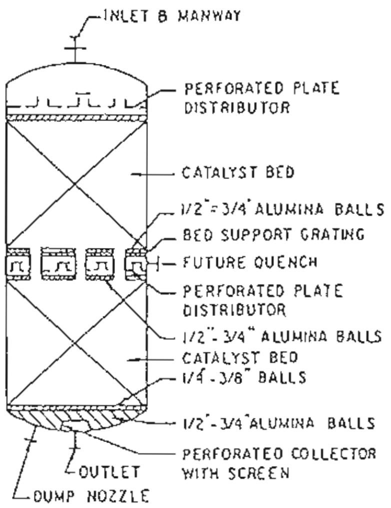


Figure 8.2. Trickle Bed Reactor for Hydrotreating 20,000B/D of Light Catalytic Cracker Oil at 370 C and 27 atm (Gianetto & Silveston, *Multiphase Chemical Reactors*, 533-563, 1986).

Dimension	Jackson (1958)	Arba *et al* (1973)	Paca *et al.* (1976)
Operating volume	—	100,000 dm^3 (total)	170 dm^3
Liquid height (L)	—	—	150 cm
L/D (tank diameter)	—	—	1.7
Impeller diameter	0.34–0.5	0.4	0.33
Baffle width/D	0.08–0.1	0.095	0.098
Impeller height/D	0.5	0.24	0.37
P/V	0.5–1.0	—	0.74
P/W	0.5–1.0	0.85	0.77
P/Y	0.5–1.0	0.85	0.77
P/Z	—	2.1	0.91
H/D	1.0–1.6	2.2	2.95

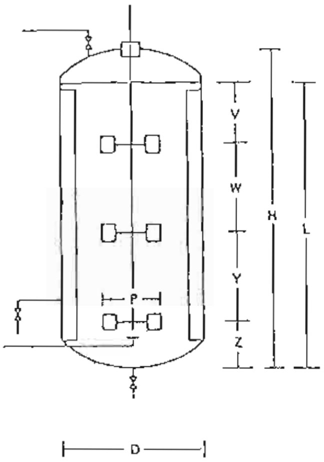


Figure 8.4. Diagram of a Fermentor with Three Impellers, with Dimensions of Typical Vessels Taken from the Literature.

Table 8.1. Typical Values of K_Ga for Absorption in Towers Packed with 1.5" Intalox Saddles at 25% Completion of Reaction (Eckert et al, *Ind Eng Chem* 59 41, 1967).

Absorbed Gas	Absorbent	K_Ga lb moles/hr ft³ atm
Cl_2	$H_2O \cdot NaOH$	20.0
HCl	H_2O	16.0
NH_3	H_2O	13.0
H_2S	$H_2O \cdot$ MEA	8.0
SO_2	$H_2O \cdot NaOH$	7.0
H_2S	$H_2O \cdot$ DEA	5.0
CO_2	$H_2O \cdot KOH$	3.10
CO_2	$H_2O \cdot$ MEA	2.50
CO_2	$H_2O \cdot NaOH$	2.25
H_2S	H_2O	0.400
SO_2	H_2O	0.317
Cl_2	H_2O	0.138
CO_2	H_2O	0.072
O_2	H_2O	0.0072

Table 8.2. Selected Absorption Coefficients for CO_2 in Various Solvents in Towers Packed with Raschig Rings (Sherwood, Pigford & Wilke, *Mass Transfer*, 305, 1975).

Solvent	$K_g a$, lb mole/(h)(ft³)(atm)
Water	0.05
1-*N* sodium carbonate, 20% Na as bicarbonate	0.03
3-*N* diethanolamine, 50% converted to carbonate	0.4
2-*N* sodium hydroxide, 15% Na as carbonate	2.3
2-*N* potassium hydroxide, 15% K as carbonate	3.8
Hypothetical perfect solvent having no liquid-phase resistance and having infinite chemical reactivity	24.0

* Basis: $L = 2{,}500$ lb/(h)(ft²); $G = 300$ lb/(h)(ft²); $T = 77°F$; pressure, 1.0 atm.

Table 8.3. Continuous-Phase Mass Transfer Coefficients and Interfacial Areas in Liquid-Liquid Contactors

Type of Equipment	Dispersed Phase	Continuous Phase	ϵ_D	τ_D	$k_L \times 10^2$ (cm/sec)	a (cm^2/cm^3)	$k_L a \times 10^2$ (sec^{-1})
Spray columns	P	M	0.05–0.1	Limited	0.1–1	1–10	0.1–10
Packed columns	P	P	0.05–0.1	Limited	0.3–1	1–10	0.3–10
Mechanically agitated contactors	PM	M	0.05–0.4	Can be varied over a wide range	0.3–1	1–800	0.3–800
Air-agitated liquid–liquid contactors	PM	M	0.05–0.3	Can be varied over a wide range	0.1–0.3	10–100	1.0–30
Two-phase cocurrent (horizontal) contactors	P	P	0.05–0.2	Limited	0.1–1.0	1–25	0.1–25

P = plug flow, M = mixed flow, ϵ_D = fractional dispersed phase holdup, τ_D = residence time of the dispersed phase (Doraiswamy & Sharma, 1984).

Table 8.4. Characteristics of Gas-Liquid-Solid Reactors

Property	(1) Trickle bed	(2) Flooded	(3) Stirred tank	(4) Entrained solids	(5) Fluidized bed
Gas holdup	0.25-0.45	small	0.2-0.3		
Liquid holdup	0.05-0.25	high	0.7-0.8		
Solid holdup	0.5-0.7		0.01-0.10		0.5-0.7
Liquid distribution	good only at high liq rate		good	good	good
RTD, liquid phase	narrow	narrower than (4)	wide	wide	narrow
RTD, gas phase	nearly plug flow		backmixed	backmixed	narrow
Interfacial area	20-50% of geometrical	like (1)	100-1500 m^2/m^3	100-400 m^2/m^3	less than (4)
MTC, gas liquid	high		intermediate		
MTC, liquid-solid	high		high		
Radial heat transf	slow		fast	fast	fast
Pressure drop	high with small d_p		hydrostatic head		

Table 8.5. Hydrodesulfurization Operating Data (In part after Satterfield, *AIChE Journal* <u>21</u> 209-228, 1975).

	Superficial liquid velocity		Superficial gas velocity				Residence time	
			ft/h (STP)		kg/m^2 · s		sec/m	
	ft/h	kg/m^2 · s	A^a	B^a	A^a	B^a	A	B
Pilot plant^b	1 to 30	0.08 to 2.5	180 to 5400	890 to 27,000	0.0013 to 0.040	0.0066 to 0.20	480 to 16	97 to 3.5
Commercial reactor	10 to 300	0.8 to 25	1800 to 54,000	8900 to 270,000	0.013 to 0.40	0.066 to 2.0	48 to 1.6	9.7 to 0.35

[a] The values of gas velocity are shown for (A) 1000 and (B) 5000 std ft^3 of H$_2$ per barrel, assuming that all the oil is in the liquid phase.

[b] The length of the pilot-plant reactor was assumed to be one-tenth the length of the commercial reactor.

PROBLEMS, CHAPTER 8

P8.01.01. REACTION ON A CATALYTIC FLAT WALL

A fluid of concentration C and linear velocity u is flowing and reacting between two wide plates a distance 2w apart, with rate equation $r_c = k_cC^\alpha$. The walls are coated with a catalyst on which the reaction rate is $r_w = k_wC_w$. Diffusion in the axial direction is small in comparison with mass transfer by bulk flow. A material balance is made over an elemental prism of unit width between y and y+dy laterally and between z and z+dz axially

$$\text{Input} = -D\frac{\partial C}{\partial y}dz + uC\,dy$$

$$\text{Output} = \text{Input} + d[-D\frac{\partial C}{\partial y}dz + uC\,dy]$$

$$\text{Sink} = r_c dV = k_cC^\alpha dydz$$

$$\text{Accumulation} = \frac{\partial C}{\partial t}dydz$$

Putting it together and dividing by dydz,

$$-D\frac{\partial^2 C}{\partial y^2} + u\frac{\partial C}{\partial z} + k_cC^\alpha + \frac{\partial C}{\partial t} = 0 \qquad (1)$$

Take the steady state,

$$-D\frac{\partial^2 C}{\partial y^2} + u\frac{\partial C}{\partial z} + k_cC^\alpha = 0 \qquad (2)$$

Boundary conditions are

At the inlet, $C(y,0) = C_0$ (3)

At the center by symmetry, $y = 0,\ \frac{\partial C}{\partial y} = 0$ (4)

At the wall, y = w, rate of diffusion = rate of reaction,

$$-D(\frac{\partial C}{\partial y})_w = k_wC_w \qquad (5)$$

Try a solution by "Separation of variables".

$$C(y,z) = f(y)g(z) \qquad (6)$$

$$- Dgy'' + ufg' + k_c(fg)^\alpha = 0 \qquad (7)$$

The variables are separable only when $\alpha = 1$. Make this assumption and rearrange,

$$\frac{D}{f}\frac{d^2f}{dy^2} = \frac{u}{g}\frac{dg}{dz} + k_c = -\lambda^2 \qquad (8)$$

The two functions of separate independent variables can equal each other only when they equal the same constant. The assumed negativity is substantiated later. The solutions of the two ODEs making up (8) are,

$$f = A\cos(\lambda y/\sqrt{D}) + B\sin(\lambda y/\sqrt{D}) \qquad (9)$$

$$g = \exp(-\frac{k_c+\lambda^2}{u}z) \qquad (10)$$

Clearly the exponent must be negative for the concentration to fall axially. Applying condition (4),

$$-A(\lambda/\sqrt{D})\ \sin(0) + B(\lambda/\sqrt{D})\ \cos(0) = 0$$

Accordingly B = 0 and the solution thus far becomes,

$$C = A\ \exp(-\frac{k_c+\lambda^2}{u}z)\ \cos(\lambda y/\sqrt{D}) \qquad (11)$$

Apply the wall condition,

$$D(\lambda/\sqrt{D})\ \sin(\lambda w/\sqrt{D}) = k_c\ \cos(\lambda w/\sqrt{D})$$

or

$$(\lambda w/\sqrt{D})\ \tan(\lambda w/\sqrt{D}) = k_w w/D \qquad (12)$$

For each value of the RHS, Eq (12) has an infinite number of solutions, for instance like on the graph. When RHS = 0.2, the successive roots are,

$$\lambda_n w/\sqrt{D} = 0.433,\ 3.204,\ 6.315,\ 9.446,\ 12.582,\ 15.271,\ldots \qquad (13)$$

To satisfy the inlet condition, try an infinite series with these values of the parameters.

$$C_0 = \Sigma\ A_n\ \cos(\lambda_n y/\sqrt{D}) \qquad (14)$$

Multiply (14) by $\cos(\lambda_m y/\sqrt{D})$ and integrate from y = 0 to w, using this trigonometric result,

$$\int_0^h \cos(\lambda_m x)\cos(\lambda_n x)dx = 0 \qquad \lambda_m \neq \lambda_n \quad (15)$$

$$0.5[h + \frac{1}{2\lambda_n}\sin(2\lambda_n h)], \quad \lambda_m = \lambda_n \quad (16)$$

The values of the coefficients in Eq (14) become,

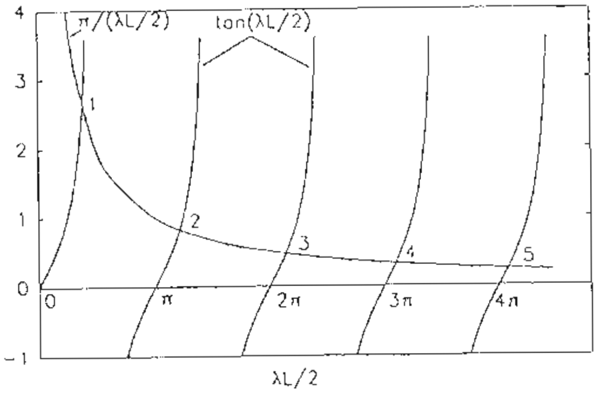
$$A_n = \frac{4C_0\ \sin(\lambda_n w/\sqrt{D})}{2\lambda_n w/\sqrt{D} + \sin(2\lambda_n w/\sqrt{D})} \qquad (17)$$

The final result is ,

$$C = \sum_n A_n\ \exp(-\frac{k_c+\lambda_n^2}{u}z)\ \cos(\lambda_n y/\sqrt{D}) \qquad (18)$$

Note that k_w and w are to be specified in Eq (12), and A_n is from Eq (17).

The average over a cross section is found by integration.



Finding eigenvalues.

P8.01.02. REACTION ON THE WALL OF A TUBE

A fluid of concentration C and linear velocity u is flowing and reacting in a tube of radius R with a rate equation, $r_c = kC^\alpha$. The tube surface is covered with a catalyst on which the reaction rate is $r_w = k_w C$. Appreciable diffusion occurs only in the radial direction. A material balance is made over a hollow cylindrical element between r and r+dr radially and between z and z+dz axially.

$$\text{Input} = -D(2\pi r)\frac{\partial C}{\partial r}\,dz + uC(2\pi r dr)$$

$$\text{Output} = \text{Input} + d(\text{Input})$$

$$\text{Sink} = r_c dV = kC^{\alpha}(2\pi r dr dz)$$

$$\text{Accumulation} = \frac{\partial C}{\partial t}\,dV = \frac{\partial C}{\partial t}(2\pi r dr dz)$$

Applying the conservation rule,

$$d[-Dr\frac{\partial C}{\partial r}dz + uCrdr] + kC^{\alpha}rdrdz + \frac{\partial C}{dt}(rdrdz) = 0$$

Dividing through by drdz,

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} = \frac{1}{D}\left(u\frac{\partial C}{\partial z} + kC^{\alpha} + \frac{\partial C}{\partial t}\right) \qquad (1)$$

In the steady state,

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} - \frac{u}{D}\frac{\partial C}{\partial z} - \frac{k}{D}C^{\alpha} = 0 \qquad (2)$$

Boundary conditions are,

At the inlet, $z = 0$, $C(r,0) = C_0$ (3)

At the center, $r = 0$, $\partial C/\partial r = 0$ (4)

At the wall, $r = R$, $C = C_w$, $-D\,\partial C/\partial r = k_w C$ (5)

Take $\alpha = 1$ and apply "Separation of variables".

$$C(r,z) = f(r)g(z) \qquad (6)$$

$$gf'' + \frac{1}{r}gf' - \frac{u}{D}fg' - \frac{k}{D}fg = 0$$

$$\frac{f''}{f} + \frac{1}{r}\frac{f'}{f} = \frac{u}{D}\frac{g'}{g} + \frac{k}{D} = -\lambda^2 \qquad (7)$$

(See P8.01.01 for the reasoning about this statement). Solve the two ODEs.

$$\frac{dg}{dz} = -\frac{k+\lambda^2 D}{u}\,g \qquad (8)$$

$$g = g_0\exp\left(-\frac{k+\lambda^2 D}{u}\,z\right) \qquad (9)$$

$$\frac{d^2 f}{dr^2} + \frac{1}{r}\frac{df}{dr} + \lambda^2 f = 0 \qquad (10)$$

The solution of this Bessel equation is

$$f = AJ_0(\lambda r) + BY_0(\lambda r) \qquad (11)$$

and

$$C = \exp\left(-\frac{k+\lambda^2 D}{u}\,z\right)[AJ_0(\lambda r) + BY_0(\lambda r)] \qquad (12)$$

For properties of Bessel functions, see for example, Walas, Modelling with Differential Equations in Chemical Engineering, 1991). Applying the condition at the center, Eq (4),

$$AJ_1(0) + BY_1(0) = 0 \qquad (13)$$

Since $Y_1(0) \Rightarrow -\infty$, the coefficient $B = 0$ and

$$C = A\exp\left(-\frac{k+\lambda^2 D}{u}z\right)J_0(\lambda r) \tag{14}$$

At the wall, Eq (5) becomes

$$\lambda R J_1(\lambda R) = (k_w R/D)J_0(\lambda R) \tag{15}$$

A plot of this equation with $k_w R/D = 1$ is shown. Successive roots are

$$\lambda_n R = 1.26,\ 4.08,\ 7.12,\ 10.30,\ \ldots \tag{16}$$

An infinite series is required to satisfy the inlet condition.

$$C_0 = \Sigma A_n J_0(\lambda_n r) \tag{17}$$

These properties are applicable:

$$\int_0^R rJ_0(\lambda_m r)J_0(\lambda_n r)dr = \begin{cases} 0 & ,\ \lambda_m \neq \lambda_n \\ \dfrac{[(\lambda R)^2+(kR/D)^2][J_0(\lambda R)]^2}{2\lambda^2}, & \lambda_m = \lambda_n \end{cases}$$

Multiply Eq (17) by $rJ_0(\lambda_m r)$ and integrate. Accordingly the coeffcients become

$$A_n = \frac{C_0\int_0^R rJ_0(\lambda_n r)dr}{\int_0^R r[J_0(\lambda_n r)]^2 dr}$$

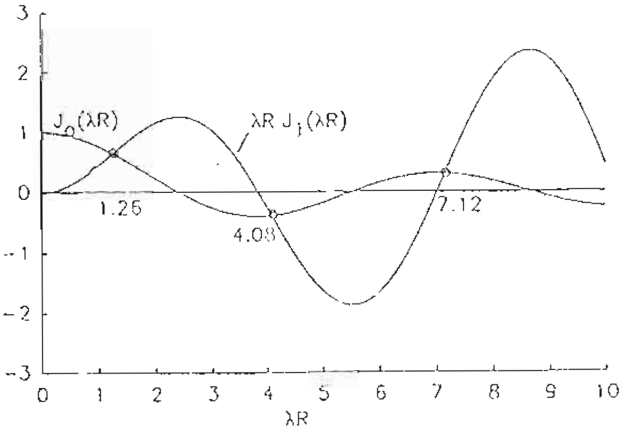
$$= \frac{2\lambda_n^2 C_0 J_1(\lambda_n R)}{[(\lambda_n R)^2+(kR/D)^2[J_0(\lambda_n R)]^2} \tag{18}$$

The final result is

$$C = \sum_n A_n \exp\left(-\frac{k+\lambda_n^2 D}{u}z\right) J_0(\lambda_n r) \tag{19}$$

The average over a cross section is found by integration,

$$\bar{C} = \frac{1}{\pi R^2}\int_0^R 2\pi rCdr \tag{20}$$



P8.01.03. SOLUTION BY FINITE DIFFERENCES

Consider the equation of P8.01.01,

$$\frac{\partial^2 C}{\partial y^2} - \frac{u}{D}\frac{\partial C}{\partial z} - \frac{k_c}{D} C^{\alpha} = 0 \qquad (1)$$

Represent the region by m divisions in the y direction and n divisions in the z direction. The concentration at a particular location or node is called $C_{m,n}$.

$$y = m\Delta y = mh \qquad (2)$$

$$z = n\Delta z = nk \qquad (3)$$

The derivatives in terms of finite differences are,

$$\frac{\partial C}{\partial z} = \frac{C_{m,n+1} - C_{m,n}}{k} \qquad (4)$$

$$\frac{\partial^2 C}{\partial y^2} = \frac{C_{m+1,n} - 2C_{m,n} + C_{m-1,n}}{h^2} \qquad (5)$$

Substitute into Eq (1).

$$C_{m+1,n} - 2C_{m,n} + C_{m-1,n} - \frac{h^2 u}{kD}(C_{m,n+1} - C_{m,n}) - \frac{h^2 k_c}{D} C^{\alpha}_{m,n} = 0 \quad (6)$$

Rearranging,

$$C_{m,n+1} = \frac{C_{m+1,n} - (2 - h^2 u/kD)C_{m,n} - (h^2 k_c/D)C^{\alpha}_{m,n} + C_{m-1,n}}{h^2 u/kD} \qquad (7)$$

Lines (7) and (8) show that the values in column n+1 are determined by the values of the preceding column, n.

$$\begin{tikzcd}
C_{m+1,n} \arrow[dr] & \\
C_{m,n} \arrow[r] & C_{m,n+1} \\
C_{m-1,n} \arrow[ur] &
\end{tikzcd} \qquad (8)$$

Whether or not the repeated determinations of column values are stable depends on the magnitudes of the increments h and k. In complex cases these may have to be found by trial. When $k_c = 0$, however, it is known that the process is convergent when

$$2 - h^2 u/kD = 0 \qquad (9)$$

Then,

$$C_{m,n+1} = 0.5(C_{m+1,n} + C_{m-1,n}) \qquad (10)$$

At the center,

$$C_{0,n+1} = 0.5(C_{1,n} + C_{-1,n}) = C_{1,n} \qquad (11)$$

At the wall, $C = C_w$, and

$$-\frac{C_{w,n} - C_{w-1,n}}{h} = (k_w/D)C_{w,n} \qquad (12)$$

The calculations are started at the inlet to the reactor where $C_{m,0} = C_0$, except at the wall where Eq (12) applies.

Alternately, instead of Eq (4) it may be preferable to use for the first derivative,

$$\frac{\partial C}{\partial z} = \frac{C_{m+1,n}-C_{m-1,n}}{2k} \tag{13}$$

with appropriate changes in the transformed differential equation.

P8.01.04. PACKED TUBULAR REACTOR HEAT AND MATERIAL BALANCES

For a process in a packed tubular reactor like that of P8.01.02, the steady material balance is derived there as

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} - \frac{u}{D}\frac{\partial C}{\partial z} - \frac{R_c}{D} = 0 \tag{1}$$

$$R_c = \exp(a-b/T)C^{\alpha} \tag{2}$$

The heat balance is made on the assumptions that conduction in the axial direction is relatively negligible and that the heat capacity is constant. The enthalpy change of reaction is ΔH_r. The components of the heat balance over a differential element are,

$$\text{Input} = -\lambda(2\pi r dz)\frac{\partial T}{\partial r} + u\rho C_p(2\pi r dr)T$$

$$\text{Output} = \text{Input} + d\ (\text{Input})$$

$$\text{Source} = -\Delta H_r R_c dV = -\Delta H_r R_c(2\pi r dr dz)$$

$$\text{Accumulation} = \rho C_p dV\frac{\partial T}{\partial t} = \rho C_p(2\pi r dr dz)\frac{\partial T}{\partial t}$$

On combining these terms and dividing out $2\pi r dr dz$,

$$-\frac{\lambda}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + u\rho C_p\frac{\partial T}{\partial z} + \Delta H_r R_c + \rho C_p\frac{\partial T}{\partial t} = 0 \tag{3}$$

At steady state,

$$-\frac{\lambda}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + u\rho C_p\frac{\partial T}{\partial z} + \Delta H_r R_c = 0 \tag{4}$$

At the wall, the temperature of the wall is T^* and the heat transfer coefficient is U, so that

$$-\lambda\frac{\partial T}{\partial r} = U(T^*-T) \tag{5}$$

At the center, by the l'Hopital Rule,

$$r = 0,\ \frac{\partial T}{\partial r} = 0,\ \frac{1}{r}\frac{\partial T}{\partial r} = \frac{\partial^2 T}{\partial r^2}$$

so the steady equation becomes at the center,

$$-2\lambda\frac{\partial^2 T}{\partial r^2} + u\rho C_p\frac{\partial T}{\partial z} - \Delta H_r R_c = 0 \tag{6}$$

Inlet conditions also must be specified, for instance as constants of functions of r,

$$C(r,0) = f(r),\ T(r,\ 0) = g(r) \tag{7}$$

P8.01.05. METHOD OF LINES FOR A PDE.

The method of lines replaces a partial differential equation with a set of ordinary differential equations. In an equation like that of P8.01.01, for instance,

$$\frac{\partial C}{\partial z} = \frac{D}{u}\frac{\partial^2 C}{\partial r^2} - \frac{k_c}{u}C^2$$

replace the radial derivative with its finite difference equivalent. Then at each radial position, m, the PDE becomes

$$\frac{dC_m}{dz} = \frac{D}{u(\Delta r)^2}(C_{m+1}-2C_m+C_{m-1}) - \frac{k_c}{u}C_m^2, \quad m = 0,\ 1,\ 2,\ \ldots \qquad (1)$$

At the center where $\partial C/\partial r = 0$,

$$C_1 = C_{-1} \qquad (2)$$

At the wall,

$$\frac{\partial C}{\partial r} = -\frac{k_c}{D}C$$

$$C_w = \frac{C_{w-1}}{1+k_c\Delta r/D} \qquad (3)$$

The equations will be written out for m = 0 (center), 1, 2, 3, 4, 5 (wall), with the indicated numerical values of the coefficients.

$$C_5 = 0.5C_4$$

$$\frac{dC_4}{dz} = 15(C_5-2C_4+C_3) - 5C_4^2$$

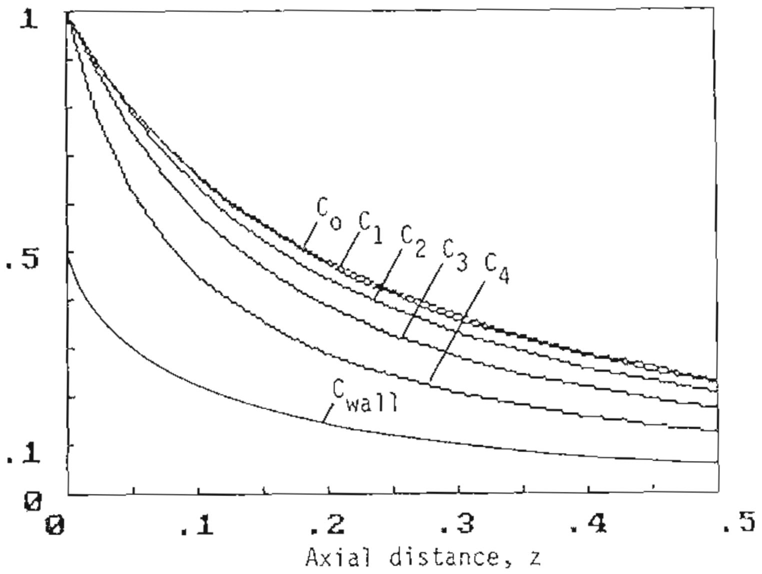
$$\frac{dC_3}{dz} = 15(C_4-2C_3+C_2) - 5C_3^2$$

$$\frac{dC_2}{dz} = 15(C_3-2C_2+C_1) - 5C_2^2$$

$$\frac{dC_1}{dz} = 15(C_2-2C_1+C_0) - 5C_1^2$$

$$\frac{dCo}{dz} = 15(2)(C_1-C_0) - 5C_0^2$$

The solution of these six ordinary differential equations is readily obtained by any ODE software. Note that the rate equation could be any function of C without complicating the solution procedure unduly. When higher axial derivatives are present, each radial equation must be reduced to a set of first order ones.



P8.01.06. HEAT AND MATERIAL BALANCES BY THE METHOD OF LINES

Apply the method of lines to the heat and material balances of P8.01.04. The differential equations that apply except at the center and the wall are,

$$\frac{\partial C}{\partial z} = \frac{D}{u}\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) - \frac{1}{u}\exp(a-b/T)C^{\alpha} \qquad (1)$$

$$\frac{\partial T}{\partial z} = \frac{\lambda}{u\rho C_p}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \frac{\Delta H_r}{u\rho C_p}\exp(a-b/T)\, C^{\alpha} \qquad (2)$$

On replacing the radial derivatives,

$$\frac{dC_m}{dz} = \frac{D}{u(\Delta r)^2}\left(C_{m+1} - 2C_m + C_{m-1} + \frac{C_{m+1}-C_m}{m}\right) - \frac{1}{u}\exp(a-b/T)C_m^{\alpha} \qquad (3)$$

$$\frac{dT_m}{dz} = \frac{\lambda}{u\rho C_p(\Delta r)^2}\left(T_{m+1} - 2T_m + T_{m-1} + \frac{T_{m+1}-T_m}{m}\right) + \frac{\Delta H_r}{u\rho C_p}\exp(a-b/T)C_m^{\alpha}$$

$$(4)$$

Eqs (3) and (4) apply for m = 1, 2, 3, ..., w-1, when C_w and T_w are the values at the wall. At the wall, T^* is the temperature of the heat transfer medium,

$$C_w = \frac{C_{w-1}}{1+k_w\Delta r/D} \qquad (5)$$

$$-\lambda\left(\frac{T_w-T_{w-1}}{\Delta r}\right) = U(T^*-T_w)$$

$$T_w = \frac{T^*+(\lambda/U\Delta r)T_{w-1}}{1+\lambda/U\Delta r} \qquad (6)$$

At the center, where m = 0,

$$\frac{dC_0}{dz} = \frac{2D}{u(\Delta r)^2}(C_1-C_0) - \frac{1}{u}\exp(a-b/T)C_0^{\alpha} \qquad (7)$$

$$\frac{dT_0}{dz} = \frac{2\lambda}{u\rho C_p(\Delta r)^2}(T_1-T_0) - \frac{\Delta H_r}{u\rho C_p}\exp(a-b/T)C^{\alpha} \qquad (8)$$

Eqs (3)-(6) are solved simultaneously for C_m and T_m as functions of axial position, z, for m = 0, 1, 2, 3, ... w.

P8.01.07. A NUMERICAL SOLUTION

Eq (7) of P8.01.03 will be solved with $k_c = 0$ and with $h^2u/kD = 2$ or 1.5. At the wall, $C_w = 0.5C_{w-1}$, $C_6 = 0.5C_5$.

In the table, the values of the top row (at n = 0) are known at the start of the calculations. Succeeding rows have the values at n = 1, 2, ..., at each particular value of m.

With 2 as the value of the constant, the concentrations fall regularly.

$$C_{m,n+1} = \frac{C_{m+1,n}+C_{m-1,n}}{2}$$

$$\left[\begin{array}{rrrrrrrrr}
 & m=-1 & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\
n=0 & 1000 & 1000 & 1000 & 1000 & 1000 & 1000 & 1000 & 500 \\
1 & 1000 & 1000 & 1000 & 1000 & 1000 & 1000 & 750 & 375 \\
2 & 1000 & 1000 & 1000 & 1000 & 1000 & 875 & 688 & 344 \\
3 & 1000 & 1000 & 1000 & 1000 & 938 & 844 & 609 & 305 \\
4 & 1000 & 1000 & 1000 & 969 & 922 & 774 & 574 & 287 \\
5 & 984 & 1000 & 984 & 961 & 871 & 748 & 531 & 265 \\
6 & 981 & 984 & 981 & 928 & 855 & 701 & 607 & 303
\end{array}\right]$$

With 1.5 for the constant, the results appear to oscillate.

$$C_{m,n+1} = \frac{C_{m+1,n}-0.5C_{m,n}+C_{m-1,n}}{1.5}$$

$$\left[\begin{array}{rrrrrrrrr}
 & m=-1 & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\
n=0 & 1000 & 1000 & 1000 & 1000 & 1000 & 1000 & 1000 & 500 \\
1 & 1000 & 1000 & 1000 & 1000 & 1000 & 1000 & 750 & 375 \\
2 & 1000 & 1000 & 1000 & 1000 & 1000 & 778 & 667 & 334 \\
3 & 1000 & 1000 & 1000 & 1000 & 852 & 852 & 519 & 260 \\
4 & 1000 & 1000 & 1000 & 901 & 951 & 630 & 568 & 284 \\
5 & 934 & 1000 & 934 & 1000 & 704 & 803 & 420 & 210
\end{array}\right]$$

P8.01.08. FINITE DIFFERENCE TREATMENT OF A PACKED BED REACTOR

The heat and material balances of a reactor with radial and axial gradients are stated in problem P8.01.04. In terms of fractional connversion, f, and for a first order reaction they are,

$$\frac{\partial^2 f}{\partial r^2} + \frac{1}{r}\frac{\partial f}{\partial r} - \frac{u}{D}\frac{\partial f}{\partial z} + \frac{k}{D}(1-f) = 0 \qquad (1)$$

$$-\lambda\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + u\rho C_p\frac{\partial T}{\partial z} + \Delta H_r kC = 0 \qquad (2)$$

$$k = \exp\left(a-\frac{b}{T+460}\right) = \exp\left(9.211 - \frac{15000}{T+460}\right) \qquad (3)$$

A solution of these equations will be made with particular values of the constants. The temperature of the heat transfer fluid in the jacket is $T^* = 500$ F, inlet temperature is 600 F and the inlet conversion is $f_0 = 0$.

finite difference equations are written with subscript m referring to the radial direction, n to the axial direction, and w to the wall. At the wall,

$$T_{w,n} = \frac{T^*+1.2T_{w-1,n}}{2/2} = \frac{500+1.2T_{w-1,n}}{2.2} \qquad (4)$$

$$f_{w+1} = f_{w-1} \qquad (5)$$

At the center,

$$T_{0,n+1} = T_{0,n}+0.8(T_{1,n}-T_{0,n}) + 2000k_{0,n}(1-f_{0,n}) \qquad (6)$$

$$f_{0,n+1} = f_{0,n}+2(f_{1,n}-f_{0,n}) + 16k_{0,n}(1-f_{0,n}) \qquad (7)$$

Elsewhere,

$$T_{m,n+1} = T_{m,n} +0.2[(1+1/m)T_{m+1,n} -(2+1/m)T_{m,n}+ T_{m-1,m}] + 2000k_{m,n}\ (1-f_{m,n}) \qquad (8)$$

$$f_{m,n+1} = f_{m,n} + 0.5[(1+1/m)f_{m+1,n} - (2+1/m)f_{m,n} + f_{m-1,n}] + 16k_{m,n}(1-f_{m,n}) \qquad (9)$$

The calculations of T and f are made for four radial increments and three axial increments. Some improvement in accuracy is obtained by using Eq (13) instead of Eq (4) of P8.01.03.

m \ n	0	1	2	3
Center, 0	600 , 0	614.4, 0.1152	627.1, 0.2171	645.1, 0.3582
1	600 , 0	614.4, 0.1152	629.6, 0.2369	643.7, 0.3552
2	600 , 0	614.4, 0.1152	626.0, 0.2369	635.8, 0.3415
3	600 , 0	602.3, 0.1152	605.4, 0.2136	606.9, 0.2779
Wall 4	554.5, 0	555.8, 0.1056	557.5, 0.1708	558.3, 0.2720

m = 0, n = 0, center

$$T_{01} = T_{00} + 0.8(T_{10}-T_{00})+2000\ k_{00}(1-f_{00})$$

$$= 600 + 0.8(600-600)+2000(0.0072)(1-0) = 614.4$$

$$f_{01} = 0 + 2(0-0)+16(0.0072)(1-0) = 0.1152$$

m = 1, n = 0

$$T_{11} = T_{10} + 0.2(2T_{20}-3T_{10}+T_{00})+2000\ k_{10}(1-f_{10})$$

$$= 600+ 0.8[2(600)-3(600)600) + 2000(0.0072)(1-0) = 614.4$$

$$f_{11} = 0 + 0.5[2(0)-3(0)+0] + 16(0.0072)(1-0) = 0.1152$$

m = 2, n = 0

$$T_{21} = T_{20} + 0.2[1.5T_{30}-2.5T_{20}+T_{10}]+2000k_{20}(1-f_{20})$$

$$= 600 +0.2[1.5(600)-2.5(600)+600]+2000(0.0072)(1-0)$$

$$= 614.4$$

$$f_{21} = 0 + 0.5[1.5(0)-2.5(0)+0]+16(0.0072)(1-0) = 0.1152$$

m = 3, n = 0

$$T_{31} = T_{30}+0.2[1.33T_{40}-2.33T_{30}+T_{20}]+2000\ k_{30}(1-f_{30})$$

$$= 600+0.2[1.33(554.5-2.33(600)+600]+2000(0.0072)(1-0)$$

$$= 602.3$$

$$f_{31} = 0+0.5[1.33(0)-2.33(0)+0]+16(0.0072)(1-0) = 0.1152$$

m = 4, n = 0, wall, $f_{50} = f_{30}$

$$T_{41} = \frac{500+1.2T_{31}}{2.2} = \frac{500+1.2(602.3)}{2.2} = 555.8$$

$$f_{41} = f_{40}+0.5[1.25f_{50}-2.25f_{40}+f_{30}]+16\ k_{40}(1-f_{40})$$

$$= 0+0.5(0) + 16(0.0066)(1-0) = 0.1056$$

m= 0, n = 1, center

$$T_{02} = T_{01}+0.8(T_{11}-T_{01})+2000\ k_{01}(1-f_{01})$$

$$= 614.4+0.8(614.4-614.4)+2000(0.0072)(1-0) = 627.1$$

$$f_{02} = 0.1152+0.5(0.1152-0.1152)+16(0.0072(100.1152) = 0.2171$$

$m = 1,\ n = 1$

$$\begin{aligned} T_{12} &= T_{11}+0.2[2T_{21}-3T_{11}+T_{01}) + 2000\ k_{11}(1-f_{11}) \\ &= 614.4+0.2[2(0.1152)-3(0.1152)+0.1152] \\ &\quad +2000(0.0086)(1-0.1152) = 629.6 \end{aligned}$$

$$\begin{aligned} f_{12} &= 0.1152+0.5[2(0.1152)-3(0.1152)+0.1152] \\ &\quad +16(0.0086)(1-0.1152) = 0.2369 \end{aligned}$$

$m = 2,\ n = 1$

$$\begin{aligned} T_{22} &= T_{21}+0.2[1.5T_{31}-2.5T_{21}+T_{11}]+2000k_{2}(1-f_{21}) \\ &= 614.4+0.2[1.5(602.3)-2.5(614.4)+614.4] \\ &\quad +2000(0.0086)(1-0.1152) = 626.0 \end{aligned}$$

$$\begin{aligned} f_{22} &= 0.1152+0.5[1.5(0.1152)-2.5(0.1152)+0.1152] \\ &\quad +16(0.0086)(1-0.1152) = 0.2369 \end{aligned}$$

$m = 3,\ n = 1$

$$\begin{aligned} T_{32} &= T_{31}+0.2[1.33T_{41}-2.33T_{31}+T_{21}]+2000k_{31}(1-f_{31}) \\ &= 602.3+0.2[1.33(555.8)-2.33(602.3)+614.4] \\ &\quad +2000(0.0074)(1-0.1152) = 605.4 \end{aligned}$$

$$\begin{aligned} f_{32} &= 0.1152+0.5[1.33(0.1056)-2.33(0.1152)+0.1152] \\ &\quad +16(0.0074)(1-0.1152) = 0.2136 \end{aligned}$$

$m = 4,\ n = 1$, wall, $f_{51} = f_{31}$

$$T_{42} = \frac{500+1.2T_{32}}{2.2} = \frac{500+1.2(605.4)}{2.2} = 557.5$$

$$\begin{aligned} f_{42} &= f_{41}+0.5[1.25f_{51}-2.25f_{41}+f_{31}]+16k_{41}(1-f_{41}) \\ &= 0.1056+0.5[1.25(0.1152)-2.25(0.1056)+0.1152] \\ &\quad + 16(0.0038)(1-0.1056) = 0.1708 \end{aligned}$$

$m = 0,\ n = 2$, center

$$\begin{aligned} T_{03} &= T_{02}+0.8(T_{12}-T_{02})+2000k_{02}(1-f_{02}) \\ &= 627.1+0.8(629.6-627.1)+2000(0.0102)(1-0.2171) = 645.1 \end{aligned}$$

$$f_{03} = 0+2(0.1152-0)=16(0.0102)(1-0.2171) = 0.3582$$

$m = 1,\ n = 2$

$$\begin{aligned} T_{13} &= T_{12}+0.2(2T_{22}-3T_{12}+T_{02})+2000k_{12}(1-f_{12}) \\ &= 629.6+0.2[2(626.0)-3(629.6)+627.1] \\ &\quad +2000(0.0105)(1-0.2369) = 643.7 \end{aligned}$$

$$\begin{aligned} f_{13} &= 0.2369+0.5[2(0.2369)-3(0.2369)+0.2171] \\ &\quad +16(0.0105(1-0.2369) = 0.3552 \end{aligned}$$

$m = 2,\ n = 2$

$$\begin{aligned} T_{23} &= T_{22}+0.2(1.5T_{32}-2.5T_{22}+T_{12})+2000k_{22}(1-f_{22}) \\ &= 626.00.2[1.5(605.4)-2.5(626.0)+629.6] \\ &\quad + 2000(0.0100)(1-0.2369) = 635.8 \end{aligned}$$

$$\begin{aligned} f_{23} &= 0.2369+0.5[1.5(0.2136)-2.5(0.2369)+0.2369] \\ &\quad + 16(0.0100)(1-0.2369) = 0.3415 \end{aligned}$$

$m = 3,\ n = 2$

$$T_{33} = T_{32}+0.2(1.33T_{42}-2.33T_{32}+T_{22})+2000k_{32}(1-f_{32})$$
$$= 605.4+0.2[1.33(557.5)-2.33(605.4)+626.0]$$
$$+2000(0.0077)(1-0.3415) = 606.9$$
$$f_{33} = 0.2136+0.5[1.33(0.1708)-2.33(0.2136)+0.2369]$$
$$+16(0.0077)(1-0.3415) = 0.2779$$

$m = 4,\ n = 2,$ wall, $f_{52} = f_{32}$

$$T_{43} = \frac{500+1.2T_{33}}{2.2} = \frac{500+1.2(606.9)}{2.2} = 558.3$$
$$f_{43} = f_{42}+0.5[1.25f_{52}-2.25f_{42}+f_{32}]+2000k_{42}(1-f_{42})$$
$$= 0.1708+0.5[1.25(0.2136)-2.25(0.1708)+0.2136]$$
$$+ 16(0.0040)(1-0.1708) = 0.2720$$

P8.01.09. DEHYDROGENATION OF ETHYLBENZENE

Data for the process of dehydrogenation of ethylbenzene to styrene in a tubular packed reactor are given by Jenson & Jeffreys (*Mathematical Methods in Chemical Rngineering*, 424, 1977). The energy and material balances are like those derived in P8.01.04. The finite difference equivalents of the first derivatives are with Eq (13) rather than Eq (4) of P8.01.03. Integration is accomplished with five radial increments. Heat transfer coefficient and temperature of the heat transfer medium are parameters studied. The number of axial increments required to make the average conversion 50% is to be found. The figures show typical variations of fractional conversion and temperatures.

$$\frac{\partial T}{\partial z} = A\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) - BR_c \qquad (1)$$

$$\frac{\partial x}{\partial z} = C\left(\frac{\partial^2 x}{\partial r^2} + \frac{1}{r}\frac{\partial x}{\partial r}\right) + DR_c \qquad (2)$$

Values of the constants are given in the reference as

$A = 0.000297,\qquad B = 37{,}000,\qquad C = 0.000427,\qquad D = 164$

At the center, the differential equations become

$$\frac{\partial T}{\partial z} = 2A\frac{\partial^2 T}{\partial r^2} - BR_c \qquad (3)$$

$$\frac{\partial x}{\partial z} = 2C\frac{\partial^2 x}{\partial r^2} + DR_c \qquad (4)$$

At the wall,

$$-k_E\frac{\partial T}{\partial r} = U(T - T') \qquad (5)$$

where T' is the jacket temperature, and k_E is the thermal conductivity.

$$\frac{\partial x}{\partial r} = 0 \quad \text{(impermeable and inert wall)} \qquad (6)$$

The rate equation is

$$R_c = k_r\left[\frac{1-x}{11+x}P - \frac{1}{K_e}\left(\frac{x}{11+x}P\right)^2\right], \quad P = \text{pressure} = 1.2 \qquad (7)$$

$$k_r = \exp\left(9.441 - \frac{11{,}000}{T}\right), \quad \text{specific rate of reaction} \qquad (8)$$

$$K_e = 0.027\exp[0.021(T - 773)], \quad \text{equilibrium constant} \qquad (9)$$

The explicit finite-difference equivalents are

$$\frac{\partial T}{\partial z} = \frac{T_{m,n+1} - T_{m,n-1}}{2k}, \quad k = \Delta z \tag{10}$$

$$\frac{\partial T}{\partial r} = \frac{T_{m+1,n} - T_{m-1,n}}{2h}, \quad h = \Delta r \tag{11}$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{T_{m+1,n} - 2T_{m,n} + T_{m-1,n}}{h^2} \tag{12}$$

with equations of the same form for the variable x.

Finite-difference equations will be formulated with five radial increments: $m = 0, 1, 2, 3, 4,$ and 5. These terms occur in the equations

$$M = \frac{Ak}{h^2} = \frac{0.000297k}{h^2} = 0.174 \tag{13}$$

$$M' = \frac{Ck}{h^2} = \frac{0.000427k}{h^2} = 0.250, \qquad \text{for stability} \tag{14}$$

It turns out that the value $M' = 0.25$ is required at the center for stability, and the corresponding other value becomes $M = 0.174$.

At the center,

$$T_{0,n+1} = 4MT_{1,n} + (1 - 4M)T_{0,n} - kBR_{c0,n} \tag{15}$$

$$x_{0,n+1} = 4M'x_{1,n} + (1 - 4M')x_{0,n} + kDR_{c0,n} \tag{16}$$

When $m = 1, 2, 3,$ and 4,

$$T_{m,n+1} = M\left(1 + \frac{1}{2m}\right)T_{m+1,n} + (1 - 2M)T_{m,n} + M\left(1 - \frac{1}{2m}\right)T_{m-1,n} - kBR_{cm,n} \tag{17}$$

$$x_{m,n+1} = M'\left(1 + \frac{1}{2m}\right)x_{m+1,n} + (1 - 2M')x_{m,n} + M'\left(1 - \frac{1}{2m}\right)x_{m-1,n} + kDR_{cm,n} \tag{18}$$

At the wall,

$$T_{5,n} = \frac{T_{4,n} + (hU/k_E)T'_n}{1 + hU/k_E} \tag{19}$$

$$x_{5,n} = x_{4,n} \tag{20}$$

The rate equation becomes

$$R_{cm,n} = 1.2k_r\left[\frac{1 - x_{m,n}}{11 + x_{m,n}} - \frac{1.2}{K_e}\left(\frac{x_{m,n}}{11 + x_{m,n}}\right)^2\right] \tag{21}$$

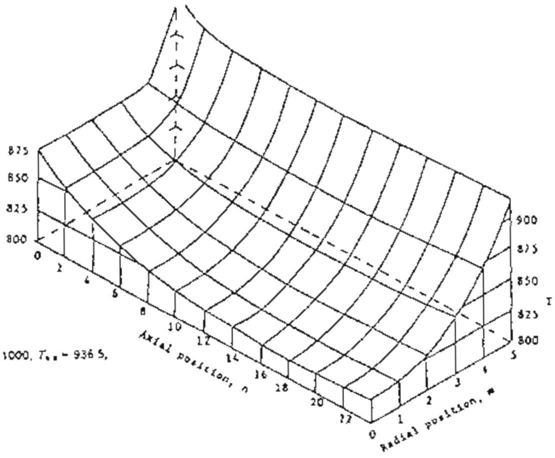
The problem solved is to find the number of steps along the axis required to make the average conversion $\bar{x} = 0.5$. Several values of jacket temperature and heat transfer coefficient are employed. Also investigated is the effect of taking the inlet temperature at the wall either the same as elsewhere at the entrance or the average with the flue gas temperature, that is,

$$T_{5,0} \overset{?}{=} T_{4,0} \qquad \text{or} \qquad T_{5,0} \overset{?}{=} 0.5(T_{4,0} + T'_0)$$

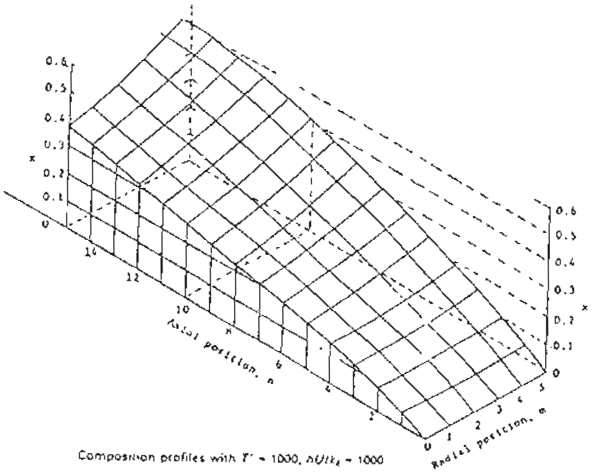
The inlet temperature of the reactants is 873°. The results are tabulated.

T_0	T'	hU/k_E	$T_{5,0}$	n at 50% conversion
873	1000	0	873	—*
873	1000	0.5	936.5	25.3
873	1000	0.5	873	26.1
873	1000	1000	1000	15.6
873	1050	0.5	962.5	21.6
873	873	0.5	873	51.2

*The adiabatic reaction temperature reaches essentially the steady conditions, $x = 0.426$ and $T = 784$, after about 70 axial increments.



Temperature profiles with $T' = 1000$, T[illegible] $= 936.5$, and $hU/k_c = 0.5$.



Composition profiles with $T' = 1000$, $hU/k_c = 1000$

P8.02.01. PSEUDO FIRST ORDER REACTION IN A LIQUID FILM

A reactant diffuses into a stagnant liquid film where the concentration of excess reactant B remains essentially constant at C_{b0}. At the inlet face the concentration is C_{a1}, Making the material balance over a differential dz of the distance leads to the second order diffusional equation. In the steady state and for unit cross section,

net transfer by diffusion = rate of reaction

$$d(D\frac{dC_a}{dz}) = kC_aC_{b0}\,dz$$

or

$$\frac{d^2C_a}{dz^2} = \frac{k_cC_{b0}}{D}C_a = \alpha^2C_a, \qquad \alpha = \sqrt{k_cC_{b0}/D}$$

The general solution is

$$C_a = A_1\exp(\alpha z) + A_2\exp(-\alpha z)$$

Application of the boundary conditions,

where $z = 0$, $C_a = C_{a1}$

where $z = z_L$. $C_a = C_{aL}$

makes the solution

$$C_a = \frac{C_{aL}\sinh(\alpha z)+C_{a1}\sinh[\alpha(z_L-z)]}{\sinh(\alpha z_L)}$$

At steady state, the rate of reaction equals the rate of input to the film.

$$r = -D(\frac{dC_a}{dz})_{C_a=C_{a1}} = \frac{\alpha D[\cosh(\alpha z_L) + C_{aL})}{\sinh(\alpha z_L)}$$

An important special case is that of complete reaction in the film, that is, when $C_{aL} = 0$ at $z = z_L$. Then

$$r = \alpha D\coth(\alpha z_L)\ (C_{a1} - 0)$$

$$= \frac{D}{z_L}(\alpha z_L)\coth(\alpha z_L)\ \Delta C_a$$

Substitute,

$$k_L = D/z_L$$

$$\beta = \sqrt{k_cDC_{b0}}/k_L = \text{Hatta number}$$

and rearrange to

$$r = k_L\beta\coth(\beta)\ \Delta C_a$$

$$= k_LE\ \Delta C_a$$

The quantity

$$E = \beta\coth(\beta)$$

is called the <u>enhancement</u> or the factor by which the mass transfer coefficient for physical absorption is to be multiplied when absorption occurs with chemical reaction in the liquid film. Some numerical values are:

β	0	0.5	1.0	2.0	3.0
E	1	1.08	1.31	2.07	3.02

<u>P8.02.02. SECOND ORDER REACTION IN A LIQUID FILM</u>

A pure gas A diffuses into a liquid film where it reacts with B from the liquid phase. Material balances on the two participants are

$$D_a\frac{d^2C_a}{dz^2} = k_cC_aC_b$$

$$D_b\frac{d^2C_b}{dz^2} = k_cC_aC_b$$

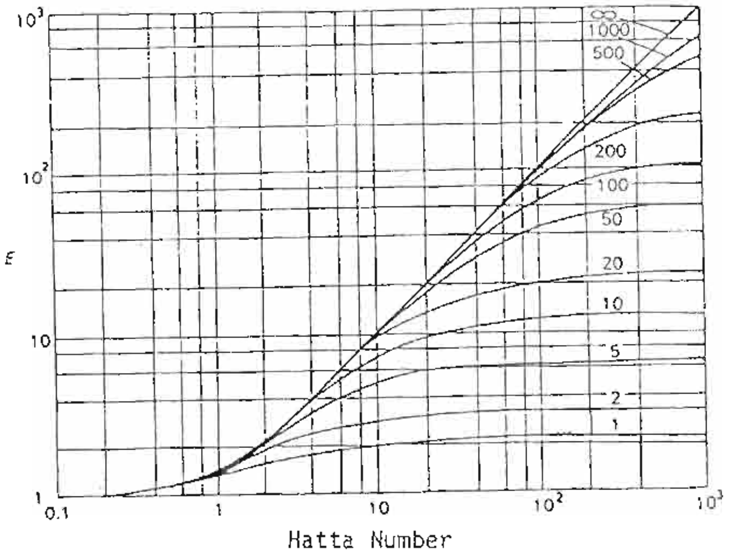
At the gas-liquid interface, $z = 0$, $C_a = C_{ai}$, $dC_b/dz = 0$. On the liquid side of the film, $z = z_L$, $C_b = C_{bL}$. The volume of the bulk liquid per unit of interfacial area is

$$V_L = \text{total volume} - \text{film volume} = \varepsilon/a - z_L$$

where ε is the fractional holdup of liquid and a is the interfacial area per unit volume of liquid. Accordingly the remaining boundary condition at z_L is

$$-D_a\frac{dC_a}{dz} = k_cC_{aL}C_{bL}(\varepsilon/a-z_L)$$

The numerical solution of these equations is shown on the plot which is due to van Krevelen & Hoftijzer (Trans Instn Chem Engrs <u>32</u> S360, 1954). The plot is of the enhancement factor E against the Hatta number β which is defined in P8.02.01. The parameters along the curves are of a ratio, $\alpha = C_{bL}D_b/C_{aL}D_a$. The uppermost curve is for a first order reaction.



<u>P8.02.03. HYDROGENATION OF FATTY ACIDS</u>

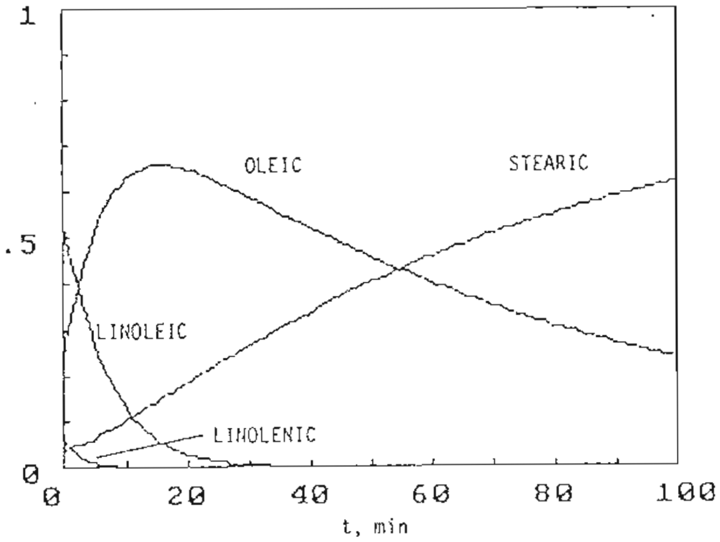
When the solution is kept saturated with hydrogen, the reaction is pseudo first order. For the sequence of fatty acids,

$$\text{Linolenic} \overset{1}{\Rightarrow} \text{Linoleic} \overset{2}{\Rightarrow} \text{Oleic} \overset{3}{\Rightarrow} \text{Stearic}$$

the specific rates are $k_1 = 0.367$, $k_2 = 0.159$, $k_3 = 0.013$/min at 175 C, 2 atm, 0.02% Ni catalyst and 600 rpm. (Swern (editor), Bailey's Industrial Oil and Fat Products, volume 2, 12, 1979). Initially A = 0.06, B = 0.53, C = 0.23, D = 0.04, Inerts = 0.14. The rate equations are

$$dA/dt = -k_1A,\quad dB/dt = k_1A-k_2B,\quad dC/dt = k_2B-k_3C,\quad dD/dt = k_3C.$$

The plot of the solution by ODE shows a peak in the concentration of the Oleic acid.



P8.02.04. REACTION IN A PACKED TOWER. CONSTANT ENHANCEMENT

A reactive absorption is done in a countercurrent packed tower. The material balance is made in terms of solute-free quantities. Inlet conditions are $X_2 = 0$, $Y_1 = 0.5$; outlet $X_1 = 0.8$, $Y_2 = 0.1$. Bottom is 1, top is 2.

G_m = mols of solute-free gas/(time)(cross section) = 100

L_m = mols of solute-free liquid/(time)(cross section) = 200

$Y = \frac{y}{1+y}$ = mols solute in gas/(mol solute-free gas)

$X = \frac{x}{1+x}$ = mols solute in liquid/(mol solute-free liquid)

The interfacial equilibrium is represented by Henry's law,

$$y_i = mx_i$$

$$\frac{Y_i}{1+Y_i} = m\,\frac{X}{1+X} \tag{1}$$

The material balance over a differential height dZ is

$$G_m dY = k_g a(p_g - p_i)dZ = k_g a\pi(y-y_i)dZ = k_g a\pi\left(\frac{Y}{1+Y} - \frac{Y_i}{1+Y_i}\right)dZ$$

$$= k_g a\pi\left(\frac{Y}{1+Y} - m\,\frac{X}{1+X}\right)dZ$$

$$\frac{k_g a\pi}{G_m}\,Z = \int_{Y_2}^{Y_1} dY/\left(\frac{Y}{1+Y} - m\,\frac{X}{1+X}\right) \tag{2}$$

The balance around the lower end of the tower is

$$L_m(X-X_1) = G_m(Y-Y_1)$$

$$X = X_1 + (G_m/L_m)(Y-Y_1) = 0.8-2(0.5-Y) \tag{3}$$

Substitute (3) into (2) and integrate for several values of Henry's law constant m. Some values are

m	0	0.1	0.2	0.3	0.4	0.5
$\int$	2.009	2.231	2.517	4.136	4.545	5.345

What is inaccurate about this solution is that k_ga depends on the extent of chemical reaction at each position in the tower. Also the equilibrium relation is more complex than linear and depends on the extent of chemical reaction. Use of a mean value of k_ga between the ends, however, gives at least an order of magnitude value of Z.

P8.02.05. FIRST ORDER REACTION IN A PACKED TOWER

A first order reaction takes place in a gas-liquid system in a packed tower. Several approximations are made:

. Average values of the gas G and liquid L rates are acceptable.

. The rate of reaction is $r = kx$ per unit volume where x is the mol fraction in the liquid.

. Liquid holdup fraction is ε

. Equilibrium is expressed by Henry's law, $y^* = mx$

. The mass transfer coefficient k_ga is constant

For the gas phase and the liquid phase,

$$Gdy = k_ga(y-y^*)dz = k_ga(y-mx)dz \quad (1)$$

$$Ldx = [k_ga(y-mx) - \varepsilon kx]dz \quad (2)$$

Solve (1) for x,

$$x = \frac{G}{mk_ga}\frac{dy}{dz} + \frac{y}{m} \quad (3)$$

from which

$$\frac{dx}{dz} = \frac{G}{mk_ga}\frac{d^2y}{dz^2} + \frac{1}{m}\frac{dy}{dz} \quad (4)$$

Substitute (4) into (2) and rearrange,

$$\frac{L}{mk_ga}\frac{d^2y}{dz^2} + \left(\frac{L}{mG} - \frac{\varepsilon k}{mk_ga} - 1\right)\frac{dy}{dz} - \frac{\varepsilon k}{mG}y = 0 \quad (5)$$

The terminal concentrations are related by the overall material balance,

$$G(y_1-y_2) = L(x_1-x_2) \quad (6)$$

Eq (5) is a homogeneous equation of the second order with constant coefficients whose solution has the form

$$y = A\exp(m_1z) + B\exp(m_2z)$$

The integration constants A and B are evaluated with the conditions $y = y_1$ when $z = 0$ and $y = y_2$ when $z = h$.

P8.02.06. MASS TRANSFER COEFFICIENT OF CO_2 IN NaOH

CO_2 was absorbed from air with 2.5 N NaOH in a 250 mm dia tower packed with 3 m of 19 mm Raschig rings. The pressure was atmospheric, 101.3 kN/m^2. At these concentration levels the equilibrium backpressures will correspond to $y^* = 0$.

gas, $G = 0.34$ kg/m^{2}s

$G_m = 0.34/29 = 0.0117$ kmol/m^{3}s

liquid, $L = 3.94$ kg/m^{2}s

inlet, $y_1 = 315$ ppm

outlet, $y_2 = 31$ ppm

Since the gas is dilute, $y \cong Y$, and the mass balance over the tower becomes

$$G_m(y_1 - y_2) = K_g aP(y - y^*)_{lm}Z$$

At the bottom, $y_1 - y_1^* = 315$ ppm

At the top, $y_2 - y_2^* = 31$ pp

$$(y-y^*)_{lm} = 122.5(10^{-6})$$

Solving for the overall mass transfer coefficient,

$$K_g a = \frac{0.0117(315-31)}{122.5(3)(101.3)} = 8.93(10^{-5})\ \text{kmol/m}^3\text{s(kN/m}^2)$$

P8.02.07. SCRUBBING OF CARBON DIOXIDE

CO_2 is to be scrubbed from air in a tower packed with 1" Raschig rings with 1.0 N Na_2CO_3 at 113 F at 10 atm and a liquid rate of L = 2000 lb/(hr)(sqft). At the bottom, $p_{CO_2} = 1.0$ atm and f = 0.95; at the top, $p_{CO_2} =$ 0.05 atm and f = 0.05, the fractional conversion to $NaHCO_3$. Equilibrium partial pressure is given by an equation of Harte et al (1933):

$$p^* = \frac{0.1803f^2N^{1.29}}{S(1-f)(365-T)} = \frac{0.1803f^2(1.0)^{1.29}}{0.0215(1-f)(365-113)} = \frac{0.0333f^2}{1-f},\ \text{atm}$$

The mass transfer coefficient is (Sherwood & Pigford, 1952):

$$k_g a = 0.00035f_1f_2f_3L^{0.64},\ \text{lbmol/(cuft)(hr)(atm)}$$

where the correction factors f_1, f_2 and f_3 are given by the graphs. The various quantities are tabulated for the bottom and the top of the column.

Item	btm(1)	top(2)
p, atm	1.0	0.05
f	0.95	0.05
p^*, atm	0.6010	0.00009
f	11.5	11.5
f_2	0.9	0.9
f_3	1.38	0.53
$k_g a$	0.1778	0.4628
$k_g a(p-p^*)$	0.07092	0.02314

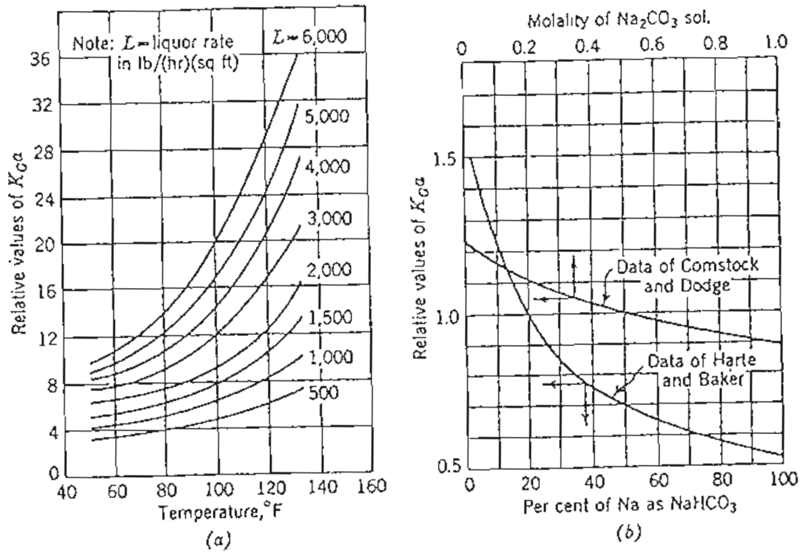
The differential material balance is

$$G_m dY = \frac{G_m}{\pi}dp = k_g a(p-p^*)dZ$$

This is integrated in terms of a log mean driving force,

$$\frac{\pi}{G_m}Z = \frac{p_1-p_2}{[k_g a(p-p^*)]_{lm}} = \frac{1-0.05}{0.04478} = 19.88$$

Thus the gas rate G_m is expressed in terms of the liquid rate L and the terminal concentrations.



Absorption of CO_2 with carbonate solutions in a tower packed with 1-in. Raschig rings. (a) Correction factor f_1 for temperature and liquid rate; (b) correction factors f_2 and f_3 for composition. [*Sherwood and Pigford*

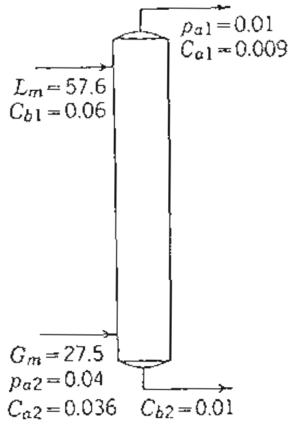
P8.02.08. SECOND ORDER REACTION IN THE LIQUID FILM

A solute A in a gas phase reacts with B in the liquid phase by a second order reaction. Some results of a numerical solution by Perry & Pigford (Ind Eng Chem 45 1247, 1953) for the enhancement factor are fitted by the equation

$$E = k_L/k_L^0 = 0.96 + 0.80\sqrt{C_b/C_a}$$

The equilibrium relation is $C_a = 0.9p_a$. Operating conditions are in the list and on the sketch. The reaction is completed in the liquid film so in the bulk liquid, $C_{aL} = 0$. Gas film resistance is negligible so $k_L = K_L$.

$p_{a2} = 0.04$ atm
$C_{b1} = 0.06$ lb mole/cu ft
$C_{b2} = 0.01$ lb mole/cu ft
$k_L^0 = 0.006$ ft/hr
$L_m = 57.6$ lb moles/(hr)(sq ft)
$G_m = 27.5$ lb moles/(hr)(sq ft)
$a = 50$ sq ft/cu ft
$\rho_m = 3.5$ lb moles/cu ft
$C_a = 0.9p_a$ (equilibrium condition)



The material balance is

$$\frac{L_m}{\rho_m}\,dC_a = K_La(C_a - C_{aL})dh = Ek_L^0C_adh = 0.006\ EC_adh$$

Integrate with Simpson's rule.

$$h = \frac{L_m}{\rho_m a}\int_{0.009}^{0.036}\frac{dC_a}{K_LC_a}$$

$$= \frac{57.6}{50(3.5)}\ \frac{0.0135}{3}[3346 + 4(3766)+6112] = 36.3 \text{ ft}$$

For comparison, without chemical reaction,

$$h = \frac{L_m}{\rho_m k_L^o a} \ln\left(\frac{C_{a2}}{C_{a1}}\right) = \frac{57.6}{3.5(0.006)(50)} \ln\frac{0.036}{0.009} = 76.3 \text{ ft}$$

The tabulation shows the calculation of the integrands.

C_a	p_a	C_b	C_b/C_a	E	K_L	$1/K_LC_a$
0.036	0.040	0.0100	0.28	1.38	0.0083	3346
0.0225	0.025	0.0350	1.56	1.96	0.0118	3766
0.0090	0.010	0.0600	6.70	3.03	0.0182	6112

P8.02.09. ABSORPTION IN A STIRRED TANK

CO_2 is to be absorbed by 2 N K_2CO_3 in a stirred tank. The pressure is $\pi = 2$ atm, inlet partial pressure is 0.7 atm and outlet is to be 0.07. The tank is charged with the solution, then the gas is charged at variable rate to maintain the desired outlet partial pressure. The residence time is to be found as a function of the fractional conversion, f.

Mass transfer coefficients have been obtained in a packed tower with 40% K_2CO_3 (6.8 mols/liter of water) (Kohl & Riesenfeld, Gas Purification, p 227, 1985).

$$K_ga/L^{2/3} = 0.43 \exp(-2.6p)$$

They are adapted to other concentrations as suggested by the Hatta number, and estimating that stirring conditions are equivalent to L = 1000 lb/(hr)(sqft).

$$K_ga = 0.43(1000)^{2/3}\exp[-2.6(0.07)]\sqrt{\frac{(1-f)N}{6.8}}$$

$$= 19.43\sqrt{1-f} \qquad (1)$$

The equilibrium relation is cited in P8.02.07. At 45 C and N = 2 it is

$$p^* = \frac{0.0333f^2N^{1.29}}{1-f} = \frac{0.0814f^2}{1-f} \qquad (2)$$

The material balance on the CSTR is

$$V'y_0 = V'y + K_ga\, V_r(p - p^*)$$

$$\tau = \frac{p_0-p}{\pi K_ga(p-p^*)} = \frac{0.7-0.07}{2K_ga(0.07-p^*)} = \frac{0.315}{K_ga(0.07-p^*)} \qquad (3)$$

The calculations are summarized in the table.

f	0	0.1	0.2	0.3	0.4	0.5	0.59
p^*	0	0.0009	0.0040	0.0105	0.0217	0.0407	0.0691
K_ga	19.43	18.43	17.38	16.26	15.05	13.74	12.44
τ	0.232	0.247	0.275	0.326	0.433	0.782	28.1

P8.02.10. NITRATION OF TOLUENE

Toluene was nitrated with mixed aqueous nitric-sulfuric acid in a stirred tank at 35 C (Barduhn & Kobe, Ind Eng Chem 48 1305, 1956). They found the reaction to occur in the acid phase with the rate equation

$$r = 518\, N_T(100\, N_n)^{0.435} \; \frac{\text{gmol nitric acid consumed}}{\text{hr(liter of acid phase)}}$$

when the starting acid was 34% H_2SO_4.

N_T = mol fraction of toluene

N_n = mol fraction of HNO_3 in the aqueous phase

An hourly charge to a CSTR is made up of

Toluene = 16.4 gmol, 1.744 liters
HNO_3 = 16.4 gmol, 0.226 mol fraction
H_2SO_4 = 24.6 gmol (34 wt%)
H_2O = 31.4 gmol
Total acid phase, 4 kg/hr, 2.395 liters/hr

Find the size of reactor and the residence time for 90% conversion of the toluene assuming it all goes to the mononitro compound.

$$N_T = 0.1$$

$$N_n = 0.1(0.226)$$

$$r = 518(0.1)(2.26)^{0.435} = 73.9 \ \frac{\text{gmol toluene}}{\text{hr(liter of acid phase)}}$$

Nitric acid balance on the CSTR,

$$16.4 = 1.64 + rV_r$$

$$V_r = \frac{16.4 - 1.64}{73.9} = 0.200 \text{ liters of acid phase}$$

$$\Rightarrow \frac{0.200(1.744+2.395)}{1.744} = 0.475 \text{ liters total}$$

$$\tau = V_r/V' = 0.475/4.139 = 0.115 \text{ hr}$$

NOTE. The coefficient and exponent of the rate equation are strong functions of the sulfuric acid concentration.

% H_2SO_4	Coefficient	Exponent
30.7	193	1.206
34.0	518	0.435
37.0	2150	0.262

P8.02.11. HYDROLYSIS OF FAT IN A SPRAY TOWER

In the hydrolysis of fats, a small amount of water dissolves in the fat and reacts to form an acid and glycerine. Then the glycerine migrates to the water phase. The differential equation representing this process was derived and checked against a plant test by Jeffreys, Jenson & Miles (*Trans Instn Chem Engrs* 39 389-396, 1961). Flow rates per unit cross section are L of the fat stream, G of the water stream.. Other symbols are,

x = wt fraction of glycerine in the L (fat) stream
y = wt fraction of glycerine in the G (water) stream
y^* = mx, glycerine equilibria
z = wt fraction of fat in the L stream
ρ = mass of fat per unit volume
w = wt of fat to produce unit weight of glycerine

The basis is a height dh of tower of unit cross section. Conditions are shown on the sketch. Balances are made on the glycerine.

$$\text{Reaction rate} = \frac{k_c\rho z}{w} dh \qquad (1)$$

$$\text{Diffusional rate} = k_ga(y^*-y)dh \qquad (2)$$

Gain of glycerine in water = amount diffused

$$-Gdy = k_ga(y^*-y)dh = k_ga(mx-y)dh$$

$$G\frac{dy}{dh} + k_ga(mx-y) = 0 \qquad (3)$$

Glycerine balance on element dh,

Inputs + source = Outputs

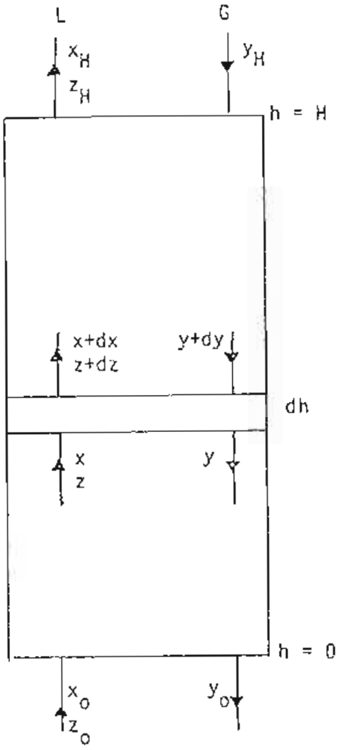
$$Lx + G(y+dy) + \frac{k_c\rho z}{w}\,dh = L(x+dx) + Gy$$

$$G\frac{dy}{dh} + \frac{k_c\rho z}{w} = L\frac{dx}{dh} \tag{4}$$

Balance around the lower end of the tower where the compositions are (x_0, y_0, z_0),

$$\frac{Lz_0}{w} + Gy = L(x + \frac{z}{w}) + Gy_0$$

$$\frac{z}{w} = \frac{z_0}{w} + \frac{G}{L}(y-y_0) - x \tag{5}$$



Substitute (5) into (4).

$$G\,\frac{dy}{dh} + k_c\rho[\frac{z_0}{w} + \frac{G}{L}(y-y_0)-x] \tag{6}$$

Solve Eq (3) for x and differentiate.

$$x = \frac{1}{m}\,(y - \frac{G}{k_ga}\,\frac{dy}{dh}) \tag{7}$$

$$\frac{dx}{dh} = \frac{1}{m}\,(\frac{dy}{dh} - \frac{G}{k_ga}\,\frac{d^2y}{dh^2}) \tag{8}$$

Substitute (7) and (8) into (6) and obtain

$$\frac{d^2y}{dh^2} - \alpha\,\frac{dy}{dh} + \beta y = \gamma \tag{9}$$

$$\alpha = \frac{k_ga}{G} - \frac{k_ga}{L} - \frac{k_c\rho}{L}$$

$$\beta = \frac{k_gak_c\rho}{L}(\frac{m}{L} - \frac{1}{G})$$

$$\gamma = \frac{k_gak_c\rho m}{GL}(\frac{G}{L}\,y_0 - \frac{z_0}{w})$$

Eq (9) is non-homogeneous second order linear with constant coefficients and can be solved readily. Boundary conditions are,

At the bottom ,h = 0, $y = y_0$; at the top, h = H, y = 0

From the solution, the value of y_0 is found at any specified H.

P8.03 01. FILM THICKNESS IN A TRICKLE BED

A packed bed of particles of diameter d_p and fractional free volume ε is modelled as a group of parallel capilaries with a perimeter

$$p = \frac{(1-\varepsilon)\pi d_p}{\pi d_p^2/4} = \frac{4(1-\varepsilon)}{d_p}$$

A theoretical equation for the thickness L of a film in laminar flow on flat surfaces inclined an angle ϕ to the vertical was derived by Cooper, Drew & McAdams (Ind Eng Chem 26 428, 1934; ChE Handbook, p 5.59, 6th edition, 1984).

$$L = \left(\frac{3\Gamma\mu}{g\rho_f(\rho_f-\rho_c)\sin\phi} \right)^{1/3}, \quad \text{cm}$$

Γ = mass flow rate/width, gm/cm s
μ = viscosity, gm/cm s
$g = 980\ \text{cm/s}^2$
ρ_f, ρ_c = densities of liquid and gas, g/cm^3

When $w = \text{g/cm}^2\text{s}$,

$$\Gamma = w/p = \frac{wd_p}{4(1-\varepsilon)}$$

Let $d_p = 0.5$, $\varepsilon = 0.5$, $\mu = 0.01$, $\rho_f = 1$, $\rho_c = 0$, $\sin\phi = 1$. Then for a range of values of w in laboratory and commercial hydrodesulfurizers,

w, $\text{gm/cm}^2\text{s}$	L, mm
0.008 lab	0.04
0.25 lab	0.12
0.08 com	0.085
2.5 com	0.26

In the bed of spheres, the film thicknesses should be appreciably greater than in the parallel capillary model, perhaps by a factor of 2 or so.

P8.03.02. TRICKLE BED PARAMETERS

The fluids of a trickle bed process have the physical properties of air-water at 50 atm and room temperature. The superficial velocities are $u_L = 0.1$ cm/s and $u_G = 10$ cm/s, bed porosity $\varepsilon_B = 0.4$, particle diameter $d_p = 0.5$ cm, densities $\rho_L = 1$ and $\rho_G = 0.06$ g/cc and viscosities $\mu_L = 0.01$ and $\mu_G = 0.0002$ gm/cm.s.

Several parameters that tell what is going on in trickle bed operation have been correlated. Apply some of those correlations from the summary of Ramachandran & Chaudhari (*Three-Phase Chemical Reactors*, 1983).

Pressure drop. The correlation of Larkin (*AIChE Journal*, 1961) is

$$\ln \frac{\Delta P_{GL}}{\Delta P_G+\Delta P_L} = \frac{5.0784}{3.531+(\ln X)^2}, \quad X = \sqrt{\Delta P_L/\Delta P_G}$$

From correlations like those of *Chem Eng Handbook* (p 5.53, 1984) the pressure drops of the two phases when flowing alone are $\Delta P_L = 217$ and $\Delta P_G = 100$ so that $X = 1.47$ and $\Delta P_{GL} = 1270\ \text{N/m}^3$ or $0.0124\ \text{atm/(m}^2\text{)(m)}$.

Liquid holdup. A result developed by Midoux et al (*J Chem Eng Japan* 9 350, 1976) is

$$\varepsilon_L = \varepsilon_B \frac{0.66X^{0.81}}{1+0.66X^{0.81}} = 0.4(0.475) = 0.190,$$ fraction of bed occupied by liquid.

Gas-liquid interfacial area. A correlation of Charpentier (*Chem Eng J* 11 161, 1976) is

$$a_B = 0.05(\Delta P_{GL}\varepsilon_B)^{1.2}\left[\frac{6(1-\varepsilon_B)}{d_p}\right]^{-0.2}$$

$$= 0.05[1260(0.4)]^{1.2}[\frac{6(0.6)}{00.005}]^{-0.2}\ 23.5\ m^2/m^3$$

compared with the geometrical area,

$$a_{geom} = 6(1-\varepsilon_B)/d_p = 72\ m^2/m^3.$$

Gas-liquid mass transfer coefficient. The correlation of Sato (*First Pacific Chem Eng Congress* p 187, 1972),

$$k_L a_B = 6.185(10^{-3}) d_p^{-0.5} u_L^{0.8} u_G^{0.8} = 8.8(10^{-0.3})\ /sec$$

Liquid-solid mass transfer coefficient. The relation proposed by Dharwadkar & Sylvester (*AIChE Journal6*, 1977),

$$k_s = 1.637 u_L Re_L^{-0.331} (\frac{\rho_L D}{\mu_L})^{2/3}$$

With oxygen diffusivity $D = 2.1(10^{-5})cm^2/s$,

$$k_s = 1.637(0.1)(\frac{0.5(0.1)(1)}{0.01})^{-0.331}(\frac{1(2.1)(10^{-5})}{0.01})^{2/3}$$

$$= 1.7(10^{-3})\ cm/s$$

Axial dispersion and the Peclet number. Michell & Furzer (*Chem Eng J* 4 53, 1972) say

$$Pe_L = \frac{u_L d_p}{D_{EL}} = (\frac{Re_L}{\varepsilon_L})^{0.7}(\frac{\mu_L^2}{d_p^3 g \rho_L^2})^{0.32}$$

In the range of $Re_L = 10$ to 100, this Peclet number is 0.2 to 0.6. In a bed 100 cm deep, say $Pe_L = 0.2$, then the vessel Peclet number is

$$Pe = 0.2(L/d_p) = 40$$

From problem P5.08.04 the variance is $\sigma^2(t_r) = 0.05$ and the Erlang parameter is n = 20. Accordingly the graph of problem P5.08.10 indicates that the conversion of a second order reaction will be close to that of plug flow for this case.

P8.03.03. THREE REACTION STEPS IN SERIES

In the steady state the diffusional rates through the gas and liquid films equal the rate of surface reaction. The concentration in the gas phase is A_g, at the interface A_i and at the surface A_S. A^* is the equilibrium value in the liquid.For a reaction of order m,

$$r = k_L a_B(A^* - A_i) = k_s a_p(A_i - A_s) = w k_m A_s^m$$

where w is the weight of catalyst per unit volume of the reactor. A_i and A_s can be eliminated.

$$A_i = A^* - \frac{r}{k_L a_B}$$

$$A_s = (\frac{r}{wk_m})^{1/m}$$

$$r = k_s a_p [A^* - \frac{r}{k_L a_B} - (\frac{r}{wk_m})^{1/m}]$$

Explicit solutions for r can be made for some values of m. When m = 1,

$$r = A^*(\frac{1}{k_L a_B} + \frac{1}{k_s a_p} + \frac{1}{wk_1})^{-1}$$

When m = - 1/2, let

$$\frac{1}{\bar{M}_A} = \frac{1}{k_L a_B} + \frac{1}{k_s a_p}$$

$$r = \frac{(wk_{1/2})^2}{2M_A}\{[1+\frac{4A^*M_A^{\ 2}}{(wk_{1/2})^2}]^{1/2} - 1\}$$

When m = 2,

$$r = \frac{M_A^{\ 2}}{2wk_2}\left[1 + \frac{2wk_2A^*}{M_A} - \left(1 + \frac{4wk_2A^*}{M_A}\right)^{1/2}\right]$$

When the rate equation is

$$r = \frac{wk_1A_s}{1+K_AA_s}$$

$$r = \frac{M_A}{2K_A}\left\{1 + K_AA^* + \frac{wk_1}{M_A} - \left[\left(1 + K_AA^* + \frac{wk_1}{M_A}\right)^2 - \frac{4wk_1K_AA^*}{M_A}\right]^{1/2}\right\}$$

When the rate equation is

$$r = \frac{wk_1A_s}{(1+K_AA_s)^2}$$

$$r^3 - r^2\left(\frac{2M_A}{K_A} + 2A^*M_A\right) + r\left(\frac{M_A^{\ 2}}{K_A^{\ 2}} + \frac{2M_A^{\ 2}A^*}{K_A} + M_A^{\ 2}A^{*2} + \frac{wk_1M_A}{K_A^{\ 2}}\right) - \frac{wk_1A^*M_A^{\ 2}}{K_A^{\ 2}} = 0$$

This cubic equation may be solved numerically.

P8.03.04. HYDROGENATION OF ACETONE IN A SLURRY REACTOR

The hydrogenation of acetone to isopropanol with a Raney nickel catalyst in a slurry reactor at 14 C and 10 atm was found to be of half order with respect to hydrogen (Lemcoff & Jameson, *AIChE Journal* 21 730, 1975). These data are known,

$k_{1/2} = 2.35(10^{-3})\ (cm^3mol)^{1/2}/g.s$

$A^* = 2.75(10^{-5})\ \text{mol/cm}^3$

$k_La_B = 0.0186\ \text{s}^{-1}$

$k_sa_p = 0.266\ \text{s}^{-1}$

$w = 0.025\ \text{g/cm}^3$

Apply Eq (4) of P8.03.03.

$$M_A = \left(\frac{1}{0.0186} + \frac{1}{0.266}\right)^{-1} = 0.0174$$

$r = 2.24(10^{-7})\ \text{mol/(slurry cm}^3\text{)/s}$

The surface concentration is

$$A_s = A^* - \frac{r}{M_A} = 2.75(10^{-5}) - \frac{2.24(10^{-7})}{0.0174} = 1.46(10^{-5})\ \text{mol/cm}^3$$

Comparison of A_s and A^* reveals substantial resistance to diffusional mass transfer.

P8.03.05. OXIDATION OF CO IN A SLURRY REACTOR

Oxidation of CO with excess oxygen in a slurry of cobalt oxide was found to have the rate equation (Ido et al, *Int Chem Eng* 16 695, 1976),

$$r = \frac{wk_1A_s}{(1+K_AA_s)^2}$$

The temperature is 120 C and the partial pressure of CO is 0.10 atm. These data are known,

$H = 5.39$, Henry's law constant

$k_1 = 6.51\ \text{cm}^3\text{/g.s}$

$K_A = 1.206(10^6)\text{cm}^3\text{/mol}$

$w = 0.025\ \text{g/cm}^3$

$k_La_B = 0.0167\ \text{s}^{-1}$

$k_sa_p = 0.25\ \text{s}^{-1}$

The liquid phase concentration is

$$A^* = \frac{p}{RTH} = \frac{0.1}{82.06(393)(5.39)} = 5.75(10^{-7})\ \text{mol/cm}^3$$

$M_A = 0.0156$

Eq (9) of P8.03.03 becomes

$$r^3 - 4.38(10^{-8})r^2 + 2.22(10^{-15})r - 1.56(10^{-23}) = 0$$

$r = 8.11(10^{-9})\ \text{mol/cm}^3\text{.s}$

The surface concentration is

$$A_s = A^* - r/M_A = 5.5(10^{-8})\ \text{mol/cm}^3$$

which is much less than A^* and indicates much diffusional resistance. The rate in the absence of diffusional resistance would have been

$$r_s = \frac{wk_1A^*}{(1+K_AA^*)^2} = 3.26(10^{-8})\ \text{mol/cm}^3\text{.s}$$

which is appreciably greater than with diffusional resistance.

P8.03.06. HYDROGENATION OF CROTONALDEHYDE. CATALYST EFFECTIVENESS

Crotonaldehyde is hydrogenated at 1 atm and 51 C in a trickle bed reactor using palladium on porous alumina as catalyst (Kenney & Sedricks, *Chem Eng Sci* 27 2029, 1972). The reaction is first order. These data are known,

$A^* = 2.8(10^{-6})$ mol/cm^3, solubility of hydrogen

$k_1 = 1.845$ cm^3/(s)(g catalyst)

$w = 0.9$ g cat/cm^3

$\phi = 31$, Thiele modulus

$k_La_B = 0.02\ s^{-1}$

$k_sa_p = 0.144\ s^{-1}$

$\varepsilon_B = 0.4$

$d_p = 0.5$ cm

From problem P7.03.06, the effectiveness of the catalyst is

$$\eta = \frac{\coth\phi}{\phi} - \frac{1}{\phi^2} = 0.0319$$

For the first order reaction the overall rate becomes,

$$r = A^*\left[\frac{1}{k_La_B} + \frac{1}{k_sa_p} + \frac{1}{wk_1\eta}\right]^{-1}$$

$$= 2.8(10^{-6})\left[\frac{1}{0.02} + \frac{1}{0.144} + \frac{1}{0.9(1.845)(0.0319)}\right]^{-1}$$

$$= 3.69(10^{-8})\ \text{mol/cm}^3\text{s}$$

P8.04.01. THE ENZYME FORMS AN UNSTABLE COMPLEX

The enzyme E is assumed to form a complex ES with the substrate S which breaks down to a product P and regenerates the enzyme (Brown, *J Chem Soc* 81 373-388, 1902).

$$S + E \underset{2}{\overset{1}{\Leftrightarrow}} ES,\quad ES \overset{3}{\Rightarrow} P + S$$

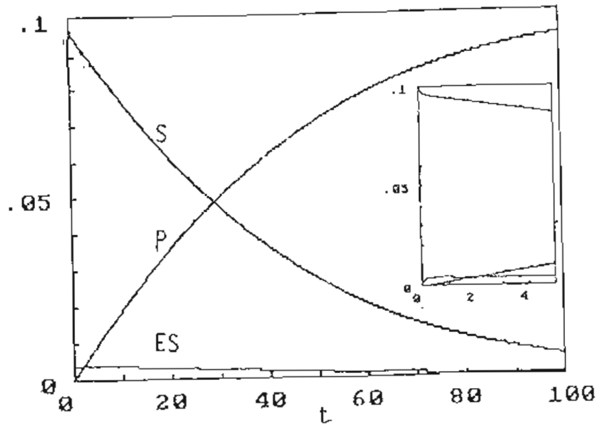
Moreover the total enzyme concentration is taken constant, $C_{E_0} = C_{ES} + C_E$. For a particular case, $k_1 = 40$ liter/mol.s, $k_2 = 5\ s^{-1}$, $k_3 =, 0.5\ s^{-1}$, $C_{S_0} = 0.1$, $C_{E_0} = 0.01$. The rate equations are

$$\frac{dC_S}{dt} = -k_1C_SC_E + k_2C_{ES} = -40C_S(0.01-C_{ES}) + 5C_{ES}$$

$$\frac{dC_{ES}}{dt} = k_1C_SC_E - (k_2+k_3)C_{ES} = 40C_s(0.01-C_{ES}) - 5.5C_{ES}$$

$$\frac{dC_P}{dt} = k_3C_{ES} = 0.5C_{ES}$$

The numerical solution of these equations is plotted. The concentration C_{ES} of the complex reaches a maximum quickly.



P8.04.02. ENZYME KINETICS. MICHAELIS-MENTEN EQUATION

The enzyme E and the reactant or substrate S are assumed to form a complex ES that then dissociates into product P and uncombined enzyme (Michaelis & Menten, *Biochem Zeit* 49 333, 1913).

$$S + E \underset{2}{\overset{1}{\Leftrightarrow}} ES$$

$$ES \overset{3}{\Rightarrow} E + P$$

If equilibrium is assumed to exist,

$$\frac{(S)(E)}{(ES)} = \frac{(s)[(E_0)-(ES)]}{(ES)} = K_m$$

where (E_0) is the total of the free and combined enzyme and K_m is a dissociation constant. Solving for (ES),

$$(ES) = \frac{(E_0)}{1+K_m/(S)} = \frac{(E_0)(S)}{K_m+(S)}$$

The rate of formation of product by first order is

$$r = \frac{dP}{dt} = k_2(ES) = \frac{k_2(E_0)(S)}{K_m+(S)}$$

Several different linearized arrangements of this equation are used for determination of the constants from rate data. With the simplified notation,

Differential equation: $r = \frac{dC}{dt} = \frac{k_1C}{1+k_2C}$ (1)

Integrated equation: $k_1(t-t_0) = k_2 \ln(C/C_0) + C - C_0$ (2)

Lineweaver-Burk: $\frac{1}{r} = \frac{k_2}{k_1}(\frac{1}{C}) + \frac{1}{k_1}$ (3)

Hanes: $\frac{C}{r} = \frac{1}{d\ln(C)/dt} = \frac{k_2}{k_1} + (\frac{1}{k_1})\ C$ (4)

Eadie: $\frac{r}{C} = \frac{k_1}{k_2} - (\frac{1}{k_2})\ r$ (5)

P8.04.03. ENZYME KINETICS WITH REVERSIBLE DECOMPOSITION

The postulated mechanism is

$$S + E \underset{2}{\overset{1}{\Leftrightarrow}} ES \underset{4}{\overset{3}{\Leftrightarrow}} E + P$$

E is the concentration of the enzyme, S that of the nutrient and P that of the product. The concentration of ES is assumed to reach a steady value.

$$\frac{d(ES)}{dt} = k_1(E)(S) - (k_2+k_3)(ES) - k_4(E)(P) \Rightarrow 0$$

The material balance on the enzyme is

$$(E_0) = (E) + (ES)$$

Accordingly,

$$(ES) = \frac{k_1(E_0)(S) + k_4(E_0)(P)}{k_2+k_3+k_1(S)+k_2(P)}$$

The net rate of formation of product is

$$r = \frac{dP}{dt} = k_3(ES) - k_4(E)(P)$$

After substitution for (ES), the rate equation becomes

$$r = \frac{k_1k_3(E_0)(S) - k_2k_4(E_0)(P)}{k_2+k_3+k_1(S)+k_2(P)}$$

P8.04.04. CELL GROWTH RATE. MONOD EQUATION

The growth rate of cells is taken proportional to the cell concentration, x, and to an empirical form of the dependence on the concentration, p, of the nutrient. That empirical form was assumed by Monod (1942) to be the same as in the Michaelis-Mewnten model for enzyme kinetics. This makes the rate of cell growth,

$$\frac{dx}{dt} = \frac{k_1p}{k_2+p}x \qquad (1)$$

Another assumption is that the change in cell concentration is proportional to the change in nutrient concentration, that is,

$$\frac{dx}{dp} = k_3$$

Solve for p,

$$p = p_0 + \frac{x-x_0}{k_3} \qquad (2)$$

and substitute into Eq (1),

$$\frac{dx}{dt} = \frac{k_1k_3(k_3p_0-x_0+x)}{k_2k_3+k_3p_0-x_0+x} \qquad (3)$$

Integrating,

$$k_1k_3(t-t_0) = \int_{x_0}^{x} \left[\frac{\beta}{x(\alpha+x)} + \frac{1}{\alpha+x}\right] dx$$

$$= \frac{\beta}{\alpha} \ln \frac{(\alpha+x_0)x}{(\alpha+x)x_0} + \ln \frac{\alpha+x}{\alpha+x_0} \qquad (4)$$

$$\alpha = k_3p_0-x_0$$

$$\beta = k_2k_3+k_3p_0-x_0$$

P8.04.05. BEST FITS OF DATA TO THE M-M EQUATION

These initial rate data of an enzyme catalyzed reaction are known:

C_s	0	1	2	3	5	7	10
r_0	0	0.20	0.22	0.30	0.45	0.41	0.50

The constants of the Michaelis-Menten equation

$$r = \frac{r_m C_s}{K_m + C_s}$$

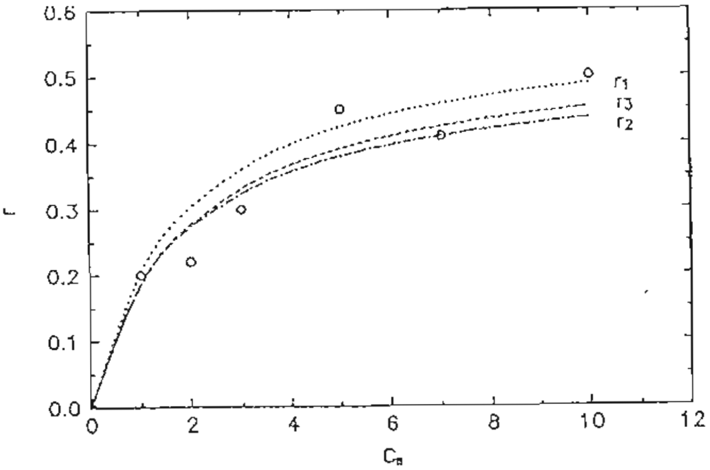
were found by best straight line fit of three linearized forms with the results shown,

$$(1)\quad \frac{C_s}{r} = \frac{K_m}{r_m} + \frac{C_s}{r_m} = 3.13 + 1.731x, \quad r_m = 0.577, \quad K_m = 1.81$$

$$(2)\quad \frac{1}{r} = \frac{1}{r_m} + \frac{K_m}{r_m C_s} = 1.946 + 3.455x, \qquad 0.514 \qquad 1.77$$

$$(3)\quad r = r_m - K_m \frac{r}{C_s} = 0.539 - 1.893x, \qquad 0.539 \qquad 1.893$$

The data have a wide scatter. The choice between the three plots of (C_s, r) is difficult to make visually, but it could be made by comparing variances. Plots (2) and (3) agree closely.



P8.04.06. A COMPETITIVE INHIBITOR

A substrate S and an inhibitor I both are acted on reversibly by the enzyme E but only S gives rise to a product P.

$$E + S \underset{2}{\overset{1}{\Leftrightarrow}} ES$$

$$E + I \underset{4}{\overset{3}{\Leftrightarrow}} EI$$

$$ES \overset{5}{\Rightarrow} E + P$$

$$r_P = k_5 C_{ES} \qquad (1)$$

The enzyme balance is

$$C_{E_0} = C_E + C_{ES} + C_{EI} \qquad (2)$$

Assume equilibria of the reversible reactions,

$$\frac{C_E C_S}{C_{ES}} = k_2/k_1 = K_S \qquad (3)$$

$$\frac{C_E C_I}{C_{EI}} = k_4/k_3 = K_I \qquad (4)$$

Put (3) and (4) into (2),

$$C_E = C_{E_0} - \frac{C_E C_S}{K_S} - \frac{C_E C_I}{K_I} = \frac{C_{E_0}}{1+C_S/K_S+C_I/K_I} \qquad (5)$$

Put (5) into (3) and the result into (1),

$$C_{ES} = \frac{C_S}{K_S}\left[\frac{C_{E_0}}{1+C_S/K_S+C_I/K_I}\right] \qquad (6)$$

$$r_P = \frac{k_5 C_{E_0}}{K_S}\left[\frac{C_S}{1+C_S/K_S+C_I/K_I}\right] \qquad (7)$$

This can be put in the Michaelis-Menten form but with term K_m dependent on the concentration of the inhibitor.

$$r_P = \frac{k_5 C_{E_0} C_S}{K_m + C_s}$$

$$K_m = K_s(1+C_I/K_I)$$

P8.04.07. LACTOSE HYDROLYSIS. SIMULTANEOUS DIFFERENTIAL EQNS

The kinetic model of lactose hydrolysis was described by Scott et al (*Biotechnol Bioeng Symp* 15 431-445, 1985) as

$$E + S \overset{1}{\underset{2}{\Leftrightarrow}} ES \overset{3}{\Rightarrow} E + P + Q$$

$$E + P \overset{4}{\underset{5}{\Leftrightarrow}} EP$$

where S, P, Q and E are lactose, galactose, glucose and free enzyme. Find dP/dt after assuming that equilibria are attained.

$$(ES) = (E)(S)/K_S$$

$$(EP) = (E)(P)/K_P$$

$$E_0 = E + ES + EP$$

$$E = E_0 - (E)(S)/K_S - (E)(P)/K_P$$

$$= \frac{E_0}{1+S/K_S+P/K_P} \qquad (1)$$

$$\frac{dP}{dt} = k_3(ES) - k_4(E)(P) + k_5(EP)$$

$$= \left(\frac{k_3}{K_S} - k_4 + \frac{k_5}{K_P}\right)(E)(P) \qquad (2)$$

$$\frac{dS}{dt} = -k_1(E)(S) + k_2(ES) = \left(\frac{k_2}{K_S} - k_1\right)(E)(S) \qquad (3)$$

Substitute (1) into (2) and (3) to obtain a pair of equations in the variables S and P, with initial conditions $S = S_0$ and $P_0 = 0$.
A numerical solution will be required.

P8.04.08. TWO DIFFERENT SUBSTRATES. NUMERICAL SOLUTION

Suppose that the following sequence describes the reactions of two different substrates catalyzed by one enzyme:

The equations relating the various concentrations are

$$E_0 = E + (ES_1) + (ES_2)$$

$$E = \frac{E_0}{1+S_1/K_1+S_2/K_2} = \frac{0.05}{1+14S_1+4.53S_2} \qquad (1)$$

$$\frac{dS_1}{dt} = -k_1(S_1)(E) + k_2(ES_1) = -70(S_1)(E)+5(ES_1) \qquad (2)$$

$$\frac{dS_2}{dt} = -k_3(S_2)(E) + k_4(ES_2) = -43.5(S_2)(E) + 9.6(ES_2) \qquad (3)$$

$$\frac{d(ES_1)}{dt} = k_1(S_1)(E) - (k_2+k_5)(ES_1) = 70(S_1)(E)-8.5(ES_1) \qquad (4)$$

$$\frac{d(ES_2)}{dt} = k_3(S_2)(E)-(k_4+k_6)(ES_2) = 43.5(S_2)(E)-12.4(ES_2) \qquad (5)$$

$$\frac{d(P_1)}{dt} = k_5(ES_1) = 3.5(ES_1) \qquad (6)$$

$$\frac{d(P_2)}{dt} = k_6(ES_2) = 2.8(ES_2) \qquad (7)$$

The input to numerical program ODE and the solution of the six differential equations are shown.

```
e = 0.05/(1+14*y(1)+4.53*y(2))

g(1)= -70*e*y(1)+5*y(3)

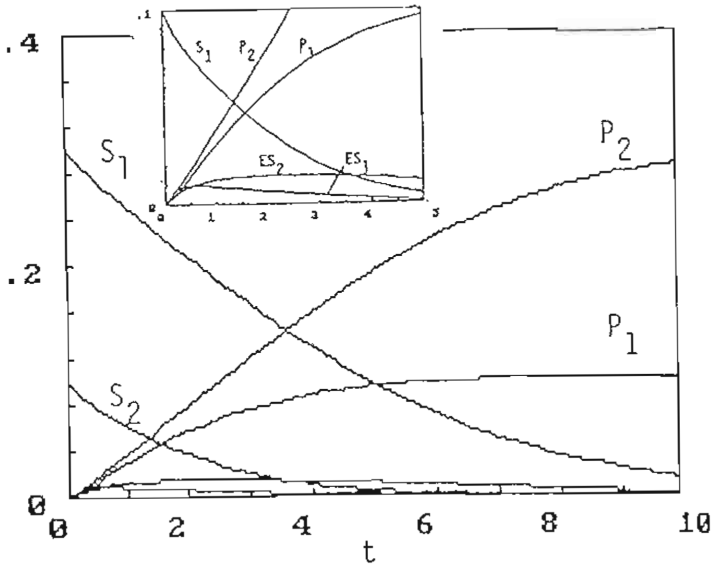
g(2)=-43.5*e*y(2)+9.6*y(4)

g(3) = 70*e*y(1)-8.5*y(3)

g(4)=43.5*e*y(2)-12.4*y(4)

g(5)=3.5*y(3)

g(6)=2.8*y(4)
```



P8.04.09. BATCH AND CSTR OPERATION WITH AN M-M RATE EQUATION

A carbohydrate decomposition has the rate equation

$$-\frac{dC}{dt} = \frac{100C}{200+C}$$

Starting concentration is $C_0 = 300$. (a) Find $C = f(t)$ of a batch reaction. (b) The feed to a CSTR is at 100 cc/min and the reactor volume is 300 cc. What is the outlet concentration?

(a) $$t = \int_C^{300} \frac{200+C}{C}\, dC = 200 \ln\frac{300}{C} + 300-C$$

C	300	250	200	150	100	50
t	0	0.86	1.81	2.89	4.20	6.08

(b) $V' = 100,\ V_r = 300,\ C_0 = 300$

$$C_0 = C + r\frac{V_r}{V'},\quad 300 = C + 3\left(\frac{100C}{200+C}\right)$$

$$C = 164.58$$

P8.04.10. MAXIMUM RATE

For a certain enzyme, $K_m = 0.01$ mol/liter. When the initial concentration of the substrate was $3.4(10^{-4})$ mol/liter, 10% was consumed in 10 minutes. (a) What is the maximum reaction rate? (b) What is the conversion after 20 min? Assume the M-M equation.

$$-\frac{dC}{dt} = \frac{r_m C}{0.01+C}$$

$$0.01\ \ln(C_0/C) + C_0\left(1-\frac{C}{C_0}\right) = r_m t$$

$$0.01\ \ln(1/0.9) + 3.4(10^{-4})(1-0.9) = 10r_m$$

$$r_m = 1.0876(10^{-4})$$

When t = 20,

$$0.01\ \ln(C_0/C) + 3.4(10^{-4})(1-C/C_0) = 1.0876(10^{-4})(20)$$
$$C/C_0 = 0.80973$$

P8.04.11. PLUG FLOW OR STIRRED TANK REACTORS

An enzyme reaction has the M-M rate equation with $r_m = 13$ mol/liter.min and $K_m = 0.03$ mol/liter. Starting concentration is $C_S = 10$ mol/liter and the flow rate is 10 liter/hr. Find conversions in plug flow and stirred tank reactors.

In plug flow,

$$-V'dC = r\ dV_r = \frac{13C}{0.03+C}\, dV_r$$

$$V_r = \int_{0.5}^{10} \frac{10(0.03+C)}{13C}\,dC = 7.3768 \text{ liters}$$

In CSTR,

$$C_0 = C + \frac{V_r}{V'}\left(\frac{13C}{0.03+C}\right)$$

$$10 = 0.5 + \frac{V_r}{10}\,\frac{13(0.5)}{0.03+0.5}$$

$$V_r = 7.746 \text{ liters}$$

P8.04.12. A TWO-STAGE CSTR

A reaction has a rate equation

$$r = \frac{7C}{10+C}\ ,\ \text{g/liter.min}$$

Feed to a two-stage CSTR is 0.5 liter/min with a concentration 50 g/liter. Each stage is 1 liter. (a) Find the effluent concentration. (b) Find the volume of a single stage reactor with the same conversion.
Two stage material balances are,

$$C_0 = 50 = C_1 + \tau r_1 = C_1 + 2\left(\frac{7C_1}{10+C_1}\right)$$

$$C_1 = C_2 + 2\left(\frac{7C_2}{10+C_2}\right)$$

$$C_1 = 38.865,\quad C_2 = 28.501 \text{ g/liter}$$

In a single stage,

$$50 = 28.501 + \frac{V_r}{0.5}\left(\frac{7(28.501)}{10+28.501}\right)$$

$$V_r = 2.0906 \text{ liters}$$

P8.04.13. HYDROLYSIS OF SUGAR. M-M EQUATION INAPPLICABLE

Invertase hydrolyzes sugar into glucose and fructose. The table gives rate data. The plot of the M-M equation in the form S/r against S is not linear. Accordingly try the mechanism,

$$E + S \underset{2}{\overset{1}{\Leftrightarrow}} ES,\quad ES + S \underset{4}{\overset{3}{\Leftrightarrow}} ESS,\quad ES \overset{5}{\Rightarrow} P + E$$

Assume equilibria are attained.

$$(ES) = K_1(E)(S)$$

$$(ESS) = K_2(ES)(S) = K_3(E)(S)^2$$

$$E = E_0 - ES - ESS = \frac{E_0}{1+K_1S+K_3S^2}$$

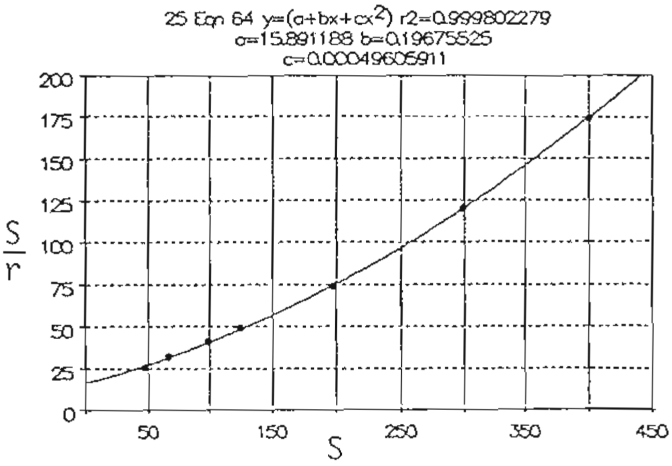
$$r = \frac{dP}{dt} = k_5(ES) = \frac{k_1k_5}{k_2}(E)(S) = \frac{k_1k_5E_0}{k_2}\left(\frac{S}{1+K_1S+K_3S^2}\right) \qquad (1)$$

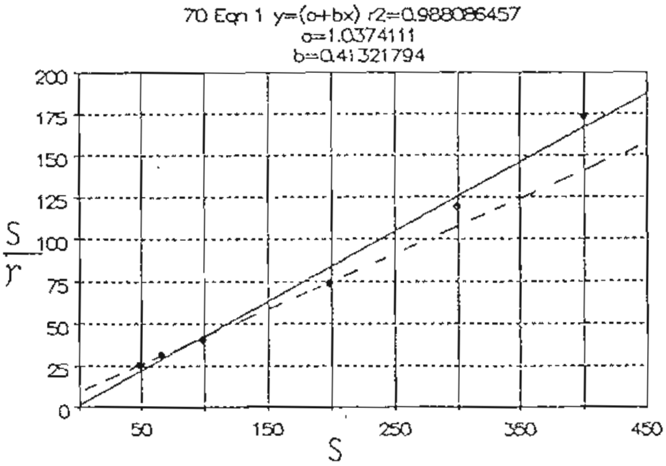
Rearrange into

$$y = \frac{S}{r} = \alpha + \beta S + \gamma S^2 \qquad (2)$$

The quadratic Eq (2) represents the data accurately and supports the assumed mechanism. This plot is compared with the linear one.

S	r	S/r
48.9	1.9	25.74
67	2.1	31.9
98.5	2.4	41.04
199.1	2.7	73.74
299.6	2.5	119.84
400.2	2.3	174





P8.04.14. INHIBITION

The reaction rates of hydrolysis of the substrate acetylcholine by an enzyme in the absence and presence of an inhibitor ($1.5(10^{-7})$ g/l prostigmine) were measured with the results tabulated. (Eadie, *J Biol Chem* 146 85-93, 1942). r_1 is in the absence and r_2 is in the presence of prostigmine. Find the parameters of the M-M equation and identify the inhibitor as competitive or noncompetitive.

The equation is plotted in linear form as

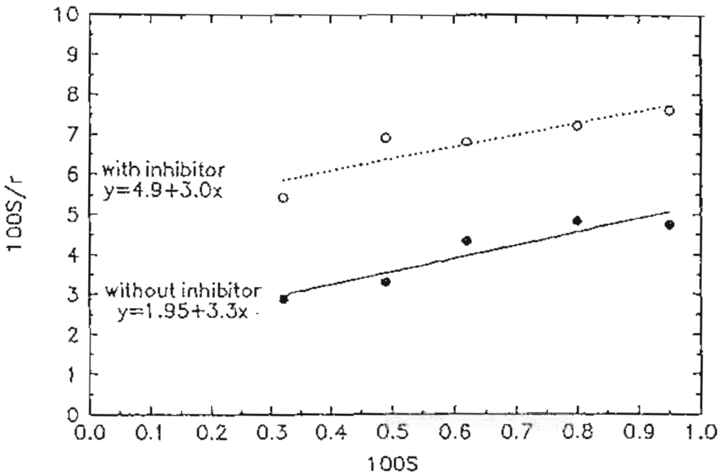
$$\frac{S}{r} = \frac{K_m}{r_m} + \left(\frac{1}{r_m}\right) S$$

The slopes are nearly the same, so the maximum rates r_m are nearly the same, but the two dissociation constants differ.

$K_{m1} = 4.9/3.0 = 1.63$, $K_{m2} = 1.95/3.3 = 0.59$

Since the maximum rate is not affected significantly, this identifies the inhibitor as noncompetitive.

S	r_1	r_2
0.0032	0.111	0.059
0.0049	0.148	0.071
0.0062	0.143	0.091
0.0080	0.166	0.111
0.0095	0.200	0.125



P8.04.15. EFFECTIVENESS OF IMMOBILIZED ENZYMES

An enzyme is immobilized by adsorption on porous pellets of a carrier. The differential equation for the concentration of a reactant in a porous spherical pellet is derived in problem P7.03.01 and integrated for a first order reaction, $r_c = kC$, in problem P7.03.06. An expression is derived for the effectiveness of the adsorbed enzyme for first order reaction as

$$\eta = \frac{3\phi \coth \phi - 1}{3\phi^2}, \quad \phi = \frac{R}{3}\sqrt{k/D}$$

For an M-M rate of reaction, the differential equation for the concentration C in the pellet is

$$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = \frac{r_m C}{D(K_m+C)}$$

In terms of new variables it becomes,

C_s = concentration of substrate at the external surface
$f = C/C_s$, $\rho = r/R$
$\beta = C_s/K_m$

$$\phi = \frac{R}{3}\sqrt{\frac{r_m}{DK_m}}$$

$$\frac{d^2f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho} = 9\phi^2\left(\frac{f}{1+\beta f}\right) \qquad (1)$$

The boundary conditions are, at the center $df/d\rho = 0$ when $\rho = 0$; at the external surface $f = 1$ when $\rho = 1$. The effectiveness of the enzyme is

$$\eta = \frac{\text{rate of diffusion into the pellet}}{\text{rate of reaction with concn } C_s \text{ on the internal surface}}$$

$$= \frac{4\pi R^2 D}{\frac{4}{3}\pi R^3\left(\frac{r_m C_s}{K_m+C_s}\right)}\left(\frac{dC}{dr}\right)_{r=R} = \frac{3D}{R}\left(\frac{K_m+C_s}{r_m C_s}\right)\frac{C_s}{R}\left(\frac{df}{d\rho}\right)_{\rho=1}$$

$$= \frac{\beta+1}{3\phi^2}\left(\frac{df}{d\rho}\right)_{\rho=1} \qquad (2)$$

Numerical solution of Eq (1) by the shooting method automatically gives the derivative at the external surface required in Eq (2).

P8.04.16. NUMERICAL EVALUATION OF EFFECTIVENESS

The effectiveness of an enzyme immobilized on a porous spherical pellet is to be calclulated with $\beta = 5$ and $\phi = 4$. The shooting method for solving Eq (1) of problem P8.04.15 is described in problem P7.03.09. Several trial values of f_0 at the center and the corresponding values at the surface, f_1 and $(df/d\rho)_1$, are tabulated. ODE is applied to the equivalent pair of equations

$$\frac{df}{d\rho} = f'$$

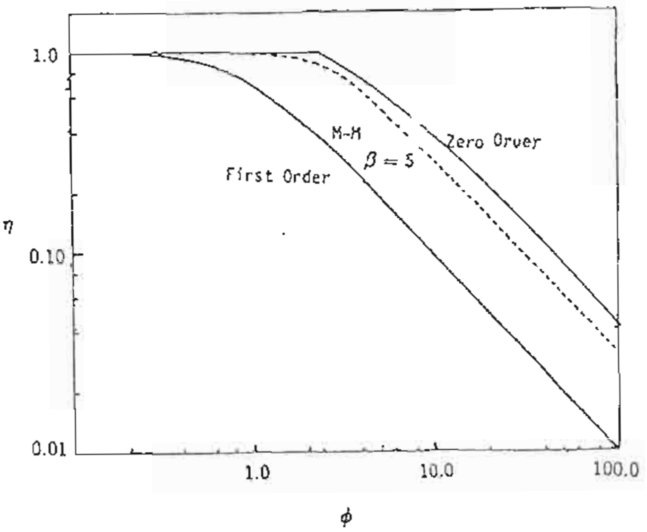
$$\frac{df'}{d\rho} = -\frac{2}{\rho}f' + 9\phi^2\left(\frac{f}{1+\beta f}\right)$$

f_0	f_1	$(df/d\rho)_1$	
0.005	2.0060	6.8462	
0.001	1.1729	6.0529	
0.0007	1.0153	4.9220	
0.000672	0.9979	4.8760	Check

Accordingly,

$$\eta = \frac{\beta+1}{3\phi^2}\left(\frac{df}{d\rho}\right)_1 = \frac{6}{3(16)}\ 4.8760 = 0.61$$

The plot is of the full range of ϕ with $\beta = 5$, and the comparison with zero and first order reactions.



P8.04.17. A THREE-STAGE CSTR

The rate equation of a reaction with an immobilized enzyme is $r = 5\eta C/(0.05+C)$. The inlet concentration to a three-stage CSTR is 1.2 and 80% conversion is required. Find the required residence time per stage when the effectiveness is 60% or 100%.

The material balances are

$$1.2 = C_1 + \eta\tau\left(\frac{5C_1}{0.05+C_1}\right)$$

$$C_1 = C_2 + \eta\tau\left(\frac{5C_2}{0.05+C_2}\right)$$

$$C_2 = C_3 + \eta\tau\left(\frac{5C_3}{0.05+C_3}\right) = 0.24 + \eta\tau\left[\frac{5(0.24)}{0.05+0.24}\right]$$

The concentrations are $C_1 = 0.8624$, $C_2 = 0.5356$, $C_3 = 0.24$.
The residence times are $\tau = 1.1907$ when $\eta = 0.6$ and $\tau = 0.0714$ when $\eta = 1.0$.

P8.04.18. CELL GROWTH RATE. MONOD EQUATION

The growth rate of *E. coli* is represented by the equation (Monod, Ann Rev Microbiol 3 371-394, 1942),

$$\frac{dC_x}{dt} = \frac{0.935C_xC_s}{0.71+C_s} \qquad (1)$$

The initial concentrations are 1.0 g/l of the cells and 10 g/l of the substrate. The yield is 0.6 g cells/g substrate consumed, or

$$\frac{C_x-C_{x0}}{C_{s0}-C_s} = \frac{C_x-1}{10-C_s} = 0.6 \qquad (2)$$

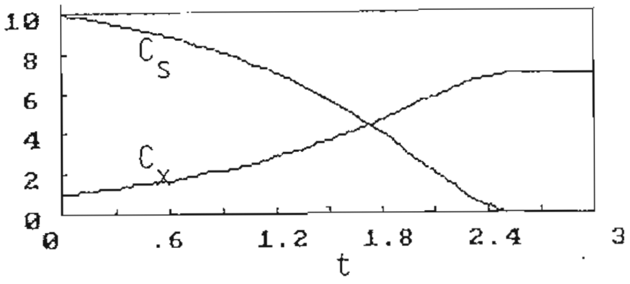
or

$$\frac{dC_x}{dt} = -\ 0.6\ \frac{dC_s}{dt} \qquad (3)$$

This equation can be put in the form

$$\frac{dC_s}{dt} = \frac{0.935C_s}{0.71+C_s}\ (0.6C_s-7) \qquad (4)$$

Eqs (3) and (4) or (3) and (1) are solved simultaneously by ODE to find the time variations of the concentrations of cells and substrate.



P8.04.19. CELL GROWTH IN A CSTR

At steady state in a CSTR the cell balance is

$$V'C_x = V'C_{x0} + V_r r_x = V'C_{x0} + V_r \frac{\mu_m C_x C_s}{K_s+C_s}$$

Solving for the residence time,

$$\tau = \frac{V_r}{V'} = \frac{K_s+C_s}{\mu_m C_x C_s}(C_x-C_{x0})$$

It is often convenient to start experiments with zero cell concentration. Then,

$$\tau = \frac{K_s+C_s}{\mu_m C_s} = \frac{K_s}{\mu_m}\left(\frac{1}{C_s}\right) + \frac{1}{\mu_m} \qquad (1)$$

(a) The tabulated data are of yeast growth in a CSTR. Inlet concentration of glucose was 100 g/l, that of the cells was zero and the volume of the reactor was 500 cc. The plot of Eq (1) has the linear equation

$$\tau = \frac{6.07}{C_s} + 3.97$$

and K_s 1.529, $\mu_m = 0.252$. The concentration of glucose is

$$C_s = \frac{K_s}{\tau\mu_m - 1} = \frac{1.529}{0.252\tau-1} \qquad (2)$$

(b) What must be the minimum flow rate to keep the yeast concentration from reaching zero?

$$C_x - C_{x0} = y(C_{s0}-C_s) = y\left(100 - \frac{1.529}{0.252\tau-1}\right) \geq 0$$

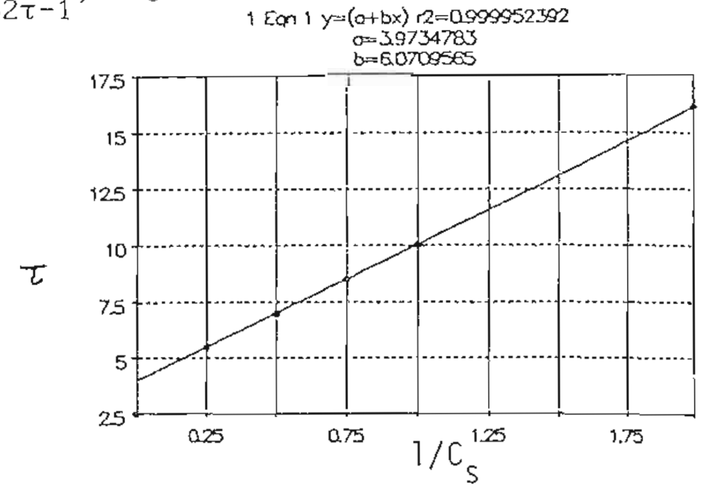
But $C_{x0} = 0$, $C_x \geq 0$ and y cancels out.

$$100 = \frac{1.529}{0.252\tau-1}$$

$\tau \geq 4.029$ hr

$V' \leq 500/4.029 = 124.1$ cc/hr

V'	C_x	C_s
31	5.97	0.5
50	5.94	1.0
71	5.88	2.0
91	5.76	4.0
200	0	100



P8.04.20. CELL YIELD AND CONSTANTS OF THE RATE EQUATION

Before the rate equation can be integrated,

$$\frac{dC_x}{dt} = \frac{\mu C_x C_s}{K_s+C_s} = \frac{\mu f(C_s)C_s}{K_s+C_s}$$

a relation is needed between C_x and C_s. The commonest relation in use is proportionality between the cell yield, ΔC_x, and the substrate conversion, $-\Delta C_s$. That is,

$$y_{xs} = \frac{C_x-C_{xo}}{C_{so}-C_s} = \text{Constant}$$

In this case the integral becomes

$$\mu(t-t_o) = (1+\frac{K_s y_{xs}}{C_{xo}+C_{so}y_{xs}})\ \ln\frac{C_x}{C_{xo}} + \frac{k_s y_{xs}}{C_{xo}+C_{so}y_{xs}}\ \ln\frac{C_{so}}{C_s} \qquad (1)$$

Suppose the yield data are

t	C_x	C_s
0	5	100
20	35	60
30	72.5	10

Inspection reveals that $y_{xs} = 0.75$. The constants μ and K_s of the rate equation may be found by substitution of the data into the integral Eq (1) and solving simultaneously.

$$\frac{K_s y_{xs}}{C_{xo}+C_{so}y_{xs}} = \frac{0.75K_s}{5+100(0.75)}\ 0.009375K_s$$

$$20\mu = (1 + 0.009375K_s)\ \ln\frac{35}{5} + 0.009375K_s\ \ln\frac{100}{60} \qquad (2)$$

$$30\mu = (1 + 0.009375K_s)\ \ln\frac{72.5}{5} + 0.009375\ \ln\frac{100}{10} \qquad (3)$$

The solution of Eqs (2) and (3) is

$\mu = 0.1206,\ K_s = 20.217$

so the rate equation becomes

$$\frac{dC_x}{dt} = -\ y_{xs}\ \frac{dC_s}{dt} = \frac{0.1206C_xC_s}{20.217+C_s} \qquad (4)$$

When y_{xs} can be found by inspection of the data, the original rate equation can be linearized as

$$z = \frac{C_s[C_{xo}+y_{xs}(C_{so}-C_s)]}{r} = \frac{K_m}{\mu} + \frac{C_s}{\mu} \qquad (5)$$

P8.04.21. A TWO-STAGE CSTR

A process has the rate equation

$$r_x = \frac{dC_x}{dt} = \frac{0.7C_xC_s}{5+C_s}$$

and the yield equation

$y_{xs} = 0.65$

with $C_{xo} = 0$, $C_{so} = 85$ and the effluent $C_{s2} = 5$. The residence times are to be found in one and two stage CSTRs.

Material balance on the first stage is,

$C_{x1} = C_{xo} + 0.65(C_{so}-C_{s1}) = 0.65(85-C_{s1})$

$$= C_{x0} + \tau r_{x1} = \frac{0.7C_{x1}C_{s1}}{5+C_{s1}}$$

$$1 = \frac{0.7\tau C_{s1}}{5+C_{s1}} \qquad (1)$$

For the second stage,

$$C_{x2} = 0.65(C_{s0}-C_{s2}) = 0.65(85-5) = 52$$

$$= C_{x1} + \frac{0.7\tau C_{x2}C_{s2}}{5+C_{s2}}$$

$$52 = 0.65(85-C_{s1}) + \frac{0.7(52)(5)}{5+5}\tau = 0.65(85-C_{s1}) + 18.2\tau \qquad (2)$$

Solving (1) and (2) simultaneously,

$C_{s1} = 49.08$ g/l

$\tau = 1.574$ hr/stage

In one stage, with $C_{s1} = 5$ in Eq (1),

$\tau = 2.857$

P8.04.22. A PLUG FLOW REACTOR

The reaction of problem P8.04.21 is to be done in a plug flow reactor with a range of starting values C_{x0}.

$$C_x = C_{x0} + 0.65(85-C_s)$$

The plug flow material balance is

$$V'dC_x = -0.65dC_s = r_x dV_r$$

$$\tau = \frac{V_r}{V'} = \frac{0.65}{0.7}\int_5^{85} \frac{5+C_s}{[C_{x0}+0.65(85-C_s)]C_s}\,dC_s$$

Because of the particular form of the rate equation (like that of an autocatalytic reaction) no reaction is possible in batch or plug flow when $C_{x0} = 0$. Inoculation with product cells must be done at the start. Practically, however, the process may get started by itself after an induction period, since the theory is not exact. Values of τ for several values of C_{x0} are tabulated.

C_{x0}	0	1	5	10	20	50
τ	∞	6.27	3.88	2.94	2.08	1.18

P8.04.23. YEAST GROWTH AND ETHANOL PRODUCTION

The results of a CSTR study of the growth of a particular yeast on glucose are tabulated (Aiba et al, Biotechnol Bioeng 10 845, 1968). The inlet stream was free of cells and ethanol. Find the rate equations for yeast cells and ethanol.

The CSTR balance on the cells is

$$C_x = C_{x0} + \tau r_x = \frac{\upsilon C_x C_s}{K_s+C_s}\tau$$

This is plotted in the linearized form,

$$\tau = \frac{1}{\mu} + \frac{K_s}{\mu}\left(\frac{1}{C_s}\right) = 2.080 + 0.5585\left(\frac{1}{C_s}\right) \qquad (1)$$

$$\mu = 0.4808,\ K_s = 0.2685$$

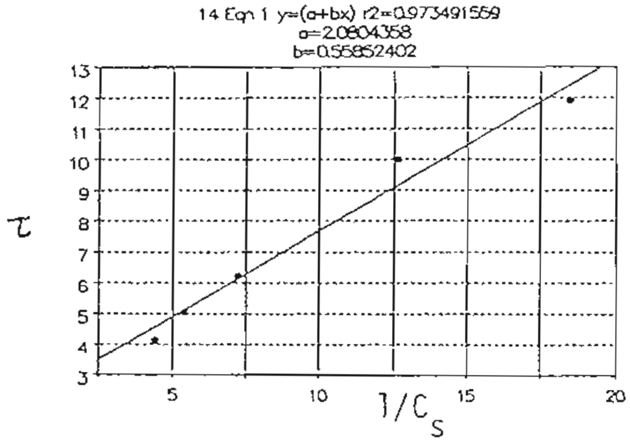
$$r_x = \frac{dC_x}{dt} = \frac{0.4808C_xC_s}{0.2685+C_s} \qquad (2)$$

For the ethanol,

$$\frac{dC_p}{dt} = \frac{dC_x}{dt}\frac{\Delta C_p}{\Delta C_x} = 3.741\,\frac{dC_x}{dt} \qquad (3)$$

The coefficient is derived in the table.

$1/\tau$	C_{s0}	C_s	$C_p=\Delta C_p$	$C_x=\Delta C_x$	$\Delta C_p/\Delta C_x$
0.084	21.5	0.054	7.97	2.00	3.985
1.100	10.9	0.079	4.70	1.20	3.917
0.160	21.2	0.138	8.57	2.40	3.571
0.198	20.7	0.186	8.44	2.33	3.622
0.242	10.8	0.226	4.51	1.25	3.608
Mean					3.741



P8.04.24. AN INHIBITORY SUBSTRATE

A rate equation for cell growth with an inhibitory substrate is assumed to be of the form (Andrews, Biotechnol Bioeng 10 707, 1968)

$$\cdot\frac{dC_s}{dt} = \frac{\mu}{1+K_s/C_s+C_s/K_I}$$

Data obtained in a CSTR are tabulated (a) Find the constants of the rate equation. (b) If the cell yield is $y_{xs} = 0.46$ g/g, what is the steady state cell concentration when $1/\tau = 0.2$?

The CSTR balance is

$$C_{s0} = C_s + \tau r_s = C_s + \frac{\mu\tau}{1+K_s/C_s+C_s/K_I}$$

Rearrange into

$$y = \frac{\tau}{C_{s0}-C_s} = \frac{1}{\mu} + \frac{1}{C_s}\frac{K_s}{\mu} + C_s\left(\frac{1}{\mu K_I}\right)$$

$$= a_0 + a_1x_1 + a_2x_2$$

Values of y, $x_1 = 1/C_s$ and $x_2 = C_s$ are tabulated. POLYMATH multilinear regression is used to find the constants. The regression equation of the points with $C_{so} = 30$ is

$$y = 0.02305 + 0.07442x_1 + 0.003123x_2$$

from which

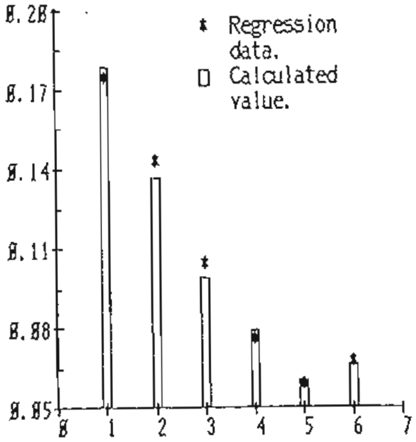
$\mu = 43.38$, $K_s = 3.2786$, $K_I = 7.3807$

Andrews suggests that the different behavior with $C_{s0} = 60$ is a result of instability. Point 6 also does not appear to be part of the family.

(b) $\Delta C_x = y_{xs}\Delta C_s = 0.46(30-0.5) = 13.57$ g/l

The regression plot suggests that point 6 may be in error.

$1/\tau$	C_{s0}	$C_s=x_2$	$1/C_s=x_1$	y
0.2	30	0.5	2	0.169
0.25	30	0.7	1.428	0.137
0.35	30	1.1	0.909	0.0989
0.5	30	1.6	0.625	0.0704
0.7	30	3.3	0.303	0.0535
0.8	30	10	0.1	0.0625
0.5	60	30	0.033	0.040
0.6	60	22	0.045	0.0439
0.7	60	15	0.067	0.0317



P8.04.25. ETHANOL BY FERMENTATION

The rate equation for the yeast cells and the yield equations for ethanol (P) and glucose (S) are given by Lee (*Biochemical Engineering*, p 181, 1992) as

$$\frac{dC_x}{dt} = 0.24(1-0.01C_p)^2\left(\frac{C_s}{1.6+C_s}\right)C_x \qquad (1)$$

$$C_x = 0.1 + 0.06(100-C_s) \qquad (2)$$

$$C_p = 0.375(100-C_s) \qquad (4)$$

Pertinent concentrations are $C_{x0} = 0.1$, $C_{p0} = 0$, $C_{s0} = 100$.

Substituting into the rate equation,

$$\frac{dC_s}{dt} = -\ 0.24(1-\ 0.00375(100-C_s))^2\left(\frac{C_s}{1.6+C_s}\right)(0.1+0.06(100-C_s))$$

This is integrated for C_s by ODE, then Eq (2) and (3) are applied, with the tabulated results.

t	C_s	C_p	C_x
0	100	0	0.1
5	96.31	1.38	0.32
10	85.44	5.46	0.97
15	59.40	15.23	2.54
20	17.57	30.91	5.05
21	8.99		
22	1.88		
23	0.0214		
24	0.0001	37.50	6.10

P8.04.26. AN EXPONENTIAL RATE EQUATION

The growth rate of a microorganism is represented by the equation

$$r_x = \frac{dC_x}{dt} = \mu[1-\exp(-C_s/K_S)]C_x$$

with $C_{s0} = 13$, $\mu = 0.365$, $K_s = 6.8$, yield equation $C_x = C_{x0} + 0.45(13-C_s)$.

(a) When $C_{x0} = 0$ and $\tau = 4$, find the steady concentrations C_s and C_x.

$C_x = 0 + 0.365\tau[1-\exp(-C_s/6.8)]C_x$

$1 = 0.365(4)[1-\exp(-C_s/6.8)]$

$C_s = 7.854,\ C_x = 0.45(13-7.854) = 2.316$

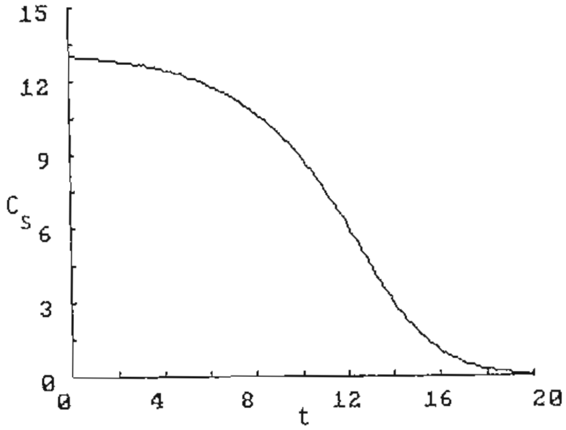
(b) When $C_{x0} = 0.1$ find the time variation of C_s in a batch reactor.

The rate equation becomes

$$\frac{dC_s}{dt} = -\frac{1}{0.45}\frac{dC_x}{dt}$$

$$= -2.222(0.365)[1-\exp(-C_s/6.8)][0.1+0.45(13-C_s)]$$

The integral by ODE is plotted.



P8.04.27. MINIMUM REACTOR SIZE

(a) Single stage. A minimum CSTR size is obtained when the rates of cell growth or substrate consumption are maxima.

$$r_x = \frac{\mu C_s C_x}{k+C_s} = \frac{\mu y_{xs} C_s(C_{s0}-C_s)}{k+C_s}$$

$$= y_{xy} r_s$$

Upon setting $dr_x/dC_s = 0$,

$$(k+C_s)(C_{s0}-2C_s)-C_s(C_{s0}-C_s) = 0$$

or

$$C_s^2 + 2kC_s - kC_{s0} = 0$$

or

$$C_{s,opt} = \sqrt{k^2+kC_{s0}} - k \qquad (1)$$

$$C_{x,opt} = y_{xs}[C_{s0}+k-\sqrt{k^2+kC_{s0}}] \qquad (2)$$

(b) Two-stage CSTR

$$C_{s0} = C_{s1} + \frac{\mu\tau_1 C_{s1}(C_{s0}-C_{s1})}{k+C_{s1}}.$$

$$\mu\tau_1 = 1 + k/C_{s1} \qquad (3)$$

$$C_{s1} = C_{s2} + \frac{\mu y_{xs}\tau_2 C_{s2}(C_{s0}-C_{s2})}{k+C_{s2}}$$

$$\mu\tau_2 = \frac{(C_{s1}-C_{s2})(k+C_{s2})}{C_{s2}(C_{s0}-C_{s2})} \qquad (4)$$

For a specified C_{s2}, put $d(\tau_1+\tau_2)/dC_{s1} = 0$. Then

$$-\frac{k}{C_{s1}^2} + \frac{k+C_{s2}}{C_{s2}(C_{s0}-C_{s2})} = 0$$

$$C_{s1,opt} = \sqrt{\frac{kC_{s2}(C_{s0}-C_{s2})}{k+C_{s2}}} \qquad (5)$$

(c) Example comparison of optimum and equal-stages CSTRs.

$\mu = 0.2$, $k = 0.5$, $y_{xs} = 0.3$, $C_{s0} = 5$, $C_{s2} = 0.5$

$C_{s1} = 1.0607$, from Eq (5)

$$\tau_1 = \frac{0.5+1.0607}{0.2(1.0607)} = 7.359$$

$$\tau_2 = \frac{(1.067-0.5)(0.5+0.5)}{0.2(0.5)(5-0.5)} = 1.246$$

For equal stages, $\tau_1 = \tau_2$,

$$\frac{k+C_{s1}}{C_{s1}} = \frac{0.5+C_{s1}}{C_{s1}} = \frac{(C_{s1}-0.5)(0.5+0.5)}{0.5(5-0.5)} = 0.4444(C_{s1}-0.5)$$

$C_{s1} = 3.112$

$$\tau_1 = \tau_2 = \frac{0.4444(3.112-0.5)}{1(0.2)} = 5.804$$

Therefore,

Optimum $\tau_1+\tau_2 = 7.357+1.246 = 8.603$

Equal stage $\tau_1+\tau_2 = 2(5.804) = 11.608$

P8.04.28. CSTR WITH RECYCLE

A yeast is cultivated in a CSTR with partial recycle of the product. Effluent from the reactor has concentrations C_x and C_s and goes to a separator where a product stream, F, has concentrations $0.3C_x$ and C_s. The recycle stream, R, likewise has concentration C_s and a material balance on X as

Recycle $= (F+R)C_x - 0.3FC_x = (0.7F+R)C_x = RC_{xr}$ (1)

This establishes the recycle concentration if desired. Material balance on the cell production with zero in the fresh feed,

$$(F+R)C_x = (0.7F+R)C_x + V_r r_x = (0.7F+R)C_x + \frac{V_r\mu C_s C_x}{k+C_s}$$

$$0.3F = \frac{V_r\mu C_s}{k+C_s}$$

$$C_s = \frac{0.3k}{\mu\tau-0.3} \qquad (2)$$

The cell concentration is given by material balance as

$$0.3FC_x = y_{xs}F(C_{s0}-C_s)$$

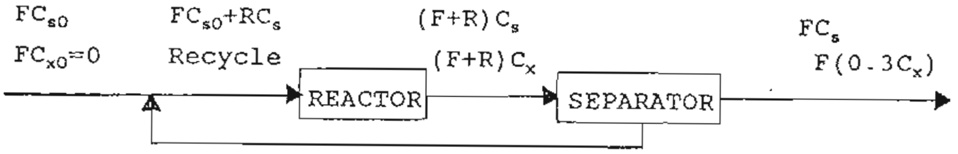
$$C_x = \frac{y_{xs}}{0.3}(C_{s0}-C_s) \qquad (3)$$

Substitute from (2). When the product concentration is made αC_x, replace 0.3 with α in Eqs (2) and (3). Without recycle,

$C_s = k/(\mu\tau-1)$ (4)

This comparison shows the greater conversion with recycle.

$\mu\tau$	0.3	1	2	5
C_s/k, with	∞	0.43	0.18	0.06
C_s/k, without	-	∞	1.43	0.25



Recycle of X = $(0.7F+R)C_x$

Recycle of S = RC_s

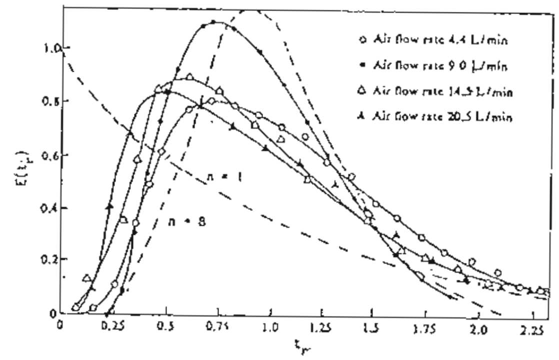
P8.04.29. RESIDENCE TIME DISTRIBUTION IN AN EIGHT-PLATE TOWER

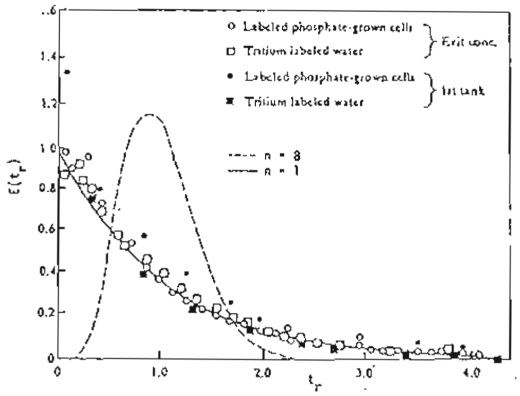
Measurements were made of RTD in an eight-plate tower under different operating conditions (Prokop et al, *Biotech Bioeng* 11 945, 1969). (a) Effect of aeration rates, salt used as tracer; the results are not clear cut, but the theoretical eight-stage distribution is approached more closely at the lower air rates. (b) Yeast cells present in the column, tritium labelled water and labelled phosphate-grown cells as tracers; one-stage CSTR performance is achieved closely.

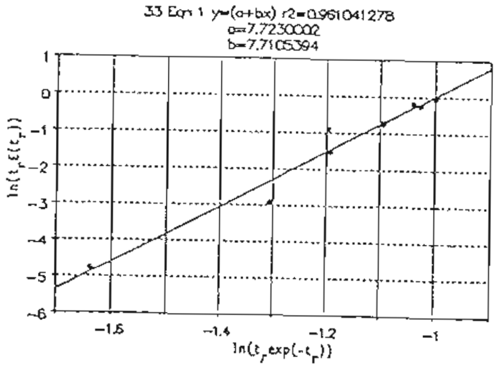
Numbers read off the graph for aeration of 9.0 L/min are:

t_r	0.25	0.5	0.75	1.00	1.25	1.50	1.75	2.00
$E(t_r)$	0.034	0.832	1.103	0.926	0.624	0.322	0.123	0.027

These data are fitted to the Gamma distribution by the procedure used in problem P5.02.04. The slope of the loglog plot and consequently the value of the parameter is n = 7.71 stages.







P8.04.30. AERATION MASS TRANSFER AND POWER

Work on the growth of a microbe shows that the critical oxygen concentration needed to maintain growth is 0.022 mmmol/liter and the oxygen utilization rate is $1.68(10^{-4})$ kmol/s m^3. Henry's law coefficient is $H = 4.75(10^4)$ atm/mol fraction. Density of the liquid is $\rho = 1050$ kg/m^3 and its molecular weight is $M = 20$. Oxygen mol fraction in air is 0.21. Find the mass transfer coefficient and the power needed.

The oxygen transfer rate is

$$K_La(C_g-C_L) = 1.68(10^{-4}) \text{ kmol/s m}^3$$

Allowing 20% excess oxygen in the broth, dissolved oxygen will be

$$C_L = 1.2(0.022)(10^{-3}) = 2.64(10^{-5}) \text{ kmol/m}^3$$

At atmospheric pressure,

$$x_g = \frac{0.21}{4.75(10^4)} = 4.42(10^{-6})$$

$$C_g = \frac{x_g\rho}{M(1-x_g)} = \frac{4.42(10^{-6})(1050)}{20(1-x_g)} = 2.32(10^{-4}) \text{ kmol/m}^3$$

The utilization rate coefficient is

$$K_La = \frac{1.68(10^{-4})}{(223.2-2.64)(10^{-5})} = 0.817 \text{ kmol/s m}^3$$

Typical superficial air velocities in fermentation are 0.1-0.5 ft/s. Take a mean value of 0.1 m/s. The power requirement is given by the equation (Van't Riet, Ind Eng Chem PDD 18 357, 1979),

$$K_La = 0.002(\Pi_g/V)^{0.7}u_s^{0.2}$$

where Π_g/V is in watts/m^3 and u_s is m/s superficial air velocity. Then

$$\Pi_g/V = (0.817/0.1^{0.2})^{1/0.7} = 1.45 \text{ W/m}^3$$

INDEX OF SUBSTANCES

INDEX OF SUBJECTS

CHEMICAL REACTION ENGINEERING HANDBOOK OF SOLVED PROBLEMS

STANLEY M. WALAS
Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence

Reactors are the basic equipment in any chemical plant. This book describes their process design in terms of numerically solved examples. It covers numerical techniques, analysis of rate data, sizes and performances of ideal reactors, residence time distributions and performance of non-ideal models, solid catalyzed reactions, behavior of porous catalysts, and reactions between multiple phases, including biochemical processes. The 1,000 plus problems are classified into 54 categories. Each of the eight chapters provides definitions and an outline of theory. Solutions are presented mostly as graphs or tables. Some key theoretical developments are given in problem form. The scope is suitable for the first undergraduate course of this topic and for beginning or graduate students, as well as review for professional engineers' examinations.

About the author

Dr. Walas has several decades of varied experience in industry and academia and is an active industrial consultant for the process design of chemical reactors and chemical and petroleum plants. He has written four related books on reaction kinetics, phase equilibria, process equipment selection and design, and mathematical modeling of chemical engineering processes, as well as the sections **Reaction Kinetics** and **Chemical Reactors** in the seventh edition of *Chemical Engineers Handbook*. He is a Fellow of the AIChE and a registered professional engineer.

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