Large-Scale Adsorption and Chromatography

Volume I

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PREFACE

My major goal in writing this book has been to present a unified, up-to-date development of operating methods used for large-scale adsorption and chromatography. I have attempted to gather together the operating methods which have been used or studied for large-scale applications. These methods have been classified and compared. The main unifying principle has been to use the same theory, the solute movement or local equilibrium theory, to present all of the methods. Mass transfer and dispersion effects are included with the nonlinear mass transfer zone (MTZ) and the linear chromatographic models. More complex theories are referenced, but are not discussed in detail since they often serve to obscure the reasons for a separation instead of enlightening. Liberal use has been made of published experimental results to explain the operating methods.

Most of the theory has been placed in Chapter 2. I recommend that the reader study Sections II and IV.A and IV.B carefully since the other chapters rely very heavily on these sections. The rest of Chapter 2 can be read when you feel motivated. The remaining chapters are all essentially independent of each other, and the reader can skip to any section of interest. Considerable cross-referencing of sections is used to guide the reader to other sections of interest.

I have attempted to present a complete review of the open literature, but have not attempted a thorough review of the patent literature. Many commercial methods have been published in unconventional sources such as company brochures. Since these may be the only or at least the most thorough source, I have referenced many such reports. Company addresses are presented so that interested readers may follow up on these references. Naturally, company brochures are often not completely unbiased. The incorporation of new references ceased in mid-May 1985. I apologize for any important references which may have been inadvertently left out.

Several places throughout the text I have collected ideas and made suggestions for ways to reduce capital and/or operating expenses for different separation problems. Since each separation problem is unique, these suggestions cannot be universally valid; however, I believe they will be useful in the majority of cases. I have also looked into my cloudy crystal ball and tried to predict future trends; 5 years from now some of these predictions should be good for a laugh.

Much of this book was written while I was on sabbatical. I wish to thank Purdue University for the opportunity to take this sabbatical, and Laboratoire des Sciences du Genie Chimique, Ecole Nationale Superieure des Industries Chimiques (LSGC-ENSIC) for their hospitality. The support of NSF and CNRS through the U.S./France Scientific Exchange Program is gratefully acknowledged. Dr. Daniel Tondeur, Dr. Georges Grevillot, and Dr. John Dodds at LSGC-ENSIC were extremely helpful in the development of this book. My graduate level class on separation processes at Purdue University served as guinea pigs and went through the first completed draft of the book. They were extremely helpful in polishing the book and in finding additional references. The members of this class were Lisa Brannon, Judy Chung, Wayne Curtis, Gene Durrence, Vance Flosenzier, Rod Geldart, Ron Harland, Wei-Yih Huang, Al Hummel, Jay Lee, Waihung Lo, Bob Neuman, Scott Rudge, Shirish Sanke, Jeff Straight, Sung-Sup Suh, Narasimhan Sundaram, Bart Waters, Hyung Suk Woo, and Qiming Yu. Many other researchers have been helpful with various aspects of this book, often in ways they are totally unaware of. A partial listing includes Dr. Philip Barker, Dr. Brian Bidlingmeyer, Dr. Donald Broughton, Dr. Armand deRosset, Dr. George Keller, Dr. C. Judson King, Dr. Douglas Levan, Dr. Buck Rogers, Dr. William Schowalter, and Dr. Norman Sweed. The typing and help with figures of Connie Marsh and Carolyn Blue were invaluable and is deeply appreciated. Finally, I would like to thank my parents and particularly my wife, Dot, for their support when my energy and enthusiasm plummeted.

THE AUTHOR

Phillip C. Wankat is a Professor of Chemical Engineering aat Purdue University in West Lafayette, Ind. Dr. Wankat received his B.S.Ch.E. from Purdue University in 1966 and his Ph.D. degree in Chemical Engineering from Princeton University in 1970. He became an Assistant Professor at Purdue University in 1970, an Associate Professor in 1974, and a Professor in 1978. Prof. Wankat spent sabbatical years at the University of California-Berkeley and at LSGC, ENSIC, Nancy, France.

His research interests have been in the area of separation processes with an emphasis on operating methods for adsorption and large-scale chromatography. He has published over 70 technical articles, and has presented numerous seminars and papers at meetings. He was Chairman of the Gordon Research Conference on Separation and Purification in 1983. He is on the editorial board of Separation Science. He is active in the American Institute of Chemical Engineers, the American Chemical Society, and the American Society for Engineering Education. He has consulted with several companies on various separation problems.

Prof. Wankat is very interested in good teaching and counseling. He earned an M.S.Ed. in Counseling from Purdue University in 1982. He has won several teaching and counseling awards, including the American Society for Engineering Education George Westinghouse Award in 1984.

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Chapter 1

INTRODUCTION

The purpose of this book is to provide a unified picture of the large number of adsorption and chromatographic operating methods used for separation. The macroscopic aspects of the processes differ, but on a microscopic scale all of these separation methods are based on different velocities of movement of solutes. The solute velocities in turn depend upon the phenomena of flow through a porous media, sorption equilibria, diffusion, mass transfer, and sorption/desorption kinetics.

Since I do not read books serially from cover to cover, but instead skip to those sections I am most interested in, this book has been written for this type of selective reading. Except for Chapter 2, the chapters are essentially independent so that the reader can start anywhere. All of the chapters do rely heavily on the local equilibrium or solute movement theory. Thus, a review of Chapter 2 (Sections III.A and B, plus possibly Section IV) would be helpful before reading other parts of the book. The remainder of Chapter 2 can be picked up as needed.

We will first look (in Chapter 2) at a physical picture of solute movement in a packed column. For most systems the separation can be predicted by combining the average rate of solute movement and zone spreading effects. The average rate of solute movement will be derived for both linear and nonlinear isotherms. This average solute wave velocity depends upon the bed porosity, solvent velocity, and equilibrium conditions, and is essentially the fraction of time the solute is in the mobile phase times the fluid velocity. The solute velocity is easily calculated and easy to use to explain the macroscopic aspects of different operating methods. Nonlinear adsorption, thermal waves, changing gas velocities, and coupled systems will all be studied. The spreading of the solute zones depends on diffusion, mass transfer rates, and sorption/desorption kinetics. The amount of zone spreading is easily determined from theories for systems with linear isotherms. From these theories one obtains the familiar rule that zone spreading is proportional to the square root of the distance traveled. For nonlinear systems which form constant patterns, the mass transfer zone (MTZ) approach will be developed.

The pictures of solute movement and of zone spreading will be combined to explain the operating methods in Chapters 3 to 8. Where necessary, the results from more detailed theories will be used to explain experimental results. Chapters 3 to 8 describe different operating methods and use the theories from Chapter 2 to explain these methods. The division of different separation methods into chapters is somewhat arbitrary. Essentially, Chapters 3 to 5 cover fixed-bed systems while Chapters 6 to 8 cover moving or simulated moving beds. These six chapters are all independent and can be read in any order, although they are cross-referenced. The development of mathematical theories is mainly restricted to Chapter 2 and, to a lesser extent, Chapter 6.

The adsorption of a single solute with simple cycles is discussed in Chapter 3. The basic type of operating cycle used is shown in Figure 1-1. The adsorption of solute occurs for some period and then the solute is desorbed either with a hot fluid or a desorbent. This is a batch process with a large number of possible variations. The method has been applied for cleaning up gas streams using a hot gas for desorption, for solvent recovery from a gas stream using activated carbon and steam desorption, for liquid cleanup using either a hot liquid or a desorbent for the desorption step, and for wastewater treatment systems. General considerations are covered in Section II of Chapter 3 and specific separations are covered in the rest of the chapter. Section II.D in Chapter 3, on the effect of particle size, will probably be of interest to all readers. Many of the common commercial adsorption processes are briefly reviewed in this chapter.

Product   Hot Fluid or Desorbent

Feed   Concentrated Solute
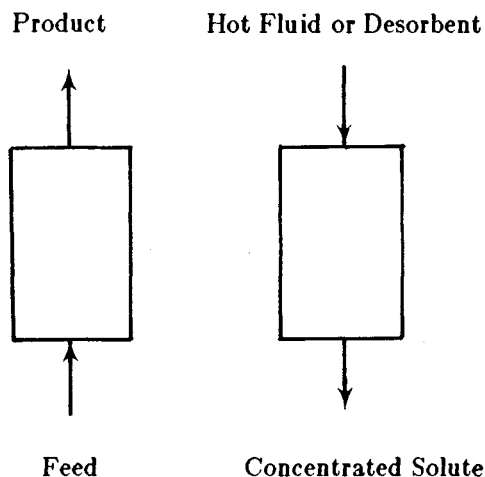
FIGURE 1-1.   Basic cycle for adsorption of a single solute. (A) Adsorption step. (B) Desorption.

Product

p_L p_H

Waste   F
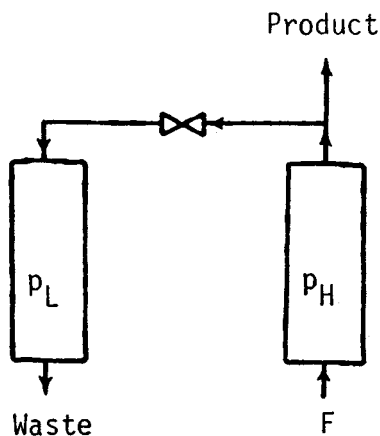
FIGURE 1-2.   Basic pressure swing adsorption apparatus.

    Chapter 4 covers cyclic operations which are somewhat more complex than those shown in Figure 1-1. Pressure swing adsorption (PSA) first adsorbs solute from a gas stream at elevated pressure and then desorbs the solute using a purge at much lower pressure. A very simple system is shown schematically in Figure 1-2. Since the volume of gas expands when depressurized, a larger volume but fewer moles of gas can be used for the purge step. Every few minutes the columns change functions. For liquid systems, parametric pumping and cycling zone adsorption are based on the shift in the equilibrium isotherm when a thermodynamic variable such as temperature is changed. Although this change in concentration is often small, a large separation can be built up by utilizing many shifts. A variety of cycles will be explored for both gas and liquid systems.

    The separation or fractionation of more than one solute by large-scale chromatography is the subject of Chapter 5. The basic method and typical results are illustrated in Figure 1-3. Solvent or carrier gas is continuously fed into a packed column and a pulse of feed is injected intermittently. Since different solutes travel at different velocities, they exit the column at
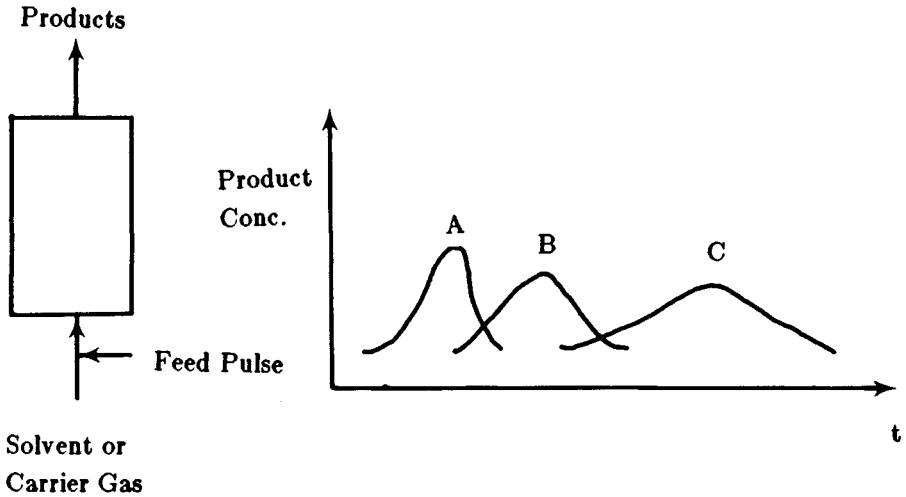
FIGURE 1-3.   Apparatus and results for chromatographic separation.

different times. Large-scale liquid chromatography, size exclusion chromatography (SEC), gas-liquid chromatography (GLC), biospecific affinity chromatography, and ion-exchange chromatography will be explored.

Countercurrent moving bed systems and simulated countercurrent systems are the subject of Chapter 6. For single solute removal the basic apparatus is shown in Figure 1-4. The function of the sorption and desorption chambers is the same as in Figure 1-1, but the countercurrent apparatus operates at steady state. To fractionate two solutes the moving bed arrangement shown in Figure 1-5 could be used. This is a steady-state apparatus for binary separation. Since it is difficult to move solids in a uniform plug flow, simulated moving bed (SMB) systems have been developed commercially. In an SMB the solid does not move. Instead, the location of each product and feed port is switched in the direction of fluid flow every few minutes. When a port location moves, an observer at that port sees the solid move in the opposite direction. Thus, countercurrent motion is simulated.

Chromatographic and simulated countercurrent processes both have advantages. These two processes are combined in hybrid chromatographic processes, which are discussed in Chapter 7. With column-switching procedures the products are removed at different locations in the column. In a moving-feed chromatograph the input location of the feed pulse moves up the column to follow the movement of solute. Then chromatographic development is used to completely separate the solutes. Moving port chromatography combines these two methods.

Two-dimensional and rotating methods are discussed in Chapter 8. The prototype two-dimensional system is the rotating annulus apparatus shown in Figure 1-6. The annulus is packed with sorbent while carrier gas or solvent flows continuously upward. Feed is added continuously at one point. The result is a steady-state separation similar to the results shown in Figure 1-3, but with the angular coordinate, θ, replacing time. Many other two-dimensional arrangements have been developed. Centrifugal chromatography, the chromatofuge, is also discussed.

Most real separation problems can be solved using any of several different operating methods. Hopefully, this compendium of operating methods will provide the designer with ideas for creating new schemes. The "best" scheme will vary depending on all the facets of the problem being solved.
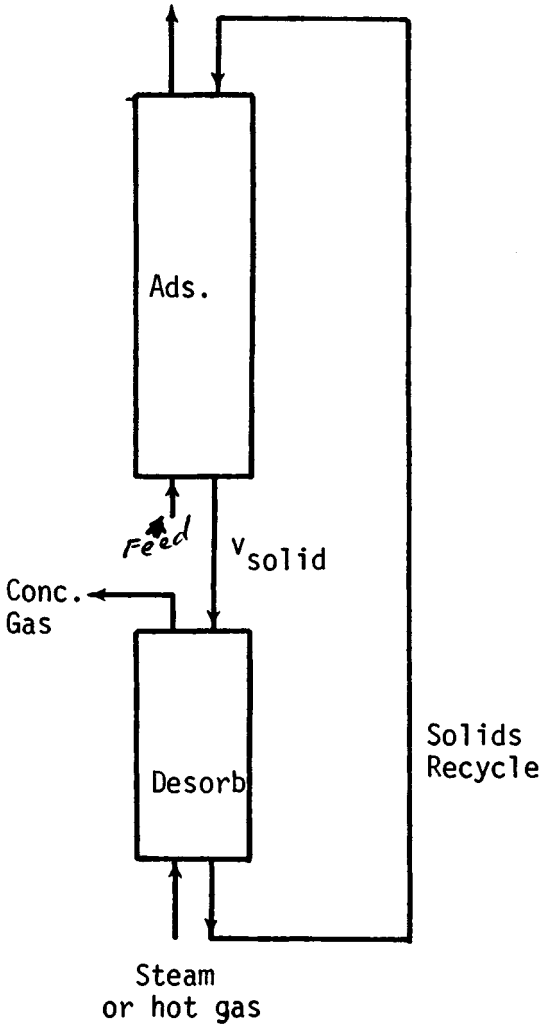
FIGURE 1-4.   Countercurrent system for single solute.
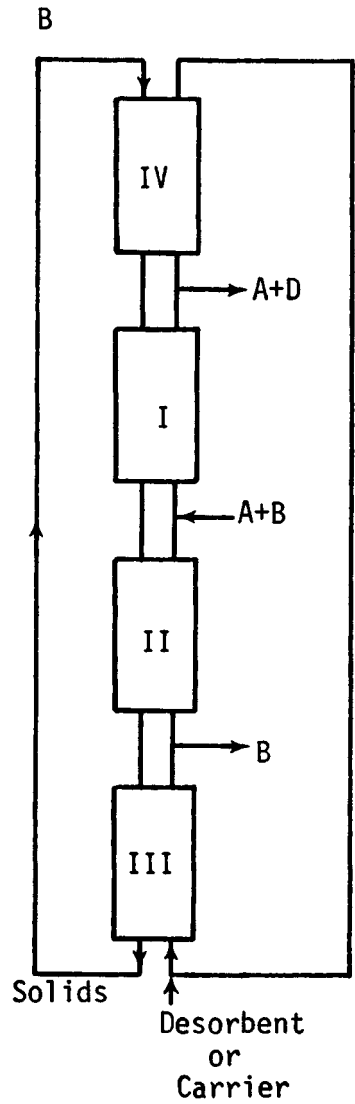
FIGURE 1-5.   Countercurrent system for fractionation of two solutes.
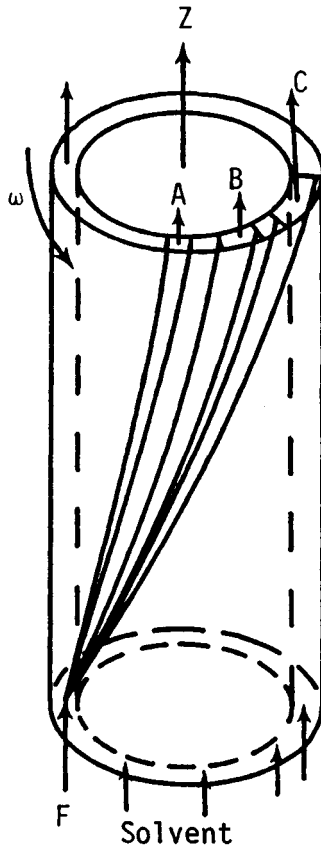
FIGURE 1-6. Apparatus and results for two-dimensional system.

Chapter 2

PHYSICAL PICTURE AND SIMPLE THEORIES FOR ADSORPTION AND CHROMATOGRAPHY

I. INTRODUCTION

What phenomena are involved in chromatographic and adsorptive separations? How do these phenomena combine to produce the desired separation? How can we simply predict the separation which will occur? In this chapter we will try to answer these and other questions. First, a physical picture of sorption will be presented. Then, equilibrium isotherms will be discussed. A physical argument will be used to explain movement of solute and energy in an adsorption column followed by a rigorous mathematical development of the equations. Zone spreading by mass transfer and diffusion will be explained mathematically for linear systems. The mass transfer zone (MTZ) or length of unused bed (LUB) approach will be introduced for nonlinear systems. The purpose of this chapter is to provide a physical understanding and relatively simple mathematical theories which will be useful in later chapters. This chapter is not a design manual; other sources should be consulted for design equations.[165,865,901,1015-1017]

II. PHYSICAL PICTURE

Commercially significant sorption operations (including adsorption, chromatography, ion exchange, ion exclusion, etc.) use sorbents which are highly porous and have large surface areas per gram of sorbent. The sorbent particles are commonly packed in a column as illustrated in Figure 2-1. In general, the particles will be of different sizes and shapes. They will pack in the column and have an average interparticle (between different particles) porosity of α. In a poorly packed bed α may vary considerably in different parts of the column. This can lead to poor flow distribution or channeling and will decrease the separation. Since the particles are porous, each particle has an intraparticle (within the particle) porosity, ϵ, which is the fraction of the particle which is void space. If the packing is manufactured uniformly, ϵ will be the same for all particles. Approximately 2% of the surface area is on the outer surface of the packing; thus, most of the capacity is inside the particles. An alternate model using a single porosity is also commonly used and is discussed in Section V.B.

The pores are not of uniform size. Large molecules such as proteins or synthetic polymers may be sterically excluded from some of the pores. The fraction of volume of pores which a molecule can penetrate is called K_d. Very small molecules can penetrate all the pores and $K_d = 1.0$ while very large molecules can penetrate none of the pores and $K_d = 0$. For a nonsorbed species, K_d can be determined from a simple pulse experiment. Very small nonsorbed species will have available both the external void volume V_o and the internal void volume V_i. Thus, small molecules will exit at an elution volume, V_e, of

$$V_e = V_o + V_i = \alpha \, V_{col} + (1 - \alpha)\epsilon \, V_{col} \qquad (2\text{-}1)$$

where V_{col} is the volume of the packed column. Since large molecules have available only the external void volume V_o, their elution volume is

$$V_e = V_o = \alpha \, V_{col} \qquad (2\text{-}2)$$
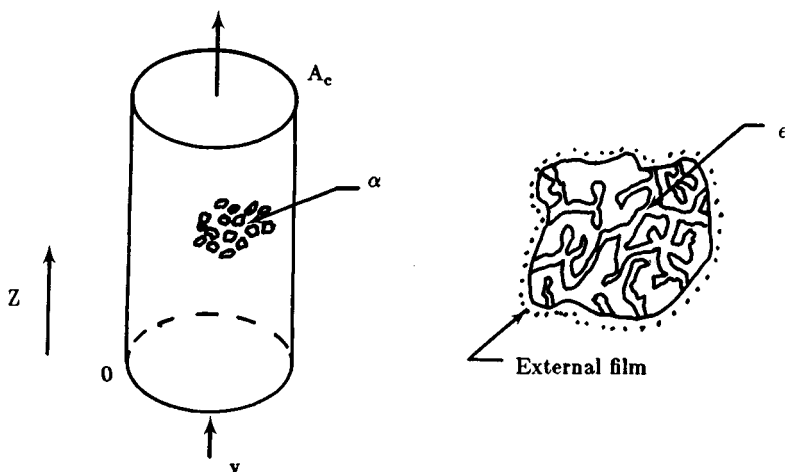
FIGURE 2-1.   Particles packed in a bed.

Equations 2-1 and 2-2 allow determination of V_o, α, V_i, and ϵ from one experiment with large molecules and one experiment with small molecules. Molecules of intermediate size can penetrate some of the pores. For these nonsorbed molecules, K_d can be determined from:

$$K_d = \frac{V_e - V_o}{V_i} \tag{2-3}$$

Size exclusion (gel permeation or gel filtration) separations are based entirely on differences in K_d.

This picture is somewhat too simple for some sorbents. Some activated carbons[792,1073] and ion exchange resins[18] have two types of pores: macropores and micropores. These particles have two internal porosities: one for macropores and one for micropores. The two internal and one external porosity can be measured by three experiments. Very small molecules will permeate all pores; large molecules will permeate only the macropores; very large molecules will stay in the external void volume. The solute movement theory presented later could be adjusted for these more complex systems, but K_d can be used to approximately include the two types of internal pores.

Molecular sieve zeolites differ from both these pictures.[105,168,645,865] The zeolite crystals form a porous three-dimensional array and have a highly interconnected, regular network of channels and cavities of very specific sizes. Thus the crystal geometry is well defined. Commercial zeolite adsorbents are pelleted agglomerates of zeolite crystals and binder. The binders have large pores and relatively little sorption capacity compared to the zeolite crystals. Typical values for void fractions are[645] interpellet = 32%, intercrystal = 23%, and intracrystal = 19% based on the fraction of the entire bed.

For the system shown in Figure 2-1, the processes which occur during a separation are as follows: Fluid containing solute flows in the void volume outside the particles. The solute diffuses through an external film to the particle. Here the solute may sorb on the external surface or (more likely) diffuse into the stagnant fluid in the pores. If the pores are tight for the solute this diffusion will be hindered. The solute finds a vacant site and then sorbs by physical or electrical forces or by a chemical reaction. While sorbed the solute may diffuse along the surface. The solute desorbs and diffuses through the pores, back across the external film, and into the moving fluid. A given molecule may sorb and desorb many

times during its stay inside a single particle. Once in the moving fluid the solute is carried along at the fluid velocity until the solute diffuses into another particle and the whole process is repeated. As far as migration down the column is concerned, the particle is either moving at the interstitial velocity, v, of the fluid or it has a velocity of zero when it is inside a particle.

A large number of adsorbents, ion exchange resins, partition chromatography supports, and size exclusion packings have been developed. The properties of these are available in the following sources: ion exchangers,[18,202,549,1016,1017,1076] size exclusion media,[549,827,1076,1109] activated carbon,[616,792,1016,1017] silica gel,[112,616,1016,1017] activated alumina,[112,438,616,1016,1017] chromatographic packings,[827,930,1076,1126] and molecular sieves.[105,112,168,616,645,865,1017] An extremely complete annotated bibliography of adsorption up to 1953 was compiled by Dietz.[321,322]

III. EQUILIBRIUM ISOTHERMS

A wide variety of equilibrium isotherms have been published.[18,105,168,645,792,825,865,1016,1017] A few of these will be reviewed for gas and liquid systems.

A. Gas Systems

For gas systems the adsorbed phase has essentially the same density as a liquid. This makes pure component equilibrium data very easy to obtain. The weight of the sorbent or the pressure can easily be measured. Many different adsorption isotherms have been developed to fit the results obtained. One of the simplest is the Langmuir isotherm.[589,629,692,809,865,1114] This isotherm is also appealing because either a simple physical picture[629,865] or a statistical mechanical argument[809,865] can be used to develop the isotherm. Langmuir assumed that at most a monolayer of adsorbate could cover the solid surface. If q is the adsorbent loading and $\bar{p}$ is the partial pressure, the Langmuir isotherm is

$$q = \frac{q_{max} \, K_A \, \bar{p}}{1 + K_A \, \bar{p}} \qquad (2\text{-}4)$$

where K_A is the sorption equilibrium constant and q_{max} is capacity at monolayer coverage. The shape of Equation 2-4 is shown in Figure 2-2A. This is known as a "favorable" isotherm, because this shape leads to sharp breakthrough curves. Since K_A is a reaction equilibrium constant, it should follow the Arrhenius relationship:

$$K_A = K_o \exp \left[-\Delta H/RT \right] \qquad (2\text{-}5)$$

The Langmuir isotherm is applicable for dilute, single-component adsorption with an inert gas present or for pure gases at low pressures.

At very low partial pressure the Langmuir equations takes the linear form:

$$q = K_A \, q_{max} \, \bar{p} \qquad (2\text{-}6)$$

The linear isotherm is extremely important not only because it is a limiting form of more complex isotherms when the solute is dilute, but also because the mathematical theories become much more tractable when the isotherm is linear.

If several solutes can adsorb the Langmuir isotherm can be extended to:[589,692,809,1114]

$$\frac{q_i}{q_{imax}} = \frac{K_i \, \bar{p}_i}{1 + \sum_{j=1}^{n} (K_j \, \bar{p}_j)} \qquad (2\text{-}7)$$
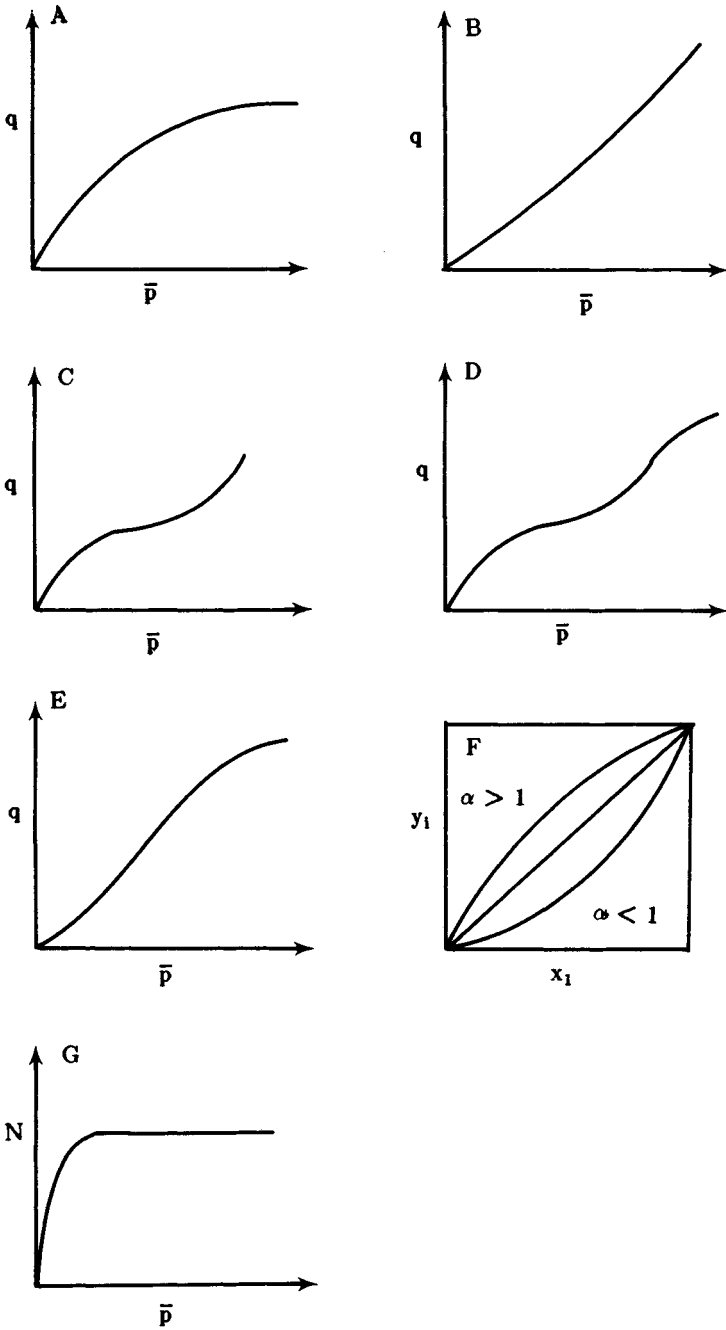
FIGURE 2-2.   Equilibrium isotherms. (A) Langmuir; (B) BET type 2 behavior (K
> 1); (C) BET type 3 behavior (K < 1); (D) BET type 4 behavior; (E) BET type 5
behavior; (F) Lewis correlation, constant α; (G) molecular sieve isotherm.

In addition to the previous assumptions, it is necessary to assume that the only interaction
of solutes is competition for sites on the adsorbent. In order for Equation 2-7 to be ther-
modynamically consistent, the monolayer coverages, q_{imax}, of all components must be equal.[652]
If the monolayer coverages differ, extra terms are required for thermodynamic consistency.[652]
Equation 2-7 predicts that less solute is adsorbed when other solutes are present. A few

systems will show cooperative adsorption where the presence of other solutes aids adsorption.[1100] Competitive adsorption is much more common.

Langmuir's isotherm is based on a specific physical picture of adsorption. The Langmuir isotherm agrees with data for some systems but not for others. (This is generally true of all isotherms. There are none that fit all systems.) When different physical pictures are used, different isotherms result. For example, by assuming that the forces involved in adsorption and in condensation are the same, and allowing for more than one molecular layer, Brunauer et al.[188,189] derived the BET isotherm. The simplest form of the BET equation is

$$\frac{q}{q_{mono}} = \frac{K\,\bar{p}}{[p^o + (K - 1)\,\bar{p}][1 - \bar{p}/p^o]} \tag{2-8}$$

where q_{mono} is the adsorbate concentration for monolayer coverage and p^o is the vapor pressure of pure solute at the adsorption temperature. The shape of Equation 2-8 depends on the values of the constants. If $K < 1$ the isotherm is unfavorable throughout and is shown in Figure 2-2B, while if $K > 1$ the isotherm is favorable at low concentrations and unfavorable at higher concentrations (Figure 2-2C). Other possible shapes which require a more complex equation[188,809,1114] are shown in Figures 2-2D and E. If $K \gg 1$ and $\bar{p} \ll p^o$ Equation 2-8 reduces to the Langmuir form. In the limit of very dilute systems Equation 2-8 becomes linear. The adsorption isotherms for many gas systems can be fit by one of the BET forms. This is true for both adsorption of a pure gas and adsorption of a gas when an inert carrier is present. Of course, just because the isotherms fit a BET form is not proof that the mechanism postulated in the derivation is correct.

As layers build up, eventually capillary condensation will occur. This will cause an inflection point in the isotherm as in Figures 2-2C and D. In the capillary condensation regime, results for adsorption and desorption will differ. Several plausible physical pictures for this hystersis have been suggested.[865]

For binary systems where both gases adsorb, Lewis et al.[589,651] developed a correlation for adsorption from the mixture compared to pure component adsorption. This equation is

$$\frac{q_1}{q_1^o} + \frac{q_2}{q_2^o} = 1 \tag{2-9}$$

where q_i^o is the amount adsorbed from a pure gas and q_i is the amount adsorbed from the mixture. With the additional assumption that the ratio

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{y_1/q_1}{y_2/q_2} = \frac{\bar{p}_1/q_1}{\bar{p}_2/q_2} \tag{2-10}$$

is a constant, Equations 2-9 and 2-10 can be used for predictions; y_i and x_i are the mole fractions in the gas and solid phase, respectively; α_{12} is a separation factor which is essentially the same as the relative volatility of a liquid vapor mixture. The shape of these isotherms is shown in Figure 2-2F.

Isotherms can also be derived from a thermodynamic argument.[809] For example, for the two-dimensional surface the pressure is replaced by the spending pressure and the volume by the area. For an ideal adsorbed solution Myers and Prausnitz[752] showed that mixture equilibrium isotherms could be predicted from pure component isotherms. The procedure has been extended to multilayer adsorption.[865,914] The ideal adsorbed solution theory has also been applied to heterogeneous surfaces.[749,1125] Unfortunately, these theories do not give a single equation which can be substituted into theories of adsorption.

Molecular sieve zeolite adsorbents behave differently than other adsorbents. Instead of

forming a surface layer the entire pore fills with adsorbed material. In addition, some solutes may be totally excluded since they are too large to fit in the pores. The loading ratio correlation (LRC)[639,645,1112] extends the Langmuir expression but replaces the monolayer capacity by the maximum attainable loading. For a pure component the loading ratio is

$$\frac{N}{N_o} = \frac{(k\bar{p})^{1/m}}{1 + (k\bar{p})^{1/m}} \tag{2-11}$$

where N is the loading on the adsorbent and N_o is the maximum attainable loading. Temperature effects can be included by using an Arrehenius relation for k and rearranging Equation 2-11:

$$\ln \bar{p} = A_1 + A_2/T + n \ln N/(N_o - N) \tag{2-12}$$

where n may also be temperature dependent. The shape of a typical molecular sieve isotherm is shown in Figure 2-2G. Equation 2-12 can be extended to multicomponent systems in the same way the Langmuir equation was extended. More detailed theories applicable to molecular sieve zeolites are discussed elsewhere.[105,168,188,589,809,865]

In gas-liquid chromatography (GLC) the phenomena is essentially absorption of the solute into the stationary liquid phase, not adsorption at a surface. At low concentrations the isotherms follow a Henry's law or linear relationship. At higher concentrations the isotherm shape is similar to Figure 2-2B. Absorption is favored as more solute dissolves in the stationary phase.

B. Liquid Systems

Adsorption from liquid systems is more complex than from gas systems. Extensive reviews are available.[589,671,750,865] Both solute and solvent compete for adsorbent surface. For dilute solutions of solid dissolved in a liquid the solvent effects can often be ignored and the Langmuir isotherm can be derived by the same procedure used for gases.[589]

$$q = \frac{q_{max} K_A c}{1 + K_A c} \tag{2-13}$$

For liquids it is common to generalize this to

$$q = \frac{a c}{1 + b c} \tag{2-14}$$

where a and b do not have to be $q_{max} K_A$ and K_A, respectively. The constants a and b can be fit to experimental data by plotting c/q vs. c. Extension to multisolute systems is analogous to Equation 2-7.

A better fit to experimental data at low concentrations can often be obtained with the Freundlich equation:[387,589]

$$q = k c^{1/n} \qquad n > 1 \tag{2-15}$$

Unfortunately, the Freundlich equation does not approach a linear isotherm for very dilute solutions, and it does not approach a limiting asymptotic value observed for many real systems.[589] Use of the Freundlich equation is discouraged.

Neither the Langmuir nor the Freundlich isotherms fit data for adsorption of organic

mixtures from aqueous solution on activated carbon. An empirical equation for multicomponent systems which fits this data is[392,865]

$$q_i = \frac{a_{io} \, c_i^{b_{io}}}{\beta_i + \sum_{i=1}^{n} a_{ij} \, c_i^{b_{ij}}} \tag{2-16}$$

of course, with five constants for one solute it is easier to fit any data. The Langmuir and Freundlich isotherms are special cases of Equation 2-16. Adsorption of organics on activated carbon has generated a ridiculously huge literature. The reader who feels compelled to attack this area can start with several reviews.[119,251,526,714,750]

For completely miscible binary liquid mixtures adsorption is complicated.[364,365,589] Over the entire range of mole fractions the component which is ''solvent'' must change. Except for molecular sieves, both components will compete for the adsorption surface. Experimental data is also much more difficult to obtain and interpret. The adsorbed layer has essentially the same density as the bulk liquid, and it is difficult to separate adsorbed material from liquid in the pores. A simple method[589] is to measure the decrease in mole fraction in component 1 (more strongly adsorbed) in the liquid.   From this a composite isotherm can be calculated

$$\frac{n_o \, \Delta x_1}{m} = n_1^s \, x_2 - n_2^s \, x_1 \tag{2-17}$$

where n_o is the original number of total moles of 1 plus 2, m is the mass of adsorbent, Δx_1 is the decrease in mole fraction of 1 in the liquid, n_1^s and n_2^s are the moles of 1 and 2 adsorbed per mass of adsorbent, and x_1 and x_2 are the mole fractions of 1 and 2 in the liquid. Three different classes of composite isotherms are shown in Figure 2-3.[589] In case A, component 1 is always most strongly adsorbed while in case B the preference switches. A negative Δx_1 on Figure 2-3B means that there is an increase in the mole fraction of component 1 in the liquid. For molecular sieves where component 2 is completely excluded from the pores n_2^s = 0 and Equation 2-17 becomes a straight line. This is illustrated in Figure 2-3C. In practice, the small amount of adsorption on the external surface will cause a slight curvature. The effect of temperature on the composite isotherm is shown in Figure 2-3D.

The composite isotherm does not give the individual isotherms directly except in the case of molecular sieves where component 2 is excluded. If it is assumed that the surface is completely covered by an adsorbed layer and that this layer is one molecule thick, then

$$\frac{n_1^s}{(n_1^s)_m} + \frac{n_2^s}{(n_2^s)_m} = 1 \tag{2-18}$$

where $(n_1^s)_m$ and $(n_2^s)_m$ are the number of moles of the pure components required to cover the surface of a unit weight of solid. This equation is essentially the same as Equation 2-9. From Equations 2-17 and 2-18, n_1^s and n_2^s can be calculated from the experimental data. Individual isotherms are shown in Figure 2-4A and B, while plots in terms of mole fractions are shown in Figure 2-4C and D. The use of Equation 2-18 does involve the assumption of a monolayer coverage. Unfortunately, for nonideal mixtures the monolayer coverage assumption is not thermodynamically consistent.[364] In these cases one must use a multilayer theory where there is a gradual change from surface to bulk properties, or a thermodynamic approach which does not postulate a physical model.[364,365]

The equations for adsorption of a solute from a very dilute solution are consistent with
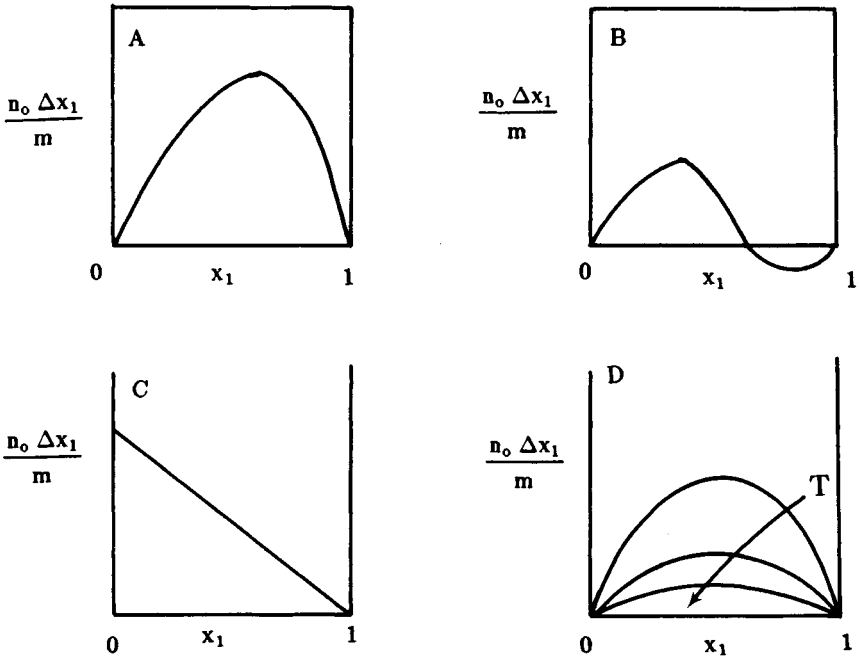
FIGURE 2-3. Composite isotherms for miscible liquids. (A) U-shaped, component 1 always preferred; (B) S-shaped, preferred component changes; (C) linear, for molecular sieves, component 2 excluded; (D) temperature effects for U-shaped composite isotherms.
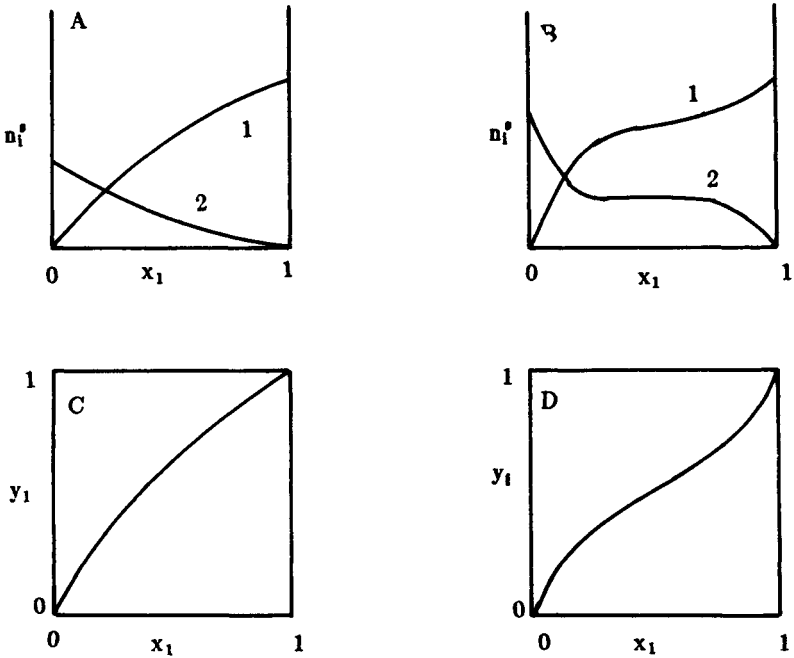
FIGURE 2-4. Individual isotherms for miscible liquids. (A,C) Component 1 always preferred; (B,D) preferred component changes.

the more general development given in Equations 2-17 and 2-18. For very dilute solutions $x_1 \simeq 0$, $x_2 \simeq 1.0$, and Equation 2-17 becomes:

$$\frac{n_o \, \Delta x_1}{m} = n_1^s \tag{2-19}$$

Thus the amount adsorbed can be determined directly from the change in concentration of the solution.

For ion exchange systems[18,484,1016] the situation is again different since ion exchange follows a stoichiometric material balance. For monovalent ion exchange

$$A^+ + R^-B^+ + X^- \rightleftarrows R^-A^+ + B^+ + X^-$$
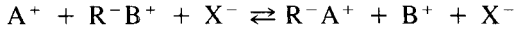
If the activity coefficients are all 1.0, the law of mass action gives an equilibrium expression

$$c_{RA} = \frac{c_{Rtotal} \, K_{AB} \, c_A}{c + (K_{AB} - 1) \, c_A} \tag{2-20}$$

where c_{Rtotal} is the total resin capacity in equivalents per bulk volume and c is the total concentration of ions in the liquid in equivalents per liter. It is convenient to work in terms of fractions:

$$y_i = \frac{c_{Ri}}{c_{Rtotal}} \quad , \quad x_i = \frac{c_i}{c} \tag{2-21}$$

Thus, for monovalent ions Equation 2-20 becomes:

$$y_A = \frac{K_{AB} \, x_A}{1 + (K_{AB} - 1)x_A} \tag{2-22}$$

For monovalent ions Equation 2-22 does not depend upon either the total ionic strength of the solution or the resin capacity (except for secondary effects due to the activity coefficients). Note that Equation 2-22 is a Langmuir-type form which will be favorable for A if $K_{AB} > 1$. The isotherms will have the same shape as those in Figure 2-2F if K_{AB} is constant. Selectivity values for a number of systems are available.[18,202,203,484,1016] Because the equilibrium forms are the same, solutions for Langmuir adsorption are also valid for binary ion exchange with constant selectivities.

For removal of a divalent ion the situation is different. Now the reaction is

$$D^{++} + 2R^-B^+ + 2X^- \rightleftarrows D^{++}R_2^- + 2B^+ + 2X^-$$
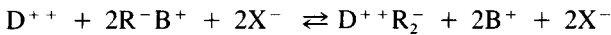
and the equilibrium expression is

$$\frac{y_B^2}{1 - y_B} = \left[\frac{1}{K_{DB} \dfrac{c_{Rtotal}}{c}} \right] \frac{x_B^2}{1 - x_B} \tag{2-23}$$

The general Langmuir form has been lost but the isotherm will be favorable for D if $(K_{DB} c_{Rtotal}/c) > 1$. Note that the isotherm now depends on both the total resin capacity and the liquid

concentration. This is important in the chemical regeneration of these systems. In real systems K_{DB} may not be constant.

IV. MOVEMENT OF SOLUTE AND ENERGY WAVES IN THE COLUMN

Separation occurs because different solutes move at different velocities. This solute movement is mainly controlled by the equilibrium, and solute movement can be predicted with a simple physical picture and some algebra. In Section IV.A a physical argument will be presented for the movement of uncoupled solutes. In Section IV.B the movement of pure energy waves will be explored and their effect on solute concentrations will be developed. In Section IV.C the "sorption effect" in gas systems will be explained. In Section IV.D, coupling effects between two solutes and between temperature and a solute are considered. The formal mathematical development will be presented in Section V.

A. Movement of Solute Waves in the Column

Solute diffuses between the moving mobile fluid and the stagnant fluid in the pores. While in the pores, solute may also adsorb on the solid (or dissolve into the stationary fluid coating the solid in GLC). Solute in the mobile phase moves at the interstitial velocity, v, of the mobile phase. Solute in the stagnant fluid or sorbed onto the solid has a zero velocity. Each solute molecule spends some time in the mobile fluid and then diffuses back into the stagnant fluid and so forth. Thus the movement of a given molecule is a series of random steps. The average velocity of all solute molecules of a given species is easily determined, but the randomness causes zone spreading.

If we consider a large number of solute molecules, this average velocity can be determined from the fraction of time they are in the mobile phase. Thus,*

$$u_{solute} = (v) \text{ (fraction solute in mobile phase)} \qquad (2\text{-}24)$$

If we consider an incremental change in solute concentration, Δc, which causes an incremental change in the amount sorbed, Δq, the fraction of this Δc in the mobile phase is

$$\text{Fraction incremental } \Delta c \text{ in mobile phase} =$$

$$\frac{\text{Amount in mobile phase}}{\text{Amount in (mobile + stagnant fluid + solid)}} \qquad (2\text{-}25)$$

For the system shown in Figure 2-1, each of the terms in Equation 2-25 is easily calculated. The incremental amount of solute in the mobile phase is

$$\text{Amount mobile} = (\Delta z \, A_c)\alpha \, \Delta c \qquad (2\text{-}26a)$$

In Equation 2-26a $(\Delta z \, A_c)$ is the volume of the column segment and α is the fraction of that volume which is mobile phase. The incremental amount of solute in the stagnant fluid is

$$\text{Amount in stagnant fluid} = (\Delta z \, A_c) (1 - \alpha)\epsilon \, K_d \, \Delta c \qquad (2\text{-}26b)$$

Here $(1 - \alpha)$ is the fraction of the fluid volume, $\Delta z \, A_c$, which is not mobile phase and ϵ is the fraction of this which is stagnant fluid. K_d tells what fraction of these pores are available to the solute. For the solid we have

$$\text{Amount on solid} = (\Delta z \, A_c) (1 - \alpha) (1 - \epsilon)\rho_s \, \Delta q \qquad (2\text{-}26c)$$

---

* This development is similar to but more complete than that in References 1051 to 1053, and 1056.

The first three terms give the volume which is solid. Since Δq is measured in kilogram moles per kilogram solid, the solid density ρ_s is required to convert from volume to weight. The solid density ρ_s is the structural density of the solid, i.e., of crushed solid without pores. Putting Equation 2-26 into Equation 2-25, we have

$$\text{Fraction} = \frac{(\Delta z \; A_c)\alpha \; \Delta c}{\Delta z \; A_c[\alpha \; \Delta c + (1 - \alpha)\epsilon \; K_d \; \Delta c + (1 - \alpha)(1 - \epsilon)\rho_s \; \Delta q]} \qquad (2\text{-}27)$$

Substituting Equation 2-27 into Equation 2-24 and rearranging we obtain:

$$u_s = \frac{v}{1 + \left(\dfrac{1 - \alpha}{\alpha}\right)\epsilon \; K_d + \left(\dfrac{1 - \alpha}{\alpha}\right)(1 - \epsilon)\rho_s \dfrac{\Delta q}{\Delta c}} \qquad (2\text{-}28)$$

The solute wave velocity, u_s, is the average velocity of the incremental amount of solute.

To use Equation 2-28 we must relate Δq to Δc. If we assume that solid and fluid are in equilibrium, then any of the equilibrium expressions developed in Section III can be used. Although a number of assumptions are now inherent in the physical derivation of u_s (see Section V), the result agrees quite well with experiment.

1. Solute Movement with Linear Isotherms

The simplest isotherm to use is the linear isotherm:

$$q_i = k_i(T)c_i \qquad (2\text{-}29)$$

Then $\Delta q/\Delta c = k_i(T)$, and Equation 2-28 becomes:

$$u_{s_i} = \frac{v}{1 + \left(\dfrac{1 - \alpha}{\alpha}\right)\epsilon \; K_{d_i} + \left(\dfrac{1 - \alpha}{\alpha}\right)(1 - \epsilon)\rho_s \; k_i} \qquad (2\text{-}30)$$

Equation 2-30 says that in the low concentration limit where the linear isotherm is valid there is a limiting solute velocity which does not depend on concentration. This solute velocity does depend upon temperature and other thermodynamic variables which change k_i. If we plot axial distance in the column z vs. time t, each solute will have a slope equal to its solute velocity. For an isothermal system this is illustrated in Figure 2-5A for a pulse of feed. The solute waves are drawn at the beginning and end of the feed pulse. Each solute moves at a constant velocity given by Equation 2-30, and the results for different solutes can be superimposed since we have assumed independent isotherms. The predicted outlet concentrations are the square waves shown in Figure 2-5B. Essentially the same results were first obtained by DeVault[320] using the equations first developed by Wilson.[1094] Obviously, the model is too simple since experimental results show zone spreading. This zone spreading will be discussed in Section VI. What is important here is that the simple theory accurately predicts where the peak maximum exit, and thus predicts whether or not a separation will occur (but not how good the separation is). The solute movement theory is simple enough to use with very complex operating methods, and it can easily be extended to nonlinear isotherms.

2. Solute Movement with Nonlinear Isotherms

In most large-scale adsorption and chromatography applications the concentrations are high enough that isotherms are nonlinear. For systems where there is only one solute $\Delta q/$
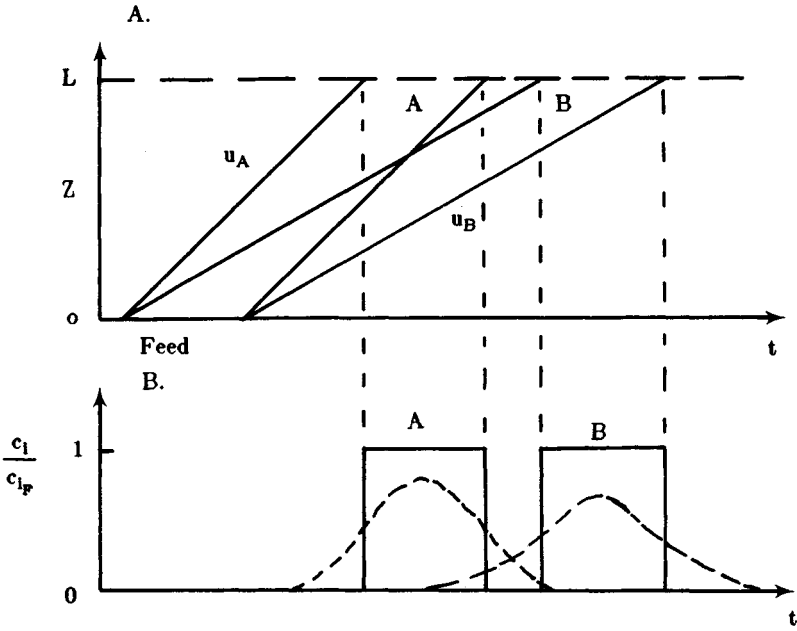
FIGURE 2-5. Solute movement theory for pulse input in an isothermal system with linear isotherms. (A) Solute movement in column; (B) product concentrations. —— Predicted; ---- experimentally observed.

Δc will be a function of the solute concentration. Hence, the solute wave velocity given by Equation 2-28 will also depend upon concentration. The specific effects actually depend upon the isotherm form used. For dilute systems the Langmuir isotherm (Equations 2-4, 2-13, or 2-14) is often a good approximation of the equilibrium data. Suppose that a column is first saturated with a concentrated solution, c_h and this is then displaced with a dilute solution, c_l (see Figure 2-6A). The value of $\Delta q/\Delta c$ now increases monotonically as concentration decreases from c_h to c_l. Thus $\Delta q/\Delta c$ can be approximated by the derivative, where Equation 2-14 has been used for the isotherm form. Equation 2-31 can be substituted into Equation 2-28:

$$\frac{\Delta q}{\Delta c} \simeq \left(\frac{\partial q}{\partial c}\right)_T = \frac{a}{(1 + bc)^2} \tag{2-31}$$

$$u_s = \frac{v}{1 + \dfrac{(1 - \alpha)}{\alpha} \epsilon K_d + \dfrac{(1 - \alpha)}{\alpha}(1 - \epsilon)\rho_s \dfrac{a}{(1 + bc)^2}} \tag{2-32}$$

This equation shows that u_s is now a function of concentration and that the solute velocity decreases monotonically as concentration decreases.

This result is easily shown on a distance vs. time diagram. Figure 2-6A shows the feed to the column when a high concentration fluid is displaced by a fluid of zero concentration. Figure 2-6B shows the z vs. t diagram. Until time t_o, all solute moves at a solute velocity u_s (c_h) which can be calculated from Equation 2-32. At t_o a "diffuse wave" or "fan" is generated. This occurs because the concentration at this point (z = 0, t = t_o) varies from c_h to c_l. Each concentration generates a solute wave with a slope u_s (c) as shown in Figure 2-6B. By choosing arbitrary concentrations between c_h and c_l, a number of solute waves in
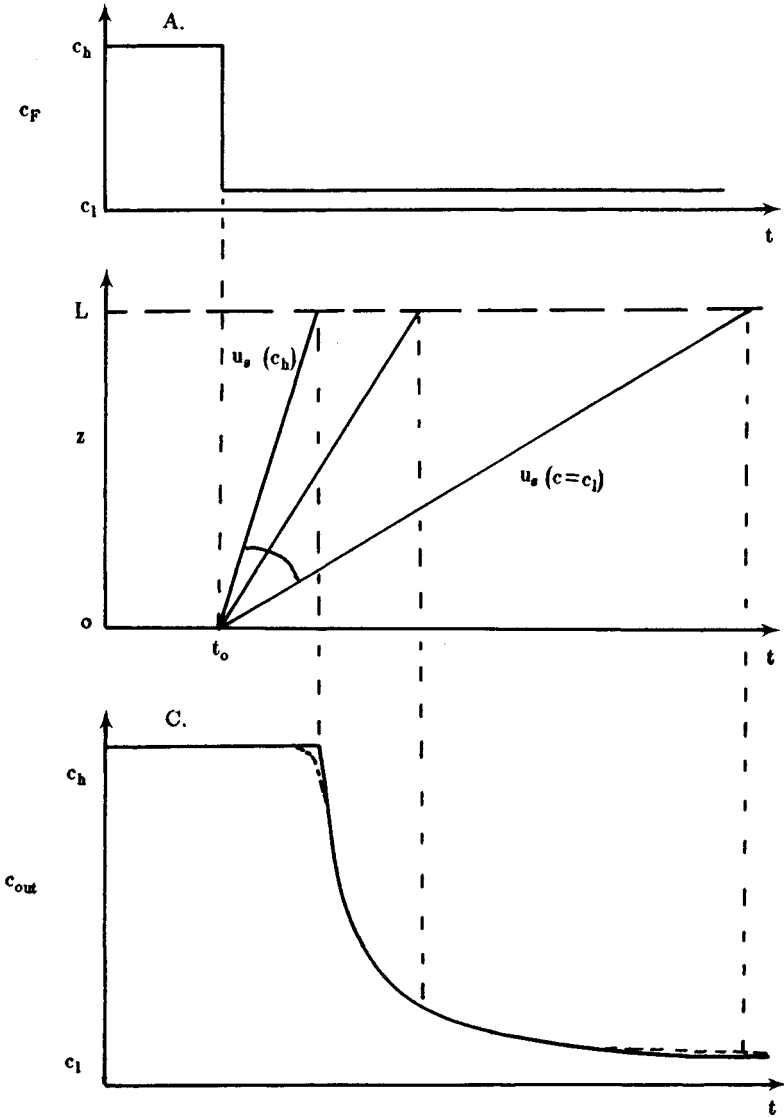
FIGURE 2-6. Solute movement theory for displacement of a concentrated solution by a dilute solution for Langmuir isotherm. (A) Feed composition; (B) solute movement in column; (C) product concentration. —— Predicted; ---- experimentally observed. Note that scales in parts A and C differ.

the diffuse wave can be drawn. In Figure 2-6C these are projected into the product concentration vs. time diagram to predict the outlet concentration profile. If the column is made longer, the spread between the fastest and slowest waves increases and the diffuse wave grows in direct proportion to the column length. This is called "proportional pattern behavior". Similar results were obtained by DeVault,[320] Walter,[1031] and Weiss[1081] using different developments, and are reviewed in several sources.[165,865,901,1015-1017]

Comparison of experimental data and predictions for the effluent concentration show that there is often excellent agreement for both adsorption[901] and for chromatography.[385] This agreement is illustrated schematically in Figure 2-6C. The reason for the agreement between theory and experiments for diffuse waves is the isotherm effect controls. Additional zone spreading caused by mass transfer resistances and axial dispersion are almost negligible.
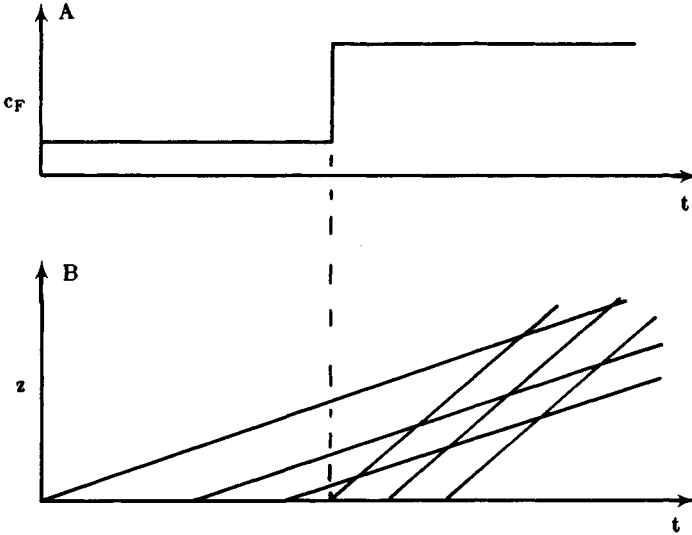
FIGURE 2-7. Concentrated material displacing dilute material for Langmuir isotherm. (A) Feed; (B) solute movement in column, Equation 2-32, impossible case.
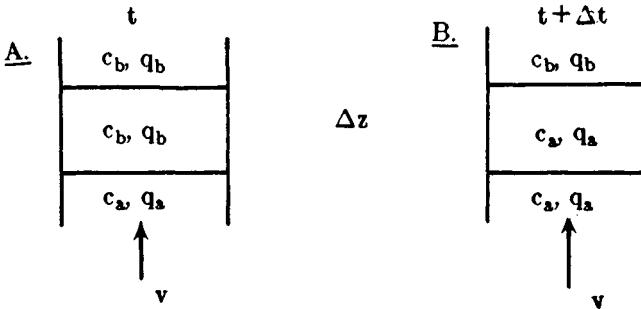
FIGURE 2-8. Control volume for mass balance for shock wave. (A) Shock wave enters control volume; (B) shock wave leaves control volume.

Any equilibrium data which is ''favorable'' and has the same general shape as the Langmuir isotherm will have similar diffuse wave behavior. The equation for other isotherms is easily derived by determining $\partial q/\partial c$ and substituting this for $\Delta q/\Delta c$ in Equation 2-28. If an isotherm equation is not available, the solute wave velocity at any concentration can be predicted by determining the isotherm slope either graphically or numerically and using this slope as the local value of $\partial q/\partial c$.

For favorable isotherms, if a dilute solution is displaced by a concentrated solution the situation is very different. Now Equation 2-32 for a Langmuir isotherm predicts that the more concentrated, faster-moving waves overtake the less concentrated, slower-moving waves. As shown in Figure 2-7B, this equation predicts a series of intersections of two waves of different concentrations. This implies that there is a region of the column where two different concentrations occur simultaneously. This is obviously physically impossible. The reason why this physically impossible prediction occurs is we assumed in Equation 2-31 that c and q were continuous functions. This is apparently not the case, and Equations 2-31 and 2-32 are not valid for the feed shown in Figure 2-7A.

Since concentration is not continuous inside the column, we must have a ''shock'' or discontinuous wave. To analyze this a macroscopic mass balance can be used. Figure 2-8

shows a macroscopic section of the column of height Δz. We wish to do a mass balance for the time period, Δt, during which the shock wave passes through this section of the column. If the shock wave velocity is u_{sh}, then the time required for the shock wave to move a distance Δz is

$$\Delta t = \frac{\Delta z}{u_{sh}} \tag{2-33}$$

In Figure 2-8, c_a and q_a are the fluid concentration and amount adsorbed *after* the shock wave has passed, where c_b and q_b refer to *before* the shock wave. We assume solid and fluid are in equilibrium at each point. For the feed shown in Figure 2-7A, $c_a = c_{low}$ and $c_b = c_{high}$. The mass balance for period Δt over segment Δz is

$$\alpha v c_a \Delta t - \alpha v c_b \Delta t - [\alpha + K_d \epsilon (1 - \alpha)](c_a - c_b)\Delta z$$

$$- [(1 - \alpha)(1 - \epsilon)] \rho_s (q_a - q_b)\Delta z = 0 \tag{2-34}$$

The first term in Equation 2-34 is input, the second term is minus the output, and the third and fourth terms are minus the accumulation in segment Δz. Substituting in Equation 2-33 and solving for the shock wave velocity we obtain:

$$u_{sh} = \frac{v}{1 + \dfrac{1 - \alpha}{\alpha}\, \epsilon\, K_d + \dfrac{(1 - \alpha)}{\alpha}\,(1 - \epsilon)\rho_s\left(\dfrac{q_a - q_b}{c_a - c_b}\right)} \tag{2-35}$$

Comparing Equations 2-28 and 2-35, we see that they are essentially the same. In Equation 2-35, $\Delta q/\Delta c$ has been defined as the difference across the shock wave. The shock wave velocity depends on $c_a = c_{high}$ and $c_b = c_{low}$ plus the isotherm. The term $(q_a - q_b)/(c_a - c_b)$ is the slope of the chord of the isotherm from the initial condition (c_b, q_b) to the final condition (c_a, q_a). This term can be calculated from the isotherm equation or from the equilibrium data. If the Langmuir isotherm is used, Equation 2-14 is substituted in for q_a and for q_b in Equation 2-35. For favorable isotherms:

$$u_s(c_{high}) > u_{sh} > u_s(c_{low}) \tag{2-36}$$

The shock wave calculation is shown in Figure 2-9. Note in Figure 2-9B that Equation 2-36 is satisfied. The product concentration shown in Figure 2-9C is a sharp jump which will be the same regardless of the column length. The shock wave shown in Figure 2-9C is different from the linear isotherm result shown in Figure 2-5B. The linear isotherm predicts no change in shape of the added pulse. If the input wave is not sharp it will stay this way with a linear isotherm. With a shock wave the diffuse input will be sharpened into a shock. This difference is illustrated in Figure 2-10. With a nonlinear isotherm the feed in Figure 2-10A will generate a series of shocks which intersect each other and eventually form a single shock wave (if the column is long enough) which gives the product concentration shown in Figure 2-10C. The linear isotherm transmits the input without change in shape (Figure 2-10B). Other developments for the shock wave are given in several reviews.[165,901,1016]

In actual practice, finite mass transfer rates, diffusion, and dispersion will spread out the shock wave as shown by the dotted line in Figure 2-9C. The sharpening effect of the shock wave illustrated in Figure 2-10 and the dispersive effects reach a balance so that a "constant pattern" is eventually obtained. Then, no matter how long the column, the shape shown by the dotted line in Figure 2-9C does not change. This S-shaped region of changing concen-
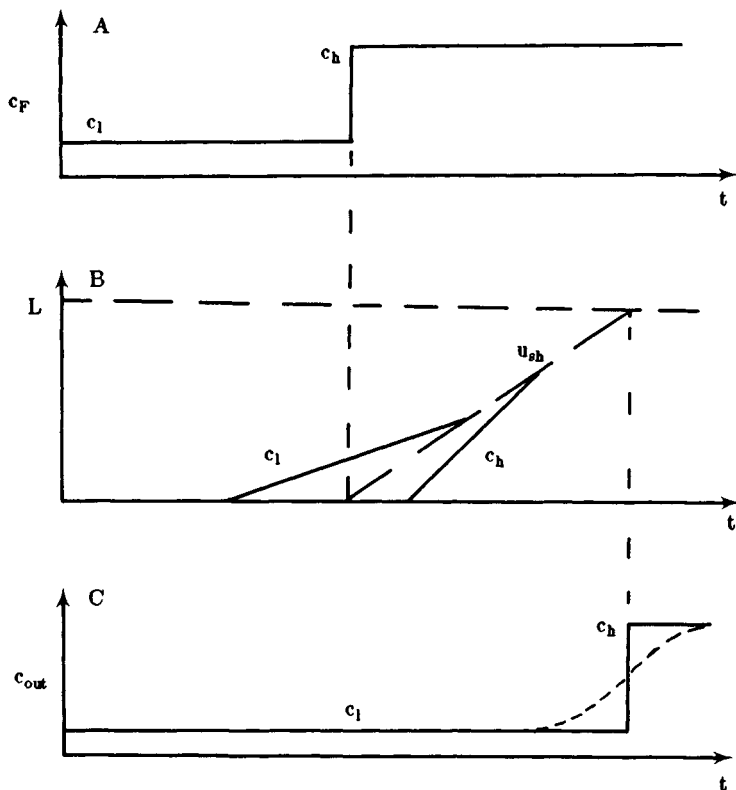
FIGURE 2-9. Concentrated material displacing dilute material for favorable isotherm. (A) Feed; (B) shock wave solution for solute movement in column; (C) predicted product concentration.

tration is called the "mass transfer zone". This constant pattern greatly simplifies the difficulty of including mass transfer in the theory and is discussed in Section VII. Once the constant pattern has been formed the movement of the mass transfer zone (MTZ) can be shown on a solute movement diagram.

This solution method for nonlinear isotherms can also be applied to monovalent, binary ion exchange[1015-1017] and to GLC.[1006] With a constant equilibrium constant the ion exchange equilibrium is given by Equation 2-22, which has the same form as the Langmuir expression. Thus, Figures 2-6, 2-9, and 2-10C could also be for binary ion exchange. Concentrations are now fractions, x_A (see Equation 2-22), of ion A. Fraction of ion B can be found as $1 - x_A$.

For GLC, the isotherms have the opposite curvature of a Langmuir isotherm and are shown schematically in Figure 2-2B. Diffuse and shock waves still occur, but in the reverse situations as for Langmuir isotherms. Thus in GLC a shock wave occurs when a dilute gas displaces a concentrated gas. The methods of constructing the diagrams are the same, but the diagrams look "backwards" compared to adsorption. With more complex isotherms such as BET type 3, 4, and 5 isotherms (Figures 2-2C to E), interacting shock and diffuse waves can occur.

B. Movement of Pure Energy Waves

If the heat of adsorption and the heat of mixing are negligible and the column is adiabatic, then we have a pure energy wave. That is, the adsorption and desorption of solutes will not affect the column temperature although temperature does affect the isotherms. These as-
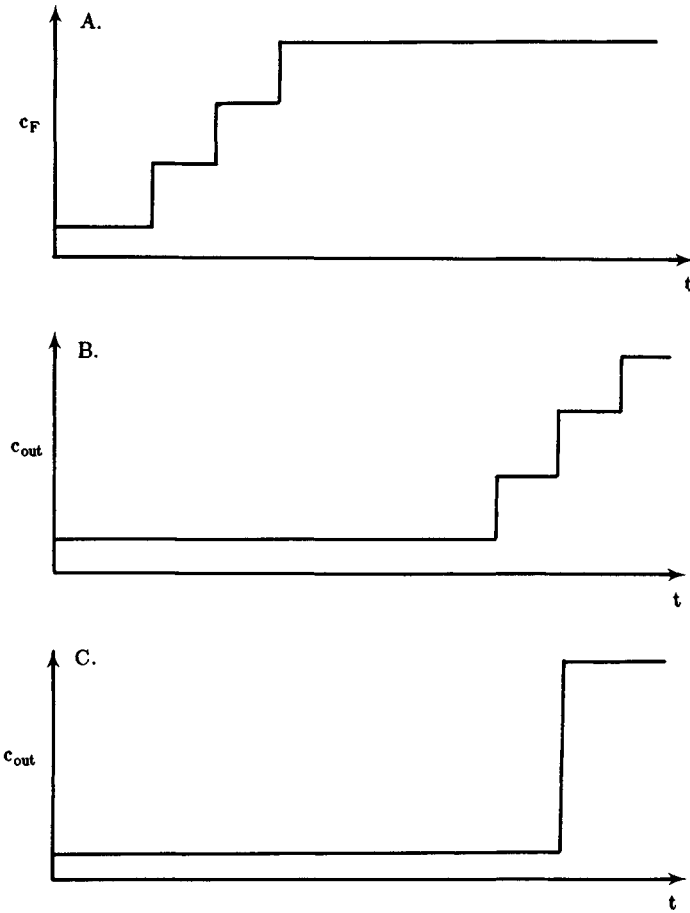
FIGURE 2-10. Effect of changing input wave. (A) Feed; (B) predicted outlet concentration for linear isotherm; (C) predicted outlet concentration for favorable isotherm.

sumptions are reasonable in many liquid systems and in very dilute gas systems. The movement of a pure energy wave can be determined from an analysis similar to that used previously for solute movement.

1. Thermal Wave Velocity

The velocity of the energy wave, u_{th}, can be found from the fraction of energy in the mobile phase times the interstitial fluid velocity.

$$u_{th} = \left(\frac{\text{Energy in mobile phase}}{\text{Total energy in segment}}\right) v \qquad (2\text{-}37)$$

The fraction of energy stored in the mobile phase is

$$\frac{\text{Energy in mobile phase}}{\text{Total energy in segment}} =$$

$$\frac{\text{Energy in mobile phase}}{\text{Energy in: (mobile + stagnant fluid + solid + wall)}} \qquad (2\text{-}38)$$

FIGURE 2-11. Movement of pure energy waves in a column. (A) Feed; (B) energy waves in column; (C) outlet temperatures. —— Predicted; ---- experimental.

$$\Delta t = \frac{\Delta z}{u_{th}} \qquad (2\text{-}42)$$

The mass balance over length Δz and time Δt is

$$\alpha v(c_a - c_b)\Delta t - [\alpha + K_d \epsilon(1 - \alpha)] (c_a - c_b)\Delta z$$

$$- [(1 - \alpha)(1 - \epsilon)]\rho_s(q_a - q_b)\Delta z = 0 \qquad (2\text{-}43)$$

Substituting in Equation 2-42 and rearranging we have

$$\left[\alpha + \epsilon(1 - \alpha)K_d - \frac{\alpha v}{u_{th}}\right](c_a - c_b) + (1 - \alpha)(1 - \epsilon)\rho_s(q_a - q_b) = 0 \quad (2\text{-}44)$$

Now u_{th} is known from Equation 2-41 and the conditions before the intersection with thermal wave, c_b and q_b, are also known. We wish to determine the values c_a and q_a after the intersection. To do this we assume local equilibrium and solve Equation 2-44 simultaneously with the isotherm equation.

For linear isotherms (Equation 2-29) this simultaneous solution is simple. After some rearrangement the result is
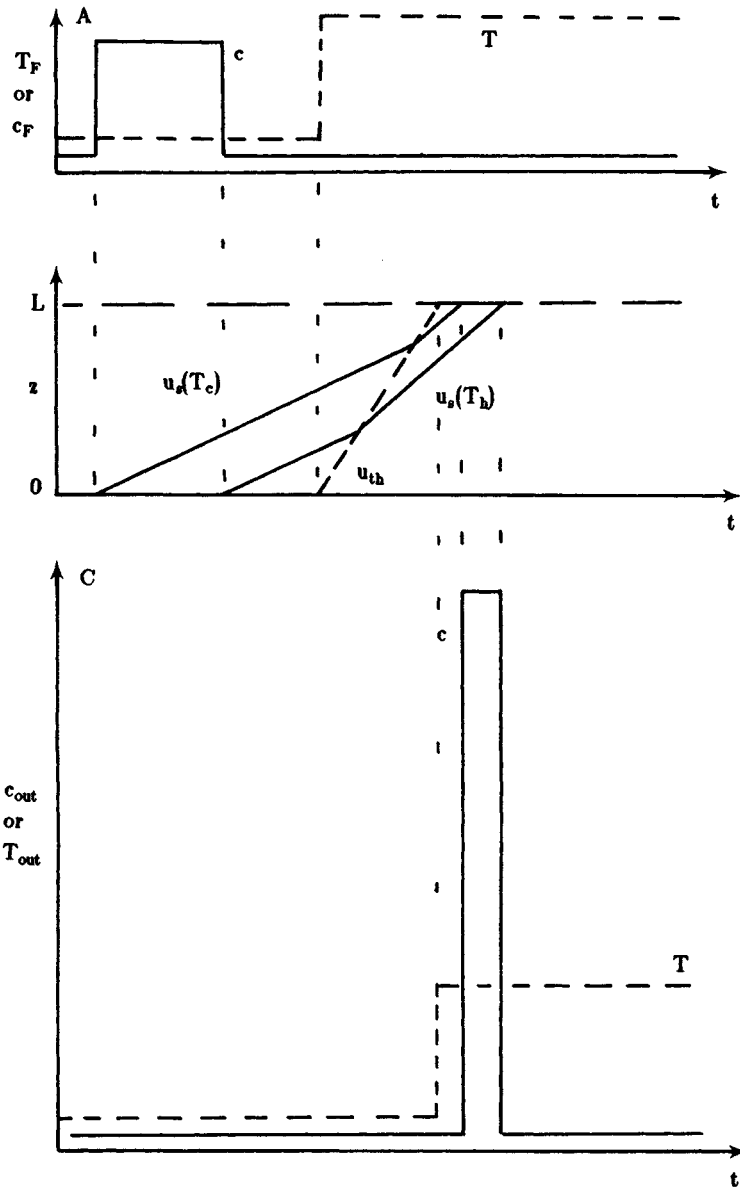
FIGURE 2-12. Effect of thermal wave on solute with a linear isotherm. (A) Feed; (B) waves in column; (C) predicted outlet concentration and temperature.

$$\frac{c(T_h)}{c(T_c)} = \frac{\dfrac{1}{u_s(T_c)} - \dfrac{1}{u_{th}}}{\dfrac{1}{u_s(T_h)} - \dfrac{1}{u_{th}}} \tag{2-45}$$

Equation 2-45 was first developed by Baker and Pigford.[74] In a typical dilute liquid system $u_{th} > u_s(T_h) > u_s(T_c)$ and Equation 2-45 predicts $c(T_h) > c(T_c)$. This is shown in Figure 2-12C.

For gas systems we may have $u_s(T_h) > u_s(T_c)$ and $c(T_c) > c(T_h)$. This is opposite to our

intuition but does agree with some experimental results. If $u_s(T_h) > u_{th} > u_s(T_c)$, Equation 2-45 predicts a negative concentration which is physically impossible. In this case the nonlinear mass balance Equation 2-44 must be solved.

An alternate way to heat or cool the column is to use a jacket or heating coils. This is called the direct mode. Now the entire length of the column is heated or cooled simultaneously. Thus, u_{th} is essentially infinite, and Equation 2-45 becomes:

$$\frac{c(T_h)}{c(T_c)} = \frac{u_s(T_h)}{u_s(T_c)} \tag{2-46}$$

If the equilibrium constant $k_i(T)$ decreases as temperature increases, Equation 2-46 predicts that $c(T_h) > c(T_c)$. That is, as solute desorbs it diffuses into the fluid and increases the fluid concentration. Equation 2-46 is valid for both gases and liquids.

For nonlinear equilibrium a simple closed form result is usually not attainable. The mass balance (Equation 2-44), and the isotherm equation often have to be solved simultaneously.

This analysis is also applicable if a thermodynamic variable other than temperature (e.g., pH) is changed. Equations 2-44 to 2-46 are valid but with u_{th} replaced by the velocity of this thermodynamic variable.

C. Effect of Velocity Changes

In the preceding two sections we assumed that the interstitial fluid velocity v was a constant. For liquids the density of adsorbed material is approximately the same as the density of the liquid. If the liquid density does not change drastically with composition, then the overall density of the liquid is roughly constant. This implies that v will be constant if the porosities are constant. A significant density change will cause v to vary; however, for liquids this is the exception, not the rule. For gases the density of the adsorbed phase is approximately the same as the liquid density. Thus when gas adsorbs there must be a decrease in volume which will cause a decrease in the velocity. When the solute desorbs, the opposite happens and v increases. This effect produces a shock wave when gas adsorbs since the faster-moving material is displacing the slower-moving material. A diffuse wave results during desorption. These effects will occur for any type of isotherm and are called "the sorption effect".

Quantitatively we can study the sorption effect by doing a mass balance for a control volume. We will assume the pores are readily available to all species. The solute mass balance over time Δt and length Δz is

$$\alpha v_a c_a \Delta t - \alpha v_b c_b \Delta t - [\alpha + \epsilon(1 - \alpha)](c_a - c_b)\Delta z$$

$$- (1 - \alpha)(1 - \epsilon)\rho_s(q_a - q_b)\Delta z = 0 \tag{2-47}$$

which differs from Equation 2-34 since v will have different velocities before and after the sorption wave. Equation 2-47 can be written for each solute. We can also write an overall balance

$$\alpha v_a \bar{\rho}_{f_a} \Delta t - \alpha v_b \bar{\rho}_{f_b} \Delta t - [\alpha + \epsilon(1 - \alpha)](\bar{\rho}_{f_a} - \bar{\rho}_{f_b})\Delta z$$

$$- (1 - \alpha)(1 - \epsilon)\rho_s(\bar{q}_a - \bar{q}_b)(\Delta z) = 0 \tag{2-48}$$

where $\bar{\rho}_{f_a}$ and $\bar{\rho}_{f_b}$ are molar densities and $\bar{q}_i$ are total amounts adsorbed. To keep the situation as simple as possible we will assume an ideal gas at constant temperature and pressure. Then the molar density is constant and $\bar{\rho}_{f_a} = \bar{\rho}_{f_b} = \bar{\rho}_f$. We will also assume that the isotherm

is linear, Equation 2-29, and that there is only one species which will adsorb plus a non-adsorbed carrier.

The analysis is different for diffuse and for shock waves. For diffuse waves we can solve both Equation 2-47 and 2-48 for $\Delta z/\Delta t$ and take the limit as $\Delta t \to 0$. This limit does exist for diffuse waves, and $\Delta c \to 0$ as $\Delta t \to 0$. The results for linear systems are

$$\lim_{\Delta t \to 0} \frac{\Delta z}{\Delta t} = \frac{\alpha}{\alpha + \epsilon(1 - \alpha) + (1 - \alpha)(1 - \epsilon)\rho_s k} \frac{d(vc)}{dc} \tag{2-49}$$

and

$$\lim_{\Delta t \to 0} \frac{\Delta z}{\Delta t} = \frac{\bar{\rho}_f \alpha}{(1 - \alpha)(1 - \epsilon)\rho_s} \frac{1}{k} \frac{dv}{dc} \tag{2-50}$$

Setting these equations equal and rearranging we eventually obtain

$$\frac{dv}{dy} = \frac{[(1 - \alpha)(1 - \epsilon)\rho_s k]v}{\alpha + \epsilon(1 - \alpha) + [(1 - \alpha)(1 - \epsilon)\rho_s k](1 - y)} \tag{2-51}$$

where y is the mole fraction of adsorbate

$$y = \frac{c}{\bar{\rho}_f} \tag{2-52}$$

Equation 2-51 can be rearranged and integrated.

$$\int_{v_{in}}^{v} \frac{dv}{v} = \int_{y_{in}}^{y} \frac{[(1 - \alpha)(1 - \epsilon)\rho_s k]dy}{\alpha + \epsilon(1 - \alpha) + [(1 - \alpha)(1 - \epsilon)\rho_s k](1 - y)} \tag{2-53}$$

The result of the integration is

$$v = \frac{v_{in}[\alpha + \epsilon(1 - \alpha) + (1 - \alpha)(1 - \epsilon)\rho_s k(1 - y_{in})]}{\alpha + \epsilon(1 - \alpha) + (1 - \alpha)(1 - \epsilon)\rho_s k(1 - y)} \tag{2-54}$$

For a diffuse wave where $y_{out} > y_{in}$, Equation 2-54 predicts that $v_{out} \geq v_{in}$ since adsorbate is desorbing.

The wave velocity can be determined by substituting Equation 2-54 into either Equation 2-49 or 2-50 and realizing that[865,1051]

$$u_{wave} = \lim_{\Delta t \to 0} \frac{\Delta z}{\Delta t} \tag{2-55}$$

The result is

$$u_{wave} = \frac{\alpha[\alpha + \epsilon(1 - \alpha) + (1 - \alpha)(1 - \epsilon)\rho_s k]v_{in}}{[\alpha + \epsilon(1 - \alpha) + (1 - \alpha)(1 - \epsilon)\rho_s k(1 - y)]^2} \tag{2-56}$$

This predicts that the wave velocity increases as y increases. Equations 2-55 and 2-56 agree with results derived by a different method.[865]

The sorption effect for a diffuse wave is shown in Figure 2-13. Note that the resulting
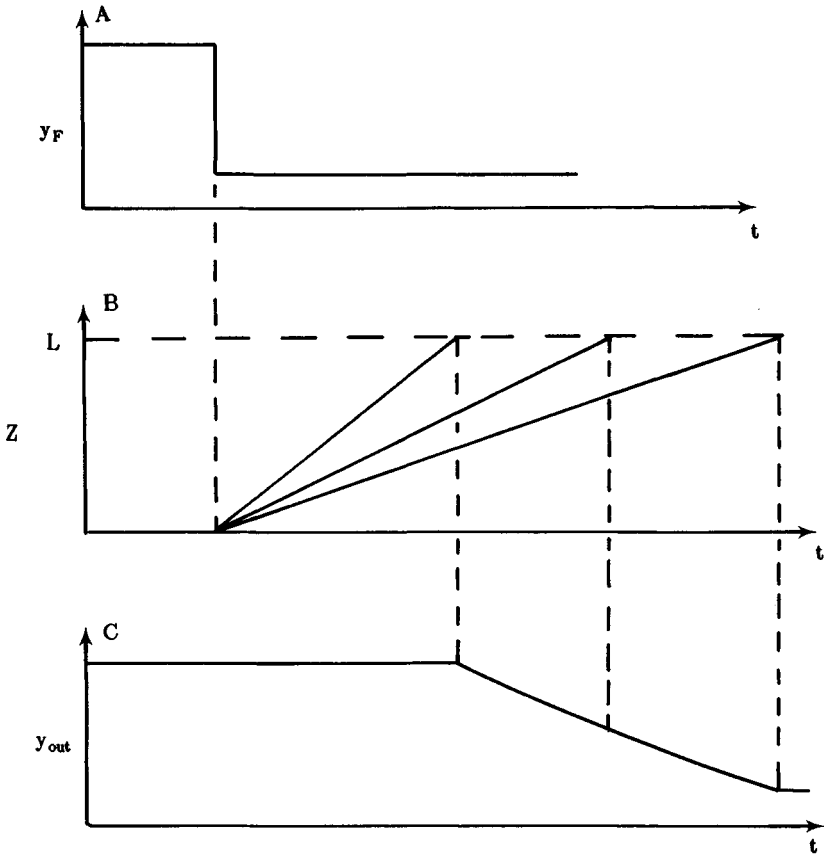
FIGURE 2-13. Sorption effect for dilute wave displacing a concentrated wave for linear isotherms. (A) Feed; (B) solution using Equation 2-56; (C) predicted product concentration.

outlet concentration is very similar to that predicted for a diffuse wave caused by a nonlinear isotherm.

When a concentrated solution displaces a dilute solution, Equation 2-56 predicts that solute waves cross. This will be similar to Figure 2-7B and is physically impossible. In this case the limit in Equations 2-49 and 2-50 does not exist. Now the balances used in Equations 2-47 and 2-48 must be over finite Δz and Δt. The time increment Δt must be related to Δz:

$$\Delta t = \frac{\Delta z}{u_{wave}} \tag{2-57}$$

Now we can solve Equations 2-47, 2-48, and 2-57 for the fluid velocity and the wave velocity. The results are

$$v_b = v_a \left[\frac{\alpha + \epsilon(1 - \alpha) + (1 - \alpha)(1 - \epsilon)\rho_s k(1 - y_a)}{\alpha + \epsilon(1 - \alpha) + (1 - \alpha)(1 - \epsilon)\rho_s k(1 - y_b)} \right] \tag{2-58}$$

and

$$u_{wave} = \frac{\alpha v_a}{\alpha + (1 - \alpha)\epsilon + (1 - \alpha)(1 - \epsilon)\rho_s k(1 - y_b)} \tag{2-59}$$
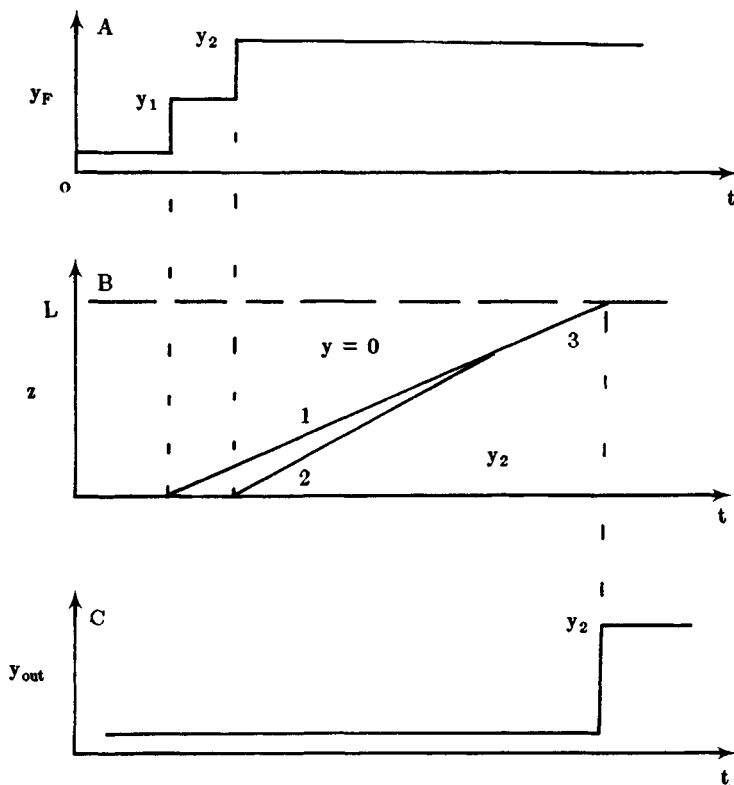
FIGURE 2-14.   Sorption effect for concentrated wave displacing a dilute wave for linear isotherms for series of steps. (A) Feed; (B) solution using Equation 2-59; (C) predicted product concentration.

where $y_a \geqslant y_b$. These results can also be obtained from a balance around the entire column. Note that the wave velocity depends on the conditions before the shock while the downstream velocity depends on conditions on both sides of the shock wave.

The sorption effect for a shock wave is shown in Figure 2-14. A series of steps are shown so that the shock wave effect will be obvious. Wave 1 sees $y_b = 0$ and has the wave velocity which would normally be expected for a linear isotherm. However, the downstream velocity $v_b < v_a$ since $y_a = y_1$. Wave 2 sees $y_b = y_1$ and thus moves faster than wave 1. The two waves eventually intersect to form wave 3. This wave sees $y_b = 0$ and has the same velocity as wave 1. The downstream fluid velocity will be different. The outlet mole fraction shown in Figure 2-14C appears as a shock wave.

For nonlinear isotherms the sorption and isotherm effects may reinforce or oppose each other. If the isotherm is favorable (Langmuir shape), both the isotherm and the sorption effects predict a shock wave when a concentrated solution displaces a dilute solution. When a dilute solution displaces a concentrated solution, both effects predict a diffuse wave. Thus the two effects reinforce each other for favorable isotherms. For unfavorable isotherms (e.g., GLC) the isotherm and sorption effects are opposite and oppose each other. Because of this opposition there is an optimum operating temperature for preparative GLC which will give quite sharp peaks.

Temperature and pressure changes will also cause velocity changes for gases. Temperature increases will increase the gas velocity. When this effect is important the molar density is not constant. The molar density can be calculated from the appropriate PVT relationship such as the ideal gas law. The effect is easily visualized for a very simple case. Assume

the ideal gas law holds, the system is isobaric, and the change in amount adsorbed is negligible compared to the total gas flow rate. Thus ρv = constant. Applying the ideal gas law, this leads to the conclusion that

$$v = T(\text{constant}) \qquad (2\text{-}60)$$

Therefore, a temperature increase increases the velocity. This means that hot waves are compressive since the upstream portion of the wave moves faster than the downstream portion. For a temperature increase from 20 to 80°C the velocity increase is about 20%. Cooling waves will be diffuse and thus increase zone spreading. For dilute isothermal systems which follow the ideal gas law:

$$v = \frac{\text{Constant}}{p} \qquad (2\text{-}61)$$

Thus a pressure drop increases the fluid velocity downstream which is dispersive. Pressure waves will also change the fluid velocity.

Changes in porosity will also change the velocity. Generally speaking, if α decreases the velocity increases. With soft gels such as Sephadex® (a polydextran) and Biogel P® (a polyacrylamide) used for size exclusion chromatography (SEC), temperature changes change the porosity if the bed is constrained. The exact effect this has on solute velocites depends on the gel used.[612] Ion exchange resins commonly swell or shrink when exchange occurs.[18,202,484,693,1016] For instance, with a carboxylic acid cation exchange resin going from the H^+ to Na^+ form the resin swells. If the bed is constrained so that expansion is not allowed the porosities decrease. The high Na^+ wave will move faster than the low Na^+ wave. This is then compressive. The reverse situation occurs and a diffuse wave results if the resin goes from the H^+ to the Na^+ form. The compressive or diffusive wave effects will be added onto the effect caused by isotherm curvature.

D. Coupled Systems
1. Two or More Solutes

When there are two or more solutes which adsorb, they will usually compete with each other for sites on the adsorbent. This was illustrated by the multicomponent Langmuir isotherm, Equation 2-7, which we will write as:

$$q_i = \frac{a_i c_i}{1 + \sum_{j=1}^{n} (b_j c_j)} \qquad (2\text{-}62)$$

Since the equilibrium for a solute depends upon the concentration of all other solutes, the movement of each solute is coupled to the movement of all other solutes which are present. For dilute solutions with constant velocity the mass balance for each solute and the solute movement equations are unchanged by the addition of additional solutes. Thus Equations 2-28 and 2-35 are the same, except $\Delta q/\Delta c$ becomes $\Delta q_i/\Delta c_i$. However, since Δq_i depends on the concentrations of all solutes present, the solute wave velocity u_{si} will depend on all c_i. The mathematical solution requires uncoupling the equations. This uncoupling can be done several different ways and is discussed in detail elsewhere.[59,385,426,485,486,536,596,657,832,836,865,982] In this section we will look at the problem qualitatively, and solve the one situation where the solutes uncouple themselves.

In Section IV.A we saw that a shock wave is produced if a concentrated solution displaces
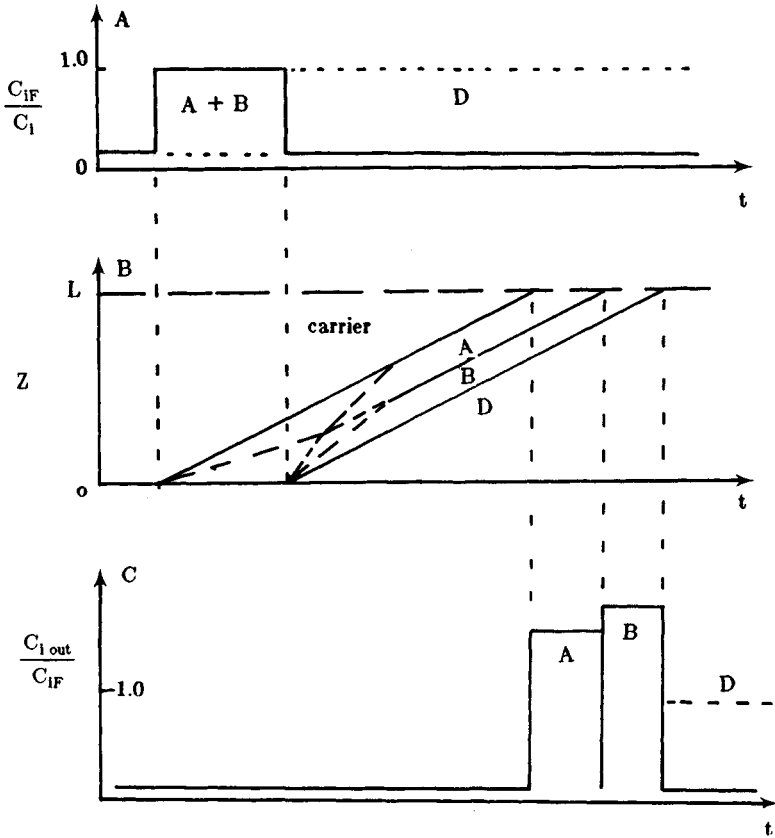
FIGURE 2-15. Displacement development with coupled solutes. (A) Feed; (B) local equilibrium theory. Solid lines can be predicted from Equations 2-35, 2-63, and 2-64. Dotted lines require more detailed theories; (C) predicted outlet concentrations.

a dilute solution when the solute has a Langmuir isotherm. In that case there really were two components present: the solute and a carrier. The solute was much more strongly adsorbed. Extending this situation to several solutes whose isotherms follow Equation 2-62 we would expect to observe a shock wave (constant pattern behavior) when a weakly adsorbed solute is displaced by a more strongly adsorbed solute. This is observed experimentally and is predicted by several theories.[59,426,486,832,865,982] If we reverse the situation and have a strongly adsorbed solute displaced by a weakly adsorbed solute a diffuse wave results.

In the case of shock waves the solutes will eventually decouple themselves. Suppose a pulse of two solutes, A and B, are displaced by a third solute, D, which is strongly adsorbed. (An example would be methane, A, and ethane, B, in hydrogen carrier being displaced by butane, D, on activated carbon adsorbent). Since the displacer, D, is pushing out less strongly adsorbed A and B, a shock wave will result. The pulse of A and B is pushing out a less strongly adsorbed material, the solvent or carrier gas, and a shock will form here also. Finally, since solute B is more strongly adsorbed than solute A, the B will displace the A. The result will eventually be a band of pure B displacing a band of pure A. Thus the final result which is observed experimentally[427,518] is four pure components separated by three shock waves. Since mass balances on A and B must be satisfied, the band widths for these solutes must become constant. This means that the shock waves must all be parallel. This condition is observed experimentally and is predicted by the theories. The solute movement diagram is shown in Figure 2-15. Prediction of the dotted lines in Figure 2-15B requires

the more complex theories[59,385,486,832,865,982] while the solid lines can be predicted based on the argument presented here.[262,320,425,518,835]

The shock wave velocities must all be equal once the pure bands are obtained. The concentration of D upstream of shock 3 is the inlet concentration of D and the concentration of D downstream of shock 3 is zero. For this particular case where the shock separates pure component D from a solution containing no D, the equations are uncoupled and u_{sh3} (Equation 2-35) does not depend on c_A or c_B. Now we know that

$$u_{sh_1} = u_{sh_2} = u_{sh_3} \tag{2-63}$$

Shock wave 1 depends only upon the concentration of A in the A band and u_{sh2} only on the concentration of B in the B band. Equations 2-63 and 2-35 can now be used to find the concentrations of A and B in their respective bands. Figure 2-15C shows that the solutes are concentrated in displacement development. Finally, the band widths can be found from a mass balance over an entire cycle.

$$(c_{iF})(t_F) = (c_{i \ band})(t_{band}) \qquad i = A,B \tag{2-64}$$

In displacement development the final products can be predicted without knowing the details of the interactions inside the column. However, calculation of the length of column necessary to get pure bands does require these details and hence the more detailed theories.

Displacement behavior only occurs if the displacing agent is strongly enough adsorbed and has a high enough feed concentration. If the weakest adsorbed solute, A, moves faster than u_{sh}, a dilute band or a separate peak of A will be formed instead of a concentrated band. This can be checked. If

$$\frac{\Delta q_A}{\Delta c_A}\bigg|_{c_A < c_{A_{band}}} < \frac{\Delta q_D}{\Delta c_D}\bigg|_{c_{D_F}}$$

then $u_{sh}(c_A) > u_{sh3}$ and the A band will be diluted. If

$$\frac{\Delta q_A}{\Delta c_A}\bigg|_{c_{AF}} < \frac{\Delta q_D}{\Delta c_D}\bigg|_{c_{D_F}}$$

$u_{sh_A}(c_{AF}) > u_{sh3}$ and a separate A peak will form. If

$$\frac{\Delta q_A}{\Delta c_A}\bigg|_{c_A = 0} < \frac{\Delta q_D}{\Delta c_D}\bigg|_{c_{D_F}}$$

then $u_s(c_A \to 0) > u_{sh3}$ and the A peak will have the diffuse tail normally expected and will be unaffected by the displacer.

Analysis of diffuse wave patterns requires the detailed theories to uncouple the equations. However, the characteristic diagrams can be understood without these theories. The characteristic diagram for three ions, which must be coupled because electroneutrality must hold, is shown in Figure 2-16A for a pulse input. The eluant, H^+, is the least strongly sorbed ion. The less-sorbed ion in the feed pulse, A^+, is pushed ahead and concentrated to form a region of pure A^+. This is shown in Figure 2-16A. This region is bounded by shocks. Then comes a region at the feed concentration. This is separated from a plateau region by a fast diffuse wave. In the fast diffuse wave the A^+ concentration drops to zero. The plateau
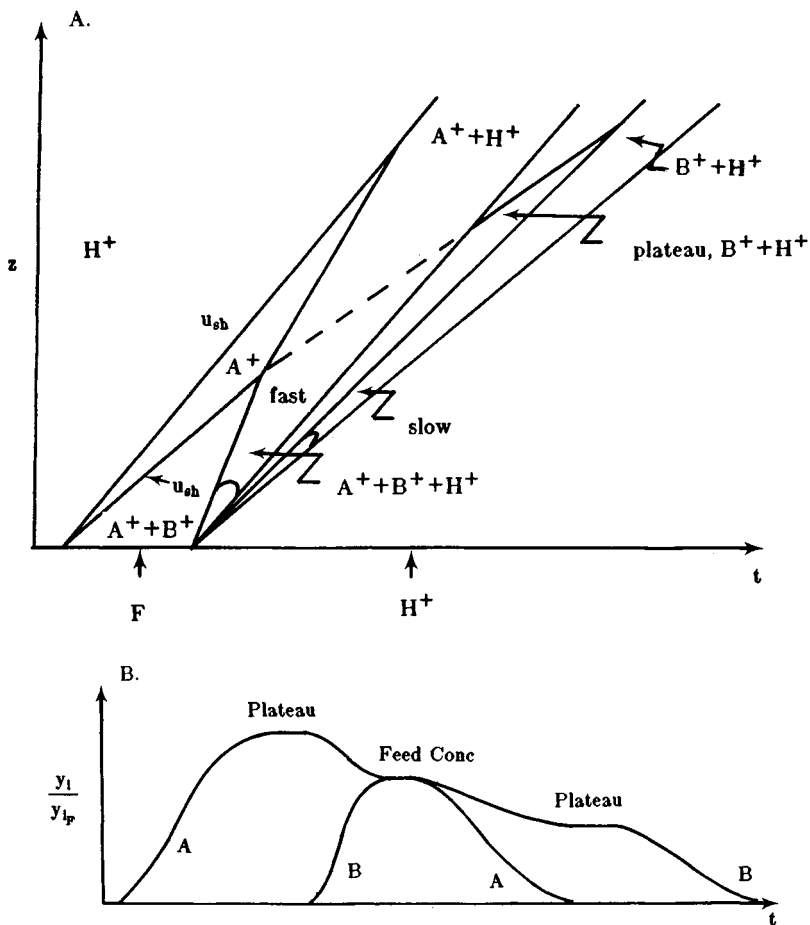
FIGURE 2-16. Coupled solutes with shock and diffuse waves. (A) Characteristic diagram for ternary ion exchange; (B) outlet concentration profiles for coupled adsorption for input of large pulse.

region contains no A^+. This plateau is separated from pure eluant by a slow diffuse wave across which the B^+ concentration drops to zero. This ordering of solutes according to their sorption characteristics demonstrates "coherence".[485,486] If given a long enough period, coupled species will always order themselves according to affinity.

Binary systems with two adsorbed species in a carrier will show a similar coupling. The observed concentration profiles for input of a long pulse are shown in Figure 2-16B for an isothermal system. Usually,[114] the fronts for both compounds form constant patterns. The concentration of component A is increased to above its feed concentration because B serves as a desorbent. After breakthrough of B, both compounds exit at their feed concentrations. When the column is eluted with a nonadsorbed species, both solutes form disperse waves. Solute B does this in two steps with a plateau in between. The results shown in Figure 2-16B can be approximately predicted using the effective equilibrium pathway method.[114] For adiabatic systems with two adsorbates the behavior is much more complex and numerical integration is required.[472]

2. Coupling with Heat of Adsorption

A second type of coupling occurs when heat of adsorption effects are important. The amount adsorbed affects the heat released, which changes the fluid tempeature. This in turn

changes the equilibrium and hence the rate of solute movement. For very dilute mixtures the amount of heat released is small and the mass and energy balances can be treated as if they were uncoupled. In exchange adsorption the net heat of adsorption is usually close to zero and the balances are uncoupled. In liquid systems the volumetric heat capacity is large and the energy is usually carried down the column past the mass transfer zone (MTZ). This effectively uncouples the balances. In gas systems which are not very dilute the coupling between the amount adsorbed and the heat of adsorption is usually important.

The mathematical techniques used to decouple solutes for equilibrium analysis will also decouple the mass and energy balances.[109,112,513a,538,865,958] To rigorously solve the problem, including mass transfer and axial dispersion, numerical solutions are required.[281,472,865,912] The equilibrium theories predict a longer breakthrough time than actually occurs and thus caution is required in their use. The approximate behavior of gas systems can be predicted by comparing the velocity of a pure thermal wave (Equation 2-41) to the solute wave velocity (Equation 2-28). For gas systems the first term in the denominator of Equation 2-41 will often be small compared to the second. In large-diameter columns the wall effect will be negligible. If adsorption is strong the first two terms in the denominator of Equation 2-28 will be small compared to the last term. Then, taking the ratio of u_{th} to u_s we have

$$\frac{u_{th}}{u_s} \simeq \frac{\Delta q/\Delta c}{(C_{P_s}/C_{P_f}) \frac{1}{\rho_f}} = R_T \qquad (2\text{-}65)$$

R_T is the cross-over ratio.[403] If $R_T \ll 1$ the solute velocity is significantly greater then the thermal wave velocity, and the thermal wave will be well behind the solute wave. If $R_T \gg 1$ the thermal wave runs ahead of the solute wave. In these two cases the temperature in the region of the solute wave can be calculated. When R_T is near 1.0, the thermal and solute waves travel together and a simple solution is not possible. Operation with R_T near one may be operationally desirable since much of the thermal energy of adsorption is stored in the column where it is available for desorption (see Chapter 3 [Section III.B]).

However, the calculation will be more difficult. Basmadjian[109] uses a different method to develop similar but more exact criteria for when the thermal wave will run ahead of the concentration wave. When shock waves are predicted, constant pattern solution methods can be used (see Section VII.A).

V. FORMAL MATHEMATICAL DEVELOPMENT OF SOLUTE MOVEMENT THEORY

In this section the simple solute movement theory will be formally developed from the complete mass and energy balances. This development is useful since it clearly spells out the assumptions inherent in the more physical development presented in Section IV. Since the basics have been presented, this section will be brief.

A. Two Porosity Model

We will first assume that the packing is homogeneous, that radial gradients in temperature, velocity, and concentration are negligible, that thermal diffusion and pressure diffusion can be neglected, that there are no phase changes other than adsorption, and that chemical reactions do not occur (reversible chemisorption is allowed). Then the solute balance on fluid and solid is[1051]

$$\alpha \frac{\partial c_i}{\partial t} + K_{d_i}(1 - \alpha)\epsilon \frac{\partial c_i^*}{\partial t} + \rho_s(1 - \alpha)(1 - \epsilon) \frac{\partial q_i}{\partial t}$$

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$$\alpha\,\frac{\partial c_i}{\partial t} + K_{d_i}(1 - \alpha)\epsilon\,\frac{\partial c_i^*}{\partial t} + \rho_s(1 - \alpha)(1 - \epsilon)\,\frac{\partial q_i}{\partial t}$$

$$+ \ \alpha \ \frac{\partial(vc_i)}{\partial z} \ - \ \alpha(E_D \ + \ D_M) \frac{\partial^2 c_i}{\partial z^2} \ = \ 0 \tag{2-66}$$

where c_i^* is the concentration of solute i in the stagnant fluid contained inside the pores and E_D and D_M are the eddy and molecular diffusivities. Assuming that a lumped parameter mass transfer expression is adequate, we obtain the following solute balance on the solid phase:

$$\rho_s(1 \ - \ \epsilon)(1 \ - \ \alpha) \frac{\partial q_i}{\partial t} \ + \ K_{d_i}\epsilon(1 \ - \ \alpha) \frac{\partial c_i^*}{\partial t} \ = \ -k_T a_p(c_i^* \ - \ c_i) \tag{2-67}$$

If the lumped parameter expression is not adequate, intraparticle diffusion terms replace the right-hand side in Equation 2-67.[865,901] For the local equilibrium assumptions the form of Equation 2-67 will be immaterial.

For the energy balance we make the additional assumptions that no electrical or magnetic fields are present, radiant heat transfer is negligible, viscous heating can be neglected, kinetic and potential energy changes are small, and either density is independent of temperature or pressure is constant. Then the energy balance for both phases is

$$\rho_f C_{P_f}\alpha \frac{\partial T}{\partial t} \ + \ \rho_f C_{P_f}\epsilon(1 \ - \ \alpha) \frac{\partial T^*}{\partial t} \ + \ \rho_s C_{P_s}(1 \ - \ \epsilon)(1 \ - \ \alpha) \frac{\partial T_s}{\partial t} \ + \ \rho_f C_{P_f}\alpha \frac{\partial(vT)}{\partial z}$$

$$-(E_{DT} \ + \ D_T)\rho_f C_{P_f}\alpha \frac{\partial^2 T}{\partial z^2} \ = \ h_w A_w(T_{amb} \ - \ T_w) \ - \ C_{P_w} \frac{W}{A_c} \frac{\partial T_w}{\partial t} \tag{2-68}$$

where T^* is the temperature of the stagnant fluid, T_{amb} is the ambient temperature, and h_w is the heat transfer coefficient for the column walls. If we assume that heat transfer into the solid can be represented by an overall linear driving force, the energy balance for the solid is

$$\rho_s C_{P_s}(1 \ - \ \epsilon)(1 \ - \ \alpha) \frac{\partial T_s}{\partial t} \ + \ \rho_f C_{P_f}\epsilon(1 \ - \ \alpha) \frac{\partial T^*}{\partial t} \ = \ -h_p a_p(T^* \ - \ T)$$

$$+ \ (1 \ - \ \epsilon)(1 \ - \ \alpha)\rho_s \Delta H_{ads} \frac{\partial q}{\partial t} \tag{2-69}$$

where h_p is the heat transfer coefficient and a_p is the surface area per unit volume.

Although already somewhat simplified, Equations 2-66 to 2-69 or the equivalent single porosity forms (see Equations 2-73, 2-74, 2-77, and 2-78) along with the isotherm expression are the usual starting points for modeling adsorption and chromatography. Now we are ready to make the additional assumptions necessary to obtain simple solutions. The first additional assumption is that stagnant fluid and solid are in equilibrium. Thus, $T_s = T^*$ and q_i and c_i^* are related by the isotherm equation. Next we assume that all parameters (e.g., α, ϵ, D_M, C_{Pf}) except density are constant. To obtain simple solutions, density is also assumed to be constant, although this assumption can be relaxed. This set of additional assumptions are often included even for numerical solutions.

To obtain analytical solutions additional assumptions are required. Usually the fluid velocity is assumed to be constant. For nonisothermal systems we usually assume that axial dispersion and diffusion terms can be neglected. The rates of heat and mass transfer are assumed to be very high. Thus $c = c^*$ and $T = T^*$, and liquid and solid are locally in equilibrium. This removes Equations 2-67 and 2-69. The column is usually assumed to be

Table 1
MODEL ASSUMPTIONS

1. Homogeneous packing
2. Thermal and pressure diffusion are negligible
3. No chemical reactions other than adsorption
4. No phase changes other than adsorption
5. No electrical or magnetic fields
6. Radiant heat transfer is negligible
7. Viscous heating is negligible
8. Kinetic and potential energy changes negligible
9. Constant α, ϵ, ρ_s, E_D, D_M, D_T, k_T, a_P, C_{P_f}, K_d, C_{p_s}, C_{Pw}, h_w, h_p, ΔH_{ads}
10. Radial gradients in q, c, T, and v are negligible
11. Lumped parameter expressions for heat and mass transfer are adequate
12. Fluid density is constant
13. Fluid velocity is constant
14a. Column is adiabatic or
14b. Column is isothermal
15. Axial thermal dispersion can be neglected
16. Axial mass dispersion can be neglected
17. Heat and mass transfer rates are very high and local equilibrium occurs
18. The heat of adsorption is negligible
19. Solutes are independent
20. The isotherm is linear

adiabatic or if the column is heated and cooled by a jacket (the direct mode) the heat transfer rates are assumed to be very high and radial gradients do not occur. For simple solutions the solutes are assumed to be independent and the heat of adsorption is neglected. With these assumptions, Equation 2-66 becomes:

$$[\alpha + K_d(1 - \alpha)\epsilon]\frac{\partial c}{\partial t} + \rho_s(1 - \alpha)(1 - \epsilon)\frac{\partial q}{\partial t} + \alpha v\frac{\partial c}{\partial z} = 0 \qquad (2\text{-}70)$$

The amount adsorbed, q, is related to c and T by the isotherm. By applying the chain rule and rearranging, Equation 2-70 simplifies to:

$$\frac{\partial c}{\partial t} + u_s\frac{\partial c}{\partial z} = -\frac{u_s}{v}\left(\frac{1 - \alpha}{\alpha}\right)(1 - \epsilon)\rho_s\frac{\partial q}{\partial T}\frac{\partial T}{\partial t} \qquad (2\text{-}71)$$

For isothermal systems, or for systems with instantaneous temperature changes or for systems with square wave changes in the feed temperature $\partial T/\partial t = 0$. Then Equation 2-71 is easily solved by the method of characteristics.[865,1051] The results are the same as shown in Figures 2-5 (for linear isotherm assumption), 2-6, and 2-9.

The energy balance Equation 2-68 simplifies to:

$$\frac{\partial T}{\partial t} + u_{th}\frac{\partial T}{\partial z} = 0 \qquad (2\text{-}72)$$

When solved by the method of characteristics, the solution to this equation is the same as Figure 2-11.[865,1051]

For easy reference the assumptions are listed in Table 2-1. This is a rather staggering list of assumptions. Fortunately, many of them are valid in most situations. As we have already seen, some of the assumptions can be relaxed. In Section VI.B we will see that by invoking assumptions 19 and 20 we can relax assumptions 16 or 17 and explore the effects of dispersion and finite mass transfer rates.

B. Single Porosity Model

Before continuing it will be useful to compare Equations 2-66 to 2-69 to the single porosity equations which are often employed. It is common to use a single porosity which we will call ϵ'. Then $(1 - \epsilon')$ includes the solid and the stagnant fluid. The mass balance equations are now

$$\epsilon' \frac{\partial c_i}{\partial t} + \rho_B(1 - \epsilon') \frac{\partial q_i'}{\partial t} + \epsilon' \frac{\partial(c_i v)}{\partial z} - \epsilon'(E_D + D_M) \frac{\partial^2 c_i}{\partial z^2} = 0 \qquad (2\text{-}73)$$

and

$$\rho_B(1 - \epsilon') \frac{\partial q_i'}{\partial t} = -k_T a_p(c_i^* - c_i) \qquad (2\text{-}74)$$

Where ρ_B is the bulk density of the solid including fluid in the pores. Comparison of Equations 2-73 and 2-74 with Equations 2-66 and 2-67 shows that $\epsilon' = \alpha$ and

$$\rho_B q_i' = \epsilon c_i^* + \rho_s(1 - \epsilon)q_i \qquad (2\text{-}75)$$

Thus the equilibrium isotherm relating q_i' to c_i must include the fluid in the pores if the single porosity equations are used. If the two porosity equations are used the equilibrium relation between q and c must not include the fluid in the pores. Unfortunately, the literature is not always clear as to how isotherms were determined. When Equations 2-73 and 2-74 are simplified and solved in the same way as Equations 2-66 and 2-67, essentially the same result is obtained except the solute wave velocity is now

$$u_s = \frac{v}{1 + \left(\dfrac{1 - \epsilon'}{\epsilon'}\right)\rho_B \dfrac{\Delta q_i'}{\Delta c_i}} \qquad (2\text{-}76)$$

With a single porosity the energy balance equations are

$$\rho_f C_{P_f} \epsilon' \frac{\partial T}{\partial t} + \rho_B C_{P_B}(1 - \epsilon') \frac{\partial T_s}{\partial t} + \rho_f C_{P_f} v \epsilon' \frac{\partial T}{\partial z}$$

$$- (E_D + D_T)\rho_f C_{P_f} \epsilon' \frac{\partial^2 T}{\partial z^2} = h_w A_w(T_{amb} - T_w) - \frac{C_{pw} W}{A_c} \frac{\partial T_w}{\partial t} \qquad (2\text{-}77)$$

and

$$\rho_B C_{P_B}(1 - \epsilon') \frac{\partial T_s}{\partial t} = -h_p a_p(T^* - T) + (1 - \epsilon')\rho_B \Delta H_{ads}' \frac{\partial q'}{\partial t} \qquad (2\text{-}78)$$

where C_B is the bulk heat capacity of the solid particles and $\Delta H_{ads}'$ is the heat of adsorption determined as a function of q'. Comparison of Equations 2-77 and 2-78 to Equations 2-68 and 2-69 with $\epsilon' = \alpha$ shows that

$$\rho_B C_{P_B} = \rho_s C_{P_s}(1 - \epsilon) + \rho_f C_{P_f} \epsilon \qquad (2\text{-}79)$$

if $T_s = T^*$. If $\partial T/\partial t = 0$, $\Delta H_{ads}'$ can be related to ΔH_{ads}.

$$\Delta H'_{ads} = \frac{(1 - \epsilon)\rho_s \Delta H_{ads}}{\epsilon \dfrac{\partial c^*}{\partial q} + \rho_s(1 - \epsilon)} \qquad (2\text{-}80)$$

If Equations 2-77 and 2-78 are simplified and solved by the same method used for Equations 2-68 and 2-69, essentially the same result is obtained except the thermal wave velocity is now

$$u_{th} = \frac{v\rho_f C_{P_f}}{\rho_f C_{P_f} + \left(\dfrac{1 - \epsilon'}{\epsilon'}\right)\rho_B C_{P_B} + \dfrac{W}{\epsilon' A_c} C_{P_W}} \qquad (2\text{-}81)$$

Either the single porosity or two porosity forms can be used. The two porosity forms are physically more realistic and are required if a combination of size exclusion and adsorption is occurring. The single porosity model is often mathematically more convenient. Care must be used when trying to convert data from one form to another.

VI. ZONE SPREADING EFFECTS FOR LINEAR SYSTEMS

We know that ignoring dispersion and mass transfer effects often give results which are physically unrealistic. Fortunately, when the solutes are independent and the isotherms are linear the mass transfer and dispersion effects can be included in the equations. This will allow us to study these effects for linear systems and qualitatively extrapolate the effects of dispersion and mass transfer to nonlinear systems. The linear results are exact for dilute solutions.

Several different types of theories have been used to study linear chromatography. We will first consider the historically important plate theories and then rate theories. Comparison of these theories gives the Van Deemter equation, which has been modified by stochastic theories. This equation predicts the zone spreading effects in linear chromatography. Next, the theories will be used to predict the resolution of two components in linear chromatography, and finally superposition of these results onto the solute movement theory results will be discussed.

A. Plate Theories

In their classical paper on liquid-liquid chromatography, Martin and Synge[695] developed a plate theory to explain zone spreading. Their model consisted of a series of stages with a stationary phase and a mobile phase. The mobile phase moved in discrete transfer steps followed by equilibrium of each stage. Mobile phase from different stages does not mix. Thus this theory really modeled the countercurrent distribution system which they had worked on before developing the chromatographic column. The result was a binomial expression which reduces to a Gaussian form. The number of stages or the plate height had to be determined experimentally.

Although none of the plate models are physically realistic, the continuous flow plate model shown in Figure 2-17 is more realistic than the countercurrent distribution model. In this plate model the column is divided into N equilibrium stages each of height H.[416,586,1008] Each component is assumed to be independent and the isotherms are assumed to be linear. A balance around stage j for solute i gives

$$c_{i,j-1} \, dV - c_{i,j} \, dV = V_M dc_{i,j} + M_s dq_{i,j} \qquad (2\text{-}82)$$
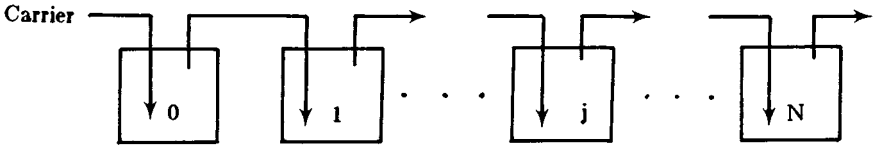
FIGURE 2-17.   Continuous flow staged model for chromatography.

where V_M and M_s are the volume of mobile phase and the mass of stationary phase on each stage. V is the volume of carrier gas. Substituting in the linear isotherm (Equation 2-29) and rearranging, we have the ordinary differential equation:

$$\frac{d\,c_{i,j}}{d\,V} = \frac{c_{i,j-1} - c_{i,j}}{V_M + k_i\,M_s}$$

(2-83)

For a pulse of F_i moles of feed into stage 0, the solution is the Poisson distribution:

$$c_{i,j} = \frac{F_i}{V_M + k_i\,M_s}\,\frac{e^{-\nu_i}\,\nu_i^j}{j!}$$

(2-84)

where the dimensionless cumulative flow of mobile phase, ν_i, is

$$\nu_i = \frac{V}{V_M + M_s k_i} = \frac{u_{si}\,t}{H}$$

(2-85)

where Equation 2-30 and the height of a stage (Equation 2-91) have been used to relate the solute velocity to the staged terms. The outlet concentration is found by setting $j = N$. Equation 2-82 has also been solved for step inputs.

With a large number of stages, Equation 2-84 can be approximated as

$$c_{i,j} = \frac{F_i}{V_M + k_i M_s}\,\frac{1}{\sqrt{2\pi j}}\,e^{-(\nu_i - j)^2/2j}$$

(2-86)

which at the column outlet is

$$c_{i_{out}} = \frac{F_i}{V_M + k_i M_s}\,\frac{1}{\sqrt{2\pi N}}\,e^{-(\nu_i - N)^2/2N}$$

(2-87)

By differentiation it is easy to show that in dimensionless terms the peak maximum occurs at $\nu_i = N$ and thus

$$c_{i_{max}} = = \frac{F_i}{V_M + k_i M_s}\,\frac{1}{\sqrt{2\pi N}}$$

(2-88)

Also, the dimensionless peak width is

$$w_i = 4\sqrt{N}$$

(2-89)

For a Gaussian peak the peak width equals 4σ where σ is the standard deviation. Thus in dimensionless terms

$$\sigma = \sqrt{N}$$

(2-90)

Equation 2-90 is easily written in terms of time by substituting in Equations 2-85, 2-88 plus a definition of plate height, H.

$$N = L/H \tag{2-91}$$

The result is

$$c_i = c_{imax}\ e^{-\left(\frac{u_{si}t}{H} - \frac{L}{H}\right)^2/2\left(\frac{L}{H}\right)} \tag{2-92}$$

After rearrangement this becomes

$$c_i = c_{imax}\ e^{-(t - t_{Ri})^2/2\left(\frac{H}{L}\, t_{Ri}^2\right)} \tag{2-93}$$

where the retention time for solute i is

$$t_{Ri} = L/u_{si} \tag{2-94}$$

By further algebraic manipulation the equation for solute concentration can be written in length units as

$$c_i = c_{imax}\ e^{-(z_i - L)^2/2LH} \tag{2-95}$$

where z_i is the location of the peak center.

Equations 2-87, 2-92, and 2-95 can all be written in the common form

$$c_i = c_{imax}\ \exp(-X^2/2\sigma^2) \tag{2-96}$$

where X is the difference from the peak maximum and σ is the standard deviation, both in appropriate units. In dimensionless units σ is given by Equation 2-90. Comparing Equations 2-93 and 2-87 in time units,

$$\sigma_t = \left(\frac{H}{L}\right)^{1/2} t_{Ri} = (LH)^{1/2}/u_{si} \tag{2-97}$$

while in length units

$$\sigma_l = \sqrt{HL} \tag{2-98}$$

This development of the Gaussian distribution and the standard deviations has been carried out at some length since different sources report different equations for the concentration profile and the standard deviation. This can be confusing, especially if the authors do not define their terms.

The staged theory correctly predicts that zone spreading is proportional to the square root of the distance traveled. This correct prediction does *not* imply that the model is "correct". Other linear theories also predict that zone spreading is proportional to $\sqrt{L}$. Since Equation 2-94 shows that the exit time for the each solute peak is proportional to L, peaks can always be separated by increasing L as long as the solute wave velocities (or distribution coefficients) differ. According to Equation 2-98, the zone spreading within the column is the same for all components except for minor differences due to different H values. Equation 2-97 shows
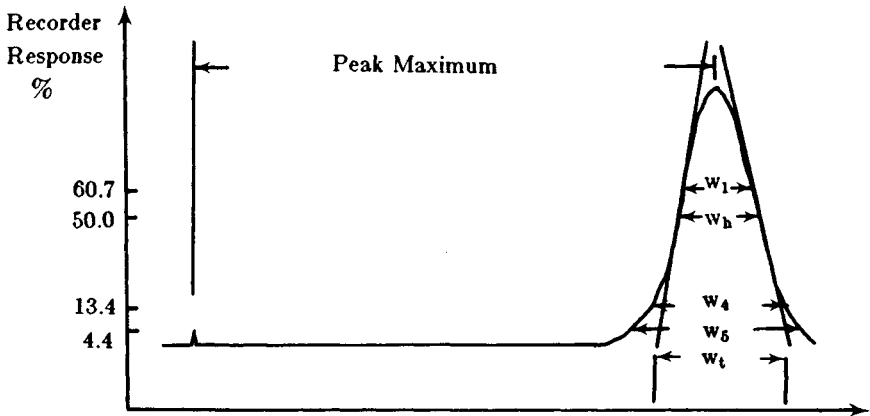
FIGURE 2-18.   Single Gaussian peak. Constants for calculation of N from Equation 2-99. $w_i = 4$, $w_h = 5.54$, $w_{4\sigma} = 16$, $w_{5\sigma} = 25$, and $w_t = 16$.

that the zone spreading with respect to time (and this is essentially what is observed on a strip chart recorder) is inversely proportional to the solute wave velocity. Slower solutes spread more. The predictions of Equations 2-97 and 2-98 are not incompatible. When the front of a solute wave just reaches the end of the column, the width of the zone inside the column is $4\sigma_l$. It takes longer to elute a slowly moving solute this distance and thus more zone spreading is observed on the strip chart.

The value of N is easily determined from an experiment. The distance (or time) that the peak maximum takes to exit and the width of the peak are measured on the strip chart as shown in Figure 2-18. Then N is

$$N = (Const) \left[\frac{peak\ maximum}{width} \right]^2 \qquad (2\text{-}99)$$

where the constant depends on which width is used[134] and values are listed in Figure 2-18. The plate height H can then be determined from Equation 2-91. The ratio is used in Equation 2-99 so that the relationship between distance on the strip chart and time divides out. The width at half height, w_h, is most common, but the use of the 5σ width will be most accurate for asymmetric peaks.[134] All methods give the same results for Gaussian peaks.

Staged models have been used as the basis for numerical simulations for both linear and nonlinear isotherms for a variety of operating methods. Unfortunately, the staged models do not tell what affects N or equivalently H, and how the values for H and N will change as the operating conditions change. The linear theory is very useful for pulse testing of columns at low concentrations to determine how well they are packed.

B. Rate Theories

The rate theories use the solute mass balance Equation 2-66 or 2-73 and the mass transfer expression Equation 2-67 or 2-74 as the starting point and then simplify these equations with additional assumptions. Lapidus and Amundson[630] solved two cases. First they used Equation 2-73 (Equation 2-66 can also be used) and for an isothermal column made all the assumptions in Table 2-1 except that dispersion is negligible. With these assumptions Equations 2-29 and 2-73 reduce to:

$$\left[1 + \rho_B \left(\frac{1 - \epsilon'}{\epsilon'} \right) k_i \right] \frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial z} - (E_D + D_M) \frac{\partial^2 c_i}{\partial z^2} = 0 \qquad (2\text{-}100)$$
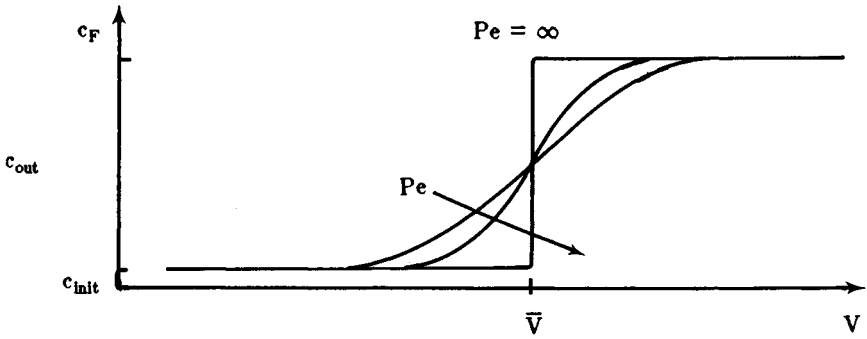
FIGURE 2-19. Response to a step input predicted by Equation 2-101.

This equation was solved for both arbitrary initial and inlet distributions and for constant initial and inlet concentrations. For constant initial and inlet concentrations a simpler, approximate solution can be obtained for columns of sufficient length.[657] For a step input this solution is

$$\left(\frac{c - c_{init}}{c_F - c_{init}}\right)_i = \frac{1}{2}\{1 + erf[(Pe_z)^{1/2} (V - \bar{V})/2(V\bar{V})^{1/2}]\} \qquad (2\text{-}101)$$

where $V = \epsilon' v A_c t$ is the elution volume, $\bar{V} = A_c L[\epsilon' + (1 - \epsilon')\rho_B k_i]$ is the volume of solution required to saturate a column of length L, and the Peclet number is $Pe_z = L v/(D_M + E_D)$. This Peclet number is now based on an effective axial dispersion which includes mass transfer effects. The error function

$$erf(u) = -erf(-u) = \frac{2}{\pi^{1/2}} \int_0^u exp(-\varsigma^2)d\varsigma \qquad (2\text{-}102)$$

is related to the normal curve of error which is a tabulated integral. The error function is also available on many computers.

The solution given in Equation 2-101 is convenient to use. For a step input an S-shaped curve is predicted. This is shown in Figure 2-19. The outlet concentration profile becomes sharper as $(D_M + E_D)$ become smaller (larger Peclet number). In the limit of an infinite Peclet number the result reduces to the solute movement theory result for linear isotherms. The concentration profiles all intersect at $1/2 (C_F + C_{init})$ at $V = \bar{V}$. The effective Peclet number can easily be obtained from experimental data. In linear systems the zone spreading effects of mass transfer and axial dispersion look the same. Thus an effective axial dispersion coefficient can model zone spreading which is caused by a combination of mass transfer and axial dispersion.

In addition to giving a simple solution, the use of linear equilibrium has the major advantage that superposition can be used to predict column behavior for a variety of situations.[502,657] Let X(L, V) be the breakthrough solution given in Equation 2-101 for an initially clean column.

$$X(L,V) = \left(\frac{c}{c_F}\right)_i = \text{Equation 2-101} \qquad (2\text{-}103)$$

Now solutions for other cases can be determined by superposition. If a column which is initially uniformly loaded is eluted with pure solvent, we can subtract the breakthrough solution from the uniform loading,

$$\frac{c}{c_{init}} = 1 - X(L,V) = \frac{1}{2}\left\{1 - erf\left[\frac{(Pe_z)^{1/2}(V - \overline{V})}{2(V\overline{V})^{1/2}}\right]\right\} \qquad (2\text{-}104)$$

If a pulse input of volume V^o is fed to an initially empty column we have first a step up and then a step down at a later time. Thus,

$$\frac{c}{c_F} = X(L,V) - X(L,V - V^o) \qquad (2\text{-}105)$$

and the result is easily generated from Equation 2-101.

In linear chromatography we are interested in a differential pulse of feed. Then we want the limit of Equation 2-105 as $V_o \rightarrow 0$. After some manipulation this is

$$\left(\frac{c}{c_F}\right)_i = V_0 \frac{\partial X(L,V)}{\partial V} \qquad (2\text{-}106)$$

Applying this to Equation 2-101 and noting that near the peak

$$\left(\frac{V - \overline{V}}{V}\right) \ll 1$$

then

$$\left(\frac{c}{c_F}\right)_i = \frac{1}{2}\frac{V_0}{\overline{V}}\left(\frac{Pe_z}{\pi}\right)^{1/2} exp\left[\frac{-Pe_z(V - \overline{V})^2}{4V\overline{V}}\right] \qquad (2\text{-}107)$$

The peak maximum occurs at $V = \overline{V}$ and the maximum concentration is

$$(c_i)_{max} = \frac{c_F}{2}\frac{V_0}{\overline{V}}\left(\frac{Pe_z}{\pi}\right)^{1/2} \qquad (2\text{-}108)$$

Although Equations 2-108 and 2-88 are defined in different terms, they both give c_{max} for a pulse input. When these equations are set equal to each other and the terms are rationalized, we find

$$Pe_z = 2N \qquad (2\text{-}109)$$

Thus the Peclet number can easily be determined from experiments from Equations 2-99 and 2-109.

In their second case, Lapidus and Amundson[630] assumed that the rate expression could be written as

$$\frac{dq'}{dt} = k_1 c - k_2 q' \qquad (2\text{-}110)$$

A special case of this equation when equilibrium is linear is the lumped parameter expression for mass transfer, Equation 2-74. The solutions obtained included untabulated definite integrals and thus are not easy to use. Van Deemter et al.[1008] were able to simplify the solution

for the input of a differential pulse in a system with linear equilibrium. If the column was large enough, their solution simplified to

$$c_i = \frac{F_i}{A_c\, v(\epsilon' + (1 - \epsilon')k')\, \sqrt{2\pi(\sigma_1^2 + \sigma_2^2)}}$$

$$\exp\left[\frac{-\left[L\left(1 + \frac{1 - \epsilon'}{\epsilon'}\, k_i\right)/v - t\right]^2}{2\left(1 + \frac{1 - \epsilon'}{\epsilon'}\, k_i\right)^2 (\sigma_1^2 + \sigma_2^2)}\right] \qquad (2\text{-}111)$$

where

$$\sigma_1^2 = \frac{2\, L\, D_T}{v^3} \qquad (2\text{-}112)$$

$$\sigma_2^2 = 2\left[\frac{(1 - \epsilon')k_i}{\epsilon' + (1 - \epsilon')k_i}\right]^2 \frac{L\, \epsilon'}{k_T\, a_P\, v} \qquad (2\text{-}113)$$

D_T is the total effective axial diffusivity. Equation 2-111 is a Gaussian distribution whose variance is the sum of the variances for diffusion and mass transfer. This solution will be employed in the next section.

Another useful solution is Thomas' solution.[974,975] Thomas solved mass balance Equation 2-73 for a single solute under isothermal conditions with negligible dispersion. He assumed that sorption was controlled by a kinetic rate expression. The two rate expressions he used are different from the mass transfer expression Equation 2-74, but his kinetic constant can be related to the mass transfer rate constant.[657,901,1015,1016] Thomas obtained solutions for Langmuir and linear systems. The linear solution is considerably simpler, and for sufficiently long columns reduces to complimentary error functions. The predicted concentration profiles for breakthrough are very similar to those shown in Figure 2-19. Superposition can be used for the linear case. For a differential pulse of feed, Equation 2-106 is valid but X is now the linear Thomas solution for breakthrough. The predicted concentration profiles from Thomas' analysis are very similar to those predicted by Equations 2-107 and 2-111. Since Thomas obtained solutions for both breakthrough and elution for Langmuir isotherms under nonequilibrium conditions, his solutions are often used as the basis for design of adsorption and ion exchange columns. The Thomas solutions are the basis for effective equilibrium pathway solutions[110-112,114] which appear to be useful for the practical design of some commercial adsorption systems.

C. Height of a Theoretical Plate

In their classic paper, Van Deemter et al.[1008] compared the continuous flow staged model results to their approximate solution, Equation 2-111, of Lapidus and Amundsen's[630] mass transfer case. They found that the height of an equilibrium stage was

$$H = \frac{2D_T}{v} + 2\left(\frac{(1 - \epsilon')k_i}{\epsilon' + (1 - \epsilon')k_i}\right)^2 \frac{\epsilon'\, v}{k_T\, a_P} \qquad (2\text{-}114)$$

Thus for linear isotherms the zone spreading caused by diffusion and mass transfer are

linearly additive. The total effective diffusivity can be expanded as the sum of molecular diffusion and eddy dispersion,

$$D_T = \gamma D_M + E_D \tag{2-115}$$

where γ is a labyrinth or tortuosity factor. Since the eddy diffusivity is proportional to velocity and particle diameter, Equation 2-115 can be written:

$$D_T = \gamma D_M + \frac{\lambda}{2} v d_p \tag{2-116}$$

Then Equation 2-114 becomes

$$H = A + \frac{B}{v} + C v \tag{2-117}$$

This equation is known as the Van Deemter equation although that seems slightly unfair to Zuiderweg and Klinkenberg. This equation is strictly applicable to linear isotherms only.

In the Van Deemter equation the A term is the eddy diffusion or flow contribution,

$$A = \lambda d_p \tag{2-118}$$

This velocity-independent term can be greatly decreased by careful design and packing of the column. Use of narrow particle size distributions also decreases the A term.[605] The B term is caused by molecular diffusion and is

$$B = 2\gamma D_M \tag{2-119}$$

In Equation 2-117 the molecular diffusion contribution is inversely proportional to the velocity. Thus this contribution becomes important at low velocities, particularly for gas systems where D_M is relatively large. The C term is due to mass transfer resistance. Since the overall mass transfer resistance can be represented as the sum of film resistances in the mobile and stationary phases

$$\frac{1}{k_T a_p} = \frac{1}{k_M a_p} + \frac{1}{k_i k_s a_p} \tag{2-120}$$

The C term can be expanded to

$$C = 2\left[\frac{(1 - \epsilon')k_i}{\epsilon' + (1 - \epsilon')k_i}\right]^2 \left[\frac{\epsilon'}{k_M a_p} + \frac{\epsilon'}{k_i k_s a_p}\right] \tag{2-121}$$

Since the mass transfer occurs by diffusion through the stagnant mobile phase in the pores and into a film of bound stationery phase, $k_M a_p$ is inversely proportional to d_p^2 and directly proportional to molecular diffusivity while k_s is inversely proportional to d_f^2; d_p is the particle diameter and d_f is the film thickness of the film coating the stationary phase. For adsorbents d_f is replaced by d_p.

A plot of H vs. velocity according to the Van Deemter equation is shown in Figure 2-20. The total H depends on the sum of the three contributions. In a well-designed and well-packed system the flow term, A, is usually quite small. Note that there is an optimum velocity for minimum H. The absolute minimum value of H is about 2 d_p. Un-
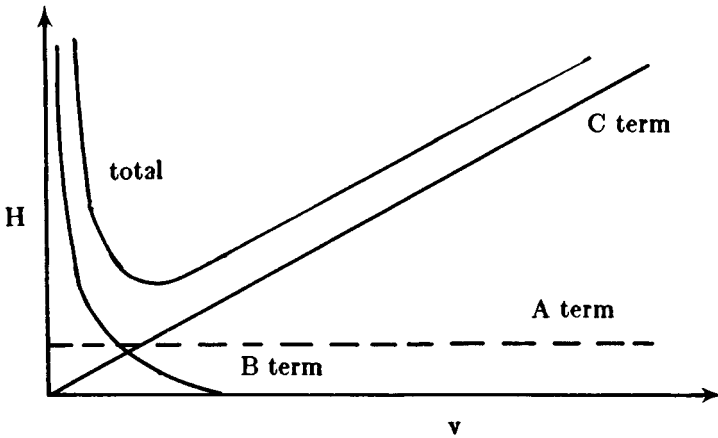
FIGURE 2-20. Variation of H with velocity according to Van Deemter equation (Equation 2-117).

fortunately, this velocity is too low for practical operation. Thus the mass transfer, C terms, usually dominate, and usually the $k_M a_p$ resistance is dominant. Thus H is essentially proportional to d_p^2 and inversely proportional to the molecular diffusivity. For very small particles (less than 10 μm) kinetics can become important and the C terms may not dominate.[517]

Many studies of zone spreading have followed the original publication of the Van Deemter equation.[354,416,517,605,870,930,1109] Using random walk and stochastic analysis, Giddings[416] was able to refine the Van Deemter equation. Several modified forms of the Van Deemter equation are in use. The classical expanded form of the Van Deemter equation is

$$H = A + \frac{B}{v} + C_M v + C_{SM} v + C_s v \qquad (2\text{-}122)$$

where the mass transfer terms have been expanded. C_M is due to extraparticle mass transfer.

$$C_M = c_M \, d_p^2 / D_M \qquad (2\text{-}123a)$$

C_{SM} is due to diffusion in the stagnant mobile phase

$$C_{SM} = c_{SM} \, d_p^2 / D_{SM} \qquad (2\text{-}123b)$$

and C_s is due to diffusion in the stationary liquid phase coating the solid or to diffusion in the solid.

$$C_s = \frac{c_s \, d_f^2}{D_s} \qquad (2\text{-}123c)$$

This last term is often very small in liquid systems. Giddings[416] assumed that lateral dispersion could move solute from slow to fast streams in the column. This flow-diffusion coupling theory gives:

$$H = \frac{B}{v} + C_{SM} v + C_s v + \cfrac{1}{\cfrac{1}{A} + \cfrac{1}{C_M v}} \qquad (2\text{-}124)$$
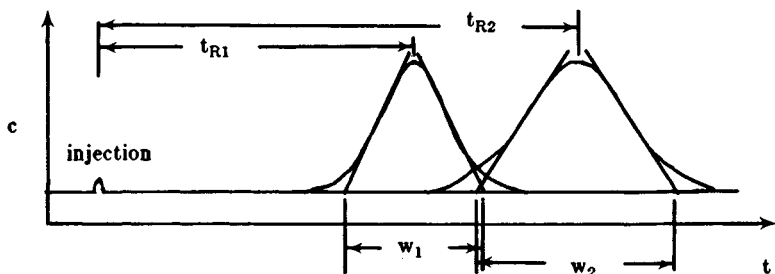
FIGURE 2-21.   Separation of two Gaussian peaks. See Equation 2-125.

where the A, B, and C definitions are unchanged. Other forms of the modified Van Deemter equation have been developed[517,605,606] and the basic predictions have been experimentally verified.[354,517,605,606,930,1109]

Since at practical operating velocities H is essentially proportional to d_p^2 and inversely proportional to D_M, zone spreading can be reduced by decreasing the particle diameter and by increasing the molecular diffusity. Decreasing d_p is discussed further in Chapter 3 (Section II.D). For liquid systems D_M can be increased by using a low-viscosity solvent or raising the temperature. However, raising the temperature also usually decreases the selectivity of the packing. The diffusivity in the pores, D_{SM}, can be increased by using large-pore packings. This is particularly important when large molecules are being separated.

Note that column diameter does not enter into any of the expressions for zone spreading. *If* the system is well designed and well packed, there is theoretically no reason why H obtained with small pulses should increase. The trick is proper design and packing of the column. Extracolumn zone broadening effects are not included in the Van Deemter equation, and can destroy the separation. Any dead zones or mixing zones in the feed system, distributors, piping, valves, and detection system can greatly increase H. All external volumes should be minimized by careful design and by placing equipment close together. Since solutes that are less strongly adsorbed (low k_i) will be more affected by extracolumn effects, the system can be tested with pulses of slow and fast solutes.[354] Skewed profiles or larger H values for the faster solutes are an indication that extracolumn zone broadening is important. Most commercial analytical chromatographs have been designed to minimize extracolumn effects. Since it always seemed less important, most large-scale adsorption and ion exchange systems have not been designed to minimize extracolumn zone broadening. This is a mistake when difficult separations are required.

Equations 2-87 and 2-111 were derived for differential pulses for systems with linear equilibrium. Thus the various forms of the Van Deemter expression, Equations 2-117, 2-122, and 2-124 are strictly valid only for this situation.

D. Resolution of Two Components by Linear Chromatography

One of the very useful things which can be done with the linear theory of chromatography is to predict the separation of two components. For Gaussian peaks the resolution between two solutes is defined as[354,416,870,930,1109]

$$R = \frac{2(t_{R_2} - t_{R_1})}{w_1 + w_2} \tag{2-125}$$

where the terms are illustrated in Figure 2-21. An R value of 1.5 represents complete separations while with an R of 1.0 the two peak maxima are separated by 4σ which is about 2% overlap. For large-scale systems with nonlinear isotherms and considerable overlap of the peaks, Equation 2-125 is not a good measure of the separation.

For differential pulse inputs in linear systems w_1 and w_2 are easily determined from the Gaussian distribution while the retention times can be found from Equation 2-94. The result is the "fundamental equation" of linear chromatography,

$$R = \frac{1}{2} \left(\frac{\alpha_{21} - 1}{1 + \alpha_{21}} \right) \frac{\overline{k'}}{1 + \overline{k'}} N^{1/2} \qquad (2\text{-}126)$$

In this equation k'_i is the relative retention of solute i,

$$k'_i = k_i V_s/V_M \qquad (2\text{-}127)$$

$\overline{k'}_i$ is the average relative retention of the two solutes, and α_{21} is the selectivity

$$\alpha_{21} = k'_2/k'_1 = \frac{k_2}{k_1} > 1.0 \qquad (2\text{-}128)$$

Thus α_{21} is the ratio of the distribution coefficients of the two solutes, and is the same as Equation 2-10.

Equation 2-126 shows that the resolution can be increased by increasing α_{21}, $\overline{k'}$, or N. Changes in α_{21} have by far the most effect. For α_{21} near 1.0 a very large number of stages are required. For α_{21} above 1.15 the number of stages becomes reasonable. This is just another way of saying that the solutes must have different distribution coefficients (different solute velocities) to separate. In large-scale systems an α_{21} above 1.50 or 2.0 is desirable. Changing the selectivity requires changing the chemistry of the system. This can be done by changing or modifying either the stationary phase or the mobile phase. When α_{21} is large, the stage requirement will be low. Thus H can be fairly large and, according to the Van Deemter equation, high velocities can be used (see Figure 2-20). Thus, increasing selectivity allows both shorter columns and high flow rates.

Another way to increase resolution is to increase $\overline{k'}$. However, as the relative retentions increase the solute velocities become slower and operating time increases. A value of $\overline{k'}$ between 4 to 6 seems to be a reasonable compromise.

Finally, resolution can be increased by increasing N. This can be done by decreasing H or increasing L. The plate height can be decreased by decreasing the particle diameter. Decreasing d_p and increasing L both increase the pressure drop so neither can be done indefinitely. If only small changes in resolution are required, increasing the column length is often the easiest thing to do. If large changes are needed, adjusting the system to change α_{21} is usually a good idea, particularly for large-scale systems where throughput is important.

In large-scale, nonlinear systems, Equation 2-126 is no longer valid. However, the qualitative conclusions drawn from this equation are valid.

E. Combining Zone Spreading Predictions with Solute Movement Theory

Exact superposition of the zone spreading predictions onto the solute movement theory is valid only for linear systems. However, we can approximately combine the results to make qualitative prediction. By adjusting the predictions with experimental data, we can develop a semiempirical theory.

The solute movement theory predicted three cases: linear systems, diffuse waves for nonlinear systems, and shock waves for nonlinear systems. For linear systems, superposition of zone spreading is valid. For diffuse waves the solute movement theory predicts that the zone spreading or band width is directly proportional to the distance traveled (see Figure 2-6B). Since linear chromatography theory predicts that zone spreading is proportional to $\sqrt{L}$, the diffuse wave effect is dominant. Thus the diffuse wave predictions shown in Figure 2-
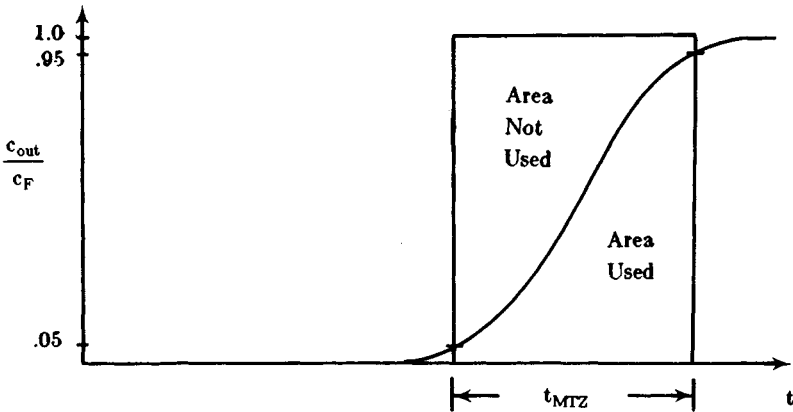
FIGURE 2-22.   Breakthrough curve for step input. LUB approach.

6C are quite accurate except at the corners. At very low concentrations the Langmuir isotherm becomes linear and thus the solute movement theory underpredicts zone spreading. At very high concentrations the Langmuir isotherm approaches an asymptote and thus also underpredicts zone spreading.

For nonlinear systems where the solute movement theory predicts shock waves, a constant pattern is generated. There is zone spreading around the shock wave (see Figure 2-9), but once developed it does not change shape. Linear chromatography results are qualitatively useful in this case. Although the zone has a constant shape for a given system, the amount of zone spreading depends on the system properties. The qualitative predictions of the Van Deemter equation will be correct. Thus if we increase the velocity in the region of Figure 2-20 where H increases then the width of the constant pattern will also increase.

The approximate combination approach has been used to model large-scale, nonlinear, coupled GLC.[463,536,864] First, the nonlinear isotherm effect, coupling effects of the solutes, and sorption effects were modeled with the local equilibrium theory. Then dispersion effects were added as if they were independent. This is an approximate procedure, but it appeared to work rather well.

VII. SIMPLE DESIGN PROCEDURES FOR NONLINEAR SYSTEMS

The solute movement theory is very useful for developing and understanding operating methods, but it is not a design method. The linear theories are useful for dilute systems, but not for most commercial processes where the isotherms are nonlinear. More complex theories have been and are constantly being developed, but have limitations for design. In this section we will outline a simple, semiempirical approach for design.

A. Mass Transfer Zone (MTZ) or Length of Unused Bed (LUB) Theories
In actual practice, shock waves will spread due to dispersion and finite rates of mass transfer. However, this spread is opposed by the isotherm and sorption effects which tend to form shock waves. The net result of these opposing forces is to form a "constant pattern" wave which does not change shape as it moves in the column. An example was shown in Figure 2-9C. Once formed the wave does not change shape as it moves down the column. This behavior will occur whenever the solute movement theory predicts a shock wave.

A common industrial design procedure for isothermal or approximately isothermal systems uses constant pattern analysis based on experimental data. What is actually measured is the "breakthrough curve" as shown in Figure 2-22. This is the outlet concentration which results

when a step input in concentration is used. The "mass transfer zone" (MTZ) is the region where concentration is changing and thus mass transfer is occurring. The length of the MTZ in time units, t_{MTZ}, is easily measured from the breakthrough curve (Figure 2-22). Usually the MTZ is arbitrarily measured from a concentration of 0.05 c_F to 0.95 c_F, since it is hard to tell exactly where the S-shaped pattern starts and ends. This problem is exacerbated by the noise typical in commercial adsorption.

We wish to use the breakthrough data to determine the MTZ length inside the column. The MTZ must move at the shock wave velocity u_{sh}. Then,

$$L_{MTZ} = u_{sh}t_{MTZ} \qquad (2\text{-}129)$$

The MTZ inside the column is the region where concentrations are changing and thus mass transfer is occurring. Upstream of the MTZ the bed is saturated at the feed concentration while downstream of the MTZ the bed contains no solute. Typically, adsorption is stopped when breakthrough just starts. Since the concentration in the MTZ is varying, the sorbent is not saturated through the entire length of the bed. Thus part of the bed is unused. The MTZ data can be used to design the column using the LUB method.

The LUB approach is based on the original work of Michaels[726] and has been applied to ion exchange and adsorption.[273,510,639,645,741,865,990] The basic idea is to determine from the breakthrough curve the fraction of the bed not used. Many different approaches which do this have been developed. We will use Figure 2-22. Inside the column the fractional bed utilization can be determined as

$$\text{Fraction of bed utilized} = \frac{L - L_{MTZ}\left(\dfrac{\text{area not used}}{\text{total area in MTZ}}\right)}{L} \qquad (2\text{-}130)$$

The ratio of area not used to total area in MTZ is the fraction of the MTZ which is not useful for adsorbing solute at the saturation concentration. This ratio can be determined from Figure 2-22. If the breakthrough curve is symmetric the ratio is 1:2. For symmetric breakthrough curves Equation 2-130 simplifies to:

$$\text{Fraction of bed utilized} = (L - 0.5L_{MTZ})/L \qquad (2\text{-}131)$$

The value of L_{MTZ} can be obtained from Figure 2-22 by use of Equation 2-129. Note that if u_{sh} is very low L_{MTZ} may be very short even though it appears long in Figure 2-22.

The amount of solute which can be held by the bed is

$$\text{Capacity} = (\text{Fraction of beds utilized})mq_{sat} \qquad (2\text{-}132)$$

where q_{sat} is the saturation capacity of the adsorbent for the given feed concentration and m is the mass of adsorbent in the column. Obviously, the capacity can be increased by increasing any of the three variables in Equation 2-132. The fractional bed utilization can be increased by increasing L or decreasing the MTZ. The MTZ will be shorter for rapid mass transfer rates or small-size adsorbent particles. The MTZ tends to be quite large for large molecules such as proteins which have low rates of mass transfer. The saturation capacity, q_{sat}, depends on the adsorbent used and the temperature. The effect of increasing L/L_{MTZ} is discussed in Chapter 3 (Section II.C).

The LUB approach has several limitations. The most obvious limitation is it is only applicable to constant pattern systems. For a favorable isotherm this would be the adsorption step. Some other approach will be required for the desorption step. The LUB approach is

strictly applicable for isothermal systems,[273] although it is often applied for nonisothermal systems with modest temperature fluctuations. Large changes in temperature can destabilize the MTZ and give nonconstant patterns.[639] The LUB approach has been adapted to nonisothermal systems,[639] but it becomes more complex. Scale-up also becomes more difficult since small columns are usually not adiabatic while large columns usually are adiabatic.

The LUB approach requires experimental data. This is really less of a disadvantage than it may seem at first since more fundamental theories also require data. Obtaining data on the chemical system which will actually be separated is very helpful if any trace components are present since they may affect the adsorbent markedly. The same particle size should be used in the laboratory column. To avoid wall effects, values of the ratio diameter/$d_p > 30$ should be used for Newtonian fluids and greater than 50 for non-Newtonian fluids.[271]

Constant pattern systems are amenable to significant mathematical simplification. The constant pattern will always form when conditions are right.[283] Because the shape of the pattern is invariant, the partial differential equations can be transformed into ordinary differential equations based on the distance from the stoichiometric front (the shock wave location). This simplification has led to a deluge of theories for constant pattern systems. These theories are reviewed in detail elsewhere.[165,510,522,657,865,901,912,990,1015-1017,1101] In the remainder of this section a simple isothermal model will be developed.[901]

The usual starting point for a theoretical analysis is Equation 2-73 plus some mass balance expression such as Equation 2-74. The constant pattern will be a function of τ,

$$\tau = t - z/u_{sh} \tag{2-133}$$

since τ is a measure of the time or distance from the center of the pattern. Neglecting axial dispersion, we can reduce Equation 2-73 to an ordinary differential equation by introducing τ. The result is

$$\epsilon' \left(1 - \frac{v}{u_{sh}}\right) \frac{dc}{d\tau} + \rho_B(1 - \epsilon') \frac{dq}{d\tau} = 0 \tag{2-134}$$

This equation has the obvious solution:

$$\left(\frac{v - u_{sh}}{u_{sh}}\right) \epsilon'c - \rho_B(1 - \epsilon')\, q = \text{constant} \tag{2-135}$$

If the bed is initially clean, $c = q = 0$ and the constant must be zero. Equation 2-135 can be written for arbitrary conditions in the wave, c and q, and for final conditions after the wave has passed, c_{final} and q_{final}. Dividing one equation by the other,

$$\frac{c}{c_{final}} = \frac{q}{q_{final}} \tag{2-136}$$

Substituting Equations 2-133 and 2-136 into Equation 2-74 we obtain:

$$(1 - \epsilon')\rho_B \frac{q_{final}}{c_{final}} \frac{dc}{d\tau} = -k_M a_p(c^* - c) \tag{2-137}$$

It is usually assumed that the stagnant fluid c^* is in equilibrium with the solid, but $c^* \neq c$. The variable c^* can then be substituted for from the isotherm and q can be removed with Equation 2-136. For example, with the general Langmuir expression,

$$c^* = \frac{q}{a - bq} = \frac{c(q_{final}/c_{final})}{a - bc(q_{final}/c_{final})} \tag{2-138}$$

Substitution of this equation into Equation 2-137 gives the simple ODE,

$$\rho_B(1 - \epsilon')\left(\frac{q_{final}}{c_{final}}\right)\frac{dc}{d\tau} = k_M a_p\left[c - \frac{c(q_{final}/c_{final})}{a - bc(q_{final}/c_{final})}\right] \tag{2-139}$$

which is easily integrated.

The MTZ can be obtained by rearranging Equation 2-139 and integrating from $c = 0.05c_F$ to $0.95c_F$. The result is

$$\Delta\tau = \frac{\rho_B(1 - \epsilon')\left(\frac{q_F}{c_F}\right)}{k_M a_p}\left\{\frac{-a}{a - \frac{q_F}{c_F}}\ln\left[\frac{0.05}{0.95}\frac{a - \frac{q_F}{c_F} - 0.95bq_F}{a - \frac{q_F}{c_F} - 0.05bq_F}\right]\right\}$$

$$+ \ln\left[\frac{a - \frac{q_F}{c_F} - 0.95bq_F}{a - \frac{q_F}{c_F} - 0.05bq_F}\right] \tag{2-140}$$

If $z = L$, $\Delta\tau = t/_{c=0.95c_F} - t/_{c=0.05c_F}$ which is the t_{MTZ}. If $t = t_{breakthrough}$, $\Delta\tau = L_{MTZ}/u_{sh}$. Equation 2-140 will be useful later on.

B. Design of Total Cycle

Someday, computer codes will exist to allow design of the total adsorption/desorption cycle for arbitrary systems. Although progress is being made and restricted but important problems can be solved quite rigorously, the day of a complete solution for any problem is not yet here. In the meantime, relatively simple procedures can be used for preliminary designs of many systems.

For the adsorption of one solute with favorable isotherms and modest heat effects the LUB approach is satisfactory. This requires column experiments as shown in Figure 2-22. During desorption a proportional pattern usually develops. The local equilibrium (solute movement) theory usually gives quite reasonable predictions for proportional pattern behavior. Thus, if the equilibrium isotherm under the conditions of desorption is determined, the solute movement theory can predict the desorption part of the cycle. This combined approach is "quick-and-dirty" but should be acceptable in most cases.

For linear systems the theories of Section VI. work very well. The major applications of these theories has been in analytical chromatography. They are useful in a limited number of large-scale chromatography applications (see Chapter 5). Nonlinear gas chromatography has been designed by superposition of local equilibrium models and dispersion. More complicated situations will usually require numerical solution of at least part of the cycle. More detailed models used are reviewed elsewhere.[59,112,165,513a,536,657,686,832,865,901,912,1006,1015-1017,1068,1073,1101] Ruthven's book[865] is a detailed, up-to-date resource for modeling.

VIII. SUMMARY

This chapter is long because it serves as a basis for all of the other chapters. Since in most adsorption and chromatography techniques equilibrium or deviations from equilibrium are the basis for separation, good equilibrium data is necessary. Although a number of equilibrium isotherms were given, the list was not exhaustive. The solute movement theory is a method for visualizing what is happening in the column. It provides a means for thinking about how equilibrium and operating methods are combining to cause the separation. Since this theory is simple compared to other theories of adsorption, it can be used as a tool to think about, explore, compare, and try on paper new operating schemes. We will be using the solute movement theory to do this in the remainder of this book.

Mass transfer and dispersion work to limit or destroy the separation. The staged models and rate theories quantify these effects. For linear systems the zone spreading effects are conveniently included in the Van Deemter equation. Thus the Van Deemter equation is a very useful tool to explain and then reduce zone spreading. The zone spreading for linear systems is proportional to the square root of the distance traveled.

For nonlinear systems with favorable isotherms a constant pattern is formed when a dilute solution is displaced by a concentrated solution. The zone spreading is now independent of distance traveled and the LUB approach can be used for design. For the same chemical system a proportional pattern (diffuse wave) will form when a concentrated solution is displaced by a dilute solution. Now the zone spreading is proportional to the distance traveled. Since the isotherm curvature controls zone spreading for proportional pattern systems, the equilibrium theories often given excellent predictions.

Chapter 3

PACKED BED ADSORPTION OPERATIONS

I. INTRODUCTION

In this chapter we will consider several common operating methods for recovery of a single solute or for removal of all solutes as a waste stream. We will also consider processes where the adsorption and desorption steps are often conceived of as two separate parts. In Chapter 4 the adsorption and desorption steps tend to be more tightly coupled. Chapters 3 and 4 complement each other, and the division between chapters is somewhat arbitrary. Chapter 5, which also covers packed beds, considers chromatographic separations where fractionation is done.

Many common industrial processes are included in this chapter. These include trace contaminant removal, drying of gases and liquids, solvent recovery with activated carbon, and wastewater treatment with activated carbon. Many of these processes can be done by several different operating methods, and thus the process will appear in several chapters. For example, solvent recovery with activated carbon is done in packed beds (Chapter 3), in countercurrent moving beds (Chapter 6), and in rotating beds (Chapter 8).

This chapter is structured to first look at the operation of a packed bed in general. Methods for desorption and for increasing the efficiency of the process are discussed. Then the specific adsorption processes are briefly covered with an emphasis on thermal desorption processes. Desorption using solvents is covered in a separate section at the end of this chapter (and in Chapter 6 [Section V.B]) and pressure swing adsorption is covered in Chapter 4.

II. OPERATION OF PACKED BEDS

A variety of operating cycles have been developed for packed bed adsorbers. In this section we will look at some of the alternatives in a general sense, and develop a background which will be useful when we look at individual processes.

A. Adsorption-Desorption Methods

Essentially, four approaches have been developed for adsorption-desorption cycles. The first is a nonregenerative design where the charge of adsorbent lasts the life of the system without being regenerated.[17,253,282] This type of system is used in sealed dual-pane windows, in some food products, and as an antidote in poisonings. This method will not be considered further here.

The second approach is to adsorb until the adsorbent is saturated and then replace the adsorbent. Totally new adsorbent may be used as in the canister of a gas mask.[666,687] Gas mask canisters are often complex mixtures of several sorbents in series, and they would be difficult to regenerate. Also, incomplete regeneration could be serious. Thus total replacement of the canister is the usual procedure. Total replacement of adsorbent in the form of canisters is also used occasionally in air purification systems for odor removal.[608,687] The adsorbent is usually activated carbon. Since the concentration of the odor-causing chemicals is usually very low, the adsorbers can be kept on stream for very long periods (often years) before the canisters have to be replaced. (Some canister systems are regenerated in place and fit into the fourth category of operating methods.) These systems will not be discussed further. Canister systems are also used in treating drinking water with activated carbon (see Section IV.B).

A similar approach is commonly used for wastewater treatment with activated carbon and for treating molasses with activated carbon, except regeneration of the carbon in a separate furnace is planned for. The regeneration may be done on or off site. The adsorption and desorption cycles are effectively decoupled. The adsorption cycle consists of loading the adsorbent into the column, adding a charge if liquids are being processed (the sweetening-on step), processing the fluid during the feed step, and then removing the used adsorbent from the column. This type of cycle is common when trace amounts of strongly adsorbed materials are removed, and the feed step can be quite long.

The third type of operation consists of loading regenerated sorbent into the column, sweetening on, doing the adsorption step, and emptying the column. The sorbent is sent to a separate vessel where it is regenerated and then immediately reused. Regeneration can be done by any of the means used for the fourth type of operation (see below). This type of operation is often used in the food and pharmaceutical industries since it clearly keeps the regeneration materials away from the process fluids. This type of system differs from the second type of operation since the adsorption and regeneration steps are fairly closely coupled, and the adsorption step cannot be designed completely independently of the desorption step.

In the fourth type of operation the adsorption and regeneration steps are done in the same vessel and the adsorbent is not transferred from one vessel to another. A typical cycle consists of adsorption, regeneration, and preparation for the next cycle.

A variety of regeneration methods are used in the third and fourth type of operations. These include:

- Noncondensing hot gas
- External heating
- Steam or other condensing hot gas
- Hot liquid
- Drain column and then use hot gas
- A gas or liquid desorbent (see Chapters 4 and 6 also)
- Brine (fluid of high ionic strength)
- Pressure swing (see Chapter 4)
- Vacuum (see Chapter 4 also)
- A combination of the above

Details of these regeneration steps will be explored when the individual processes are considered.

The steps required to prepare the column for the next adsorption step depend on the regeneration step. In some cases where hot gas is used for regeneration no preparation step is required, while in other cases the bed may have to be cooled. When steam is used for regeneration, the bed may need to be dried and/or cooled. When desorbent or brine are used, they need to be washed out from the column. With pressure swings and vacuum regeneration the pressure needs to be increased to the operating pressure. In addition to these steps, a backwash may be used to remove suspended solids which have been trapped on the bed. Also, a sweetening-on step may be needed to add a concentrated viscous material to the column, and a sweetening-off step may be used before the regeneration step to recover valuable feed material in the column.

B. Desorption Cycles

When the adsorbent is to be regenerated in the same vessel or in a separate vessel which is closely coupled to the adsorption step, the desorption or regeneration step is crucial to the commercial success of the process. Despite the importance of desorption, many articles in the literature look at only the adsorption step instead of the entire cycle. If only the

FIGURE 3-1. Co-flow regeneration. (A) Steps in cycle; (B) concentration profile in column at end of feed step; (C) concentration profiles in column during regeneration. 1, Early in regeneration step; 3, end of regeneration.

adsorption step is looked at, incorrect conclusions may be drawn about desired operating conditions. It is important to always consider the entire cycle.

Regeneration can be done with either co-flow (in the same direction as the feed in the adsorption step) or counter-flow (in the opposite direction to the feed). Co-flow regeneration is shown schematically in Figure 3-1A. Either up-flow or down-flow may be used. The feed step is continued until breakthrough occurs as shown in Figure 3-1B. With co-flow regeneration the regeneration fluid flows in the same direction and pushes the concentration profile through the previously clean part of the bed. This is illustrated in Figure 3-1C where the concentration profiles are shown for three times during the regeneration step. Co-flow desorption thus contaminates the clean part of the bed, which is undesirable.

Counter-flow regeneration is shown schematically in Figure 3-2A. The feed step is essentially the same as in co-flow systems, and the concentration profile at breakthrough is illustrated in Figure 3-2B. Regeneration is now done in the opposite direction as shown in Figure 3-2C. With counter-flow operation the clean end of the bed stays clean. Regeneration is seldom run long enough to completely clean the column. Thus a residual amount of solute (the "heel") is often left in the column. With co-flow (Figure 3-1C) this residual will appear in the product during the next feed step. With counter-flow regeneration the residual is at the feed end of the column, and the solute can be readsorbed.

The solute movement theory developed in Chapter 2 can be used to compare co- and counter-flow regeneration. The advantages of counter-flow are most evident when the isotherms are nonlinear and have a favorable shape (Langmuir or Freundlich). Consider a case where a hot fluid is used for regeneration. (The solute movement theory can also be applied to other regeneration methods.) Heating decreases adsorption and makes the solute wave velocities higher (Equations 2-28, 2-32, or 2-35). The resulting solute movement diagrams for co- and counter-flow are shown in Figures 3-3A and B, assuming the thermal wave is faster than the solute waves. Co-flow does not produce a pure final product unless the column is completely regenerated. A pure product can be produced with counter-flow even though the column is not completely regenerated. In addition, the diffuse wave which is generated during the regeneration step can be partially recompressed (or swallowed by the shock wave)
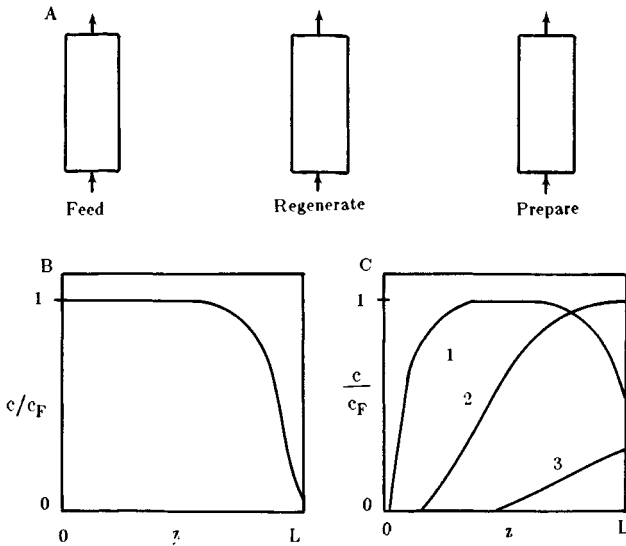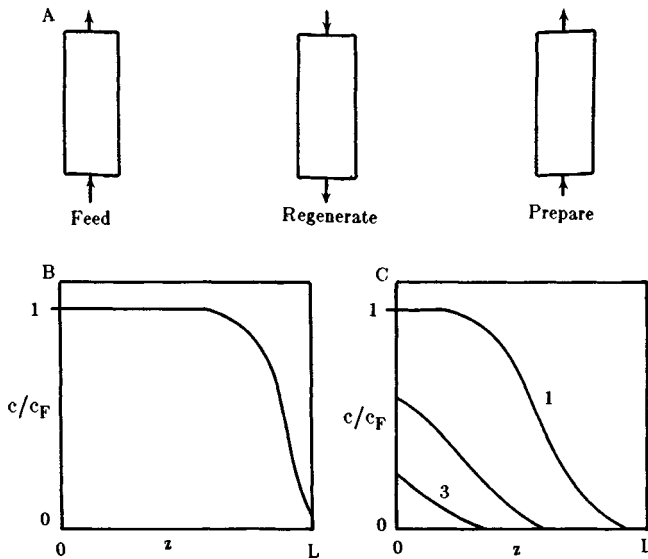
FIGURE 3-2. Counter-flow regeneration. (A) Steps in cycle; (B) concentration profile in column at end of feed step; (C) concentration profiles in column during regeneration. 1. Early in regeneration; 3, end of regeneration.

as shown in Figure 3-3B. The step increase in concentration when feed is added causes a shock wave which decreases in slope as less concentrated material is intersected, and the diffuse wave disappears. Counter-flow regeneration is usually used for adsorption systems because of these advantages. The adsorbate will leave the column as a quite concentrated peak which then tails when the diffuse wave exits. Thus, adsorption columns can serve as concentrators for dilute streams, and may be the cheapest way to concentrate. Co-flow has advantages for fractionation systems where a heel can often *not* be left in the column and is used in chromatography (Chapter 5) and in simulated countercurrent systems (Chapter 6).

In some cases the cooling period shown in Figures 3-3 is not required.[109] This is the case when the thermal wave set up by the cool feed solution moves faster than the concentration wave (see Section III.B). Even when a cooling step is desirable it can usually be much shorter than shown in Figures 3-3A and B. A short cooling step followed by feed will push the hot fluid out of the column before the solute wave breaks through.

How much regeneration should be done? Partial regeneration keeps the MTZ inside the column, and makes the regeneration product much more concentrated in solute. This procedure also minimizes the amount of desorbent or purge fluid required. (Of course, there are situations where it is desirable to completely regenerate the bed, but they are unusual.) A loading diagram can be constructed using the equilibrium curve and the solute movement diagram shown in Figure 3-3B. Figure 3-4A illustrates the loading in the bed when partial regeneration is used. Note that the useful capacity is considerably less than the total capacity, but regeneration is stopped at a convenient time. Typically, this would be some multiple of the adsorption time so that several columns can be used to allow continuous processing of the feed. Complete regeneration is shown in Figure 3-4B. For systems with nonlinear "favorable" isotherms desorption is slower than adsorption. This occurs because the MTZ during the adsorption step approaches a constant shape while the diffuse wave during desorption grows proportionally to the distance traveled. With longer desorption periods, the useful capacity increases, but the capacity/time and the outlet concentration of the purge stream decrease. Thus, partial regeneration is usually favored. This is particularly true when the isotherm is very nonlinear and the diffuse wave would show considerable tailing. This
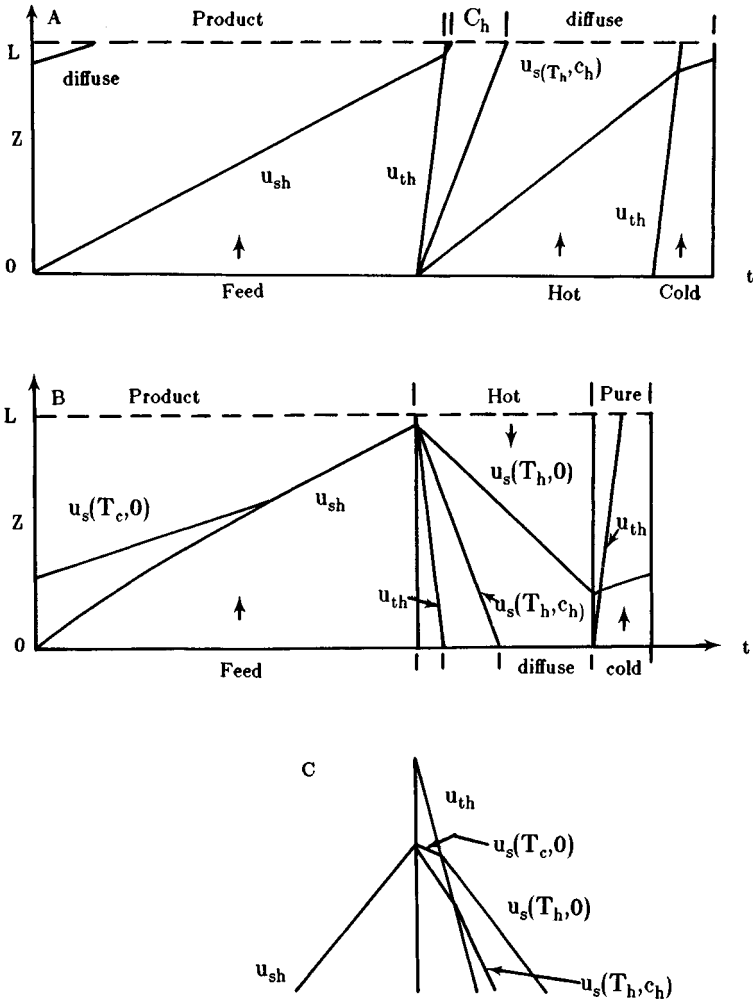
FIGURE 3-3. Solute movement diagram for system with nonlinear isotherms. (A) Co-flow; (B) counter-flow; (C) blown-up diagram for intersection of thermal waves and solute waves for counter-flow.

situation occurs in drying of gases and in solvent recovery with activated carbon. As a general rule it is best to keep the system small and to cycle fairly rapidly.

C. Increasing Fractional Use of the Bed

The fractional use of the bed for the situation shown in Figure 3-4A can be very low. This results in a very low adsorbent productivity (kilogram of adsorbate per kilogram adsorbent-hour) and thus may require rather large beds. In addition, the concentration of adsorbate in the purge product may be quite low. Several methods can be used to increase the fractional bed use and increase the productivity.

For the usual situation for adsorption where the isotherm is nonlinear and the shape is "favorable", the fractional bed use can be increased by increasing the bed length. With favorable isotherms a constant pattern wave is formed and the MTZ will reach a constant length. Then as the bed length, L, increases the ratio L_{MTZ}/L decreases and the relative length of the bed which can be fully loaded increases. This effect is shown in Figure 3-5[676] for the adsorption part of the cycle only. There is a decreasing rate of improvement as the
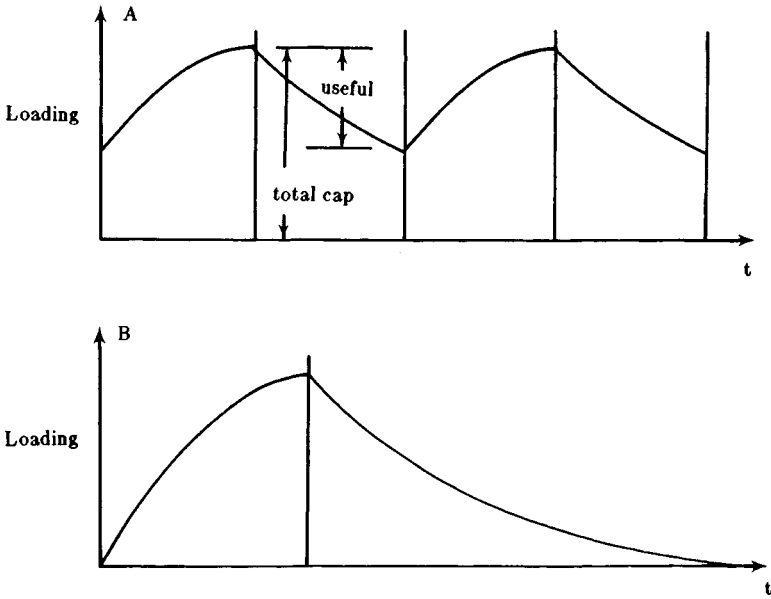
FIGURE 3-4. Total column loading during cycle. (A) Partial regeneration; (B) total regeneration.
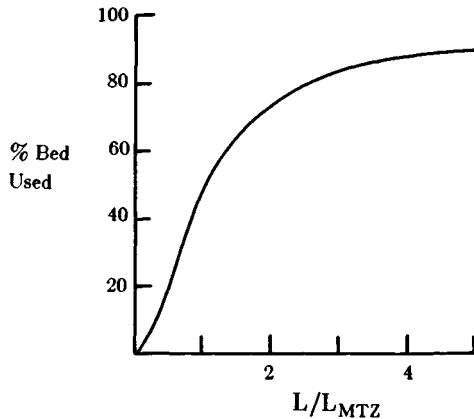
FIGURE 3-5.   Fraction of bed used as function of L/
L_{MTZ}. (From Lukchis, G. M., *Chem. Eng.*, 80(13), 111,
1973. With permission.)

bed length increases past two to three times the L_{MTZ}. The appropriate bed length thus depends very heavily on the length of the MTZ, and thus on the mass transfer rate and the equilibium isotherm. Increasing the bed length will also increase the pressure drop. The fractional use of the bed and the sorbent productivity can be increased by decreasing the particle diameter. This is discussed in detail in Section II.D.

The bed utilization can also be increased by using layered beds. One way of doing this is to use one layer of large-diameter particle followed by a layer of the same adsorbent of a considerably smaller diameter.[382b] In the first layer the pressure drop will be low, but the MTZ will be quite long. If the isotherm is favorable the MTZ will be sharpened in the second layer since there is less resistance to mass transfer in the smaller particles. The layered bed can then have a small L_{MTZ} at the outlet which means a small ratio of L_{MTZ}/L
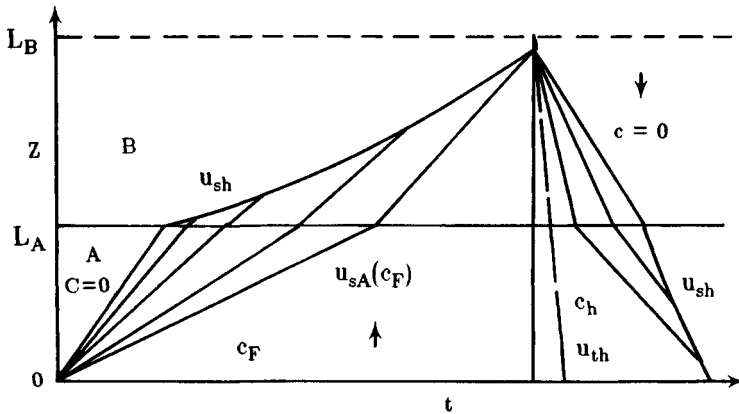
FIGURE 3-6. Solute movement diagram for layered beds. Adsorbent A has unfavorable isotherm while B has a favorable isotherm.

and hence a large fractional bed use. At the same time the pressure drop will be considerably less than a bed which was entirely small particles. Use of this procedure has been reported with two sizes of zeolites.[112]

A second way to use layered beds is to use two different adsorbents.[12,112,268,1016] If a cheap adsorbent with a modestly favorable isotherm is covered with an expensive adsorbent with a very favorable isotherm, the shock wave will be tightened up when it reaches the second layer. Thus, bed utilization will be higher or a purer product will be produced but at lower cost. This procedure is done with mixtures of silica gel and zeolite molecular sieve, and other combinations of adsorbents. Layered beds of different adsorbents are also used to remove several adsorbates from the feed stream. A unique application of this concept is on spacecraft.[308,309]

Another use of layers is to use a guard bed which protects the main bed from contaminants which might polymerize or irreversibly adsorb. The guard bed can use sorbent which has lost some of its capacity, but is still useful.

The two layers could be two different sorbents which have different isotherm curvatures. If a layer of adsorbent with an unfavorable isotherm is covered with a layer with a favorable isotherm, the column will have particularly advantageous properties. A diffuse wave will form in the adsorbent with the unfavorable isotherm during the adsorption step. This diffuse wave will be refocused in the second layer of adsorbent. The result at the outlet of the column will be a shock (constant pattern) wave. Then the bed utilization during the adsorption step can be quite high. During counter-flow desorption a diffuse wave will form in the bed with the favorable isotherm, but this wave will be refocused in the layer of adsorbent with an unfavorable isotherm. The result is a shock wave at the feed end of the column. This type of system can then have tight constant patterns during both adsorption and desorption. This situation is illustrated using a solute movement diagram in Figure 3-6. Note that when dispersion is ignored the diffuse waves can be recompressed. In Figure 3-6 sorbent B has a favorable isotherm while sorbent A has an unfavorable isotherm. This could be achieved by using an adsorbent such as activated carbon for sobent B, and a reverse-phase chromatographic packing for sorbent A. The wave slopes vary when the boundary between sorbents is passed. Since the isotherms have different curvatures, the waves can either speed up or slow down at the transition point. The exact shape of the solute movement diagram will depend on the sorbents and their isotherm shapes. With only one adsorbent a diffuse wave must form during either the adsorption or regeneration steps. This two-layer procedure has been studied for ion exchange systems.[595]
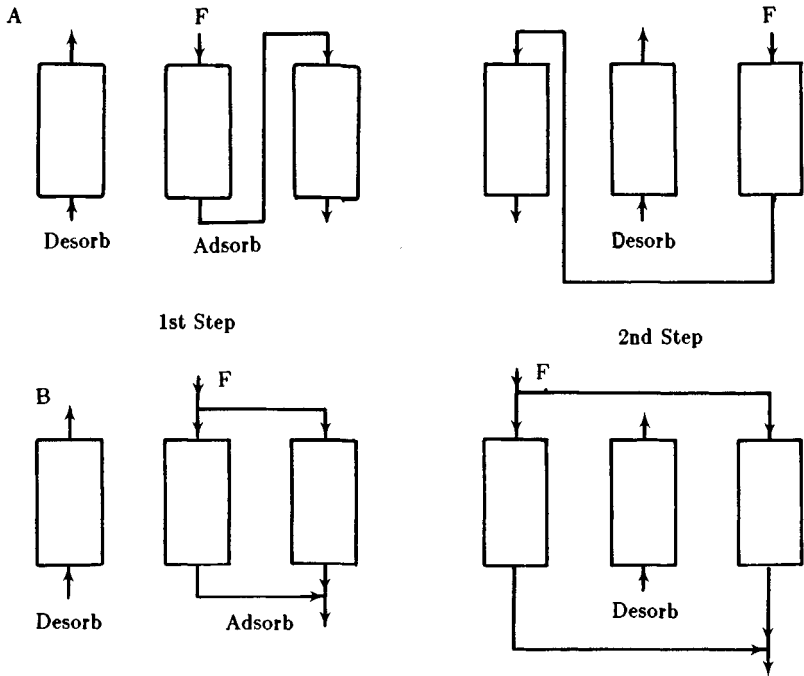
FIGURE 3-7.   Increasing bed utilization. (A) Series arrangement; (B) parallel arrangement.

For removal of a divalent ion by ion exchange the column can be operated so that equilibrium is favorable for sorption of the divalent ion during the loading step and unfavorable for the divalent ion during the regeneration step. This is possible since the equilibrium expression, Equation 2-23, depends on the total equivalents per liter of ions in the solution. The result will be shock waves during both loading and regeneration steps, and a minimum of dispersion. This approach is commonly used for water softening where concentrated sodium chloride solution is used for regeneration. This approach does not appear to be generally applicable to adsorption.

Another procedure which can be used to increase fractional bed use is to use multiple beds either in series (Figure 3-7A) or in parallel (Figure 3-7B). In the series case, two or more columns are connected in series while the other column(s) is regenerated. The first column in the series can be totally saturated while the MTZ is held in the remaining columns. The freshly regenerated column is put on at the tail end of the series. If counter-flow regeneration is used, the column does not have to be completely regenerated. This procedure is commonly used,[247,327,380,382b,469,522,527,557,591,655,677,687,785, 946,954,1016] particularly for systems with long MTZs such as activated carbon wastewater treatment.[327,380,522,527,557,591,785]

Many theoretical studies of the series systems have been reported[247,327,591,655,946,954] using numerical methods to solve the equations. An alternate way to use columns in series, but with only two columns, is discussed in Section III.A. and shown in Table 3-1. When there are several columns in the series at one time the method is often called a "merry-go round", and is related to simulated moving bed techniques (see Chapter 6, Section V.A.).

In the parallel system shown in Figure 3-7B, the bed which will be desorbed next is run past the allowable breakthrough concentration, but the product concentration is kept below acceptable levels.[380,527,946] The parallel arrangement has the advantage of a lower pressure drop, but always has a lower bed utilization and a less concentrated effluent than the series case.[946] The solute movement theory for nonlinear isotherms can easily be used to analyze both the series and the parallel cases.

Table 3-1
NO$_x$ CYCLE[556]

Step 1. Col. 1 adsorbing
Col. 2 desorbing

Step 2. Col. 1 adsorbing
Col. 2 cooling

Step 3. Col. 1 adsorbing
Col. 2 adsorbing in series
behind Col. 1

Step 4. Col. 1 desorbing
Col. 2 adsorbing

Step 5. Col. 1 cooling

Col. 2 adsorbing

Step 6. Col. 1 adsorbing in series
behind Col. 2
Col. 2 adsorbing
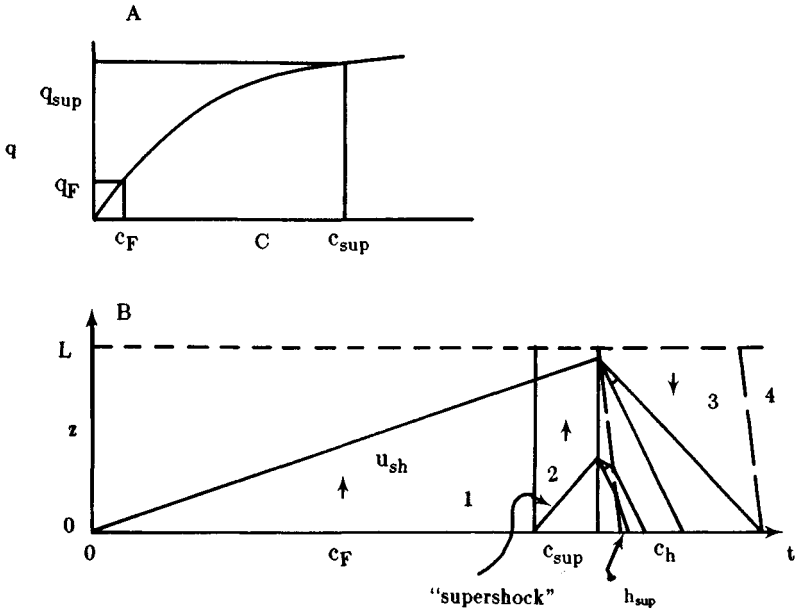
FIGURE 3-8. "Superloading" procedure. (A) Illustration on equilibrium diagram; (B) solute movement diagram. 1, Feed step; 2, "superloaded"; 3, solvent rinse; 4, water rinse.

A final method for increasing the bed utilization is the "superloading" or two-feed adsorption concept.[381,382,382a,1026] An adsorbent bed was used to remove phenol from water. The bed was regenerated with acetone followed by a water rinse. The eluant from regeneration was distilled and acetone was the distillate product. The bottoms product separated into two layers: a phenol-rich layer which was recovered and an aqueous layer with 10% phenol (a process flow sheet is shown later in Figure 3-20). This layer was sent to the adsorption column at the end of the usual loading step. Even though the bed was saturated with phenol at the feed concentration, the bed still had considerable capacity for phenol at the very high concentrations in the waste aqueous phase. This is shown schematically for a favorable isotherm in Figure 3-8A. This superloading procedure increases the concentration of phenol in the bed and thus gives a higher concentration feed to the distillation column. This procedure should be adaptable to other adsorption problems. It would be generally applicable whenever two feeds of different concentration need to be processed. The more concentrated feed enters after the dilute feed. This procedure is roughly analogus to a distillation column with two feeds. The solute movement diagram for superloading is shown in Figure 3-8B. The superloading produces a shock wave, the velocity of which can be calculated from Equation 2-28. During regeneration an acetone wave and two diffuse waves will be formed. Complete

regeneration of the column is not required, and a heel can be left in the column. The solute movement diagram can look different depending on the isotherm shape and the periods for each step.

D. Intensification of Adsorption: Particle Diameter Effects

Particle diameter has a major effect on the behavior of the packed bed. In this section we will explore this effect for packed bed adsorption systems. The changes in analytical liquid chromatographic columns over the last 25 years have been tremendous. By decreasing the particle size and increasing the pressure drop, column lengths and analysis times have decreased by almost two orders of magnitude. Unfortunately, very little of this process intensification has appeared in large-scale adsorption or chromatography. In this section we will show that many packed bed commercial adsorption systems can operate with shorter columns and faster cycles to increase the productivity of the adsorbent by at least an order of magnitude. This requires decreasing the particle diameter, but can be done with *no* increase in total pressure drop. Continuous systems have different requirements (see Chapter 6, Sections II and III) and this section does not apply to moving bed systems.

In Chapter 2, Section VI.C we saw that under most circumstances the plate height for linear systems is directly proportional to d_p^2. If pore diffusion controls this is absolutely true. Thus, N is proportional to (L/d_p^2). By decreasing the particle diameter we can increase N and thus shorten the MTZ, or we can decrease both d_p and L while keeping N constant.

Decreasing the particle diameter also affects the pressure drop. For laminar flow, which is almost always the case in chromatography and adsorption, the pressure drop equation is[138,549]

$$\Delta p = \frac{v\mu L}{Kd_p^2} \qquad (3\text{-}1)$$

For rigid particles the permeability K can be calculated from[138]

$$K = \frac{\alpha^3}{150(1 - \alpha)^2} \qquad (3\text{-}2)$$

while for deformable gel particles[549]

$$K = K_o \exp\left(-\frac{a\,\Delta p}{L}\right) \qquad (3\text{-}3)$$

In this section we will restrict ourselves to rigid particles. Equation 3-1 shows that the total pressure drop is proportional to (L/d_p^2) which is exactly the same functional dependence as N.

For process intensification we can decrease both the particle diameter and L, keeping (L/d_p^2) constant. Now Δp and N are unchanged. The zone of changing concentrations (MTZ) requires the same number of stages in the column, N_{MTZ}, and the fractional length of the MTZ is the same

$$\frac{L_{MTZ}}{L} = \frac{N_{MTZ}}{N} = \text{constant} \qquad (3\text{-}4)$$

Thus the fraction of the column which can be used per cycle is unchanged. Since the column is shorter it will saturate faster. Thus, the cycle period is decreased by the same factor as

L. Over many cycles the throughput is unchanged but the adsorbent productivity [moles throughput]/[(kg adsorbent) (hour)], increases by the same factor as L decreased. The faster cycling and the shorter column length cause this increase in productivity. The smaller particle diameters allows one to shorten the bed and cycle faster.

An alternate solution is used commercially by the Graver Company.[623] They attach very small particles to fibers to give a system with very rapid mass transfer and low pressure drop. However, currently these systems are not regenerated.

The productivity argument was based on the Van Deemter equation which is valid for linear systems. How about nonlinear systems? The distance that shock and diffuse waves travel is proportional to time. Thus if the cycle time and L are decreased by the same factor, the fraction of the column length traveled by the wave is unchanged. This can be seen by changing both L and t in Figures 2-6 and 2-9. Since the zone spreading in a diffuse wave is proportional to L, the fraction of the column occupied by the diffuse wave will be unchanged when L and t are both decreased. For constant pattern waves the width of the MTZ depends on a dynamic balance between dispersion and the compressive effects of the shock wave. Equation 2-140 shows that L_{MTZ} is inversely proportional to $K_m a_p$. If pore diffusion controls, $K_M a_p$ is inversely proportional to d_p^2 and thus L_{MTZ} is proportional to d_p^2. If we scale by L/d_p^2, L/L_{MTZ} is constant and the fractional bed use remains constant.

The question of whether the column will scale L/d_p^2 can also be asked using the Thomas solution for Langmuir isotherms (e.g., see References 901 or 1016). When this is done it is easy to show that if pore diffusion controls, the number of transfer units is proportional to L/d_p^2 and Equation 3-4 is valid if (L/d_p^2) is constant. A good example of this is to rework example 10.6 in Reference 901 to include this scaling. This is shown in Table 3-2. The problem consists of adsorbing 10 mol % methane from hydrogen at 10 atm and 25°C on activated carbon. Flow rate was 100 ft³/min and the adsorption time was 10 min. Cases 1 to 3 were previously reported.[901] The authors concluded that there was an advantage in decreasing particle size from 4 to 10 mesh, but not from 10 to 20 mesh. Case 4 is a new calculation which uses 20-mesh particles but reduces the period so that n and nT (terms in the Thomas solution[901]) are kept at the same value as in Case 2. This results in a bed which is roughly four times smaller than Case 2, has a period roughly four times shorter, but has essentially the same number of transfer units and the same pressure drop. Thus, Case 4 has the same relative bed utilization as Case 2 but with an adsorbent productivity which is roughly four times greater. There is an advantage to decreasing the particle size if the cycle period is also decreased.

In this example, scaling was done to keep the number of transfer units n constant and not exactly as $1/d_p^2$. Scaling by $1/d_p^2$ would have reduced the column length by a factor of 4 instead of the 3.92 actually observed. This problem does not scale exactly as $1/d_p^2$ since $k_t a_p$ is not negligible in the determination of $k_T a_p$, and $k_f a_p$ is proportional to $1/d_p^{1.415}$. The difference is not very significant and there is still an obvious advantage in decreasing d_p, L, and the adsorption period.

So far, only the adsorption step has been discussed. Can the desorption step also be done faster? The answer is yes, if certain conditions are met. The time for the desorption step will also scale by the same factor used to decrease the column length. For thermal desorption the time for the thermal wave to break through is proportional to L. Thus the fraction of the desorption period required for breakthrough is constant. The analysis of Van Deemter et al.[1008] could be applied to the energy balance. The result would be a Van Deemter equation for the number of thermal stages in the column. If thermal pore diffusion controls, then N_{th} will be proportional to (L/d_p^2). This means that

$$\frac{\text{Width thermal transfer zone}}{L} = \text{constant} \tag{3-5}$$

Table 3-2
EXPANDED RESULTS OF THOMAS CALCULATION FOR EXAMPLE 10.6 OF SHERWOOD ET AL.[901]

Case	dp (cm)	Period (min)	$k_p(k_M)$ (cm/sec)	$a(a_p)$ (cm²/cm³)	Superficial Vel (cm/sec)	k_f (cm/sec)	$\kappa(k_T)$ (cm/sec)	$\kappa a\ (k_T a_p)$	n	nT	Length (ft)	Adsorbent volume (ft³)	Δp in, H_2O
1	0.476 (4 mesh)	10	0.0327	8.26	3.0	1.06	0.0364	0.300	30.6	17.65	10.05	185.7	0.42
2	0.168 (10 mesh)	10	0.0927	23.4	3.0	2.02	0.1016	2.38	160.9	143	6.63	122.5	2.24
3	0.0841 (20 mesh)	10	0.0185	46.6	3.0	3.05	0.200	9.33	579.9	562.4	6.12	113.1	8.26
4	0.0841	2.55	0.0185	46.6	3.0	3.05	0.200	9.33	160.9	143	1.69	31.2	2.29

Note: Cases 1 to 3 are from Sherwood et al.[901] with a minor correction in case 1. Case 4 is same particle diameter as case 3, but has period selected so that n and nT are same as in case 2.

as long as (L/d_p^2) is constant. Since there is no change in the fraction of the bed covered by the thermal transfer zone, the period of desorption will scale in the same way as L. Thus, if the column length is decreased by a factor of ten then both the adsorption and desorption periods are decreased by a factor of ten, and the adsorbent productivity is increased by a factor of ten. Obviously, this does not apply for a jacketed, externally heated system since radial heat transfer will not be speeded up. If a large proportion of the energy is used heating the ends of the column, energy use will increase with rapid cycling. This can be controlled with insulation.

If the desorption is done with a solvent or desorbent, similar arguments can be used to show that the desorption time will scale in the same way as L does if (L/d_p^2) is constant.

Another common method is pressure swing adsorption (see Chapter 4). Usually, the time for the pressure wave to pass through the system is not important since this time is much shorter than the cycle time. If the bed is tight and cycle times are short, pressure waves can be very important;[558] however, for most pressure swing adsorption (PSA) systems at least a modest process intensification is possible without any changes in the operating principle.

Decreasing the particle diameter and the column length will affect the design of the adsorber. Suppose we decrease d_p by a factor of $\sqrt{10}$ and to keep (L/d_p^2) constant decrease L by a factor of 10. The cycle time will also be decreased by a factor of 10. The following factors must be included in the new design.

1. The smaller particles must be carefully packed to avoid channeling effects.[653] Large-scale columns have been efficiently packed with small particles.[159,342,558] Thus this can be done with care. For the examples considered here the decreases in d_p are not huge. Use of the same small-diameter particles in both laboratory- and large-scale systems could make scale-up easier since wall effects are less likely to be important in the large-scale system,[271] and mass transfer inside the particles will be the same.
2. A tight fractionation of particle size is required. This is always desirable since the largest particles control H while the smallest particles control the pressure drop. As d_p decreases it is important that $\Delta d_p/d_p$ not increase. Until there is a market for them, the small particles may be more expensive, or may have to be specially ordered. This may make this intensification process uneconomic in a particular case, but tends to be a *Catch 22* situation.
3. The particles should be spherical since this will reduce channeling.[653]
4. The packing should be stable and have a long life. Adsorbents which rapidly foul will not be very useful in a separation which requires rapid cycling.
5. The end fittings need to be redesigned. The column is now short and fat, and end effects could be much more important than in long columns. Proper distribution will probably require a change in end fitting design. Short, fat columns are common in large-scale gel permeation chromatography[544,549,800] because the gels are compressible. Similar designs could be used for rigid particles, and have been used in ion exchange systems.[26,342] In addition to proper distribution the ratio (dead volume to packed volume) must be controlled. Since the packed volume has decreased by a factor of ten, careful column design is required to keep this ratio small. This is particularly important for liquid systems.
6. Smaller particles are easier to fluidize. Thus, a hold-down screen or frit will be required. This is particularly important with rapid back-and-forth cycling. If a significant change in d_p is done (greater than that illustrated in Table 3-2), the support plate and the hold-down plate will have increased pressure drops. If this becomes a problem the column diameter can be increased to lower the pressure drop. A significant increase in productivity can be obtained in many commercial systems before this problem becomes significant.

7. The piping and valves connected to the column must be designed to keep the dead volume small.
8. The control valves and other equipment must be capable of cycling faster. For thermal systems this should be no problem since the cycle is reduced from hours to minutes. For common PSA systems the cycle will be reduced from minutes to 10 to 30 sec. Since faster cycles are operated commercially,[558] this should not be a problem.
9. The feed must be free of suspended solids. This is a most important requirement. Beds packed with small particles are highly efficient filters. A dirty feed will clog such a bed and cause the pressure drop to increase rapidly. Very small amounts of suspended solids can be handled if feed flows downward and an upward flow elution step is used. Fluidized bed equipment (see Sections II and III in Chapter 6) is well suited to handling dirty feeds.

This process intensification will have a minor impact on the operating cost, except for depreciation. Some other tradeoffs are possible to simultaneously intensify the process and decrease the operating cost. Equation 3-1 shows that pressure drop will be constant if $(v\ L/d_p^2)$ is constant. The velocity is easily decreased without changing the throughput by increasing the column diameter. Suppose we decrease d_p by a factor of $2\sqrt{10}$, decrease L by a factor of 10, and double the column diameter. For constant throughput Δp will be unchanged, the amount of adsorbent will be decresed by a factor of 2.5, and the number of stages will increase. The number of stages increases since in the usual range of operating conditions where pore diffusion controls H is proportional to $v\ d_p^2$ (see Equations 2-122, 2-123a, and 2-123b and Figure 2-21) and thus N is proportional to $(L/v\ d_p^2)$. With larger N a higher fraction of the bed can be utilized and desorption will be more efficient. This means less energy in a thermal desorption, less desorbent in a chemical desorption, or less product loss in a pressure swing desorption. Thus both capital and operating costs will decrease. As Figure 3-5 shows, this method is useful when L/MTZ is less than 2 to 3. Similar tradeoffs can be made if modest increases in pressure drop are allowable.

There are situations where this process intensification may not work. With many ion exchange systems swelling of the resins occurs and space must be available for this swelling. Because of this extra dead volume it may be impossible to keep the rate (dead volume/column volume) small if d_p and L are both decreased. However, ion exchange systems with small resin particles, rapid cycling, high resin productivity, and very small resin inventories are available commercial.[26,342] In activated carbon systems where the carbon is regenerated in a furnace, very small particles may cause problems during the regeneration. First, the furnace may have to be redesigned; second, the loss in weight and hence diameter may be too large for small-diameter particles. In some designs where the packing is moved periodically it may be difficult to properly move small particles and there will be a limit to how much d_p can be reduced. There are many other adsorption systems where process intensification is feasible and probably is economic.

How much can the particle diameter be decreased? This question cannot be answered without careful design and economics studies. However, some of the technical limits can be delineated. As the particle diameter decreases, film diffusion will become increasingly important. Since $k_f a_p$ is approximately proportional to $(d_p)^{-1.4}$ instead of $(1/d_p)^2$, H will no longer scale as d_p^2. Thus the exact scaling used will no longer be applicable. Although N could still be held constant, the pressure drop would have to be increased. In the range of particle sizes currently used, pore diffusion usually controls and this limit is not important. This is the case in the example shown in Table 3-2. For particles less than 10 μm in diameter, kinetic effects can be important, and the scaling may break down.[517] The use of alternate procedures such as attaching small particles to a fiber[623] or making the adsorbent as fibers[28,725] probably allows further reductions in the particle diameter.

More important current limitations are the ability to pack small particles in short, fat columns, and the ability to design short, fat columns with small dead volumes. Perhaps the ultimate is to dispense with particles entirely and use a homogeneous sheet of packing with uniform pores. This could be made from fused particles or by polymerizing a gel as is currently done in gel electrophoresis. This ultimate step will require a total rethinking of the design of adsorption and chromatography systems.

III. ADSORPTION OF GASES WITH THERMAL REGENERATION

Gas adsorption processes with thermal regeneration are very common industrially. Thermal regeneration changes the equilibrium parameters and dilutes the adsorbate in the gas phase since a sweep gas is used to remove the adsorbate. These two effects combine to cause desorption. A variety of operating methods have been developed for these processes. In this section we will briefly look at trace contaminant removal, drying and sweetening, and solvent removal with activated carbon. Most of these systems are designed to use particles that are too large, and thus the columns are too big and cycles are too long.

A. Trace Contaminant Removal

One of the simplest and most common applications of adsorption is the removal of trace contaminants. This application takes advantage of the usual favorable shape of adsorption isotherms. At very low adsorbate concentrations in the gas the amount adsorbed can be very high. Since the feed concentration is low, the saturation of the adsorbent at higher concentrations never controls the process. A shock wave with a very low velocity will form during the adsorption step and very long adsorption periods can be used. When very long adsorption periods or intermittent adsorption periods are used, one critical question is how much residual capacity remains.

Regeneration may be done off-line or the adsorbent may be discarded. This is economical because of the very long periods between regeneration. When regeneration is done *in situ,* a counter-flow of hot gas is usually employed. In some cases one column is sufficient since regeneration is so infrequent. With more frequent regeneration two or more columns are used with one or more columns adsorbing while the remainder are being regenerated and then cooled in preparation for the next adsorption step.

Odor control is a special case since parts per million or less of some chemicals can produce an odor problem. Activated carbon often has a high affinity for the odor-causing chemicals and is used as the adsorbent. With low concentrations and a very nonlinear isotherm a sharp shock wave is formed, and the MTZ will be very short. Thus, thin layers of packing can be used. Usually, pressure drop must be minimized since the blower horsepower is the largest operating cost. Designs which maximize the surface area and have a very short bed depth are used. These include annular systems such as canisters and corrugated bed systems.[608,687] Examples of these systems are discussed in detail elsewhere.[608,687]

A considerable amount of work has gone into developing processes for removal of sulfur compounds. Removal of SO_2 is commonly done with a thermal cycle.[17,253,274,588] A zeolite molecular seive can be used to adsorb SO_2 in the tail gas from a sulfuric acid plant. The tail gas typically has between 2000 to 4000 ppm SO_2, which is too low for making sulfuric acid but much too high to exhaust. The molecular seive effectively adsorbs SO_2 in the presence of CO_2, and can be easily regenerated. Desorption is done counter-flow with air heated in a furnace. During desorption the SO_2 exits as a peak starting at around 0.3% and then rising to about 4% before subsiding.[274] This gas is returned to the acid plant where it results in a 2 to 3% increase in acid production. Removal of H_2S (sweetening) is discussed in the next section.

Molecular sieves can also be used for NO_x removal.[17,253,556,588,608] The sieves adsorb NO_2

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but not NO; however, in the presence of oxygen the NO will react to form NO_2. The gases need to be dried first since water will be preferentially adsorbed by the sieves, thus deactivating the sieve. With no water present the sieves can be regenerated by counter-flow at 150°C. If water is present 250°C is required. The recovered NO_2 is returned to the acid plant. More efficient bed use and higher NO_2 concentrations in the purge gas can be obtained by using two columns in series.[556] The cycle for doing this is listed in Table 3-1. This cycle could be adapted for other adsorption problems when regeneration can be done faster than the adsorption step.

Another example of trace component adsorption with thermal regeneration of the adsorbent is the removal of traces of mercury vapor from air.[17,253,730] A gas stream containing mercury with 1 to 2 ppm(v) can be reduced to less than 1 ppb(v) with a proprietary adsorbent. Regeneration is done counter-flow with hot air. When the effluent gas is cooled, droplets of liquid mercury condense and are removed in a separator. The gas from the separator is mixed with fresh feed and returned to the adsorber. Since regeneration takes a maximum of 2 days and adsorption can last for 7 days, one adsorber will sit idle for 5 days.[730] Higher bed utilization could be obtained by using the two-column scheme shown in Table 3-1, but at the cost of a higher pressure drop and hence higher blower operating costs. This would be an inexpensive way to increase the capacity of existing systems.

B. Drying and Sweetening of Gases

Adsorptive drying of gases followed by thermal regeneration has been a standard unit operation for many years.[112,206,253, 268,301,529,571,575,608,616,645,687,706,731,865,1017,1079] Basmadjian's review[112] is particularly complete and up to date. A large amount of data on properties of adsorbents and equilibrium isotherms are available in Basmadjian's review[112] and in other sources.[12,206,608,616,645,865, 1017] Equilibrium isotherms such as Equations 2-4, 2-8, and 2-11 have been used. Pressure swing adsorption (PSA) is also used for drying gases and is covered in Chapter 4 (Section II). Other separation methods, such as condensation and glycol drying,[529,608,706] are also used for drying gases. Adsorption has the advantage of drying to very low final humidities, but may not be the best method for hot saturated gases. In this case a combination of methods such as cooling and condensation followed by adsorption may be the best method. For example, reducing the temperature from 50 to 25°C reduces the water concentration from 12.2 to 3.1 v/v%, and this decrease obviously decreases the load on the adsorption dryer.[731] After partial condensation, the liquid droplets must be removed from the gas stream in an efficient vapor-liquid separator.

The basic adsorption system will use two beds if the MTZ is short, and three beds with the option of running two in series if the MTZ is long. Silica gel and activated alumina can give dew points from −40 to −50°C, while zeolite molecular sieves are capable of giving dew points as low as −100°C. The beds are usually regenerated with a hot gas although open steam or external steam heating are also used. A regeneration temperature of 350 to 400°F is typically used except for zeolite molecular sieves which require 500 to 700°F.[608] Counter-flow regeneration is more energy-efficient than co-flow regeneration, but the latter is simpler and has lower capital costs. Thus both counter- and co-flow regeneration schemes are used. The bed is often cooled co-flow to the feed direction before reintroducing the feed. One desires to operate with high adsorbent productivity, low product losses, and low energy use. Fast cycles tend to increase adsorbent productivity, particularly if the bed utilization is fairly high. Short beds with fast cycles have been recommended for drying in LNG plants.[418] Bed utilization can be increased by using beds in series, short beds with small-diameter particles, or an adsorbent such as molecular sieves which have a short HETP. However, excessive pressure drops must be avoided. Using a layer of silica gel or activated alumina followed by a layer of molecular sieve will keep pressure drops low, minimize costs, and keep bed usage high[112,268] (see Section II.C).

Product losses occur at the beginning of the regeneration step. Gases in the void spaces and in the head spaces will be swept out and lost. It may be possible to recycle these gases to the on-line column to avoid loss. Minimizing the head spaces will help minimize these losses and will help reduce energy requirements. Minimizing the HETP increases the bed utilization and helps to reduce product losses. Several methods for reducing the energy use have been developed:

1. Counter-flow regeneration will reduce energy usage. Incomplete regeneration as illustrated in Figure 3-2C will reduce energy requirements per kilogram of product.
2. Internal insulation can be helpful to decrease the amount of energy used to heat the shell.
3. When compressed air is dried the heat of compression can be used to regenerate the bed. This is done by feeding the hot compressed air directly to the regenerator, and then to a cooler and liquid-vapor separator before the adsorption dryer.[106] When this is done no supplemental heating is required. This approach could probably be applied to other gases which need to be compressed and dried.
4. When the thermal wave velocity is greater than the solute wave velocity, it may be possible to operate without a cooling step.[109,112,783] The cold feed gas then serves as the coolant. To prevent premature breakthrough of the adsorbate, a very short cooling step which cools only the feed end of the column may be used, but commercial operation without any cooling operated without problems for more than 1 year.[783]
5. Operating so that the thermal wave stays inside the bed during the feed step will reduce the energy requirements. This requires that the cross-over ratio, Equation 2-65, be near 1. This type of operation keeps the heat of adsorption inside the bed where it is available for desorption. Pressure swing adsorption (see Chapter 4, Section II) uses this principle, and recently[399,403,404,625] this method has been used commercially to thermally regenerate dryers removing water from the ethanol-water azeotrope. With large amounts of water the temperature increase in the bed can be 15°C or higher. A cross-over ratio, R_T of about 1.0 is required, which usually means fairly high water content in the feed gas. This operation might be aided by adding a small amount of inert material with a high heat capacity with the adsorbent. Layers of inert material in a heat regenerator at the end of the bed can also help conserve energy.
6. When hot gas desorption is done at elevated pressures, the system will often be mass transfer-controlled. Roughly half of the energy in the desorbent gas will be used for heating the adsorbent and for desorption.[252] Less desorbent and less energy would be used if desorbent were fed until thermal breakthrough occurred, and then the gas were shut off. After a delay period for mass transfer, desorbent gas would be started again to sweep out the interstitial gas. Another delay period would be followed by another pulse of desorbent gas. This procedure would be continued until sufficient desorption has occurred. This delay procedure will save energy, will probably take longer, will be more difficult to operate, and will result in increased dispersion because of diffusion during the delays. Naturally, an alternative is to reduce the pressure during desorption.

These methods are also applicable to the processes discussed in Sections II.A and C.

One major problem in gas drying is the slow loss in adsorbent capacity with time.[112,206,253,529,571,575,616,645] An adsorbent lifetime of from 1 to 4 years is common when natural gases are dried, although much shorter lifetimes can occur. This drop in activity is usually due to the irreversible adsorption of heavy trace components. Guard beds using partially deactivated adsorbent can help protect the active dryer. Another solution is to use 3 Å zeolite molecular sieves. The large molecules which irreversibly adsorb cannot fit into the very small pores of the 3 Å sieve. The price for using 3 Å sieves is somewhat lower
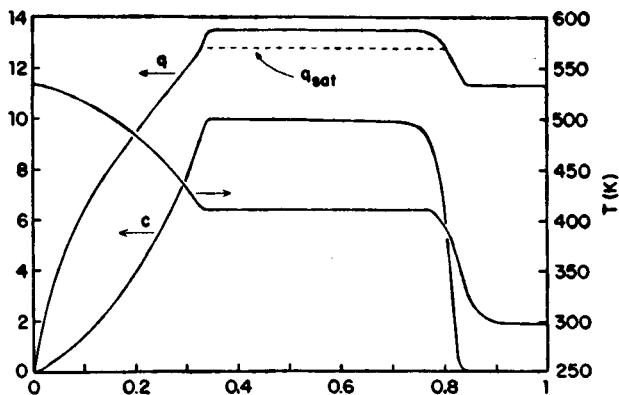
FIGURE 3-9. Concentration and temperature profiles predicted by staged model for regeneration of molecular sieves adsorbing water. (From Friday, D. K. and LeVan, M. D., *AIChE J.*, 28, 86, 1982. With permission.)

mass transfer rates and thus somewhat longer MTZs. When the adsorbent does deteriorate with time, it is common to reduce the cycle time as aging occurs. When the necessary cycle time becomes so short that the column can no longer be regenerated in the available time, the adsorbent must be replaced.

Another cause of deterioration of the adsorbent is the presence of liquid water in the bed. This is particularly detrimental for silica gel beds. Separators are commonly placed upstream of the beds to remove any entrained water. The separator will also help to remove suspended sulfur particles in natural gas streams.[783] A guard bed of liquid water-resistant adsorbent before the high-capacity gel bed can also help prevent problems. However, Friday and Levan[389,391] used a staged model to show that condensation of liquid can occur in the bed during a co-flow regeneration step. This was previously unexpected and has since been collaborated with the local equilibrium theory[390] and by experiments.[391] The concentrations and temperatures predicted inside the bed by the staged model are shown in Figure 3-9.[389] When the solid phase concentration exceeds the saturation concentration, condensation will occur. Physically this high concentration occurs because of "roll-up" of the adsorbate. The first part of the column becomes hot and removes the adsorbate. This adsorbate catches up to the colder part of the bed where the highly concentrated gas is adsorbed (in essentially the same way as "superloading") and the concentration shoots up. When the saturation concentration is exceeded, condensate forms in the pores. In small capillaries the saturation concentration may be well below the saturation limit determined from vapor pressures. The condensate will revaporize when the thermal wave arrives.

Many other theories have been applied to gas drying and are reviewed in detail by Basmadjian[112] and Ruthven.[865] In the simplest case where very little water is present, isothermal theories can be used. However, since heat effects are usually important in drying, the theories usually need to be nonisothermal. The simplest nonisothermal theories which include heat of adsorption effects are the coupled equilibrium theories discussed in Section III.D.2. An alternative is to use the local equilibrium theory with "effective equilibrium curves".[110-112,865] Complete numerical solutions of the partial differential equations have also been done, but many of these solutions are flawed since the mass balances are not satisfied.[112] Carefully done numerical analyses can fit the experimental results for adiabatic drying.[818,865] Industrially, modifications of the MTZ or LUB approach are often used for design,[112,252,399,608,642,645,734] including the results from a large number of experimental runs in both laboratory- and large-scale systems.
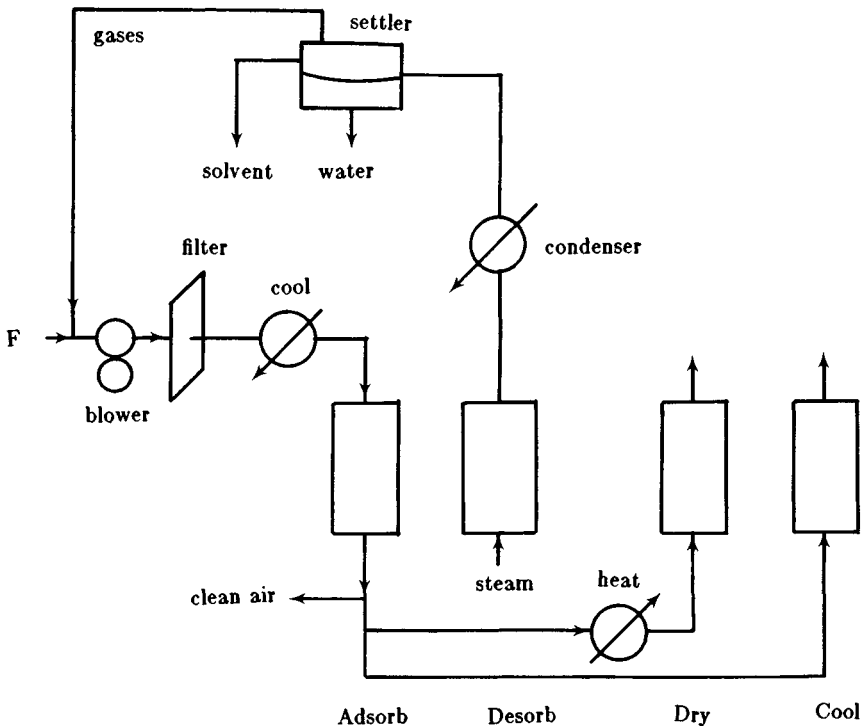
FIGURE 3-10. Typical activated carbon solvent recovery system.

Gas sweetening operations are similar to drying except H_2S, CO_2, and H_2O are all removed.[112,206,253,261,608,616,645] These gases can lead to several problems. First, the acids can attack molecular sieves and special acid-resistant grades must be used. Second, carbonyl sulfide, COS, is formed by the reaction of H_2S and CO_2 which is catalyzed by molecular sieves.[261] Unfortunately, the COS is not as strongly adsorbed as the H_2S, and will break through early. The use of 5 Å sieve appears to minimize the catalysis. Removal of the acid gas prior to dehydration may be necessary to prevent this problem. A third point is that carbon dioxide is less strongly adsorbed than either hydrogen sulfide or water. Thus the system can be operated to remove all three gases or just water and hydrogen sulfide. If carbon dioxide is allowed to break through it will peak at a concentration above its feed concentration because it will be desorbed by the H_2S. Simultaneous removal of acid gases and dehydration with molecular sieves is practiced in small peak shaving LNG plants.[418]

C. Activated Carbon Solvent Recovery

An extremely common but somewhat specialized process is the removal and recovery of solvent from air using activated carbon. This process has been used commercially since the 1920s. A glance at some older references[123,672,687,688] shows that surprisingly, the basic system is almost unchanged, except for more sophisticated controls, in almost 60 years of use. This may mean that major innovations are overdue.

1. Basic System

The basic system for solvent recovery with activated carbon in fixed beds is shown in Figure 3-10. The air stream is usually collected at one quarter to one half of the lower explosion limit when the gas stream is air. Any increases in the solvent concentration will decrease the capital and operating costs. This gas stream is forced through a filter to remove

any particulates which might clog the packed beds, and is often cooled. The operation is usually at 80 to 90°F. Cooling is both a safety precaution and a method for making adsorption more efficient. The gas is then sent to the carbon adsorber and the clean gas is either reused or exhausted. The most common desorption method is to use steam counter-flow to the gas flow. Steam is very convenient because of its large latent heat. The steam-solvent mixture is condensed and sent to a settler if water and the solvent are immiscible. The noncondensible gases are recycled through the adsorber. After desorption is complete, the carbon may be dried and then cooled. These steps are optional and it may be possible to return the hot, wet carbon back into adsorption service.

A large variety of solvents can be recovered with activated carbon systems. Solvents with molecular weights from about 45 to 200 can usually be recovered. Lower molecular compounds tend to be too weakly adsorbed while the higher molecular weight compounds are difficult to desorb.

With minor modifications, the system shown in Figure 3-10 is a standard unit operation for solvent recovery.[123,165,297,395, 560,571,608,616,618,638,667,672,687,688,690,786,990,996,1016] A variety of packaged units are available.[13,27,28,251,302,305, 355,560,689,696,710,725,789,797,798,927,1027,1095] The usual configuration for the adsorber is to lay the column horizontal and support a horizontal layer of carbon. This gives a maximum surface area and minimizes the pressure drop in the bed. Since power for the blower is a major cost, minimizing Δp is a major consideration. The pressure drop is readily determined from charts[157,687,996] or from general equations for flow in packed beds.[138,157] The usual range is from 0.5 to 30 in. of water pressure drop. Relatively shallow beds with gas velocities from 60 to 120 ft/min are commonly used. Either downward or upward flow of the gas can be used. Downward flow is often used since there is much less bed churning and attrition of the carbon. When upward flow is used, the gas velocity should satisfy.[157,640]

$$\frac{G^2}{\rho_G \, \rho_B \, d_p \, g} < 0.0167 \tag{3-6}$$

to prevent lifting the bed. Equation 3-6, G is the mass velocity of the gas and g is the acceleration due to gravity. When adsorption is strong, annular columns can be used to maximize area and minimize pressure drop.[28,165,725] In small units vertical columns are often used. Other configurations for activated carbon adsorption are discussed in Chapter 6 (Section II.A.2 and II.A.3) and Chapter 8 (Section II.C).

Steam is most commonly used for desorption, since it often has numerous advantages. A lot of energy can be put into the column very quickly to heat the shell, the carbon, and desorb the adsorbate. The steam should be at such a pressure that it will condense at least 30°C above the boiling point of the solvent. The steam purge also serves to dilute the adsorbate and sweep it from the column. Water can often be left on the column and its evaporation during the adsorption step keeps the temperature from rising substantially. This water can easily be exhausted to the atmosphere and the water does not have to be recovered. Many solvents are immiscible with water and the solvent can be recovered by condensing the vapor and separating the two phases. The solvent can often be reused without further processing. When the solvent is miscible with water, the solvent can be recovered by distillation. Unfortunately, this greatly increases the cost of the system. If the solvent forms an azeotrope with water, separation becomes even more expensive, and alternate desorption steps may be preferable.

Complete desorption is usually not employed since an excessive amount of steam would be required. Thus the column loading during the cycle looks like Figure 3-4A. Design is usually for a working capacity of 25 to 30% of the capacity at saturation.[1027] This often leads to a working capacity which is about 7.5 wt % of the weight of the carbon. The usual
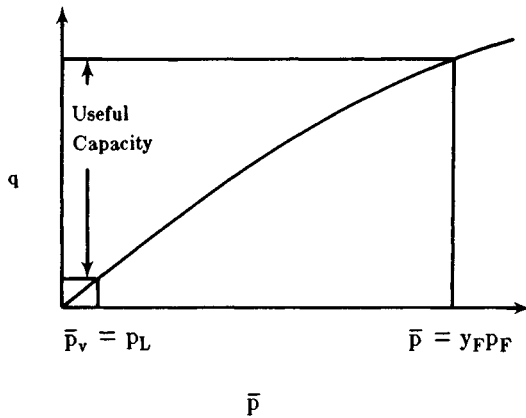
FIGURE 3-11. Steam usage during desorption. (From Danielson, J. A., Ed., *Air Pollution Engineering Manual*, Publ. #AP-40, EPA, Research Triangle Park, N.C., May 1973.)

range for steam use is from 1 to 5 lb of steam per pound of adsorbate recovered. The effect of time of desorption on the amount of steam required is shown in Figure 3-11.[297] More solvent can be recovered by desorbing for longer periods, but at the price of increased steam use. Only about 10% of the energy in the steam is used for desorption. The rest either exits the column or is used to heat the shell and the carbon. Much of this energy can be recovered (up to 70%[797]) and used elsewhere in the plant.

If the solvent is miscible with water the bed is usually dried after desorption to reduce the amount of water fed to the distillation columns downstream. Pebble bed regenerators can often be used to heat the air used for drying and keep heating costs down. If the bed does not have to be dried, the evaporation of water left on the bed will keep the bed temperature from rising excessively. However, excessive humidity (>50% relative humidity) is detrimental to adsorption since water condenses in the pores because of capillary condensation.[618,851,996] The adsorbed water blocks the organics from some of the pores. This reduces the column capacity and results in quicker breakthrough of the organics.[442] Thus, a short drying period may be desirable. Drying can also be done with a cooling step.[701] If the inlet gas is above approximately 50 to 60% relative humidity the condensation of water will interfere with solvent adsorption. To solve this problem it may be necessary to preheat the gas to decrease the relative humidity. The cost of doing this is that operation will be at a higher temperature where adsorption is weaker. An alternative is to dry either the feed gas or the product.

The cooling step shown in Figure 3-10 can often be skipped since the thermal wave usually moves faster than the solute wave. However, in some cases hot activated carbon is a catalyst for undesirable side reactions and the cooling step is required to limit reaction. The cooling step also removes about 30% of the water and can increase solvent recovery by approximately 4%.[701,786] Thus, in many situations cooling will be economical.

The entire process shown in Figure 3-10 should be automated. For safety reasons (carbon beds can burn) a maximum temperature of about 150°C should be set. Cooling the air before it enters the adsorber also serves as a flame arrester and makes the process safer. If trace quantities of materials which can polymerize are present, guard beds can be used to protect the main bed.

After the adsorber, the vapors are cooled and condensed. In an integrated plant some of this heat can be recovered. The noncondensible gases should be returned to the adsorber since they will be saturated with the solvent.

Costs for carbon adsorption systems have been published.[104,1013] Small-scale systems (less

than 10,000 lb of carbon) are usually purchased as packaged units. The cost data shows an economy of scale since the exponent in the cost equation based on the weight of carbon is 0.481.[1013] Larger systems are usually custom designed and here the exponent, 1.20, is greater than one and there is no economy of scale. When distillation is required, the distillation system may control the costs.

2. Alternatives

A variety of alternate operating procedures have been developed. First, the basic column shape can be changed. Canisters[1027] or annular shapes[28,616,725] can be used to either provide easy replacement of the carbon or large cross-sectional area for flow. Continuous flow (see Chapter 6, Section II.A.2 or II.A.3) and rotating beds (see Chapter 8, Section II.C) have also been used in some applications, particularly for larger-scale systems.

Carbon forms which are different from the usual granular activated carbon have been recently developed. Carbon fibers[28,583a,682,725] reportedly make the adsorption sites more accessible to the gas phase and reduce mass transfer resistance. The fibers are supposed to be easier to regenerate, but adsorptive forces are weaker and some low molecular weight solvents are not strongly retained. Nonwoven felt-like structures with high carbon contents have recently been developed.[29] but are not yet commercial. Monolithic blocks of fused granular activated carbon have also been developed. These systems should have very short MTZs, but will have to be used in thin layers since pressure drop per centimeter will be high.

A variety of alternate desorption techniques have been developed for special cases. Steam has the disadvantage of adding water to the system and the alternatives try to avoid this. The alternatives may also have an advantage at remote locations where steam is not available.

1.   Hot gas desorption has been mentioned as an alternative for many years,[395,667] but only recently has it become fairly common commercially.[13,210,824] The advantage of using a hot inert gas for desorption is that solvent recovery can be done by condensation (perhaps after passing through a desicant column) and distillation columns are not required for solvents which are miscible with water. The disadvantage is large volumes of hot gas are required to transfer the required amount of heat into the column. This can conveniently be done by recycling the same gas through the column, the condenser, and the heater. Heat pumps are useful for reducing energy requirements.[210,824] The outlet concentration of the desorbed solvent and the amount of hot gas used can be minimized by stopping the desorption cycle shortly after the peak of solvent concentration leaves the column. This will follow thermal breakthrough. This leaves a large heel in the column which will be resharpened by the shock wave during adsorption. Rapid cycles minimize energy requirements. The addition of heating coils, which are steam heated, inside the column can also help desorption. Unfortunately, the heat transfer coefficients are quite low inside the bed. The theories used for drying of gases with thermal regeneration (see Section III.B.) can be adapted to hot gas desorption of solvents.

2.   A second commercial approach is to use vacuum desorption.[30,667,687,711,830] Vacuum systems again have the major advantage of avoiding contamination with water. The total pressure is reduced to below the partial pressure of the adsorbate and desorption occurs. Unfortunately, if concentrations are low the required pressure can be very low. With low feed concentrations the useful feed capacity of the bed can be quite low. This is illustrated with the equilibrium isotherm shown in Figure 3-12. The partial pressure of the feed gas is $\bar{p} = y_F p_F$. During evacuation all nonadsorbed gases are removed and $y \rightarrow 1.0$. Thus the partial pressure during the lowest part of the vacuum desorption is $\bar{p}_v = p_L$. If y_F is low, $y_F p_F$ will be near $\bar{p}_v$, resulting in a small swing
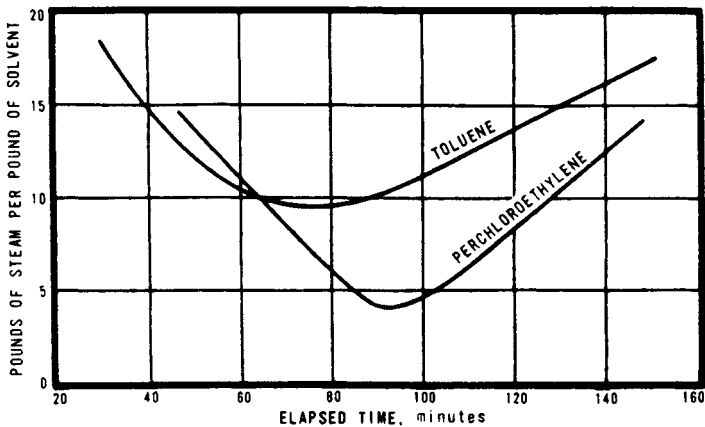
FIGURE 3-12. Isotherm for vacuum desorption system, amount adsorbed vs. partial pressure.

in partial pressures and the resulting useful bed capacity will be small (see Figure 3-12). Vacuum operation has proven to be economical only when the concentration of recovered solvents is high (3 to 50 vol %[30]). In these cases the vapor produced during regeneration may be as high as 95 vol % solvent. This is safely above the upper explosion limit. A common application of vacuum regeneration has been for recovering gasoline vapors in gasoline storage or loading facilities. In this application the adsorbers will rapidly pay for themselves.

3. A third type of desorption process which is still under development is the use of a solvent for the desorption. This can be done by a liquid-liquid extraction-type process or with a supercritical fluid.[312] An alternative is to use a vapor desorbent which is then condensed and separated from the recovered solvent.[1062] The hot desorbent is removed from the bed with steam or with a hot inert gas. Unfortunately, this approach requires complete desorption of both solvent and desorption agent to avoid contamination of the purified air and to avoid cross-contamination of solvent and steam systems.

4. A fourth alternative is to not recover the solvent and to regenerate the carbon in a kiln. This is particularly useful when only traces of a very high molecular weight solvent must be removed.

5. The fifth alternative is really a variant of steam desorption. The solvent is adsorbed on the carbon and then desorbed. Then, instead of condensing and trying to recover the solvent, the steam, solvent, air mixture is burned with additional air and any additional fuel required.[1028] The advantage of this approach over straight incineration of the dilute gas stream is that much less gas needs to be heated, and much less or no additional fuel is required. The incinerator can be used as the boiler to heat the steam needed for desorption. Often the energy requirements for the steam can be met by the incineration. Of course, this approach does not produce as valuable a product as the processes which recover solvent.

Some of these alternative desorption techniques are also applicable to the other adsorption systems discussed in this chapter.

3. Theories

Until recently, very few theoretical studies of solvent recovery with activated carbon had been published in the open literature. Most design seems to have been done on the basis of experience and pilot plant measurements.[395,638,996] Recently, some theoretical results have
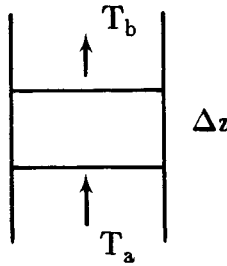
FIGURE 3-13.   Segment of column for thermal shock
wave when steam is added to the column.

been published, and with slight modification the solute movement theory can be applied to this system.

The solute movement theory is directly applicable to the adsorption or feed step. Since equilibrium isotherms of most solvents on activated carbon are nonlinear and favorable, a shock wave usually forms [$(1 + Kc_F)$ is fairly large]. The thermal wave requires some modification to include the effect of condensation of steam. Because of the condensation of steam a thermal shock wave will result. The energy balance can be done over a segment of the column of length Δz as shown in Figure 3-13. In order for the thermal wave to traverse the entire segment the time interval, Δt, must be related to Δz by

$$\Delta t = \Delta z / u_{steam} \tag{3-7}$$

If we assume a constant vapor velocity, v, before and after the thermal shock wave, and constant heat capacities a simple expression for the thermal shock wave velocity can be derived. Since saturated steam is usually used, we will choose T_a as the reference temperature so that the condensed liquid water has an enthalpy of zero. The energy balance over segment Δz and time interval Δt is

$$\text{In} - \text{Out} - \text{Accumulation} = 0 \tag{3-8}$$

This becomes

$$\alpha v(\Delta t) \rho_f[C_{Pf}(T_a - T_{ref}) + y_{STM}\lambda_w] - \alpha v(\Delta t) \rho_f[C_{Pf}(T_b - T_{ref}) + y_{w_b}\lambda_w]$$

$$-\Delta z\Big\{(\alpha + \epsilon(1 - \alpha)) \rho_f[C_{Pf}(T_a - T_{ref}) + y_{STM}\lambda_w - C_{Pf}(T_b - T_{ref}) - y_{w_b}\lambda_w]$$

$$-(1 - \alpha)(1 - \epsilon)\rho_s C_{ps}(T_{sa} - T_{sb}) - \frac{W}{A_c} C_{pw}(T_{wa} - T_{wb})\Big\} = 0 \tag{3-9}$$

where λ_w is the latent heat of water, and y_{STM} and y_{w_b} are the mole fractions of water in the steam and in the bed before regeneration. Assuming thermal equilibrium so that $T_f = T_s = T_w = T$, substituting in Equation 3-7, and solving for u_{steam} we obtain:

$$u_{steam} = \frac{[C_{Pf}(T_a - T_b) + \lambda_w(y_{STM} - y_{w_b})]v}{\left[1 + \frac{\epsilon(1 - \alpha)}{\alpha}\right][C_{Pf}(T_a - T_b) + \lambda_w(y_{STM} y_{w_b})] + \left[\frac{1 - \alpha}{\alpha}\right](1 - \epsilon)\frac{C_{Ps}\rho_s}{\rho_f}(T_a - T_b) + \frac{W}{A_c}\frac{C_{pw}}{\rho_f\alpha}(T_a - T_b)} \tag{3-10}$$
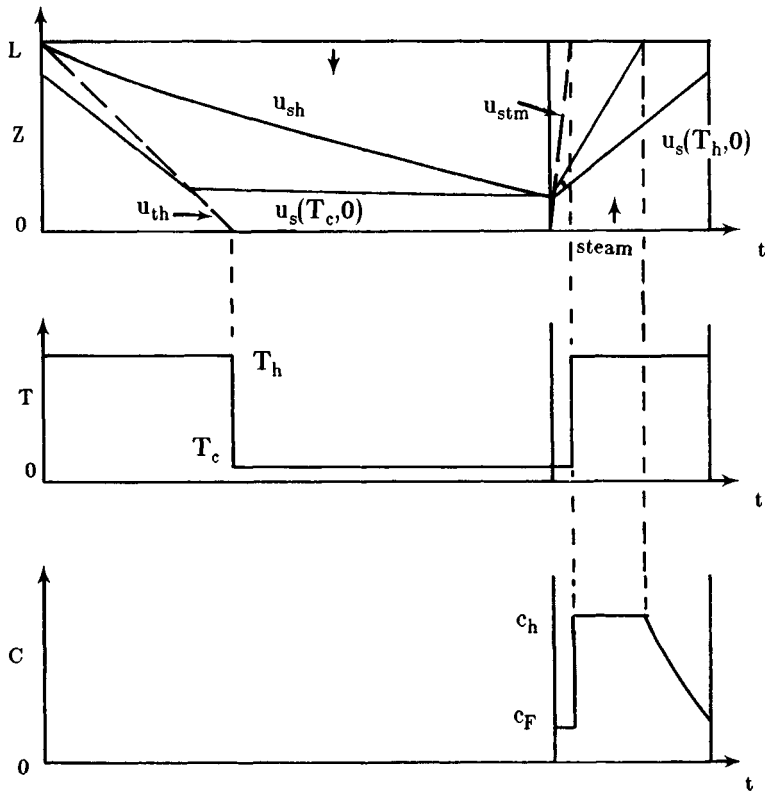
FIGURE 3-14. Solvent recovery with activated carbon and steam desorption. (A) Solute movement theory for solvent recovery with activated carbon. Nonlinear isotherms, no cooling or drying steps; (B) predicted temperature profile; (C) predicted solute concentration profiles.

This equation should be compared to Equation 2-41, which gives the thermal wave velocity when there is no condensing steam. If a noncondensible gas is used ($y_{STM} - y_{w_b}$) is approximately 0 in Equation 3-10, and the terms ($T_a - T_b$) will cancel out. The result is then Equation 2-41. Since the latent heat effect is quite large compared to the specific heat effects, Equation 3-10 predicts a steam wave velocity which is close to v. As was mentioned earlier, this is the major advantage of using a condensible vapor; the column can be rapidly heated.

Following the steam wave will be a diffuse wave as the solvent desorbs. The entire operation is illustrated in Figure 3-14A. The predicted temperature and composition profiles are shown in Figure 3-14B and C. Note that delays in appearance of the temperature and concentration changes are predicted. A separate cooling step is not shown in this figure and cooling results from the addition of the cool feed gas. Note that the diffuse wave which results during steam regeneration is not completely removed from the column, but is re-captured during the next adsorption step by the shock wave. Figure 3-14 is an oversimpli-fication since the following are ignored:

- Velocity changes when the gas is heated.
- Spreading of the shock wave.
- Spreading of the thermal and steam waves.
- The effects of the heat of adsorption and desorption. These effects can be quite large when fairly concentrated streams are adsorbed.
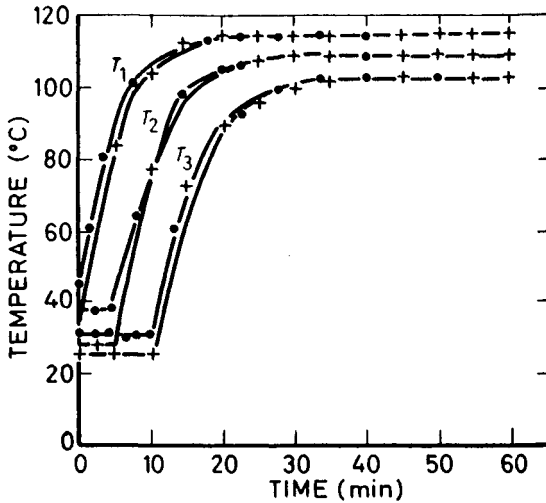
FIGURE 3-15. Outlet temperature profiles during steam desorption. T_1 is near steam inlet to column while T_3 is near outlet; + and ● are data points for two different runs. (From El-Rifai, M. A. et al., *Chem. Eng.*, 269, 36, 1973. With permission.)

- Condensation of solvent in the column during desorption. In drying operations adsorbate can condense during the desorption step.[389,390] This might also occur with steam desorption.

Even though this model is quite simple it does a reasonable job of predicting the qualitative behavior. Other theories for solvent recovery with activated carbon have been developed.[214,350,434,701,875] The one closest to that presented here is a local equilibrium model which includes coupling of solute and energy effects.[214] This model is similar to those used for other coupled systems (see Chapter 2, Section IV.D.2).

The adsorption step can be modeled as a constant pattern solution since the equilibrium isotherms are favorable. In many cases a first-order irreversible kinetics model[434] can be used. This is valid since in many cases the isotherm is so steep that a good fit is obtained. The advantage of this approach is a very simple solution can be obtained[434]

$$\ln \frac{c}{c_F} = \frac{k_A \, c_F}{\rho_B \, q_{sat}} \, t \, - \, \frac{k_A \, m}{Q \, \rho_B} \tag{3-11}$$

where m is the weight of carbon used, Q is the volumetric flow rate, and the first-order rate constant k_A can be fit to the data. A plot of log c/c_F vs. t gives k_A from the slope. This irreversible equation was an excellent fit up to 50% of breakthrough.[434] Since the adsorption step is rarely run past the start of breakthrough, this is a good semiempirical model. Note that temperature effects are included in the empirical rate constant. The sharp breakthrough curves predicted by this model have been observed experimentally.[434,875] However, when very large temperature increases are observed a semiempirical model such as this would have to be treated with caution for scale-up since energy losses from the bed are diameter dependent.

The steaming step has been studied experimentally.[350,875] Typical experimental results are shown in Figure 3-15.[350] The lag or dead time shown in Figure 3-15 is predicted by the solute movement theory in Figure 3-14. The zone spreading is what we would expect for a constant pattern-type system with finite rates of heat transfer. The data of Figure 3-15 could be empirically fit to a lumped parameter-type model.[350]
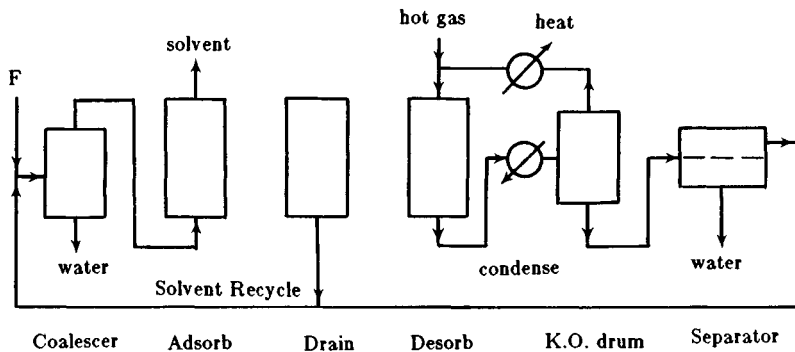
FIGURE 3-16. System for adsorptive drying of liquids.

A detailed numerical model has been used to explore the behavior of carbon adsorbers for acetone recovery with and without cooling steps.[701] The cooling step reduced the temperature and removed about 30% of the water from the bed. Both of these effects increase adsorption of acetone during the feed step. The net result was a 4% increase in acetone recovery. This increase was sufficient to make addition of a cooling step economical.

Obviously, solvent recovery with activated carbon followed by steam desorption is a problem which has not been completely solved theoretically. Numerical models will be required to solve the complete problem.

IV. ADSORPTION OF LIQUIDS WITH THERMAL REGENERATION

In contrast to gas systems, where *in situ* thermal regeneration is very common, in liquid systems it is less common. Thermal regeneration of activated carbon is separate kilns or furnaces is quite common, and is discussed in Section IV.B.

A. Drying Liquids

The drying of liquids by adsorption is practiced commercially.[112,206,301,467,615,745,1115] A schematic diagram of the usual method is shown in Figure 3-16. The liquid feed should first be sent to a coalescer or knock-out drum to remove water droplets. The feed is then sent to the adsorption column which can be packed with activated alumina, silica gel, zeolite molecular sieves, or other desicants. Since the water content in the organic liquid is often very low, the adsorption period may be quite long.

Once breakthrough starts, the column is drained to remove unadsorbed solvent contained in the void spaces. This recovered solvent is recycled to the adsorber during the adsorption step. Draining also reduces the amount of energy required for the desorption step since the drained solvent does not have to be vaporized. If the solvent fits into the pores, it may be difficult to drain this liquid from the pores. A vacuum may be used to help remove this solvent.[615] Another possibility would be to pack the adsorbent in a centrifuge (see Chapter 8, Section III). An alternate solution is to use an adsorbent such as a 3 Å or possibly 4 Å zeolite molecular sieve which has pores which are too small for the solvent to penetrate.

After drainage, the column is usually desorbed with an inert hot gas. Nitrogen, carbon dioxide, butanediol, air, butane, and other gases have been used. The higher the heat capacity of the gas the more rapid heating and desorption will be. After condensation to remove water and residual solvent, the gas can be reheated and recycled. Burying heating coils in the bed allows the use of steam condensation to aid the inert gas purge.[205] The temperature of the regeneration must be high enough to desorb the water, but not so high as to cause excessive coking. For gasoline drying,[745] 400 to 450°F was suggested. Coking problems can

also be controlled by using a zeolite molecular sieve with pores small enough that the solvent will not fit into pores[301,467] or by using vacuum to remove all the solvent before thermal regeneration.[615]

Theories for liquid drying have not been extensively reported in the literature and more research would be quite helpful. Available equilibrium theories to predict isotherms are excellent when the solvent adsorption is negligible, but are inadequate when there is competitive adsorption of the solvent and water.[112] More theoretical and experimental work is needed for the competitive adsorption case. Very little modeling of the column behavior has been done. The solute movement theory could easily be applied to the adsorption step when the solvent does not adsorb. This theory will be similar to other applications of the theory. This theory can also be applied to the regeneration step if it can be assumed that all of the liquid has drained out. The result will be similar to Figure 3-3. Note that the feed step in the solute movement diagram is in the liquid phase while the regeneration step is in the vapor phase. Thus different physical properties need to be used to calculate the wave velocities in the different steps. Unfortunately, so many assumptions are involved in this theory that it is not useful for design purposes. The length of unused bed (LUB) or MTZ approach has been applied to the adsorption step,[745] but this was done empirically. Apparently, no models for the drainage or regeneration steps have been published. Obviously, this should be a fruitful area for future research.

B. Activated Carbon Water Treatment

Water treatment with activated carbon is commonly used and has developed almost as a completely independent technique. In this section we will discuss the use of packed columns which are then unloaded so that the carbon can be thermally regenerated in a separate furnace or kiln. For home treatment of relatively clean water the entire canister is usually replaced, and the carbon is discarded. Many reviews on water treatment with activated carbon have appeared[4,251,291,474,526,679,687,714,793,926,944,1069] which are more detailed than this section. Stirred tanks (see Chapter 6, Section I.A.4), pulsed moving beds (see Chapter 6, Section III.A), and fluidized or expanded beds (see Chapter 6, Section II.A.1) are also commonly used. We will first discuss the treatment of drinking water with activated carbon and then wastewater treatment.

Activated carbon has been used for treating drinking water at least since Biblical times.[582,687,811] The systems are commonly used in bottling plants to remove trace amounts of impurities such as chlorine.[582] The chlorine is removed by the reaction

$$2Cl_2 + 2H_2O + C = CO_2 + 4HCl$$

The carbon will last for 6 months to 2 years before being exhausted. Either fresh carbon may be used or the carbon may be regenerated in a kiln.

Activated carbon is commonly used in homes to remove traces of obnoxious chemicals.[32] Schematic diagrams of two typical under-the-sink units are shown in Figure 3-17.[32] The column type shown in Figure 3-17A has a lot longer effective length and worked better to prevent breakthrough. The annular systems had the tendency to have premature breakthrough, and could concentrate less strongly held chemicals and produce a concentrated pulse of these chemicals during extended operation.[32] These adsorbers are made so that some suspended matter will settle out in the housing. Water with a lot of suspended matter must be prefiltered or the adsorber will clog. The beds are usually replaced instead of being regenerated. A major disadvantage of these systems is that the typical homeowner has no reliable way, other than taste, to determine when breakthrough has occurred. Thus the systems are either discarded too soon or left on line too long. Because of the long life of these systems, the homeowner is likely to forget the unit and replace the cartridge only after it is obviously
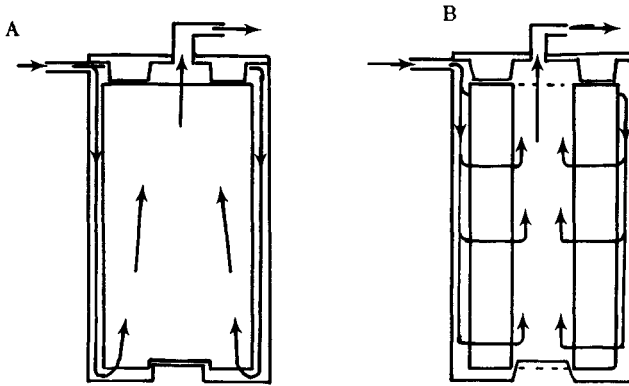
FIGURE 3-17.   Household activated carbon adsorber for treating tap water.
(A) Column type; (B) annular type. (From *Consumer Reports*, 48(2), 68,
1983. With permission.)

not working. Development of an easy way to determine when to replace the cartridge would
be a major advance.

Activated carbon treatment of wastewaters is often done with packed columns which are
periodically unloaded so that the carbon can be separately regenerated. Since the molecules
are large and the pores are small, mass transfer zones (MTZs) tend to be quite long, and it
is common to use columns in series. The adsorption cycle is often very long. During this
long cycle some apparent regeneration of the carbon often occurs. This regeneration may
be due to bioregeneration where organisms growing on the surface of the carbon break down
adsorbed species.[21,222,327,368,714,715,945,1034] When biodegradation occurs, the column can be
left on-line indefinitely and some BOD and COD reduction will occur. This continuous
operation without regeneration can be used for the first column in a series of columns. An
alternate reason for the partial regeneration is very slow mass transfer into micro-
pores.[715,792,1073] Transfer into the macropores is quite rapid and breakthrough occurs quickly.
If given enough time, some of the solutes will diffuse into the micropores and adsorb there.
This opens up the sites in the macropores and appears as a partial regeneration. Support for
this view of partial regeneration comes from equilibrium studies which show that equilibrium
of large solutes on activated carbon can take 30 days.[791] Probably, both slow adsorption and
biodegradation occur in commercial systems. There does not appear to be a great synergism
between the bacteria and carbon, but this question has not been completely resolved. As
Benedek[715] stated: "there is a bottomless amount of literature", and no attempt to review
this literature will be made here.

Wastewater treatment differs from many other purification problems since the feed is
usually not well characterized and the components in the feed can vary drastically over time.
Laboratory studies are commonly used for design.[8,130a,213,291,327,679,772,1075] Unfortunately,
advances in modeling techniques are not very helpful if the nature of the contaminated
wastewater is not known. Designing the large-scale system from small-scale column studies
is usually cheaper than completely characterizing the system and then obtaining the required
equilibrium data. Equilibrium equations such as Equation 2-16 or more complex forms need
to be fit to the data. Wastewaters also often contain suspended solids which will clog a
packed bed. Expanded or semifluidized beds (see Chapter 6, Section II.A.1) and stirred
tanks (see Chapter 6, Section II.A.4) are commonly used when suspended solids would be
a problem. The breakthrough curve for an expanded bed can be very close to that obtained
with a packed bed;[702] thus, there may be little penalty involved in using an expanded bed.

Regeneration of the activated carbon usually involves sending it to a separate furnace or
kiln. This may be done on-site or by off-site contractors. Since some of the carbon capacity

is usually lost, the regenerated carbon is usually mixed with virgin make-up carbon. The subject of thermal regeneration of activated carbon in separate furnaces or fluidized beds is beyond the scope of this book. Interested readers are referred to the extensive literature on the subject.[141,251,255,256,259,270,314,473,489,557,594,607,664,665,679,704,713,811,815,826,880,899,905,1001,1002,1005,1024] Typical losses of carbon range from 4.5 to 8% per regeneration.[905] When on-site regeneration is used, the carbon adsorbers usually work quite well, but the regeneration furnace can cause considerable operating problems.[314]

Alternatives to thermal regeneration include biological regeneration which is usually slow and incomplete, wet-air oxidation,[227,421] solvent regeneration,[251,284,507,664, 952,1110] and supercritical fluid regeneration.[312,530,739] In solvent regeneration the organics are desorbed with a solvent which must then be steamed off the carbon. This method often gives incomplete desorption, but has the major advantage of recovering the organics. When the adsorbate is valuable solvent regeneration can be economical. The supercritical fluid regeneration schemes are still experimental at this time. See Section V.B. and C for more details of both these methods.

The solute movement theory can be applied to wastewater treatment with activated carbon if the solutes are assumed to be independent. The results will be similar to the other solute movement diagrams shown in Chapter 2 and in this chapter. Unfortunately, this simple model is not adequate for design since it does not include mass transfer effects which are *very* important in these systems. The LUB or MTZ approach (see Chapter 2, Section VII.A) can also be used when experimental data is available. This approach is commonly used for industrial design.[522,1069]

Theories which try to predict column behavior from first principles are much more difficult since the feed is often not well characterized, the feed is variable, and activated carbon is a very complex material. Most theories ignore the first two problems and try to model adsorption for a well-defined, constant concentration feed. Single pore models[166,223,327,654,686,714,722,981,1033] can give good agreement between theory and experiment, but cannot show the relaxation effect predicted by two pore models.[791,1073,1075] Multicomponent Langmuir isotherms are popular for theoretical studies, but cannot give a good fit to the experimental data. Multicomponent Freundlich-Langmuir isotherms (Equation 2-16) are more versatile[686] and give better fits; however, with a lot of constants the better fits do not have theoretical significance. Ideal Adsorbed Solution (IAS) theory was capable of giving excellent fits to the isotherms,[981,1033] and could be used to accurately predict breakthrough curves for well-characterized laboratory systems. Solutes can be grouped together if their equilibrium data and mass transfer coefficients are within a factor of two.[719] A model including bacterial growth has recently been developed.[1034] All of these more detailed models require numerical solutions.

V. GAS AND LIQUID ADSORPTION WITH DESORBENT REGENERATION

An alternative way to desorb is to use a desorbent or solvent to remove the adsorbates. The desorbent may be removed before the next feed step, or the feed may be started immediately following the desorption. In any case, the recovered adsorbate will be contaminated with the desorbent, and equipment to recover the desorbent is required. Both gas and liquid systems are done commercially, but data in the literature are relatively scarce. Reducing particle diameter and designing shorter columns with faster cycling would generally be advantageous.

A. Gas Systems

Gas systems are regenerated with desorbent when thermal or pressure swing desorption cycles are not adequate to remove the adsorbate. Desorption is done both with less strongly
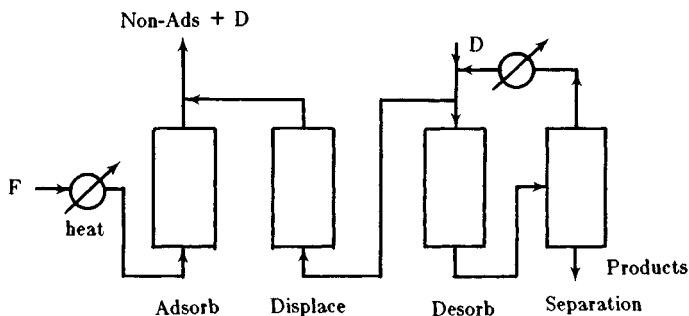
FIGURE 3-18.   General flow sheet for separation of *n*-paraffins using a desorbent for desorption.

adsorbed gases[17,62,107,219,253,254,578,627,641,645,678,852,865] and with more strongly adsorbed gases.[107,678] The use of less strongly adsorbed gases is much more common. When the desorbent gas is not adsorbed, the method is often known as purge gas stripping. These systems can be considered a type of gas chromatography with backflushing where one of the components is not adsorbed and the other is quite strongly adsorbed (see Chapter 5, Section IV.C). When the purge gas is adsorbed but less strongly than the adsorbate, the operation is often known as displacement desorption.* In these systems the desorbing gas competes for sites with the adsorbent and helps to remove the adsorbent from the system.

The major commercial application is separating medium molecular weight (C_{10} up to C_{20}) straight chain hydrocarbons from branched chain and cyclic hydrocarbons.[17,62,219,253,254,578,627,641,645,865] There are a variety of commercial processes which differ mainly in the details of the desorption method used. A general process flow sheet is shown in Figure 3-18. The commercial gas-phase processes would typically use counter-flow desorption and then some separation method to recover the product from the desorbent. Fairly rapid cycles with incomplete desorption are usually used. When the more strongly adsorbed material is fed to the column, a shock wave forms which recompresses the diffuse wave formed during desorption. The bed loading will be similar to Figure 3-4. The second step in Figure 3-18 displaces nonadsorbed fluid in the external pores, and is quite short. All of the processes use 5 Å zeolite molecular sieves as the sorbent. The straight chain hydrocarbons can diffuse into the pores and thus be adsorbed while the branched and cyclic molecules are too large to fit into the pores. The linear paraffins are strongly adsorbed even at 350°C. Since thermal decomposition becomes excessive above this temperature, thermal swings cannot be used. The paraffins can be desorbed with a high vacuum,[62] but it is then difficult to provide the high heat needed for desorption. Pressure swing systems are commonly used for separation of lower molecular weight straight chain hydrocarbons (see Chapter 4, Section II).

The ideal desorbent would rapidly remove the adsorbate, be easy to displace from the bed, be easy to separate from the products, and satisfy the usual desirable characteristics of being nontoxic, nonflammable, readily available, and inexpensive. So far, this magic material has not materialized. Purge gas stripping operations usually use gases such as nitrogen or hydrogen, which are easy to recover from the adsorbate, have high diffusivities, are relatively safe, and are inexpensive. Unfortunately, they do not do a good job of pushing strongly adsorbed materials from the bed. These purge gas systems are used for octane improvement at from 100 to 300 psia and 600 to 800°F.[219] They are also used in chromatographic-type systems (see Chapter 5). Applications of the solute movement theory and other theories to these chromatographic-type systems are considered in Chapter 5.

For the harder to desorb *n*-paraffins, a desorbent which adsorbs helps to push the materials

---

*   Note that there can be some confusion in nomenclature. In displacement chromatography (see Chapter 2, Section IV.D.1 and Chapter 5, Section IV.B) the desorber is more strongly adsorbed.

from the bed. Among the desorbents which have been used are *n*-pentane, *n*-hexane, ammonia, and alkylamines. The higher the molecular weights of the *n*-paraffins being purified the stronger the desorbent should be adsorbed. Processes have been developed by BP, Exxon, VBB Leuna Werke, Shell, Texaco, and Union Carbide. The general flow sheet will be similar to Figure 3-18 and details of the processes are given elsewhere.[62,219,254,641,645,865] Since an exchange adsorption is occurring, the processes are almost isothermal. A qualitative understanding of the operation can be obtained with the local equilibrium model with coupled solutes. Quantitative predictions for these isothermal systems can be obtained using the effective equilibrium pathway method.[114]

B. Liquid Systems

Solvent extraction has been studied for desorption of both activated carbon[227,284,507,952,1110] and resin[381,382,382a,382b,1026] systems. A flow sheet for recovery of a solute from water using activated carbon is shown in Figure 3-19A.[952] The heavily loaded wastewater is fed to the adsorber. After breakthrough occurs, the carbon is regenerated with a solvent. The effluent from the column is sent to a separation scheme such as distillation where both the solvent and the organics are recovered. The column is then drained and steamed to remove the solvent. After condensing the steam, the solvent-water mixture must be separated by suitable means. If water and the solvent are immiscible, it may be possible to send the water layer from the liquid-liquid separator to the adsorber at the end of the adsorption step. This is then a form of two-feed adsorption (see Section II.C.). When the water is highly loaded with organics, this method is reported to be cheaper than thermal regeneration since the organics are recovered.[952,1110] One disadvantage of this approach is that quite complete steam regeneration is required or the water may become contaminated with solvent. (An alternative is the waterwash shown in Figure 3-20.) Economics will also depend heavily on the cost of the solvent-organics and solvent-water separation steps. Thus solvent choice will be very important.

The solute movement theory can be applied to part of this cycle if the velocity of the solvent wave is known. Experimentally,[952] the solvent (acetone) seemed to displace water by plug flow. Then the solvent wave velocity will be

$$u_{solvent} = \frac{v}{1 + \left(\dfrac{1 - \alpha}{\alpha}\right)\epsilon\, K_d} \tag{3-12}$$

The solute movement diagram for the adsorption and desorption steps is shown in Figure 3-19B. During desorption the organic will exit at its feed concentration, and then a large peak will follow breakthrough of the solvent wave. This peak is followed by a diffuse wave. These predictions are qualitatively correct as illustrated by the experimental results shown in Figure 3-19C.[952] A more detailed model, including mass transfer, was solved by finite difference methods.[952] These theoretical results are shown in Figure 3-19C as a solid line and agree well with the experimental results. The effective equilibrium pathway approach[114] can also be applied to these systems.

Solvent desorption of organics adsorbed from water onto polymeric resin systems has been used commercially for several pollution problems. A variety of flow sheets are used depending on the organic being recovered. The method used for recovery of phenol is shown in Figure 3-20.[367,381,382,382a] Before breakthrough of the phenol the wastewater flow to the adsorption column is halted and the column is "superloaded" with 10% phenol from the separator (see Section II.C.). The column is then regenerated with the solvent (acetone or methanol) and then rinsed with water to remove the solvent. The solute movement diagram was shown in Figure 3-8 when the superloading[367,381,382,1026] procedure was discussed. Resin life was over 2 1/2 years and thus is not a problem.[382]

A

B

C.
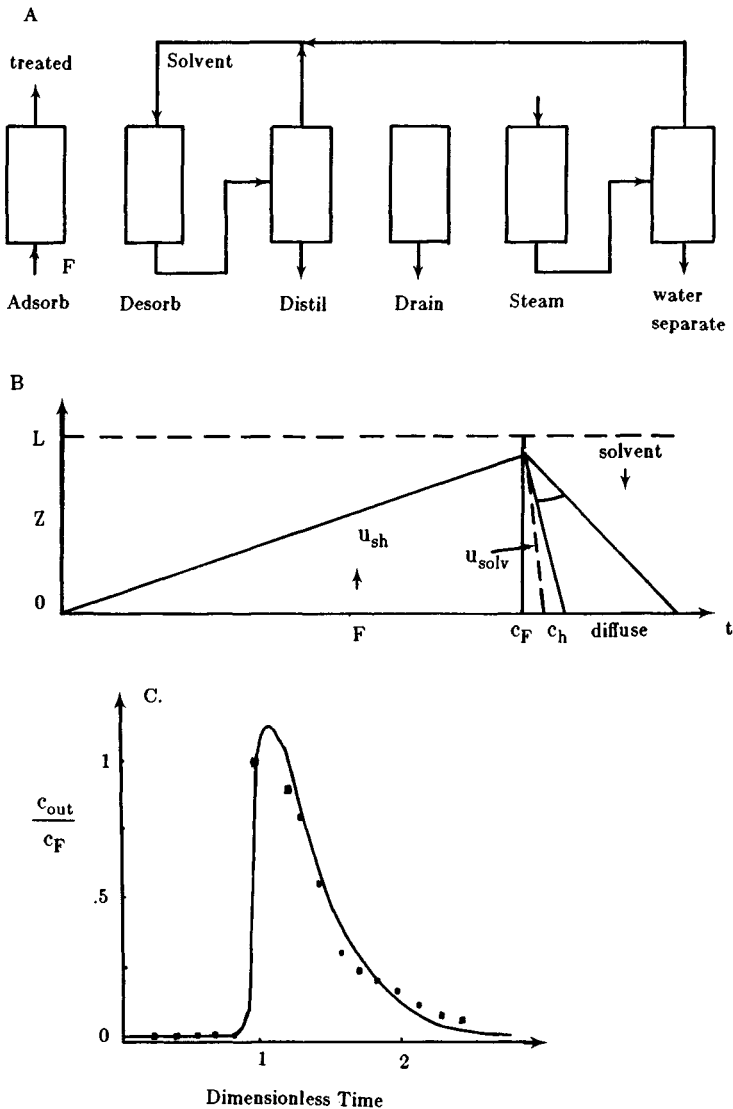
FIGURE 3-19. Desorption of activated carbon with solvent. (A) Operating cycle; (B) solute movement diagram; (C) experimental results for removal of phenol using acetone as solvent.[952]

The resin systems can also be thermally regenerated with steam. This is done commercially for recovery of chlorinated and aromatic hydrocarbons.[381] The cycle consists of adsorption of the organic from the wastewater, draining, and desorption with steam. Usually, the organic can be recovered by condensing the vapors and using a liquid-liquid separator.

C. Supercritical Fluids

Supercritical fluids have recently been introduced as a method for desorption.[312,530,739,804] Typically, solute would be adsorbed from the liquid phase and then the column would be drained. Desorption would be done with a supercritical fluid with carbon dioxide and water being likely candidates. The adsorbate would be recovered from the supercritical fluid by reducing the pressure and/or varying the temperature. One attraction of the method is the tremendous changes in solubility of compounds in supercritical fluids when the fluid is near
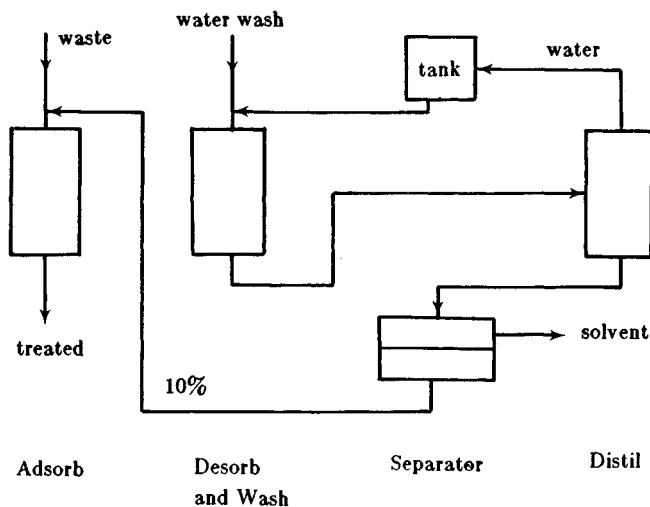
FIGURE 3-20. Phenolic removal and recovery system using polymeric adsorbent and "superloading".

the supercritical temperature and pressure. Thus desorption of many adsorbates will be rapid and the recovery of the adsorbate is simple, but may be costly. Operation is at mild temperatures and thus will be advantageous for thermally sensitive compounds. Also, supercritical CO_2 is nontoxic, has about the same solubility and density as liquids, but the diffusivity is about an order of magnitude higher, and the viscosity an order of magnitude lower. Thus the desorption step should be rapid with a minimum of extra zone broadening caused by mass transfer rate limitations. Pumping the CO_2 is also inexpensive.

Experimental data[804] for the desorption of acetic acid, phenol, and alachlor from both activated carbon and polymeric resinous adsorbents shows that supercritical CO_2 is an effective desorbent. The weaker and less nonlinear the adsorption the more effective the supercritical CO_2 was for removing the adsorbate.

Supercritical fluid desorption does not look like a simple or cheap process. The process requires high-pressure vessels and compressors. Pressure swing versions require compression of the supercritical fluid to high pressures after decompression to recover the adsorbate. Thus operating costs will not be low.[804] A method for recovering energy could greatly decrease operation costs. If used, I expect that the process will be used only for the recovery of expensive products such as flavor ingredients and pharmaceuticals. Even for these compounds the method will have to compete with other separation methods.

Supercritical fluid extraction of caffeine from coffee has been practiced commercially in Germany for many years, but commercial applications of supercritical fluids for desorption have not been reported. Pilot plants have been constructed and are available for lease.[31,739]

D. Ion Exchange Systems (References)

Ion exchange systems are usually operated in a fashion similar to solvent-desorbed adsorption systems. In ion exchange systems the regenerant is usually a solution which is concentrated in the regenerating ion. Because of the special nature of ion exchange resins (e.g., swelling of the resin) and because of the special nature of some cycles (such as using mixed beds for demineralization), the operation of ion exchange systems may be somewhat different than adsorption systems. The underlying chemistry of ion exchange is different and is more closely related to extraction.

A detailed coverage of ion exchange systems is beyond the scope of this book. Ion exchange systems are covered where their operation is quite similar to that of adsorption systems (see

Chapter 4 [Sections III and IV], Chapter 5 [Section VIII.A], Chapter 6 [Sections II.A, III.A, and III.B], and Chapter 8 [Section II]. For packed bed applications the reader is referred to any of the large number of excellent review papers and books.[16,18,56,201,322,334,431,484,493,621,656,753,854,933,943,942,1016,1017]

VI. THE FUTURE OF PACKED BED OPERATIONS

I feel somewhat sheepish making guesses about the future of these packed bed operations since most of them are already used commercially. However, there are a few trends which are fairly evident.

First, efforts at reducing energy use in adsorption operations will continue. This will result in more extensive use of beds in series, of two or more layers of adsorbent in a bed, of short cycles which leave a considerable heel in the column, and of methods such as "superloading", which increase the concentration of effluent. Energy reduction efforts will also focus on better ways to regenerate columns. This will include more use of vacuum, solvents, or desorbents, and other ways to replace thermal methods. This also will include an increased rate of replacement of traditional adsorbents with improved adsorbents. An example of this is the use of polymeric resins instead of activated carbon. Efforts to improve thermal desorption techniques will continue. There will probably be more widespread use of cycles without a cooling step, of systems where the thermal wave remains in the column, and more coupling of the adsorption process with other parts of the plant to use waste heat for desorption.

I expect to see a vast increase in efforts to intensify the use of adsorption systems. More systems will be designed with smaller-diameter particles. These systems will be considerably shorter than existing systems, and will operate on much shorter cycles. Thus they will have higher adsorbent productivities. The use of special forms of adsorbents with low mass transfer resistances will also allow rapid cycles and higher productivities. In addition, spherical adsorbents which can be packed to give more efficient columns will be used more widely.

Detailed theoretical understanding of many of the processes lags our ability to apply these processes. Advances in understanding activated carbon systems in both gas and liquid applications should continue; however, they will be slow particularly for wastewater treatment. Understanding of some of the less common methods such as purge gas stripping or purge gas desorption will come when the theoretical experts focus their attention on these areas.

Overall, there will be many small changes which will result in the increased application of packed bed adsorption techniques for solving a wider variety of separation problems.

Chapter 4

CYCLIC OPERATIONS: PRESSURE SWING ADSORPTION, PARAMETRIC PUMPING, AND CYCLING ZONE ADSORPTION

I. INTRODUCTION

In this chapter we consider three cyclic adsorption processes. Essentially, pressure swing adsorption (PSA) adsorbs material at high pressure and desorbs it at low pressure using part of the pure product as a countercurrent reflux. Parametric pumping is similar except a thermodynamic quantity other than pressure is varied. In cycling zone adsorption a thermodynamic variable is changed to force the separation, but flow is unidirectional. The division between Chapters 3 and 4 is somewhat arbitrary. The major difference is that the processes discussed in this chapter were developed with the entire cycle in mind. The processes in Chapter 3 tend to be a separate desorption step attached to an adsorption step.

II. PRESSURE SWING ADSORPTION (PSA) AND VACUUM SWING ADSORPTION (VSA)

Pressure swing adsorption (PSA) was first developed by Skarstrom,[917,918] who called the process "heatless adsorption". Since the process was first announced in 1959, there have been many important modifications to the original process. PSA has attracted considerable interest because of its simplicity and low capital investment. PSA is now really a class of processes which are used commercially for drying air, recovering hydrogen, producing oxygen or nitrogen from air, separating hydrocarbon gases, and several specialty applications. Several reviews of the PSA process have appeared.[248,583,627,643,723,825,865,919,988,1051] Vacuum swing adsorption (VSA) is somewhat similar but desorption is done by drawing a vacuum. This process is also used commercially for air separations.

A. Basic PSA Method

One logical place to start to examine PSA is the basic two-column Skarstrom-type system[917,919] shown in Figure 4-1. The high-pressure feed enters the right column where the solute is adsorbed under high pressure p_H. The product gas exits at high pressure and is essentially free of solute. A portion of this pure high-pressure gas is expanded and used as a countercurrent purge in the left column which is at low pressure. After a half cycle period of a few minutes, the columns switch. The feed repressurizes the left column and the left column produces high-pressure product. The right column is depressurized to p_L and then is purged counter-flow to the feed with a fraction of the high-pressure product. After a start-up period, a cyclic steady state is reached where a pure high-pressure product and a somewhat concentrated, low-pressure waste gas are produced. At the cyclic steady state each cycle is time dependent and outlet concentrations vary with time, but the same cycle repeats over and over. The low pressure (p_L) is usually slightly above atmospheric while the high pressure (p_H) depends either on the gas supply pressure or the desired purity and recovery of the product.

This method was first developed for drying compressed air with a desiccant as adsorbent;[917] 3 days were required for start-up with an initially saturated desiccant to dry a 4000 ppm feed gas to 2 ppm. Eventually the product contained less than 1 ppm moisture. This start-up is shown in Figure 4-2.[919] If a dry desiccant were used initially a dry product gas would be produced immediately.[600] The major cost of operation is the loss of product (in this case compressed air) in the waste gas. This loss results in a relatively low recovery of product and has been one of the major problems with PSA systems.
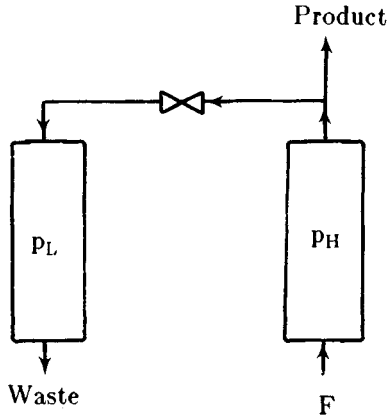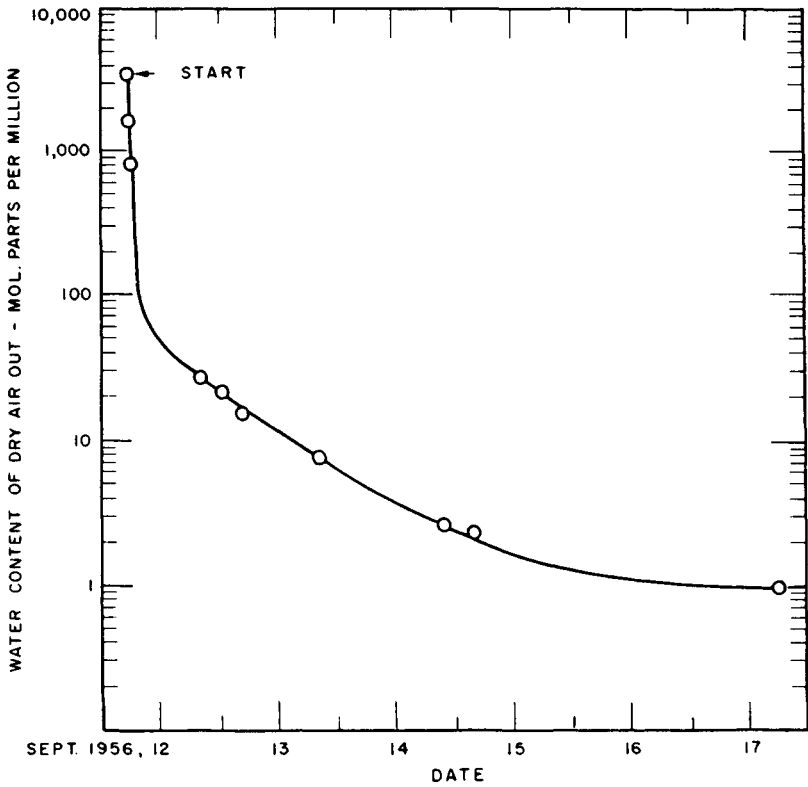
FIGURE 4-1. Skarstrom-type two-column pressure swing adsorber.

Drying out of adsorption drying system using heatless fractionation.
Flows: wet air in: 1.0 scfm, 40 psig, 3,800 ppm H_2O
dry air out: 0.5 scfm, 40 psig, as shown
regeneration air out: 0.5 scfm, 0 psig
Adsorbent: Mobilbeads, 1 lb each chamber
Cycle time: 3 min dry, 3 min regenerate

FIGURE 4-2. Start-up of PSA air dryer.[919]

With a few modifications the local equilibrium theory developed in Chapter 2 can be used to explain the primary aspects of PSA. This has been done for the two-column system shown in Figure 4-1[224,900] and for other PSA configurations (see Section V). In addition to the assumptions in Table 2-1 (some of which have been relaxed in some analyses), the gas is usually assumed to be ideal and pressure drops are neglected. The solution of the mass balances for solute A for isobaric periods is[224]

$$u_s = \frac{v}{1 + \left(\dfrac{1 - \alpha}{\alpha}\right)\epsilon + \dfrac{1 - \alpha}{\alpha}(1 - \epsilon)\,\rho_s\,k_i} \qquad \text{Isobaric} \qquad (4\text{-}1)$$

which is the same as Equation 2-30 with $K_d = 1.0$. The fluid velocity v is usually different during the adsorption and purge steps.

During the blowdown (depressurization) step solute is desorbed and carried towards the outlet end of the column. Thus the mole fraction of solute y in the gas increases and the solute wave moves towards the outlet of the column. Since solute is adsorbed during the repressurization step, the solute mole fraction decreases. The change in the positions of the solute waves during the blowdown or repressurization steps is predicted by equilibrium theory[224] to be

$$\frac{z_{\text{after}}}{z_{\text{before}}} = \left(\frac{p_{\text{after}}}{p_{\text{before}}}\right)^{-\beta_A} \qquad (4\text{-}2)$$

where z is measured from the closed end of the column and

$$\beta_A = \frac{\alpha + (1 - \alpha)\epsilon + (1 - \alpha)(1 - \epsilon)\rho_s\,k_{\text{inert}}}{\alpha + (1 - \alpha)\epsilon + (1 - \alpha)(1 - \epsilon)\rho_s\,k_A} \qquad (4\text{-}3)$$

If the inert gas does not adsorb $k_{\text{inert}} = 0$. β_A is the ratio of the amount of inert gas which could be stored in the column to the amount of adsorbate which could be stored. The change in mole fraction corresponding to Equation 4-2 is

$$\frac{y_{A,\text{after}}}{y_{A,\text{before}}} = \left(\frac{p_{\text{after}}}{p_{\text{before}}}\right)^{\beta_A - 1} \qquad (4\text{-}4)$$

The simple equilibrium theory assumes that fluid and solid are always in equilibrium. The exact path taken depends on the way pressure is decreased or increased. However, the final state does not depend on the path when equilibrium is assumed. For nonequilibrium processes the details of the blowdown and repressurization steps become important.

Equation 4-2 predicts that the solute waves move towards the open end of the column during depressurization and towards the closed end of the column during repressurization. This happens because gas is flowing in these directions during these two steps. Equation 4-4 predicts that the solute mole fraction in the gas increases during depressurization and decreases during repressurization. During depressurization the total pressure drops and thus the partial pressure of adsorbate will decrease. The adsorbate will then start to desorb. Since adsorbate is desorbing, the mole fraction of adsorbate in the gas y must increase. The opposite behavior occurs during repressurization. Thus the predictions of Equations 4-2 and 4-4 agree with our physical intuition. More detailed analyses of the depressurization step result in much more complex results.[849]

This simple theory can now be applied to the two-column system shown in Figure 4-1.
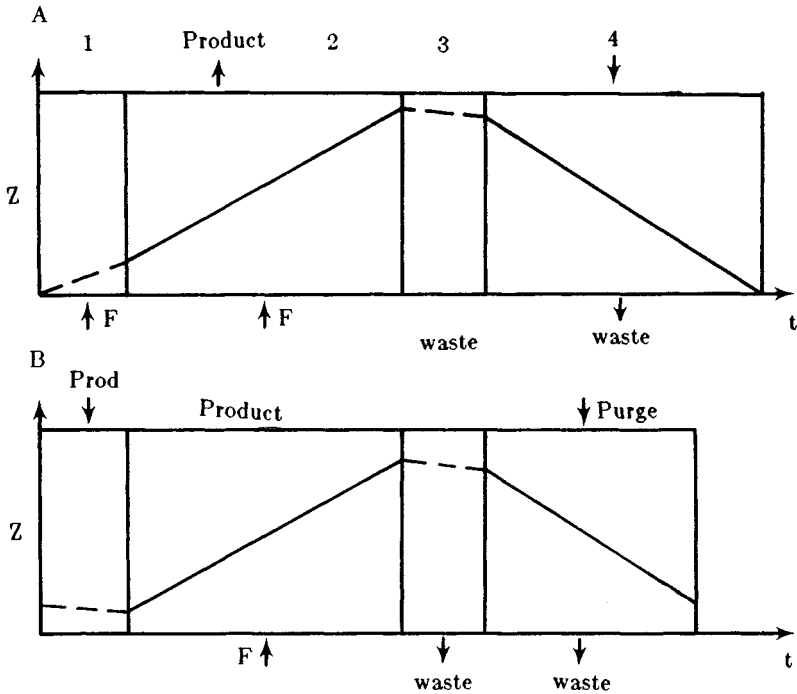
FIGURE 4-3.   Solute movement diagrams for PSA, Step 1, repressurization; 2, adsorption at p_H; 3, depressurization (blowdown); 4, purge at p_L. (A) Using feed to repressurize. (B) Using product to repressurize.

Each column undergoes four steps: repressurization with feed, adsorption at p_H, depressurization, and purge at p_L. The solute movement diagram for one column of this system is shown in Figure 4-3A. The dotted lines in the blowdown and repressurization steps indicate that the exact paths are not known during these steps since the pressure history is not known. However, the end points are known from Equation 4-2.

Figure 4-3A is drawn with a higher velocity during the purge step than during adsorption. Typically the volumetric purge to feed ratio, $\gamma = V_{purge}/V_{feed}$, is greater than 1.0. The local equilibrium theory with linear isotherms predicts that any $\gamma \geq 1$ will be sufficient.[224,900] In practice, dispersion and finite mass transfer rates cause spreading of the waves and a $\gamma > 1$ is required. A range of 1.1 to 1.5 has been suggested.[919] One major advantage of PSA processes is a large amount of product can be produced even though γ is greater than one. This is possible because of the expansion of the product gas when the pressure is dropped. If the ideal gas law is followed the ratio of moles of purge to moles to feed is

$$\frac{n_{purge}}{n_{feed}} = \frac{p_L}{p_H}\frac{V_{purge}}{V_{feed}} = \gamma\frac{p_L}{p_H} \tag{4-5}$$

The fraction of feed which appears as product will be high if the pressure ratio, p_H/p_L, is high. This expansion effect is one of the major reasons PSA has become a successful commercial process while cycling zone adsorption and parametric pumping have not.

Many variations of the PSA process have been developed. One of the simplest is to repressurize with pure product instead of the feed. This variation is shown in Figure 4-3B. The purge step in Figure 4-3B is drawn with a shorter period and hence a lower γ than in Figure 4-3A. Industrial practice[988,1029] and theoretical calculations[220,599,1106] show that more

FIGURE 4-4. Loading in a PSA column when removing an adsorbate with nonlinear isotherms.

product is produced when the column is repressurized with product. Since repressurization with product can be considered as more reflux, this does make sense.
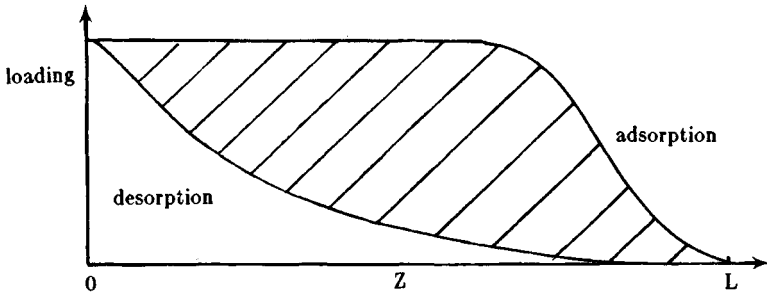
In many industrial separations the adsorbates will have nonlinear isotherms. Then a shock wave will be formed during the feed step in Figures 4-3a and 4-3b, and a diffuse wave will occur during the purge step. The solute movement theory is easily adapted to these steps. The blowdown and repressurization steps are more difficult to calculate. The effects of nonlinear isotherms are shown schematically in Figure 4-4 where the loading is plotted vs. the axial distance in the column. A constant pattern wave forms during adsorption and feed is stopped when breakthrough occurs. A proportional pattern (diffuse wave) forms during the purge step. Usually, the column is not completely purged; instead, most of the mass transfer zone (MTZ) remains in the column as a heel. This makes the waste gas more concentrated and uses less purge gas. The working capacity of the bed is represented by the lined region in Figure 4-4. With slow mass transfer the two MTZs will be quite long, and the working capacity can be a very small fraction of the total bed capacity (much less than shown in Figure 4-4). Highly favorable isotherms will give sharp adsorption fronts but very diffuse desorption fronts. The opposite is true for highly unfavorable isotherms. The optimum isotherm shape is a compromise, and is probably close to linear. A higher working capacity can be achieved by using smaller-diameter particles, decreasing L, and increasing the column diameter. This procedure can keep Δp constant while decreasing L_{MTZ}/L and increasing adsorbent productivity (see Chapter 3 [Section II.D]).

Comparison of the solute movement (local equilibrium) theory with experiment[375,900,1099] consistently shows that the local equilibrium theory overpredicts the separation. Considering the very restrictive assumptions made in the derivation, this is not surprising. The agreement between theory and experiment is illustrated in Figure 4-5,[900] which also illustrates the importance of the purge to feed ratio, γ. Figure 4-5 shows the lowest CO_2 concentration observed during a cycle. The outlet gas concentration during a cycle is time dependent, and a series of waves or scallops are actually observed.[900,1099] When mass transfer rates are slow and the separation is kinetically controlled, the observed separation may be the opposite of the local equilibrium theory predictions.[1098,1099] Thus extreme care should be used in employing this simple theory. More complex and accurate theories should be used for design (see Section V).

Adsorber operation is not isothermal. During the adsorption of water vapor from air the adsorber heats up from 2 K[217] to 4 K.[257] This heat is "stored" in the bed and thus is available during the regeneration step. During the regeneration step the bed temperature will drop to 2 to 4 K below the feed temperature. With concentrated systems (50% CH_4) the temperature excursion can exceed 50°C[220,1106] although much smaller temperature increases are seen with faster cycles. In normal operation the relatively fast PSA cycles allow for heat storage since the thermal waves do not have time to break through. If thermal breakthrough did occur
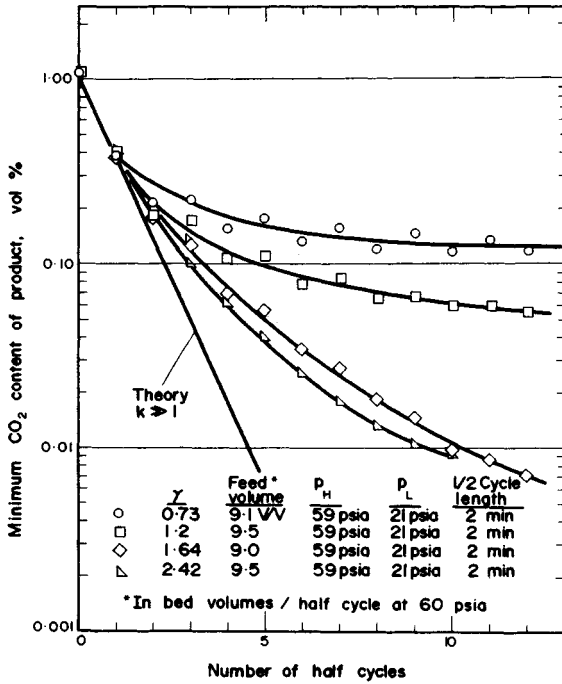
FIGURE 4-5. Removal of CO_2 from He by two-column PSA.[900]
(From Shendalman, L. H. and Mitchell, J. E., *Chem. Eng. Sci.*,
27, 1449, 1972. With permission.)

during the cycle, some of the stored heat would be lost. This problem can be solved by adding a nonadsorptive heat storage material to the column.[512,1103] This also decreases the amplitude of the temperature variations, which is desirable. However, the volumetric capacity of the adsorber at the feed temperature will drop since less adsorbent is present. With large temperature variations it may be desirable to couple two columns so that they can exchange heat.[1103] When these columns are operated out of phase, each will be heated or cooled as required.

Most theories have ignored temperature changes and assumed the bed is isothermal. Even if one ignores this temperature variation there will be an optimum temperature for operation. At low temperatures adsorption becomes easier but regeneration becomes more difficult. For hydrogen purification with molecular sieves the optimum range was 10 to 15°C.[1066] Most commercial systems work better when it is cool, and thus a penalty is paid in very hot locations. Operation at higher temperatures may be advantageous if impurities adsorb less. Cyrogenic temperatures are advantageous for separating rare gases.[988] When temperature effects are included in the analysis, adiabatic operation results in lower purities than the ideal isothermal operation.[258]

Gas velocities are typically in the range from 0.01 to 0.5 m/sec. For most systems where internal diffusion controls, velocities in this range will give an average residence time longer than the characteristic time for mass transfer, d_p^2/D_M. Sharp adsorption fronts result, and a clean separation can be obtained.

B. Building Blocks for PSA and VSA Cycles

Many PSA cycles have been developed. One way to look at the multitude of cycles is to look at the individual steps which can be employed. These steps are delineated below:

(1a) Repressurization with feed or (1b) repressurization with high-pressure product or (1c) repressurization by pressure equalization. Steps 1a and 1b were illustrated in Figures 4-3A and B. The repressurization can start from the low pressure p_L and go to p_H, or it can go from an intermediate pressure to p_H or from one intermediate pressure to another. Partial repressurization is used when pressure equalization steps are employed. Repressurization with pure product is in a counter-flow direction to the feed.

(2) Feed (adsorption) at p_H. This step is usually employed to produce the high-pressure product.

(3) Pressure equalization. When one column needs to be repressurized and another depressurized, this can be partially done by equalizing pressure between the two columns.[75,130,218,300,477,1066] This step reduces the amount of product gas lost to waste and thus increases recovery. Pressure equalization may be done several times by matching a column with the column closest to its pressure. Blowdown gas can also be saved in a reservoir for later use in pressure equalization.[643] Commercial systems with ten or more columns have been built to take advantage of pressure equalization.[218,477,1066] Obviously, valving and control systems become more complex as the number of columns increases. Pressure equalization can be done from either end of the column.[477] For instance, at the start of depressurization pure or almost pure product gas can be recovered by depressurizing co-flow with the feed gas direction.[300,477] The material can be recovered as product or be used to repressurize a column counter-flow to the feed direction. During later depressurizations flow should be counter-flow since impurities are being desorbed. Now this gas should be fed cocurrently to the feed direction in the column being partially repressurized. Pressure equalization can also be done by hooking together the two ends of the columns to have both co- and counter-flow depressurization and repressurization simultaneously,[75] or by having feed gas and repressurization gas enter simultaneously.[300] In all cases it is desirable to keep impurities away from the product end of the column.

(4) Blowdown (depressurization). Blowdown may go from p_H to p_L as in Figures 4-1 and 4-3, or partial blowdown to p_L may be used when pressure equalization steps are used. During blowdown some solute desorbs. Thus a certain amount of regeneration occurs during the blowdown step. In some processes this is the only regeneration since separate purge or vacuum regeneration steps are not employed.[33,375,504,558,580,617, 999,1098] Blowdown is usually counter-flow, but a period of co-flow blowdown can be useful for removing the less adsorbed gas[220,1106] or producing product.[300] The co-flow blowdown period will usually be short, and is usually followed by counter-flow blowdown.

(5) Purge (regenerate) at p_L. Usually pure high-pressure product gas is expanded and used to purge the column at the low pressure. This is done counter-flow to the feed direction. Sometimes the purge gas is obtained during blowdown of other columns.[300]

(6) Vacuum regeneration. A vacuum can be used to regenerate the column. This may be done instead of the purge step,[34,35,75,190,330,737,969] or in addition to a purge step.[602,603,910,911] Vacuum operation works best when the mole fraction of the strongly adsorbed gas in the feed is fairly high (see Figure 3-11). Vacuum operation minimizes the loss of nonadsorbed product gas, but pulling the vacuum requires a vacuum system and columns usually need to be larger in VSA systems (no purge step). These cycles are also often longer than PSA cycles, and thus adsorbent productivities are lower. Operating costs are often lower since recoveries can be higher and less gas is compressed.[190] Vacuum regeneration can also separate binary gas streams although the more strongly adsorbed gas will not be at extremely high purities.[190,915] These processes are used for simultaneous recovery of oxygen and nitrogen from air. For air separations PSA is favored when energy is cheap and capital is expensive, and VSA is favored in the opposite case.[190]

(7)   Purification step (high-pressure rinse or reflux). This procedure is used when there are multiple solutes to be recovered[758,910,911,1064] or removed[915] (see Section II.D) or when a binary mixture is to be completely separated.[737,1064] The less adsorbed solute is swept out at high pressure with either pure carrier gas or a reflux of more strongly adsorbed solute. A compressor may be required to repressurize the reflux gas.[737,911,1064] Flow would usually be cocurrent with the feed gas.

(8)   Delay. Some processes[33,558,580,1098] use a delay step where there is no flow in or out of the column. This delay period gives slowly diffusing solute time to adsorb or desorb and gives time for pressure waves to move in the column.[558,580]

These steps can be arranged into a very large number of different processes. The appropriate combination will depend upon the desired objective. As in all classification schemes, some processes cannot be conveniently broken down into the steps listed here.

Additional procedures can be used to develop unique PSA processes. A mid-bed withdrawal line[330,583,643,988] is useful since it gives quite large turndown ratios and can help pull off fairly pure streams of the more strongly adsorbed solute. Magnetically stabilized moving beds (see Chapter 6 [Section II.A.3]) have been adapted to combined pressure and temperature swings.[475] Multiple adsorbents have been used for several purposes. A guard bed packed with a weak or partially deactivated adsorbent is useful to prevent poisoning of the main bed.[7] Packing a column with activated carbon and a desiccant will remove both traces of hydrocarbons and water from compressed air.[587] A layer of desiccant plus zeolite is used commercially to produce dry oxygen from air while a layer of desiccant plus carbon sieve is used commercially to produce dry nitrogen.[35,756] A VSA system with desiccant columns and an adsorbent for nitrogen can dry the air and then separate it into oxygen and nitrogen.[915] In general, two adsorbents packed in series can be used to remove two solutes. Two layers of adsorbent could also be used to sharpen constant pattern (shock) waves. This can be done by placing a layer of small-size particles with a low HETP on top of a layer of larger particles (with a low Δp). Two adsorbents with different selectivities can also be used for multicomponent separations (see Section II.D).

C. PSA and VSA Cycles for Bulk Separations

The usual industrial applications of PSA have been for bulk separations. Impurities are removed and sent to a waste stream. In some cases, e.g., air drying or oxygen purification from air, the waste gas is simply discarded. In other cases, such as hydrogen recovery, the waste gas has value as a fuel. In bulk separations no attempt is made to fractionate the gas into different solutes. In this section some of the basic cycles for bulk separations will be discussed. No attempt will be made to exhaustively cover the many cycles illustrated in the several hundred PSA and VSA patents. Useful reviews cover some of these processes.[219,583,627,643,825,865,919,988,1051]

1. "Slow" Cycles

The "slow" cycles have cycle periods of a few minutes. These processes can be described as combinations of the steps discussed in the previous section. Usually, the solute movement theory gives an adequate qualitative description of the process. (This is not true for carbon sieves which work by a kinetic effect.[37,602,756]) Flow sheets for many processes are in the reviews by Lee and Stahl[643] and by Tondeur and Wankat.[988]

Most one-column systems do not have a source of gas for the purge step. Thus the system either uses only the blowdown step for regeneration or vacuum for regeneration. A typical one-column system[375,504] using only blowdown for regeneration is shown in Figure 4-6A. This cycle is quite simple, but will have difficulty producing as pure a product as systems with purge or vacuum regeneration. Purge can be obtained with reservoirs[64] or dead vol-
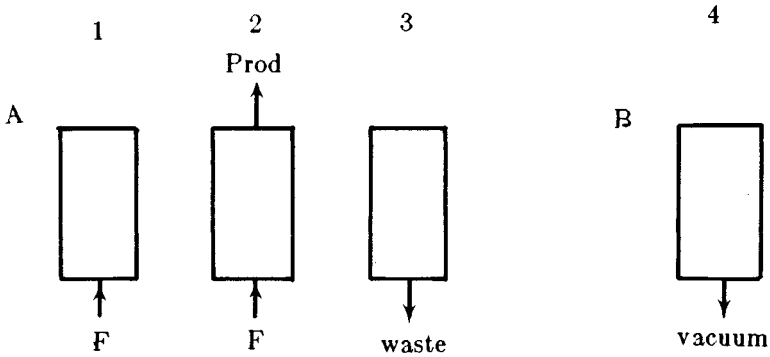
FIGURE 4-6. One-column PSA systems (A) Using only blowdown for regeneration. Step 1, repressurization; step 2, adsorption at p_H; 3, blowdown. (B) Addition of vacuum regeneration step.

ume.[250] A one-column system with vacuum regeneration would either add a vacuum regeneration step as shown in Figure 4-6B, or the feed in Figure 4-6A would be at close to atmospheric pressure and the waste stream would use a vacuum. Vacuum regeneration can do a more thorough job of removing solute and thus produce a purer product gas. However, a vacuum system is required and capital costs tend to be larger. Neither type of one-column system can use pressure equalization steps.

The original two-column configuration[917,919] shown in Figure 4-1 is commonly used for drying compressed air. Small-scale package units are available.[36,310,409,563,782,1079] A variety of desiccants can be used in the column. One-column systems with a reservoir for purge gas storage are also used for drying small quantities of compressed air.[64] Their behavior is similar to two-column systems. The compressed air dryers can be designed to knock out entrained liquids in an action similar to a cyclone before the air enters the dryer. Considerations for design and an empirical design procedure are available.[64] Packaged two-column systems for oxygen and nitrogen recovery from air are also available.[37,756] Molecular sieve zeolites are used when pure oxygen is desired,[300,627,643,919] and carbon sieves are used when pure nitrogen is desired.[37,561,602,603,723] Two-column VSA systems using zeolite molecular sieves have been used to produce both oxygen and nitrogen from air.[190] Packaged units for other separations are also available.[409,519,712] The two-column systems are simple and can produce a very high-purity product, but losses of product gas in the waste stream are often fairly high.

The carbon sieve process is of interest since it is the "only known commercial process using difference in intraparticle diffusivity . . . "[578] as the basis for the separation. The equilibrium adsorption of oxygen and nitrogen are approximately the same. However, the oxygen diffuses into the pores much faster and acts as if it is more strongly adsorbed. This carbon sieve system has been built with both vacuum[561,602,603,723] and atmospheric purge[37] operation, usually using two-column systems. The cycle is very similar to the Skarstrom cycle in Figure 4-1, but the reason for separation is different and the solute movement theory is not applicable. One advantage of the carbon sieve systems is predrying of the gas is usually not required. Capillary condensation of water occurs only if the relative humidity is high. This condensation will decrease the adsorption capacity, but does not affect the selectivities.[953] Carbon sieves will probably be used for other commercial separations since they can be made very selective.[216]

Multiple-column systems allow for pressure equalization steps and thus are capable of higher recoveries. From three[7,300,519,643,988] to ten or more[218,477,643,988,1066] columns have been used. More columns allow for additional pressure equalization steps. This is useful if the high pressure is high enough.[1066] For low-pressure operation additional columns are not
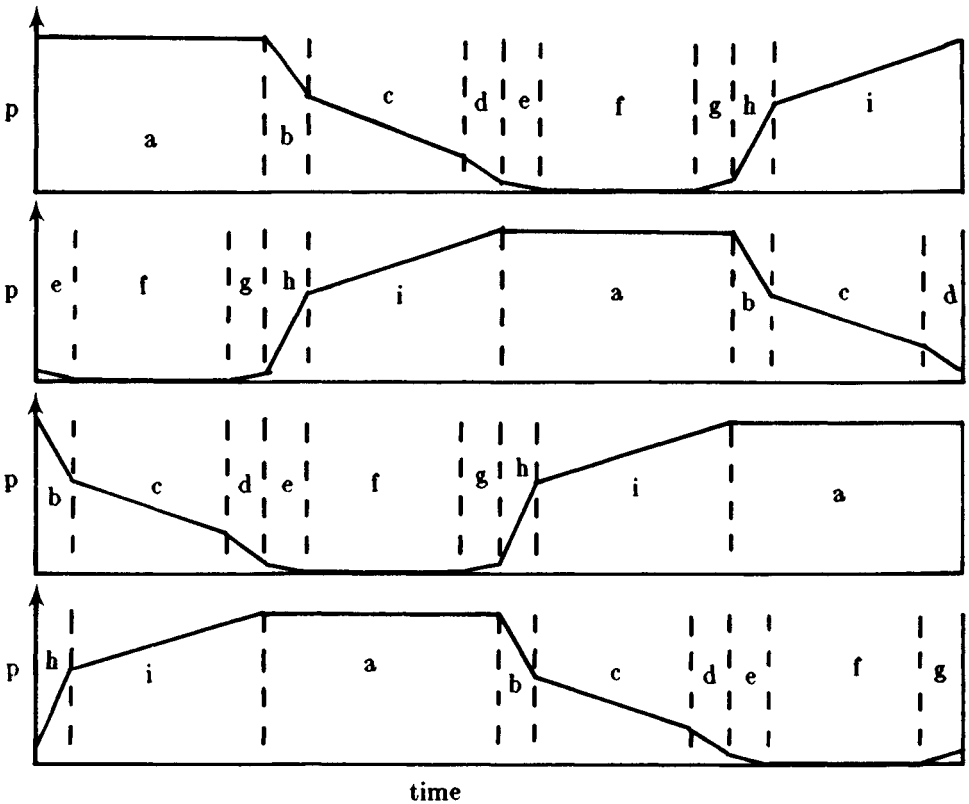
FIGURE 4-7.   Pressure-time diagram explaining operation of four-bed PSA system with pressure equalization steps. (From Watson, A. M., *Hydrocarbon Processing, 62,*(3), 91, 1983. With permission.)

useful. The operation of a four-bed system with pressure equalization is illustrated by the pressure vs. time diagram shown in Figure 4-7.[1066] Adsorber 1 first is in the adsorption mode (step a) and then the void space gases, which are mainly hydrogen, are expanded (step b) and used to partially pressurize column 2. The gas from further depressurization of column 1 (step c) is used to purge column 3 while gas from step d is used for the initial repressurization of column 3. The final depressurization (step e) is a blowdown operation. Regeneration (step f) is done with expanded gas from column 4 which is also used for the first repressurization step g. The second repressurization (step h) uses gas from column 2 while the final repressurization (step i) uses pure H_2 product. Timing is set so that the short periods — b, d, e, g, and h — are all of equal duration. Then from Figure 4-7 periods,

$$a = e + f + g \quad , \quad a = h + i \quad , \quad i = c + d$$

This allows easy development of the cycle. Extension to more columns allows for more pressure equalization steps and thus recovery of a higher percent of the hydrogen. Naturally, the valving manifolds and control systems become more complex as more columns are added.

Economics have been presented for four-bed systems.[1097] Multibed PSA systems have been used for a variety of industrial separations. Hydrogen recovery is done with three or more (usually more) beds.[219,287,1097] Over one billion SCFD of H_2 are recovered worldwide.[219] Large-scale oxygen recovery systems use multibed systems. Over 200 PSA systems for oxygen recovery have been installed.[219] Light *n*-paraffins have been commercially recovered by two- or three-bed PSA since 1961.[66,219,723]

One should also remember that it may be advantageous to use PSA or VSA in conjunction with other separation techniques. For example, combining PSA or VSA and cryogenic separation can give both high hydrogen purity and high recovery.[1035,1097]

2. *"Rapid" Cycles*

Rapid cycle systems operate with considerably shorter periods (usually less than 30 sec), may not satisfy the classification scheme presented in Section II.B, have higher productivities than the classical PSA systems, and can often not be adequately explained by equilibrium models. These methods may represent the wave of the future.

A rapid cycle PSA system which uses one to three columns has been commercialized for removal of nitrogen from a nitrogen-ethylene stream[33,341,558,559,578,580] and for production of medical oxygen.[219] This system is shown schematically in Figure 4-8A with one column. The 1- to 5-ft long column is packed with small particles (40 to 80 mesh) which have a fairly high pressure drop and a low HETP. The cycle is as follows:[33,558,580]

Feed:	0.3 to 1.0 sec
Delay:	0.5 to 3.0 sec
Exhaust:	5 to 2.0 sec

The feed valve is open during the feed step and the exhaust valve is open during the exhaust step. The product valve controls column pressure but it is always open. Nonadsorbed or less adsorbed gas is collected as product while the adsorbed impurities and some carrier gas leave as exhaust. Similar processes but without the delay step were reported earlier.[617,999]

To understand the operation of this process, consider the pressure profiles shown in Figure 4-8B.[580] During the feed step (1) the pressure profile monotonically decreases as expected. The delay step (2) allows the pressure wave to penetrate into the column further. When the exhaust valve is opened the pressure immediately drops at the feed end. Early in the exhaust period (3) there is a pressure maximum in the column and gas flows to both ends from the center of the bed. Late in the exhaust period (4) the column continues to be purged. The feed, delay, and part of the exhaust step produce product while the exhaust step both depressurizes and regenerates the bed. The concentration profiles in the bed are shown in Figure 4-8C.[580] Note that a rather small fraction of the bed (between curves 1 and 3) is available as a useful capacity.

The productivity (kilogram of product per kilogram adsorbent per day) of this one-bed system for recovery of 90% oxygen from air was 2.3 compared to 0.5 for standard three-bed PSA systems.[558] The oxygen recovery was 38% compared to 40% in the PSA system.[59] Thus a much smaller system can be used at the price of a somewhat lower recovery. Somewhat higher recoveries are achieved with the three-column system.[341,578]

An interesting comparison which was not made would be to use a smaller packing in the standard PSA system, but keep L/d_p^2 constant so that both N and Δp are constant. The cycle period would also be reduced by a factor d_p^2. The amount of feed processed per hour would be essentially unchanged. This should give roughly the same separation as the standard PSA system but the productivity would be considerably higher (see Chapter 3 [Section II.D]). For example, a decrease in d_p by a factor of $\sqrt{5}$ (to about 25 mesh) would reduce L by a factor of 5 (to around 1 to 2 ft). The cycle time would be reduced by a factor of 5 (to about 35 to 60 sec). The amount of product should be about the same but the productivity would increase by approximately a factor of 5. Thus the faster cycling greatly increases productivity. These suggested modifications of standard PSA cycles have not been tried. If they worked they would significantly increase the productivity. One possible problem area which needs to be checked experimentally is whether the pressure waves adversely affect the operation. In large-diameter systems the resulting column would be short and fat, and would not satisfy

A.

B.

C.
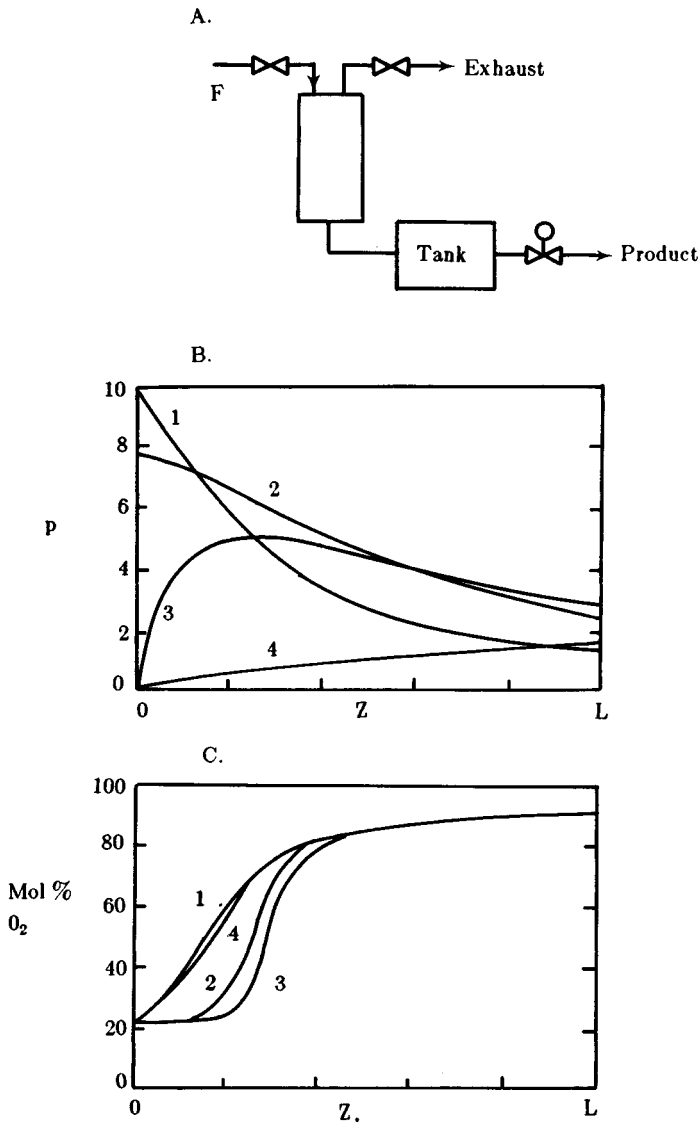
FIGURE 4-8.   Rapid cycle PSA process. (A) Single column system. (B) Pressure profiles. 1, Middle of feed; 2, middle of delay; 3, early in exhaust; 4, late in exhaust. (C) Concentration profiles in bed producing 90% oxygen. (From Flank, W. H., Ed., *Adsorption and Ion Exchange with Synthetic Zeolites*, ACS, Washington, D.C., 1980, 275. With permission.)

rules of thumb for L/D. However, short fat columns are successfully operated (see Chapter 3 [Section II.D] and Chapter 5 [Sections VI and VIII]) for other sorption operations. Less waste gas could be achieved by modifying the scaling procedure. If d_p were reduced by a factor of $\sqrt{5}$ and L by the same factor the pressure drop can be kept constant by increasing the cross-sectional area by $\sqrt{5}$ (v decreases by $\sqrt{5}$). The number of stages or the number of transfer units will increase significantly (by a factor of 5 in linear systems with pore diffusion control), resulting in sharper breakthrough curves and a more concentrated waste gas. This can be done with simple cycles and with higher adsorbent productivity.

A second very short cycle system called the "molecular gate" with significantly higher productivities has been developed by Keller and Kuo.[579,581] A schematic diagram of this
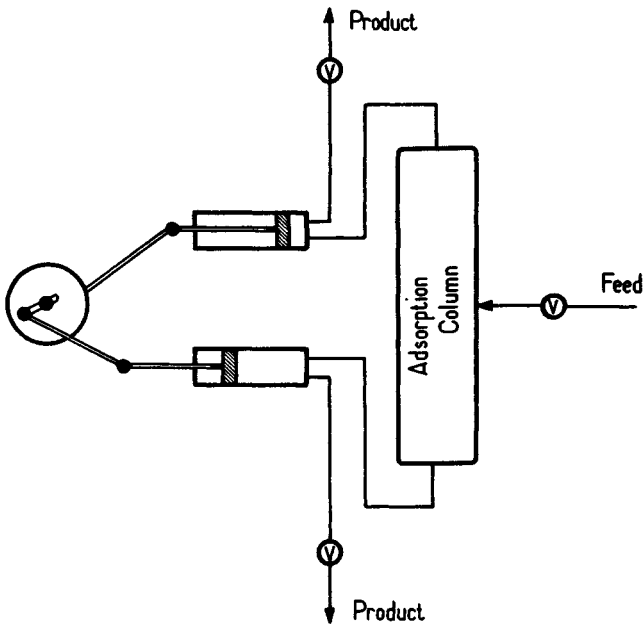
FIGURE 4-9. Center feed, refluxed PSA system.[581]

process is shown in Figure 4-9. The pressurized feed enters the column somewhere between the two ends. The two pistons have different amplitudes and operate out of phase. Thus during parts of the period both push in, during parts one pushes in and the other retracts, and during parts both retract. This results in complex pressure profiles and flow patterns. The process essentially has large reflux ratios at both ends. During part of the cycle the column pressure rises above the feed pressure which effectively shuts off the feed to the column. The more strongly adsorbed solute concentrates in the piston with the larger amplitude while the least strongly held gas concentrates in the piston of smaller amplitude. For separation of 15 psig air the optimium ratio of volume small piston to volume large piston was about 0.25. The optimum phase angle was approximately a 45° lead of the smaller piston. This phase angle caused the flow direction to reverse when the flux from the particles to the gas reverses. Both pistons operated at 30 rpm, although higher frequencies are now used.[579] Productivities for N_2 ranged up to 85.2 and for oxygen up to 15.7. For high-purity N_2 plus argon (99.9%) with 98.5% recovery and simultaneous 95% oxygen with 99.8% recovery the productivities were 4.42 and 1.35. Other gases were also separated, including a 50:50 mixture of H_2 and CH_4. Almost no temperature increase was observed because of the rapid cycling between adsorption and desorption. To some extent this device can be considered a type of pressure swing parametric pump (see Section III).

The local equilibrium model is not satisfactory for explaining these results. The cycle periods (2 sec or less) are too short to approach equilibrium, and kinetic effects are important. Models, including diffusion in and out of a single particle, are qualitatively successful.[579]

So far commercialization has not been announced. Since the pistons are compressing and expanding the gas, energy reuse is critical to keep operating costs low. The major problem with commercialization has been capital expense and the use of rotating equipment.[579] However, the ability to simultaneously produce high-purity oxygen and nitrogen or high-purity hydrogen and methane in a relatively simple device is a breakthrough. Other cycles which can do this are quite complex or require a vacuum. This achievement shows that PSA can produce high-purity products with very low recoveries. This should spur further PSA research.

A.

B.

C.
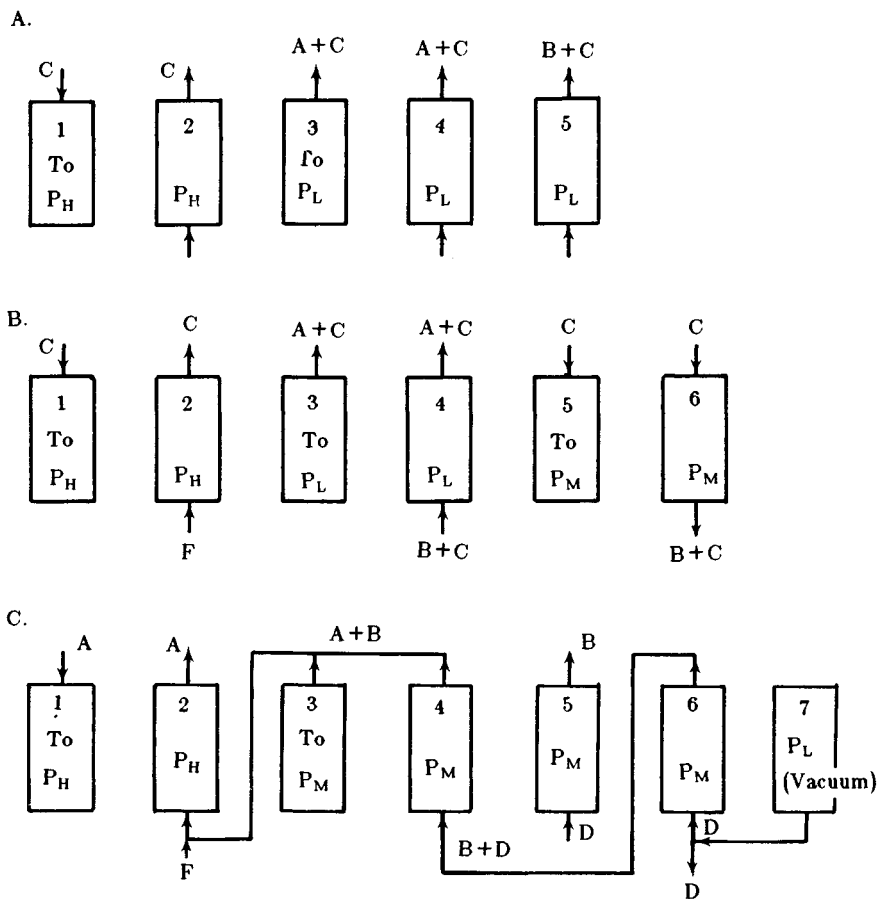
FIGURE 4-10. Multicomponent PSA cycles. A, B, D are solutes and C is carrier gas. (A) No flow reversal. Step 1, repressurization; 2, high-pressure adsorption; 3, blowdown; 4, purification; 5, cocurrent purge. (B) With flow reversal. 1, 2, and 3 same as Part A; 4, purification using expanded B and C from Step 6; 5, partial repressurization; 6, countercurrent purge. (C) With vacuum. 1, Repressurization; 2, feed; 3, blowdown; 4, purification; 5, product; 6, purification; 7, vacuum.

D. PSA Cycles for Fractionation

PSA was first developed as a bulk separator. Recently some attention has been paid to developing PSA and VSA cycles which can fractionate several solutes. Essentially, three approaches for PSA separation have been used. One approach uses a single adsorbent and uses a cycle with a purification step to separate dilute solutes from each other, but the solutes are not separated from the carrier gas.[758] The second type of approach modifies the standard PSA cycles by adding a cocurrent blowdown step.[220,1106] The third type of approach uses two adsorbents with different selectivities.[598,910,911,1064] VSA systems with a single adsorbent are used commercially for simultaneously production of oxygen and nitrogen.[190,915]

Two PSA cycles with a single adsorbent for separating solutes were developed[758] and are shown in Figure 4-10A and B. The cocurrent flow system shown in Figure 4-10A works very much like an elution chromatograph which is producing its own pure carrier in step 2. The faster-moving solute A in carrier gas C is eluted from the column in steps 3 and 4 while solute B remains in the column. Solute B in carrier gas is eluted co-flow during step 5. Additional solutes can be separated by adding more steps. The system shown in Figure 4-10B has similar steps 1, 2, and 3. In purification step 4 a mixture of solute B and carrier gas C is used to remove A from the column. The column is then partially repressurized to

medium pressure P_M and the column is purged counter-flow in step 6. Some of the product gas from step 6 is expanded and used as reflux in step 4. An alternate cycle would skip step 5, operate step 6 at pressure P_L, and use a compressor for the reflux gas.

Analysis of these cycles by the solute movement theory is straightforward for linear systems.[758] The cocurrent cycle is useful for separations where the selectivity between solutes A and B is small while the countercurrent cycle works best when the selectivity is large. The same conclusion can be drawn for elution chromatography systems (see Chapter 5). These schemes can both be considered gas chromatographs and offer an alternate way of operating large-scale gas chromatographs. They have the disadvantage of chromatographs that a heel of component A cannot be left in the column in either scheme. A heel of component B can be left in the column in the system shown in Figure 4-10B. This will be an advantage for nonlinear systems.

A VSA system similar to that shown in Figures 4-6A and B can simultaneously produce fairly pure weakly adsorbed gas and strongly adsorbed gas. This is done commercially for production of oxygen and nitrogen from air using zeolite molecular sieves.[190,915] The weakly adsorbed oxygen is produced as product during the adsorption step which is operated near atmospheric pressure. The more strongly adsorbed nitrogen is then desorbed under vacuum. A higher-purity oxygen should be obtained if the column is repressurized counter-flow with oxygen product instead of with feed. A higher-purity nitrogen product is obtained if a co-flow nitrogen flush is added after the feed step to remove oxygen in the voids.[915]

Multicomponent separations similar to the system shown in Figure 4-10B can be done by adding a vacuum desorption step. One possible cycle is shown in Figure 4-10C. All three components adsorb with A adsorbing least and D most. After repressurization with pure A (step 1) and processing of feed plus recycle gas (step 2), a co-flow blowdown (step 3) is used to remove A from the system. Step 4 is a further purification step to remove A if the co-flow blowdown is insufficient. In step 5 pure B is produced by purging co-flow with D. In step 6 the remainder of species B is removed either by co-flow blowdown and/or a purge step. Finally, in step 7 species D is removed by vacuum desorption. Pressure equalization steps can easily be added to the cycle. Required compressors and vacuum pumps are not shown in the figure. The advantage of using a vacuum is all components can be recovered as fairly pure products.

Concentrated binary mixtures can be separated into two products with greater than 90% purity by adding a co-flow blowdown step to the usual four step PSA cycle: repressurize, adsorb, counter-flow blowdown, and purge.[221,1106] The co-flow blowdown has the same function as the purification step shown in Figure 4-10. A heel of the faster-moving component cannot be left in the column, but a heel of slower-moving component can be left in the column. A cycle with co-flow repressurization, adsorption, and co-flow blowdown was capable of partial separation of hydrogen and methane.[1026] Ternary mixtures were separated with a cycle consisting of pressurization, adsorption, co-flow blowdown and counter-flow vacuum evacuation,[220] which is similar to the cycle in Figure 4-10C. The most strongly adsorbed component, H_2S, was concentrated but was not recovered as a pure stream.

Systems with two adsorbents choose adsorbents with different and if possible reversed selectivities for the solutes.[598,1064] With two adsorbents of reversed selectivity for the two components relatively simple schemes can be devised for completely separating a binary mixture.[1064] If one two-column PSA system (Figure 4-1) is packed with one adsorbent and another two-column PSA system is packed with the other adsorbent, the two systems can be operated in parallel. Each system produces a pure high-pressure gas which is the less adsorbed component with that adsorbent. The waste gases from each system are compressed and sent to the complementary system for cleanup. Each of the two-column systems act like normal PSA systems, and thus a heel of the adsorbed component can be left in each system.

Multicomponent systems can be fractionated using more complex two-adsorbent

schemes.[619,910,911] One of these cycles[910] has a high-pressure feed step, high-pressure purification step, several pressure equalization steps, blowdown step, purge step, vacuum desorption step and repressurization. Six columns with one adsorbent and three with the other are used. A mixture of hydrogen, carbon dioxide, methane, and carbon monoxide was separated using BPL-activated carbon and 5 Å molecular sieves. A primary product of high-purity hydrogen, a secondary product of high-purity carbon monoxide, and a tertiary product with hydrogen, methane, and carbon monoxide were produced.[910]

If one desires to fractionate all the solutes but not separate them from the carrier gas, simple two-adsorbent systems can be used.[1064] The apparatus for doing this is illustrated in Figure 4-11A. The lower column is packed with adsorbent A which selectively adsorbs solute 1 but very weakly adsorbs solute 2. The second column is packed with adsorbent B which strongly adsorbs solute 2 (the relative adsorption of solute 1 by this adsorbent is irrelevant). During the feed step solute 1 is retained by the first column while the second column retains solute 2. This is illustrated in Figure 4-11B. At the end of the feed step solute 2 is present in the void spaces of the first column. This solute is pushed into the second column during the high-pressure purification step. Now the first column contains only solute 1 plus carrier gas while the second column contains solute 2 plus carrier gas. Each column is separately depressurized and purged with carrier gas. Repressurization can be done either with product or with feed sent to the first column. This cycle is easily extended to systems with more components.[1064] Since solute 1 must pass through column A, a heel of solute 1 cannot be left in column A; however, a heel of solute 2 can be left in column A and a heel of solute 1 can be left in column B. Thus both solutes can be recovered as fairly concentrated mixtures in the carrier.

Other fractionation schemes for "slow" cycles are easily developed using different combinations of the basic processing steps. The "fast" cycles can also be adapted to binary and perhaps multicomponent separation. There is considerable commercial interest in fractionation of gas mixtures. It remains to be seen if PSA and VSA fractionation schemes become widely used for these separations.

III. PARAMETRIC PUMPING

Parametric pumping (PP) is similar to PSA in that flow reversal (or reflux) is employed after a thermodynamic variable has been changed. However, PP utilizes the shift in the isotherm when temperature or another thermodynamic variable is changed to force the separation, and not the large expansion of purge gas which is used in PSA when pressure is decreased. Thus the molar reflux ratio in PP is usually much higher than in PSA. This, of course, is a disadvantage, but it is hard to see how to avoid this problem when liquids are separated. This high reflux ratio and the resulting marginal economics have kept PP from being commercialized except in one brief instance (see Section III.E). PP was originally developed by Wilhelm and co-workers[856,962,1089-1092] at Princeton University. The process has been extensively studied and reviewed[233,449,450,840,956,957,959,1040,1051] by academics since Wilhelm's original work. Grevillot's[449] review is particularly up to date and thorough.

A. Batch Direct Mode Thermal Parametric Pump

To explain how parametric pumping works we will start with the batch direct mode process shown in Figure 4-12. The column is jacketed and the entire column is heated and cooled externally (direct mode). Fluid flows upwards when the column is hot and is stored in the top reservoir. The column is cooled during a delay period and then fluid flows downward into the bottom reservoir. The column is heated and this cycle repeats. When the column is hot, adsorption of a single solute will be weak and the solute wave velocity will be high. When the column is cooled, the solute is more strongly adsorbed and the solute wave velocity

schemes.[619,910,911] One of these cycles[910] has a high-pressure feed step, high-pressure purification step, several pressure equalization steps, blowdown step, purge step, vacuum desorption step and repressurization. Six columns with one adsorbent and three with the other are used. A mixture of hydrogen, carbon dioxide, methane, and carbon monoxide was separated using BPL-activated carbon and 5 Å molecular sieves. A primary product of high-purity hydrogen, a secondary product of high-purity carbon monoxide, and a tertiary product with hydrogen, methane, and carbon monoxide were produced.[910]

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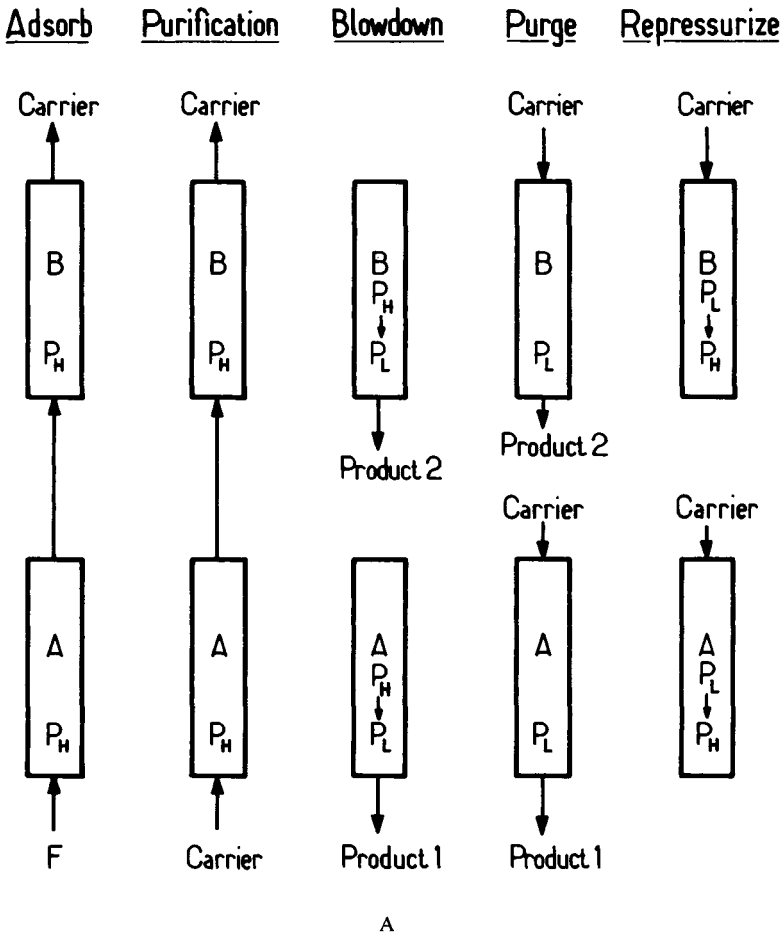## Adsorb   Purification   Blowdown   Purge   Repressurize

A

FIGURE 4-11.   Multiple adsorbent PSA system for fractionation. (A) Apparatus. (B) Solute movement diagram for linear isotherms. (From Wankat, P. C. and Tondeur, D., *AIChE. Symp. Ser.*, 81(242), 74, 1985. With permission.)

is low. Thus, upward movement of solute will be greater than downward movement and solute will tend to concentrate in the top reservoir.

The solute movement theory is easily applied to batch PP. The solute wave velocities are given by Equation 2-30 for linear systems and Equation 2-28 for nonlinear systems. The parametric pump is often started up with the entire column and the bottom reservoir in equilibrium at the hot temperature. Then solute movement can be followed on a plot of axial distance z vs. time t. Every time the temperature switches the solute will redistribute according to Equations 2-44 or 2-46 for linear isotherms in the direct mode. The solute movement diagram for a linear system is shown in Figure 4-12C. As can be seen, solute eventually is "pumped" to the top reservoir. The concentration at any time and location can be predicted if the type of reservoir is specified so that external mass balances can be written. The usual assumption has been that the reservoirs are completely mixed. Then in Figure 4-12C everything exiting the column from a to b is at c_i (the initial concentration). During the next half cycle this material enters the column from the top reservoir during the period from b to c. The material leaving the column during the cold half cycle has undergone one temperature change from hot to cold. Since more material is adsorbed, this portion will be diluted. From Equation 2-46,
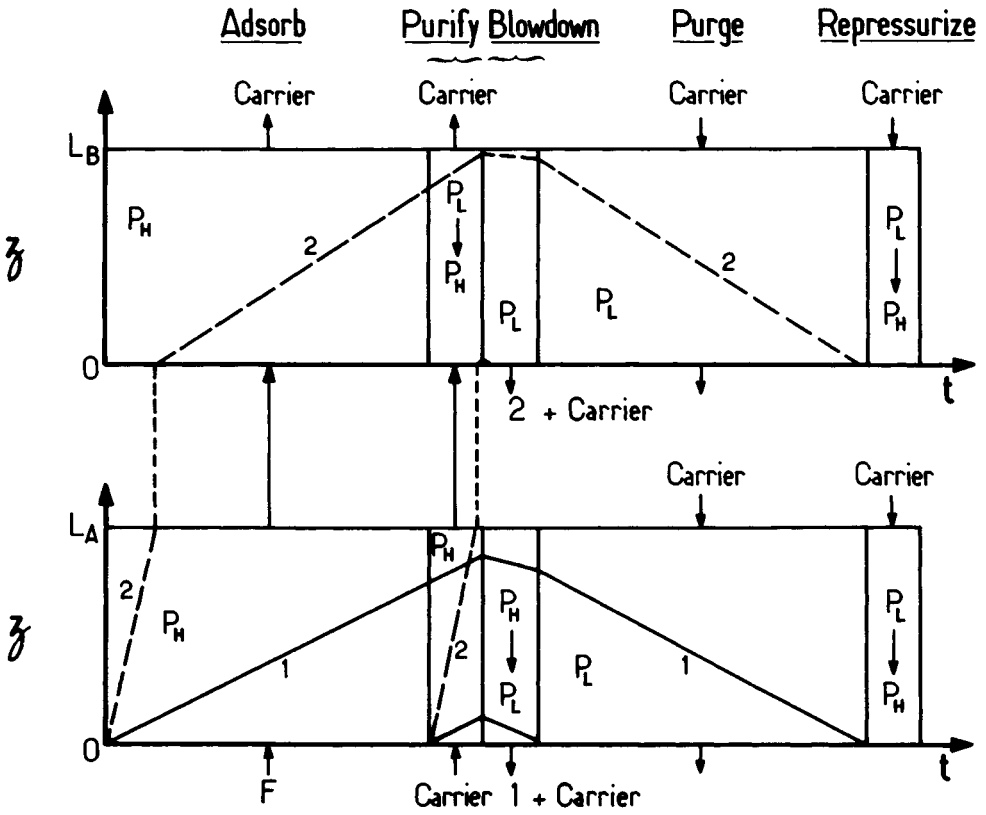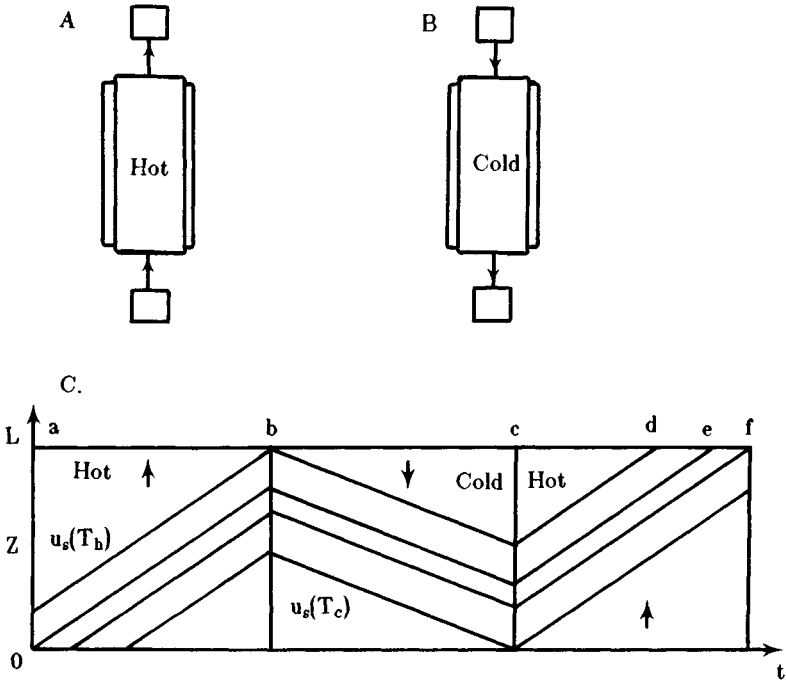
FIGURE 4-11B

FIGURE 4-12.   Batch direct mode thermal parametric pump. (A) Hot half cycle. (B) Cold half cycle. (C) Solute movement diagram for system with linear isotherms.

$$c_{bot}(cycle\ 1,\ cold)\ =\ c_i\ \frac{u_s(T_c)}{u_s(T_H)} \tag{4-6}$$

During the next cycle, the solution leaving the top of the column from c to d was at c_i, but it underwent a temperature change from cold to hot and was concentrated.

$$c_{cd}\ =\ c_i\ \left(\frac{u_s(T_H)}{u_s(T_c)}\right) \tag{4-7}$$

The solute exiting from d to e and from e to f both started at c_i and both underwent first a hot-to-cold temperature change and then a cold-to-hot temperature change. These changes cancel and the concentration from d to f remains c_i. The average concentration for the second cycle is

$$c_{top,2}\ =\ c_{cd}\left(\frac{\overline{cd}}{\overline{cf}}\right)\ +\ c_i\left(\frac{\overline{df}}{\overline{cf}}\right) \tag{4-8}$$

The relative distances are easily determined from the solute wave velocities. This process can be continued for any number of cycles.

For linear isotherms a closed form solution for bottoms concentration can be obtained.[58,805] In terms of the variables defined here this solution is

$$c_{bot,cycle\ n}\ =\ c_i\left[\frac{u_s(T_c)}{u_s(T_H)}\right]^n \tag{4-9}$$

The bottoms concentration is predicted to decrease exponentially and the separation factor will increase exponentially as the number of cycles increases. The top reservoir concentration asymptotically approaches a limiting concentration where essentially all of the solute is pumped into the top reservoir. The theory also predicts that each half cycle should be short enough to avoid breakthrough of solute directly from one reservoir to the next.

This simple theoretical description of parametric pumping appeared after the classical experiments of Wilhelm and Sweed[1092] were published. Their results for the separation of toluene from *n*-heptane on silica gel are reprinted in Figure 4-13.[1092] The separation factor $>10^5$ was considered astounding, but it really means that the bottom reservoir concentration was quite low. The separation increased when the temperature difference was greater and when the cycle period was longer (slower flow) since this allowed a closer approach to equilibrium. Note that for the first 15 to 20 cycles the separation factor does increase exponentially. The local equilibrium (solute movement) theory gave a surprisingly good fit to the data.[805] However, this was a semiempirical use of the theory. The equilibrium parameter was fit to the PP experiments and was not obtained from equilibrium data. When equilibrium data is used, the solute movement theory overpredicts the separation. The equilibrium theory cannot explain the differences between curves A and B. With longer cycles and hence slower flow rates operation is closer to equilibrium.

A large number of other mixtures have been separated by batch direct mode PP.[196,233,237,449-453,840,846,879,956,957,959,1040,1051] When ionic mixtures are separated, the physical picture is slightly different from the picture presented earlier. Because of electroneutrality, if one ion is desorbed when the temperature increases, the other ion must be sorbed. Thus one ion must concentrate at the hot end of the column and the other at the cold end. This binary separation of ions is experimentally observed.[196,205,451] Complete separation of the two ions can be obtained by using a center feed system.[205,456] The linear solute movement theory is unable to explain the observed results, but the nonlinear theory with shock and diffuse waves (see Chapter 2
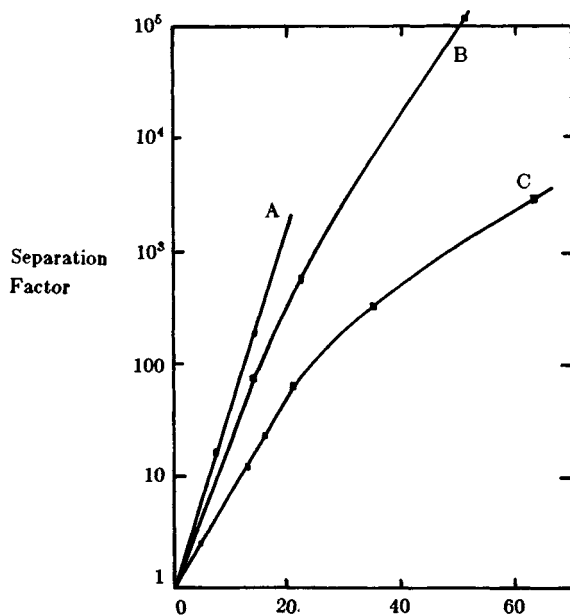
FIGURE 4-13.   Batch direct mode thermal parametric pumping separation of toluene from *n*-heptane on silica gel. (A) 140-min cycle, 70 to 4°C, (B) 30-min cycle, 70 to 4°C; (C) 8.5-min cycle, 70 to 15°C. (From Wilhelm, R. H. and Sweed, N. H., *Science*, 159, 522, 1968. With permission.)

[Section IV.A.2]) does qualitatively explain the results.[205] As usual, the model overpredicts the separation. In addition to the separation of ions, the PP experiments show a change in total concentration.[196,451-453] This effect was recently explained with the local equilibrium theory based on the temperature dependence of Donnan electrolyte partition.[453]

There are situations where the local equilibrium theory is qualitatively wrong. Reverse separations have been observed.[237,846] These reverse separations will usually be caused by slow rates of mass transfer so that the process is kinetically controlled. (Of course, this is not necessarily bad. A kinetically controlled separation could be developed.) Other possible causes have been delineated.[846] In most cases the local equilibrium model is qualitatively correct; thus, we will use the local equilibrium model to explain other PP procedures. For design and optimization the local equilibrium model is *not* adequate and more detailed theories are required (see Section V or the reviews by Rice[840] or Grevillot[449]).

B. Batch Recuperative Mode Parametric Pump

In the "recuperative" or "traveling wave" mode the column is adiabatic and the entering fluid is heated or cooled. This process is illustrated in Figure 4-14A. The solute movement diagram for a linear system is shown in Figure 4-14B. Note that the temperature does not change until the thermal wave has passed. Thus, breakthrough of the thermal wave is desired so that concentration changes will be observed at the ends of the column.[961] When the solute waves intersect the thermal wave, the concentrations change according to Equation 2-45 for linear systems. The solute wave velocities change because the distribution coefficient depends on temperature. Analysis of start-up is very similar to the batch direct mode analysis shown in Equations 4-6 to 4-9. When properly operated (i.e., with breakthrough of the thermal waves), large separations are predicted for the recuperative mode. The local equilibrium theory predicts complete removal of solute from the cold reservoir, but the more detailed STOP-GO theory predicts finite separation factors which are somewhat less than the direct
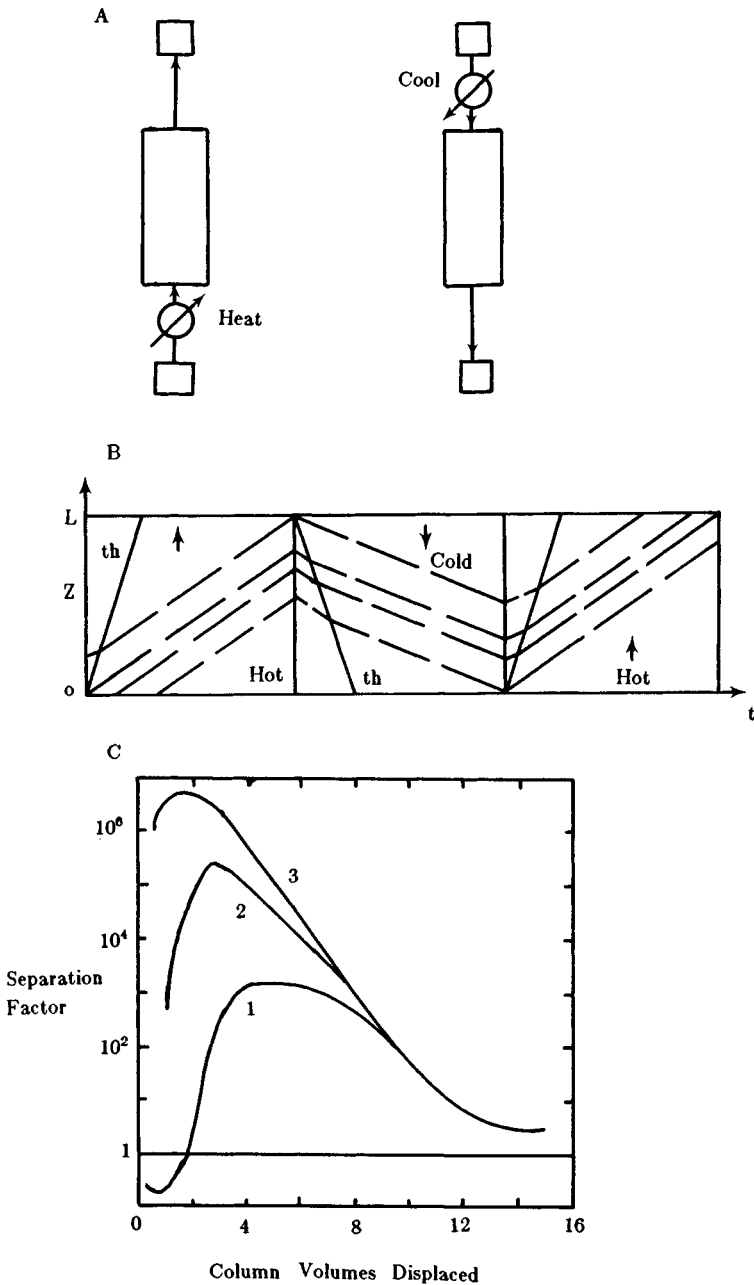
FIGURE 4-14. Batch recuperative mode thermal parametric pumping. (A) Column operation. (B) Solute movement diagram for system with linear isotherms. (C) Simulation using STOP-GO model. 1, recuperative mode; 2, recuperative mode with three intermediate heat exchangers; 3, direct mode.[961] (From Sweed, N. H. and Rigaudeu, J., *AIChE Symp. Ser.*, 71(152), 1, 1975. With permission.)

mode results for slow cycling.[961] This is shown in Figure 4-14C.[961] As shown in this figure, the recuperative mode results can be improved by using intermediate heat exchangers which will reduce the lag time for the temperature to change. Thermal breakthrough is desired to avoid the small reverse separations predicted with low fluid displacements. With fairly rapid cycling or with short delay periods for the direct mode temperature changes, the recuperative mode separation can be greater than the direct mode.[9]

The recuperative mode has two major advantages for large-scale separation. First, in large-diameter systems it is much easier to scale-up than the direct mode. Slow radial heat transfer is a problem in the direct mode and special designs would be required.[940] However, laboratory-scale direct mode systems are simpler than the recuperative mode so most thermal experiments have used the direct mode. Second, in continuous or semicontinuous operation the energy use of the recuperative mode is significantly less than in the direct mode plus it is easier to recover energy. In one calculation the recuperative mode used 10 to 15 times less energy than the direct mode.[1048] In addition, the recuperative mode can be used for thermodynamic variables other than temperature.

Unfortunately, the early recuperative mode experiments operated without breakthrough of the thermal wave and the separations were very small.[856,1089,1091] The reason for these small separations was not understood and at the same time the direct mode was giving very large separation factors.[1091,1092] Research shifted away from the recuperative mode and it has only been quite recently that properly operated thermal, recuperative mode simulations[961] and then experiments[9] have been conducted. The simulations shown in Figure 4-14 show that the early experiments with fluid displacements from one to two column volumes per cycle would be expected to have low separation. Experimental results are discussed in the next section.

The majority of the research reported in the literature refers to the direct mode. However, since the one industrial application of PP used the recuperative mode (see Section III.E) and other large-scale uses would probably also use the recuperative mode, I will emphasize the recuperative mode in the remainder of this chapter. Direct mode theories and experiments are included in Tables 4-1 and 4-2.

C. Open Systems: Continuous and Semicontinuous Operation

In large-scale applications a continuous or semicontinuous system is preferable to a batch system. These have been called "open" systems as compared to the "closed" batch systems. The early recuperative mode systems[1090,1091] were semicontinuous systems with fresh feed introduction. The most extensive studies of continuous and semicontinuous systems have been with direct mode systems.[5,235,236,240,242,243,446,447,844,960] Continuous recuperative mode operation has been analyzed using the solute movement theory[1048] and was used commercially in the Sirotherm process (see Section III.E).

Many different continuous or semicontinuous systems could be used. One possible configuration is shown in Figure 4-15.[1048] This can represent either a single column, semicontinuous system, or a two-column continuous system. When two columns are used, this system is quite similar to the two-column PSA system shown in Figure 4-1. With open systems the reflux ratios at the top and bottom of the column become very important variables. The reflux ratios are defined as equivalent to internal reflux ratios in distillation.

$$R = \frac{\text{fluid returned to column}}{\text{fluid exiting column}} \qquad (4\text{-}10)$$

When both R_T and R_B equal one, the system is at total reflux and becomes a batch system. As with distillation or PSA the higher the reflux ratio, the better the separation, but the lower the productivity.

The solute movement theory is easily applied to open systems.[1048] This can be done either for start-up or for the cyclic steady state. Start-up will be similar to batch operation (Figure 4-14B). At the cyclic steady state the cycle repeats itself every cycle. This is shown in Figure 4-15B for linear isotherms for the case where $u_{th} > u_s(T_h) > u_s(T_c)$, and in Figure 4-15C for nonlinear isotherms where $u_s(T_h, 0) > u_{th} > u_s(T_c, c_F)$. In an open system with top feed the volumetric displacement during the cold (downward) portion of the cycle must

Table 4-1
APPLICATIONS OF LOCAL EQUILIBRIUM MODEL

Application	Operation	Ref.
Development of basic model for two-column system with linear equilibrium, and comparison with experiments.	PSA	506,900
More detailed linear equilibrium model. Carrier gas can adsorb.	PSA 2 Columns	224
Comparison of linear model to experiment. Discussion of situation where model fails.	PSA	1099
Continuation of model[224,900] including sorption effects. Linear isotherms. Required numerical solution.	PSA	599
Application of theory[224] to one-column system. Linear isotherms.	PSA	504
Theory for one-column system. Both linear and nonlinear isotherms. Comparison with results for air drying. Nonlinear isotherms required numerical solutions.	PSA	375
Use of theory[224] for multicomponent separation. Developed feasible regions to achieve separation.	PSA	758
Use of linear theory[224] for systems using two adsorbents to fractionate solutes.	PSA	598,1064
Use of linear theory to study transient performance.	PSA	600
Development of theory for rapid cycle, one-column system including pressure drop. Linear isotherms. Required numerical solutions. Comparison with data for N_2-CH_4 separations.	PSA	999
Study of purge step for both adiabatic and isothermal operation. Sample calculations for CO_2 and CH_4,N_2 or H_2. Isothermal assumption can seriously underpredict purge gas requirements.	PSA	913
Basic development of model for batch systems with linear isotherms. Graphical and analytical solution. Semiempirical data fitting. Direct mode.	PP	805
Generalization of solution.[805]	PP	58
Development of model and graphical solution for direct mode.	PP	962
Letter on effect of nonlinear isotherms.	PP	833
Effect of nonmixed reservoirs in direct model batch. Linear isotherms.	PP	979
Batch method for multicomponent separation direct mode linear isotherms.	PP	195
Comparison of sinusoidal and square waves. Very little difference when equal displacements are compared. Batch direct mode, linear isotherms.	PP	839
Donnan concentration effects, batch direct mode. Comparison with experiments.	PP	453
Model for coupled, nonlinear systems. Batch and open systems, direct mode.	PP	205
Application of linear model in design of direct mode system with shell-and-tube heat exchanger.	PP	940
Analysis of batch recuperative mode.	PP	961
Theory of direct mode open systems. Development of external equations. Linear isotherms.	PP	236,242,243,446
Analysis of open recuperative mode systems. Mixed and unmixed reservoirs. Comparison of energy use in direct and recuperative modes.	PP	1048
Analysis of open, direct mode systems nonmixed reservoirs with dead volume. Good agreement between theory and experiment.	PP	288
Application of model to direct mode, open system for separation of two noncoupled solutes. Theory overpredicts experimental separations.	PP	1100
Comparison of theory and experiment. Equilibrium parameters obtained from separate experiments. Theory overpredicts observed separations.	PP	9,788,879,895

Table 4-1 (continued)
APPLICATIONS OF LOCAL EQUILIBRIUM MODEL

Application	Operation	Ref.
Comparison of theory and experiment. Semiempirical fit since parameters obtained from PP experiments.	PP	5,235,242—244,805
Use of two adsorbents for binary and multicomponent separations. Direct and recuperative mode in open systems.	PP	1064
Development of theory and analytical equations for direct mode linear equilibrium.	CZA	464
Direct and traveling wave modes. Linear and nonlinear equilibria. Reasonable comparison of theory and experiment.	CZA	74
Traveling wave with linear equilibrium and Arrhenius temperature dependence. Optimized.	CZA	721
Traveling wave with Langmuir isotherm and Arrhenius temperature dependence. Reasonable agreement with experiments.	CZA	601
Multicomponent traveling wave system with focusing. Linear equilibrium.	CZA	1043
Direct and traveling wave modes, multicomponent separation. Linear and nonlinear equilibria for uncoupled solutes.	CZA	1044
Direct mode, concentrated systems with nonlinear equilibrium. Effect of layered beds and recycle.	CZA	388
Forced direct mode to simulate traveling wave of controlled velocity. Linear and nonlinear isotherms. Uncoupled, multicomponent. Reasonable comparison with experiment.	CZA	376
Use of linear theory for fractionation systems using two adsorbents.	CZA	1064
Comparison of theory with experiment.	CZA	903
Gas system with focusing. Large heat of adsorption couples thermal and solute wave. Reasonable agreement between theory and experiment. Development of feasibility conditions.	CZA	537—541
Theory for chromatothermography.	—	993

Table 4-2
MORE COMPLEX MODELS FOR CYCLIC SEPARATIONS

Model	Operation	Ref.
Used method of characteristics to obtain ODE which was solved by finite differences for two-column system. Assumed isothermal, linear equilibrium, ideal gas, negligible Δp, and no axial dispersion. Good agreement with experiment.[900]	PSA	736
Ignore dispersion and mass transfer. Assume linear equilibria and use D'Arcy's law for pressure drop. Solve one-column system by finite differences. Reasonable agreement with experiments.	PSA	969
Assume isothermal and ignore diffusion. Solve mass balance and rate equations by numerical integration. Good agreement with data on drying air in two-column system.	PSA	217
Nonisothermal and isothermal systems with linear equilibria. Use numerical integration. Adiabatic case shows considerably less separation then isothermal case.	PSA	258
Theory above[258] compared to experiments for air drying. To obtain agreement needed to use high values for mass transfer coefficients.	PSA	257
Linear, well-mixed cell model applied to one- and two-column systems. Sample calculations for recovery of He from the HE-CH$_4$ mixture.[249] Comparison between theory and experiment for one-column system[250] (Figure 4—5A).	PSA	249,250

Table 4-2 (continued)
MORE COMPLEX MODELS FOR CYCLIC SEPARATIONS

Model	Operation	Ref.
Nonlinear, well-mixed cell model. No details of model given, but results compared well with experimental data for drying air.	PSA	375
Equilibrium staged, countercurrent distribution type model. Few details. Agreed well with finite difference model.[b11] One-column system.	PSA	969
Equilibrium staged model for rapid cycle one-column system.	PSA	617
Overall mass balance model for two-column system. Assumes complete bed equilibrium at end of cycle. Agreement between theory and experiment poor, but improves with longer cycle times.	PSA	1067,1087
Overall mass balance model with MTZ of assumed length.	PSA	333
Mass balance model treating cyclic steady state as a steady countercurrent contactor. Used for N_2, CO, H_2, and air-drying examples.	PSA	952a
Pore diffusion model for mass transfer with thermal equilibrium (nonisothermal). Ideal gas law, loading ratio correlation equilibrium. Negligible Δp. Numerical integration. Applied to separation of concentrated H_2/CH_4 mixture,[1105,1106] $H_2/CH_4/$ H_2S separation,[220,1105] H_2/CO[1105] mixtures, and $H_2/CH_4/CO_2$[1105] separation.	PSA	220,1105,1106
Empirical approach for small-scale systems for drying compressed air. Comparison with experiments.	PSA	64
Numerical analysis using orthogonal collocation for isothermal system with one adsorbate and an inert carrier. Two-bed Skarstrom-type system.	PSA	819,965
Equilibrium and linear driving force model applied to H_2/CO mixtures.[221,1105] Nonisothermal but with thermal equilibrium. Hybrid Freundlich-Langmuir isotherm. Numerical integration. Application of equilibrium model to explore use of inert material to slow down thermal wave[1104] and to explore heat exchange between two columns.[1103]	PSA	221,1103,1105
Modeling of depressurization step. Numerical analysis. Applied to depressurization only, not complete cycle.	PSA	849
Detailed modeling of open system, thermal, recuperative mode PP for ion exchange resins. Used 2nd order Langmuir equation and included pore diffusion. Model solved by finite difference. Excellent agreement between theory and experiment. This remains the most detailed PP modeling.	PP	856
Solved PDE by finite difference. Include mass transfer inside particles and used an effective surface diffusivity. Thermal, direct mode basket PP.	Basket PP	703
Zero order reaction with Langmuir kinetics and first order reaction with linear kinetics. Utilizes Thomas-type solution method. Numerically calculates results.	PP with reaction	585
General integral analysis. No numerical calculations.	PP	516
Frequency response solutions of partial differential equations for thermal, direct mode. Effect of radial heat transfer. Calculation of optimal ultimate separation conditions. Good agreement with experiment.[844,845] Consideration of design problems.[844]	PP	377,378,836— 838,840,844,845
Deans and Lapidus mixing cell model with 50 stages. Direct[1091,1092] and recuperative[1091] mode calculations. Calculation of maximum separation region.	PP	1091,1092
Mixing cell model for direct mode, thermal PP. Calculated number of cells from Van Deemter equation (see Equation	PP	465

Table 4-2 (continued)
MORE COMPLEX MODELS FOR CYCLIC SEPARATIONS

Model	Operation	Ref.
2—117), but to achieve fit to experimental data this had to be adjusted. Also developed a near equilibrium model and assumed each cell was at equilibrium. Matrix manipulation used for solution of both theories.		
Near equilibrium model for direct mode, thermal PP as chemical reactor	PP	52
STOP-GO algorithm. During GO step all fluid in cell is discretely transferred to next cell. During STOP step heat and mass transfer occur. Solve ODE during stop step numerically. Good agreement with data[1089,1092] for direct thermal mode.	PP	962
Apply STOP-GO algorithm to recuperative thermal mode. Good agreement with data.[856]	PP	961
Apply STOP-GO algorithm to gas PP. Modified to allow for pressure equalization and axial mixing. Model qualitatively agreed with data.	PP	552
Applied STOP-GO to thermal, direct mode PP in batch and open systems. Very good agreement for batch.	PP	960
Use STOP-GO algorithm to optimize several open, thermal, direct mode PP. Good agreement between theory and experiment.	PP	447
Use STOP-GO to compare continuous recuperative mode PP and conventional thermally regenerated adsorption.	PP	445
Analyzed open, pH PP with circulation using STOP-GO algorithm.	PP	239
Equilibrium staged analysis for direct mode PP. Models with continuous flow of fluids and with discrete transfer and equilibrium steps. Reasonable agreement with extraction PP.	PP	1038
Equilibrium stage analysis for direct mode system. Graphical solution.	PP	1030
Use of equilibrium staged analysis to stimulate direct mode multicomponent PP. Good agreement with experiments when number of stages was estimated from PP data.	PP	1100
Graphical analysis based on discrete transfer, equilibrium staged model.[1038] Developed analogy between PP and distillation.	PP	454,455
Use of graphical analysis[454,455] to simulate separation of Ag^+ and Ca^{2+}. Fit data to find HETP. Studied reflux effects.	PP	451
Use of graphical analysis[454,455] to simulate direct thermal mode PP.	PP	449,459,757,1030
Use of graphical analysis[454,455] for multicolumn, pH recuperative mode PP. Reasonable agreement between theory and experiment.	PP	245
Staged graphical analysis with one equilibrium stage for direct, thermal mode basket PP.	Basket PP	441
Equilibrium staged analysis applied to extraction PP. Used matrix formalism to study transient and cyclic steady states. Good agreement between theory and experiment.	Extraction PP	871
Equilibrium staged analysis applied to extraction PP with chemical reaction.	Extraction PP	440
Comparison of local equilibrium model, STOP-GO, integration of PDE and discrete transfer, discrete equilibrium model. Related parameters of different models.	PP	338
McCabe-Thiele type graphical analysis for distillative adsorption with equal[841] and unequal solids loadings.[604]	Adsorptive-distillation (3-phase PP)	604,841

Table 4-2 (continued)
MORE COMPLEX MODELS FOR CYCLIC SEPARATIONS

Model	Operation	Ref.
Pore diffusion model for Langmuir isotherm with Arrhenius temperature dependence. Numerical solution. Good agreement between theory and experiment for separation of CH_4-H_2 and CH_4-H_2-H_2S.	CZA	248,991,992
Perturbation analysis for sine wave temperature change in direct mode. Linear isotherms. Include diffusion of solute inside pores. Good agreement between theory and experiment. Extended to multizone systems.[597]	CZA	597,601,903
Equilibrium staged analysis with discrete transfer and equilibrium steps. Traveling wave mode. Good agreement between theory and experiment when pH wave velocity was determined from experiments.	CZA	194,331
Equilibrium staged analysis with discrete transfer and equilibrium for direct[1039] and traveling wave[1041] thermal operation in extraction. Good agreement with extraction experiments.	CZ extraction	1039,1041
Discrete transfer and equilibrium steps in equilibrium staged model applied to multicomponent CZA. Linear isotherms.	CZA	1043
Continuous flow equilibrium staged model for direct mode CZA. Good agreement between theory and experiment.	CZA	759
Mixing cell model applied to gas separation with focusing. Good fit with data, but a low estimate of gas heat capacity had to be used.	CZA	541
Mixing cell model. Prove that a cyclic steady state exists for cocurrent (CZA) flow. A cyclic steady state was found in numerical simulations for countercurrent flow (PP) but a general proof was not found.	PP, CZA	635

be greater than that in the hot portion. Thus with equal velocities the period of the cold portion of the cycle T_c must be greater than the hot portion T_h. The larger the shift in equilibrium with temperature the lower the reflux ratio can be and the more pure bottom product will be produced. In Figure 4-15B and C, a bottoms concentration of zero is predicted. In actual practice, some solute will be observed in the bottom product. In Figure 4-15C a case where $u_s(T_h, c_F) > u_{th} > u_s(T_c, c_F)$ is shown. The solute movement theory will predict infinite concentrations if linear isotherms are used. The use of nonlinear isotherms shows a large increase in concentration before the thermal wave during the hot cycle. This results in a shock wave as shown in the figure. Figure 4-15C is drawn for a nonoptimum case since solute waves can pass directly from the bottom to top reservoirs. With a much shorter cycle this would be prevented, a more concentrated top product could result, and R_B would be reduced, producing more product. Timing is very important in all the cyclic separation procedures.

Experimental results for the removal of dilute concentrations of phenol from water on Duolite ES 861 are shown in Figure 4-16[9] for a system similar to that shown Figure 4-15A. The local equilibrium model overpredicts separation after the first four cycles, but separation factors up to 10^3 were obtained experimentally. Larger separations would be obtained if the column were adiabatic. In large-diameter columns heat losses through the wall would be much less a problem.

In general, the product concentrations and energy use depend not only on the solute movement in the column but also on the details of the reservoir. If separation is not complete the separation can be increased by using nonmixed or segregated reservoirs which retain partial separation instead of mixing everything together.[979] Energy use can also be reduced with selective recycle.[1048] Thus, for the system shown in Figure 4-15A, energy use will be
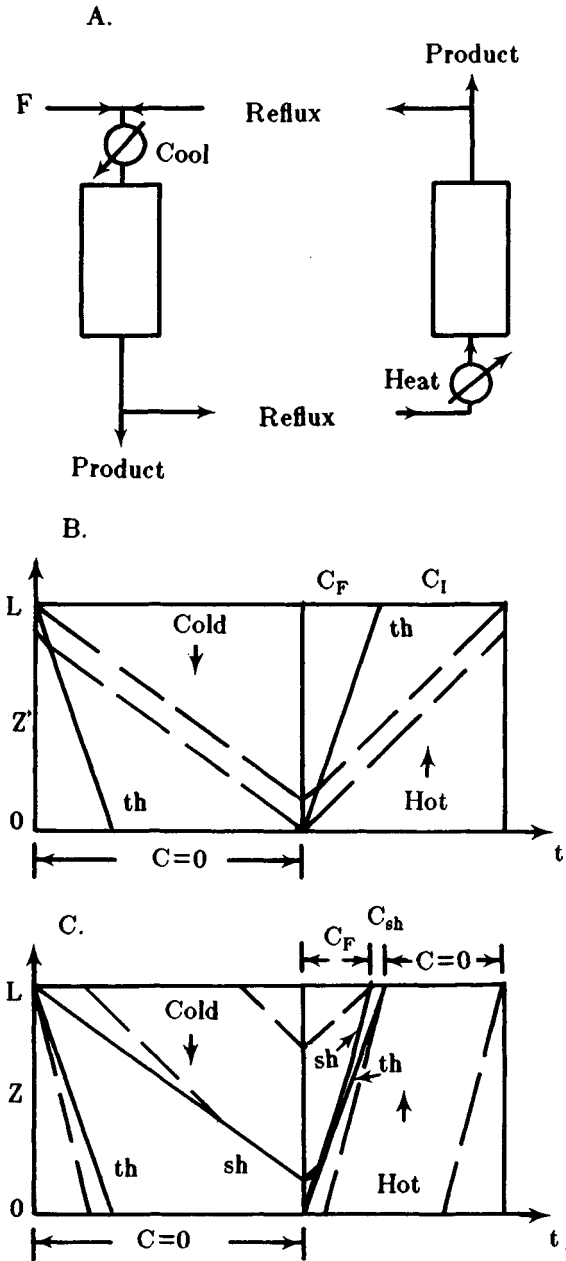
FIGURE 4-15. Semicontinuous recuperative mode system. (A) Cycle used; (B) solute movement diagram for linear isotherms; (C) solute movement diagram for nonlinear isotherms.

reduced if the products are always withdrawn after the thermal wave has broken through. This allows one to reflux all of the hot material for the next hot step and all of the cold material for the next cold step. Segregated reservoirs were used in the commercial Sirotherm process[535] for reflux of specific streams.

D. Modifications and Extensions of PP

A large number of modifications and extensions of parametric pumping (PP) have been
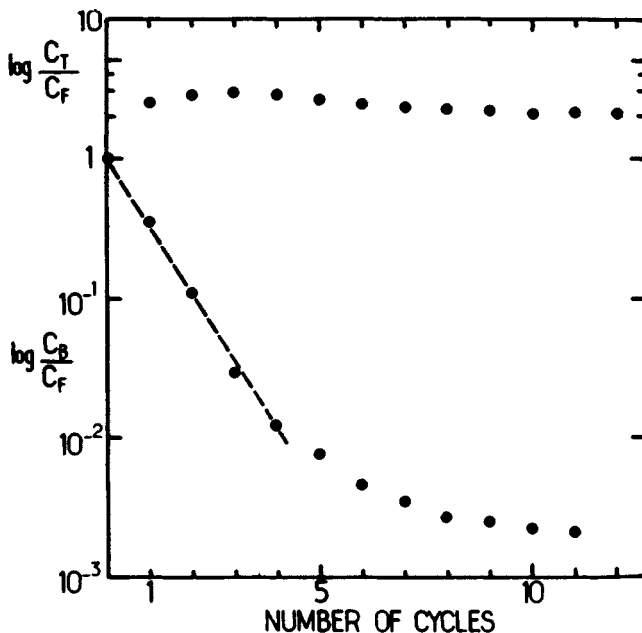
FIGURE 4-16. Recuperative thermal mode parametric pumping separation of phenol from water. Dotted line is local equilibrium theory. (From Almeida, F. et al., *Physicochemical Methods for Water and Wastewater Treatment*, Elsevier, Amsterdam, 1982, 169. With permission.)

developed since 1966. In this section we will briefly consider these. Theories are outlined in Section V.

Any thermodynamic variable which affects the equilibrium can be used in a parametric pump. These have included pH,[237,239,241,244,245,514,869,895] pH and electric field,[238,514] pH and ionic strength,[234] chemicals which complex with the solute,[225] and pressure (see Section II.C.2). The recuperative mode is used when chemicals are added. The added chemical can either compete with the solute for the adsorbent[869] or change the solute in free solution so that it is less adsorbed.[225,234,237-239,241,244,245,895] The latter approach has advantages since less chemical may be consumed and it may be possible to reuse the chemical. Chen and co-workers developed a number of different operating methods.[225,234,237-239,241,244,245,514] The simplest are one-column systems similar to Figure 4-16 but with a pH addition and control system replacing the heat exchanger.[244,869,895] The solute movement diagrams for these systems are similar to Figure 4-16C and D. Two-column center feed systems[237] should be useful for separating two proteins, but reverse separations were observed. This equipment is similar to the center feed systems used for separating mixtures of two ions[205,456] (except the ionic separations were direct mode operations). Multicolumn systems using both cation and anion exchangers were used for continuously separating proteins.[241,245] Fairly high separation factors were obtained with continuous operation. When a single resin is used, complicated cycles have been developed.[234,239] One such cycle[239] is shown in Figure 4-17. The circulation steps are used to make the concentrations and pH values equal. These protein separations by pH parametric pumping use pH values which bracket the isoelectric point of the desired protein. The protein will either strongly adsorb or not adsorb at all depending on the pH. The separation can be improved by applying an electrical field during the upflow steps.[514]

Adsorption or ion exchange is not necessary to develop a parametric pump. A thermal mode size exclusion parametric pump has been developed.[612] The apparent cause of the

pH₂   pH₂   Prod   pH₂   pH₂   F, pH1

1   2   3   4   5   6   7   8

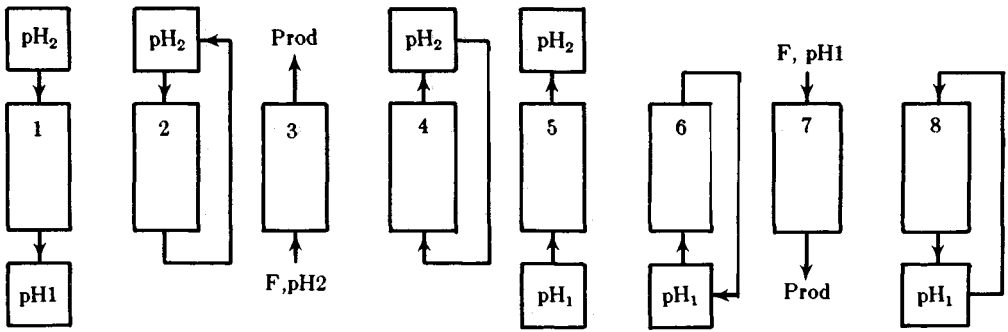pH1   F,pH2   pH₁   pH₁   Prod   pH₁

FIGURE 4-17.   Cycle for pH parametric pumping protein separation.[239] Step 1, downflow; 2, circulate; 3, bottom feed; 4, circulate; 5, upflow; 6, circulate; 7, top feed; 8, circulate.

separation was changes in porosities of the size exclusion gel when the temperature was varied. If there is no adsorption, u_s is given by Equation 2-28 with $\Delta q/\Delta c = 0$. Changes in either α or ϵ will change the solute velocity.

Two-adsorbent systems with different selectivities can be used for completely separating a binary mixture or for fractionating two solutes.[1064] If only one adsorbent is available, fairly complex cycles can be used for fractionation by PP,[1100] but cycling zone adsorption appears to work better (see Section IV).

Electrochemical PP[774-777] has been used for removing sodium chloride from water and could potentially be used for desalting brackish water. The amount adsorbed on the carbon depends on the electrostatic charge and a parametric pump can be operated electrochemically. Since there are no Faradic reactions and no electron transfer, the energy usage could be very low. This technique is still under development.

Parametric pumping has been applied to the separation of gas systems.[505,551,552,788] The amount of separation achieved has been significantly less than that predicted by the local equilibrium theory.[788] Problems with gas systems are high dispersion, low heat transfer rates, and in closed systems raising the temperature to decrease adsorption also increases the pressure which increases adsorption. A combined PSA thermal PP process which eliminates the problems has been developed.[505] PSA and cycling zone adsorption (CZA) seem to work better with gas systems than thermal PP.

Other types of equipment have been used for PP. Instead of using pumps, an oscillating gravity flow system can be used.[844] Although simple in concept, in practice unequal flow in the two columns caused the separation to deteriorate. "Tea bag"[959] or "basket"[441,703] systems pack the sorbent in a bag or basket and then move this basket back and forth between the hot and cold reservoirs. This is a one-stage system and the amount of separation is limited. PP has also been extended to extraction systems[817,1038] and electrodialysis.[976-978]

Adsorptive-distillation can be considered a type of three-phase parametric pump.[604,841,842] Each stage undergoes the cycle:

● Adsorption on solid from liquid phase (equilibrium)
● Drain
● Vapor phase desorption using heat and vacuum
● Charge with liquid

This cycle is thus similar to drying of liquids (see Chapter 3 [Section IV.A]) except it is operated more like distillation. The vapor from desorption of stage $n - 1$ is condensed and mixed with the liquid from draining stage $n + 1$. This is then the charge to stage n for the next cycle. The flow of liquid and vapor in the opposite directions gives a countercurrent-

type flow. At cyclic steady state the mass balances can be rearranged into forms which are essentially the same as the operating equations for distillation. The system was conveniently analyzed with a modified McCabe-Thiele diagram using a pseudo-equilibrium curve.[841,842] The pseudo-equilibrium depends on adsorption equilibrium and not vapor-liquid equilibrium as does distillation. Thus, adsorptive distillation may be favorable when relative volatilities are close to one, but selectivity in adsorption is large. Since only theoretical results have been reported, several important questions remain unanswered. These include equipment configurations which allow convenient construction and scale-up, and methods for energy reuse.

PP systems work best when there is a large change in the equilibrium when the thermodynamic variable is varied. For thermal cycling, equilibrium isotherms will often follow an Arrhenius relationship. Large values of ΔH give large changes in the isotherm. For many adsorbents the entropy change on reaction, $\Delta S \approx 0$. Then, if $|\Delta H|$ is large, the free energy change of the reaction, $|\Delta G|$, is also large and the adsorption is essentially irreversible. To have a large $|\Delta H|$ and a modest $|\Delta G|$, the entropy change on adsorption, ΔS, must be a large negative value. This is the case for some biochemical affinity systems.[230] For example, some monoclonal antibody systems for antigen purification have changes in the dissociation complex of two orders of magnitude when temperature is increased from 4 to 43°C. If denaturing does not occur, similar biochemical systems may present future applications for PP and CZA. Affinity chromatography has been tried in PP,[225,895] but the separations obtained were not outstanding. Careful choice of chemical systems for PP should result in much more impressive separations.

E. Commercial Use of Parametric Pumping: The Sirotherm Process

The one advertised commercial use of PP was the Sirotherm process[69,144,146,147,152,153,155,198,535,897,963,966] developed by CSIRO, ICI Australia, and Australian Technology Engineering and Processes (AUSTEP). The Sirotherm process uses a combination weak acid/weak base ion exchange resin which can be thermally regenerated.[574] The regeneration occurs because of the more than 30-fold increase in the ionization of water when the temperature is raised from 25 to 85°C. The major problems in development of the Sirotherm process have been in resin development. The earlier resins oxidized and lost their capacity fairly rapidly.

A variety of operating techniques[69,144,146,147,152,153, 155,198,535,897,963,966] have been tried with Sirotherm. In small-scale plants the operation used counter-flow regeneration using the heated tails as regenerant. This is a form of recuperative mode PP although it was apparently developed independently of Wilhelm's work. Several small demonstration plants using this cycle have been operated in Australia for desalinating brackish water.[147] A temperature difference of about 60°C was used. Cycle period was about 1 hr and the yield of purified water was from 70 to 90%. The largest fixed-bed Sirotherm was a 600,000 ℓ/day unit at ICI Australia's Osborne plant which started up in 1976. This Sirotherm unit has apparently been shut down. It is convenient to combine Sirotherm with other ion exchange processes. For example, a presoftening system before the Sirotherm system is convenient since the presoftener increases the capacity of the Sirotherm process, and the presoftener can be regenerated with the concentrated Sirotherm effluent.

Co-flow operation, which is essentially a CZA-type procedure, has also been used.[198] In this application, co-flow regeneration was less efficient than counter-flow regeneration. The major problems with this plant[198] were in the pretreatment section. Because of the very low oxygen levels required by the early resins, vacuum degassing was required. This took 30% of capital and 40% of operating costs.[198] Newer resins are more tolerant of oxygen.[146,147,963]

In large-scale systems continuous operation appears to be cheaper than fixed-bed plants.[69,147,198,963] The major advantages of continuous plants are it is much easier to exclude

First Half Cycle   Second Half Cycle

A

F → [Hot] →   F → [Cold] →

B

F → [Hot] — [Cold] →   F → [Cold] — [Hot] →

C

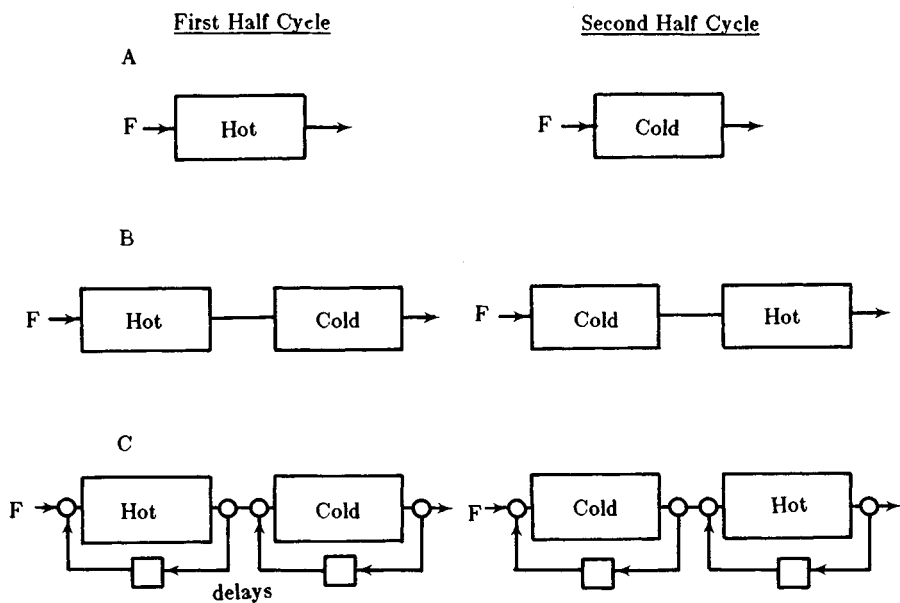F → [Hot] — [Cold] →   F → [Cold] — [Hot] →

delays

FIGURE 4-18. Direct thermal mode cycling zone adsorption. (A) Single zone; (B) two zone; (C) two zone with recycle and delays.

oxygen which translates into longer resin life, and the equipment will be smaller. These advantages are important since fixed-bed Sirotherm does not appear to be economic when compared to reverse osmosis or electrodialysis.[198,966] Ashai-type continuous systems with normal Sirotherm resins, pipe-flow reactors, and fluidized beds with magnetic resins have been used (see Chapter 6). The future of this process appears to focus on continuous plants, and thus PP apparently has lost its one commercial application.

IV. CYCLING ZONE ADSORPTION (CZA) AND CHROMATOTHERMOGRAPHY

Cycling zone adsorption (CZA) and chromatothermography were developed independently and had different purposes. CZA was developed as a large-scale system for bulk separation while chromatothermography was developed as a type of analytical chromatograph. I have juxtaposed these methods because they are very similar. Both processes use unidirectional flow and both methods can use focusing to increase the separation.

A. Direct Mode Cycling Zone Adsorption

The basic ideas of CZA were first presented by Pigford and co-workers,[74,805] and several reviews have been written.[450,1051,1058] In the direct thermal mode the columns are externally heated or cooled, and the temperature is cycled between the hot and cold temperatures. A single zone device is shown in Figure 4-18A. Note that feed enters the column continuously and reflux is not used. Since the change of the isotherm with temperature is usually modest, the separation obtained in a single zone will be modest. This separation can be multiplied by adding additional zones as shown in Figure 4-18B. When the adsorbent is hot, solute is weakly adsorbed and a concentrated solution exits the column. If this solution is sent to a cold column which already contains solute, the concentration will be increased further when the column is heated since solute must desorb. Thus a peak of material which has been concentrated twice will exit the hot column in Figure 4-18B if the fluid and adsorbent have undergone two temperature changes from cold to hot. Thus correct timing is essential.
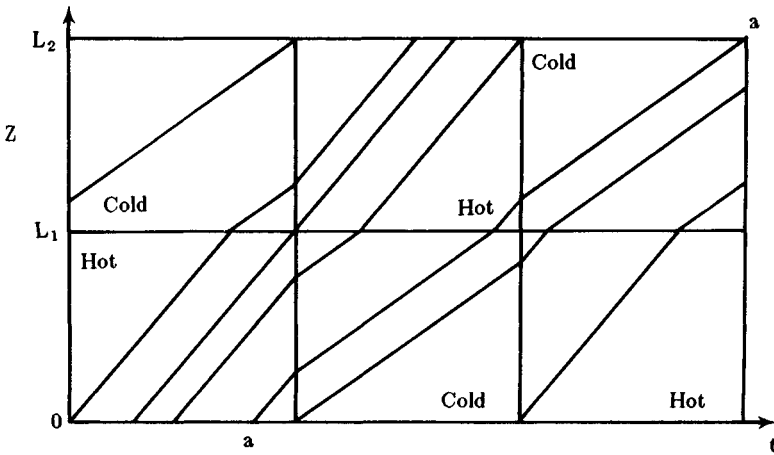
FIGURE 4-19.   Solute movement theory for two-zone, direct mode CZA with linear isotherms.

Additional separation can be obtained by controlled recycle of portions of the product stream[388,850] as shown in Figure 4-18C. The concentrated peaks leaving the column when the column is hot need to be delayed during recycle so that the peaks enter the column while it is cold. Then, when the column is heated for the next cycle, the concentrated peaks will be further concentrated. Delay can be obtained with a column packed with an inert solid or with a coil of small-diameter tubing. Further separation can be obtained by packing the bed with alternating layers of packing with different temperature dependence.[388] By using two adsorbents with different selectivities, a modified CZA system with recycle can be used to fractionate mixtures of solutes.[1064]

The solute movement model is easily applied to CZA.[74,806,1058] The solute movement diagram which results is shown in Figure 4-19 for a system with linear isotherms. The basics of the calculation are essentially the same as for PP except there is no flow reversal. When fluid enters zone 2, which is at a different temperature than zone 1, the solute velocity changes because k_i changes; however, the fluid concentration does not change since the adsorbent in zone 2 has not changed temperature. By counting the number of times the adsorbent changes temperature, the concentration of any characteristic can be determined. Thus, characteristic a-a undergoes two changes of adsorbent temperature from hot to cold and, according to Equation 2-46, its concentration will be doubly diluted. The diagram for the single-zone system shown in Figure 4-18A will look like the zone 1 portion of Figure 4-19. Extension to nonlinear isotherms is straightforward.

Closed form solutions can be obtained for systems with linear isotherms. When the system is properly timed, the maximum separation factor is[464]

$$\frac{c_{conc}}{c_{dilute}} = 2\left[\frac{1 + k(T_c)}{1 + k(T_h)}\right]^m - 1 \qquad (4\text{-}11)$$

where m is the number of zones. This is the same exponential increase that is observed with batch PP but the number of zones has replaced the number of cycles. If dispersion or nonlinear isotherms are included, the batch direct mode PP can ultimately obtain more separation than CZA. The reason is that because of flow reversal, PP keeps the product end of the column free of solute, and the mass transfer zone (MTZ) stays inside the column. In CZA the MTZ moves through the column and all parts of the column see high and low solute concentrations. If there is significant tailing or dispersion complete cleanup is difficult. However, as we will see in the next two sections, CZA has advantages in some cases.

A number of experimental separations have illustrated direct mode CZA. These include the separation of acetic acid from water on activated carbon with one[74,806] and two zones,[74] separation of methane from helium on carbon,[806] separation to toluene and *n*-heptane on silica gel,[850] separation of oxygen from air with 5 Å molecular sieve,[1010] separation of methane from nitrogen on silica gel,[142] and the removal of sodium chloride from water using mixed beds.[420,633,903] Direct mode CZA has been extended to extraction where diethylamine was removed from water using toluene as solvent.[1039] Direct mode CZA can also be operated by changing electrical potential of the adsorbent.[347,644] In all cases the outlet product exits as a peak concentration followed by a valley of low concentration. If timing is incorrect, shoulders with a concentration equal to the feed concentration will appear.

B. Traveling Wave CZA and Focusing

Thermal traveling wave CZA is analogous to recuperative mode PP; the feed is heated or cooled and a thermal wave passes through the column. The equipment for this is quite simple and is illustrated in Figure 4-20A. Additional separation can be obtained by adding additional zones and heat exchangers in series or with recycle, but timing is crucial. A lag may have to be built into the connection between zones or in the recycle line. For a liquid system where $u_{th} > u_s$ the concentrated portion of the wave should always undergo temperature changes from cold to hot while the dilute part of the wave should go from hot to cold.

Analysis by the solute movement theory is straightforward. For liquids where u_{th} is usually greater than u_s, Equation 2-45 predicts there is more concentration in a single-zone traveling wave system than in a single-zone direct mode system (Equation 2-46). This is collaborated by experimental results for thermal traveling wave CZA with liquid systems.[74,601,806] This is also true in thermal traveling wave cycling zone extraction.[1041] Similar results are obtained when a thermodynamic variable other than temperature is used if the wave velocity is greater than the solute velocity. This was observed for separation of dipeptides from water using waves of dichloroacetic acid.[760]

As the thermal wave velocity* approaches the solute wave velocity the solute movement theory (Equation 2-45) predicts better separation. The solute movement diagram for a linear system with $u_s(T_H) > u_{th} > u_s(T_c)$ is shown in Figure 4-20B. Once a solute wave intersects the thermal wave it is "trapped" there. If the solute moves faster than the thermal wave, the solute will enter a cold region and must slow down. If the solute moves slower than the thermal wave, the solute will be heated up and must speed up. An infinite concentration is predicted at the thermal wave and a zero concentration everywhere else. This result is physically impossible. Equation 2-45 predicts negative concentrations under these circumstances. The reason why the local equilibrium theory predicts physically impossible results is the linear isotherm is not adequate at high concentrations. When a nonlinear favorable isotherm such as a Langmuir isotherm is used, physically reasonable results are obtained. This is shown in Figure 4-20C.[1044] The concentration at the thermal wave builds up to a high enough level so that the solute wave velocity in the cold region becomes greater than the thermal wave velocity. This leads to a region of very high concentration, c_I which exits *ahead* of the thermal wave. This is shown in Figure 4-20D.[1044] The wave velocities in Figure 4-20C are in the order,

$$u_s(T_H, c_F) > u_s(T_c, c_I) > u_{sh}(T_c, c_I) > u_{th} > u_s(T_c, c_F) > u_{sh}(T_c, c_F) > u_s(T_c, 0) \quad (4\text{-}12)$$

A long period of zero concentration will follow the diffuse wave. Thus with the appropriate thermal wave velocity a single-zone system can achieve an excellent separation. This con-

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* Other thermodynamic variables can be used instead of temperature.
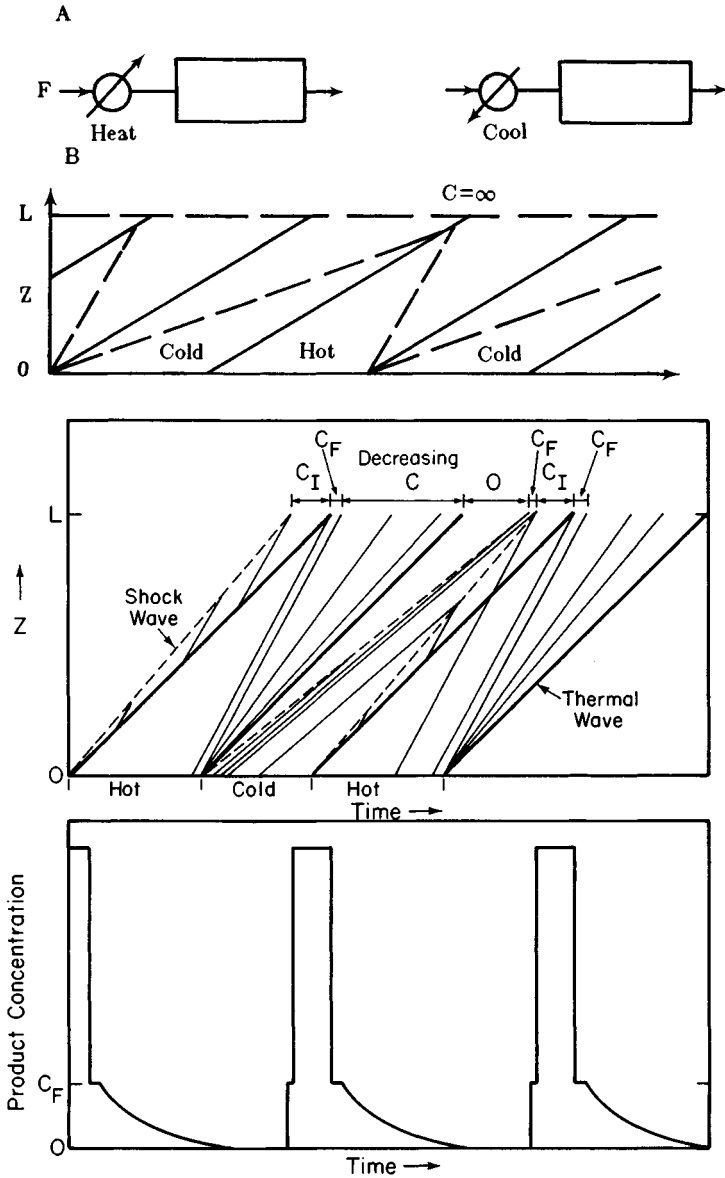
A

F →⊘→ [   ] →

Heat

B

→⊘→ [   ] →

Cool

FIGURE 4-20.   Single-zone traveling wave cycling zone adsorption. (A) Equipment; (B) solute movement theory for linear isotherms with $u_s(T_H > u_{th} > u_s(T_c)$; (C) nonlinear favorable isotherms; (D) product concentrations predicted in part C. (From Wankat, P. C., *Chem. Eng. Sci.*, 32, 1283, 1977. With permission.)

centrating effect has been called focusing, trapping, or the Guillotine effect, and it is a powerful tool.

In liquid systems the natural thermal wave velocity is usually too high to obtain focusing, but other thermodynamic waves will illustrate focusing. The separation of fructose or glucose from water using pH waves is an examples of this.[194,331] The removal of fructose from water is shown in Figure 4-21.[759] These results are at the cyclic steady state. Note that there is a long period of almost complete removal of the fructose and a concentrated peak which exits ahead of the high pH wave. The theoretical results were obtained with an equilibrium staged theory with four stages.[759] Focusing was also obtained in cycling zone extracting of dyes from water using Na_2CO_3 concentration as the cyclic variable.[1063]
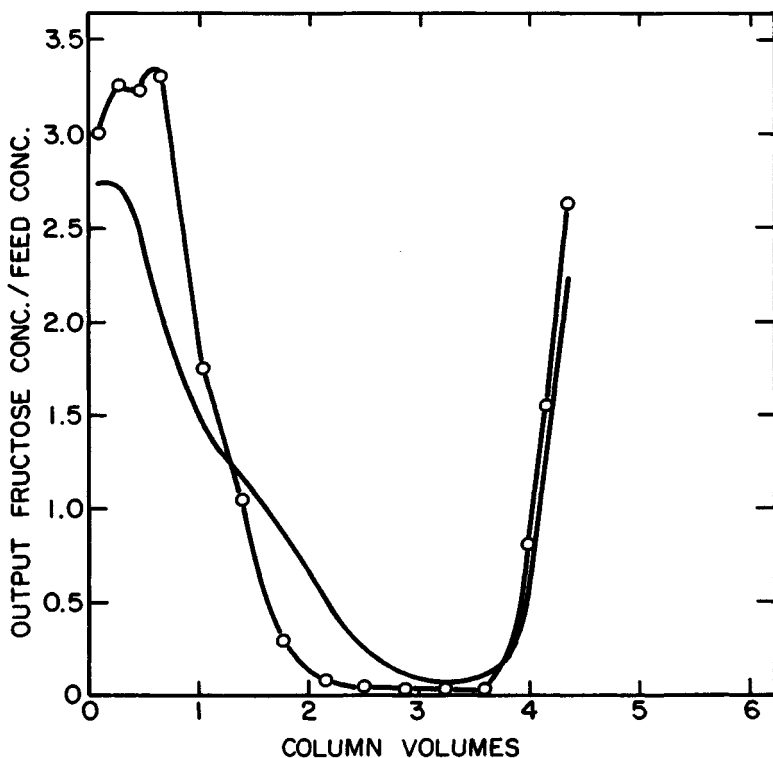
FIGURE 4-21. Separation of fructose from water by traveling wave CZA using pH waves. o——o, Data ——— . equilibrium staged theory. (From Nelson, W. C. et al., *Ind. Eng. Chem. Fundam.*, 17, 32, 1978. With permission.)

Focusing can occur in gas systems but the analysis is more difficult since the concentration and thermal waves are usually coupled by the large heat of adsorption (see Chapter 2 [Section IV.D.2]). Focusing was observed in adsorption studies.[113,784,986] In thermal traveling wave CZA in gas systems focusing has been more extensively studied than in liquid systems.[537-541,987,992] If a temperature wave of the right amplitude is used for a gas within the correct concentration range, focusing will occur. This is illustrated in Figure 4-22[541] for the removal of *n*-pentane from isopentane on 5 Å molecular sieve. Note that the cyclic steady state is rapidly attained. The product is roughly half pure iso-pentane and half a pulse concentrated in *n*-pentane. The pulse exits before the peak in the thermal wave. Because of energy losses, the thermal wave is considerably attenuated. Separation will be easier in a large-diameter column where the heat losses are proportionally less.

The conditions for occurrence of focusing in gas systems have been extensively studied.[539-541,991] Essentially, the hot and cold temperatures must bracket the "reversal temperature" T_r and the concentration of strongly adsorbed compound must not be too high. The reversal temperature is defined as the temperature at which the initial slope of the isotherm equals the ratio of the heat capacities of packing to mobile phase.[541]

$$\left(\frac{d\bar{q}}{dp}\right)_{\substack{\bar{p}=0 \\ T=T_r}} = \frac{C_{ps}}{C_{pg}}\left(\frac{M_1}{M_0}\right)\frac{1}{p} \qquad (4\text{-}13)$$

where $\bar{p}$ = partial pressure, p = total pressure, M_1 and M_0 are the molecular weights of the adsorbed and nonadsorbed species, C_{ps} and C_{pg} are the mass specific heats of the solid and the nonadsorbed gas. If we define $f(p)$ as
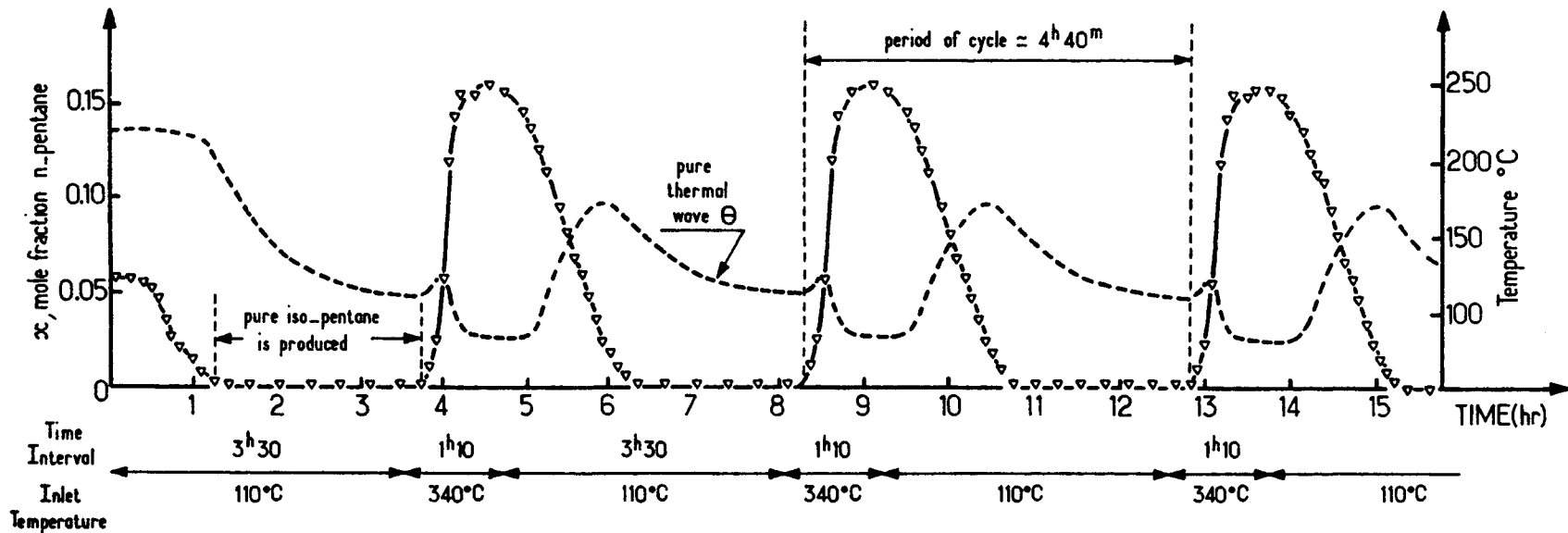
FIGURE 4-22.   Traveling wave CZA of *n*-pentane and iso-pentane on 5 Å molecular sieve. (From Jacob, P. and Tondeur, D., *Chem. Eng. J.*, 31, 23, 1985. With permission.)

$$f(p) = \frac{M_1}{M_0} \frac{C_{ps}}{C_{pg}} \frac{\bar{p}}{p} \qquad (4\text{-}14)$$

this function can be plotted on a graph of q vs. p along with the isotherms. If the cold isotherm lies entirely above the curve and the hot isotherm lies entirely below f(p) up to the partial pressure of the feed, then focusing can occur. This condition sets limits on hot and cold temperatures and the feed concentration. The recovery of pure component can be increased by using recycle.[541]

In Section II.A we saw that PSA systems had an optimum operation temperature. Gas CZA systems will have an optimum operating pressure. As pressure increases the equilibrium loading increases and with constant mass flow rate the gas velocity decreases which means a longer contact time.[992] These phenomena favor increased adsorption. However, pore diffusion will be slower at higher pressures, particularly for tight pores. Adsorbents with large pores will have high optimum pressures while those with small pores will have lower optimum pressures.

The gas separations with focusing have considerable promise for large-scale application. Large systems have been designed, but apparently none have been built yet.

C. Multicomponent CZA

Focusing can be used to develop multicomponent CZA systems. Essentially, the idea is to focus each solute at a different wave boundary. This was first illustrated theoretically[1043] using the solute movement theory and has since been shown experimentally[331,376,1036,1063] and with more detailed theories.[331,759] The basic idea is illustrated in Figure 4-23 for the local equilibrium theory with linear isotherms. (Obviously, nonlinear isotherms are physically more realistic as shown in Figure 4-20.) A series of steps in temperature is input as in Figure 4-23A. The temperature levels are selected so that

$$u_A(T_2) > u_A(T_1) > u_{th} > u_A(T_c)$$

$$u_B(T_2) > u_{th} > u_B(T_1) > u_B(T_c) \qquad (4\text{-}15)$$

Then solute A will be focused at the $T_c - T_1$ boundary and solute B at the $T_1 - T_2$ boundary. If a continuous temperature gradient were used, each solute would concentrate at the temperature where the wave velocity of the solute equaled the thermal wave velocity.

There are difficulties in putting this idea into practice. In many liquid systems the natural thermal wave velocity is too high and the criterion for focusing cannot be met. If waves other than temperature are used, focusing can occur. This was first illustrated by fractionating dyes using cycling zone extraction with Na_2CO_3 concentration as the cyclic variable.[1063] In a packed column partial fractionation of fructose and glucose was obtained using pH as the cyclic variable.[331] Considerable dispersion of the pH wave and interaction between the sugars decreased the separation somewhat. The method is applicable to gases also. For the system hydrogen, methane, and hydrogen sulfide on activated carbon, a region of almost pure hydrogen, a region quite concentrated in methane with no H_2S, and a region with all three gases was obtained.[1036] This would be useful for feeds containing small amounts of H_2S.

Excellent fractionation of three solutes was obtained by overriding the natural thermal wave velocity.[376] This was done by using a column with a jacket divided into sections as shown in Figure 4-24A.[376] The temperatures in each jacket section are changed as shown in Figure 4-24B. This direct mode system simulates a traveling wave with any desired thermal wave velocity and is similar to chromatothermography (see next section). One of the resulting separations for the separation of acenaphthylene, anthracene, and pyrene is shown in Figure 4-24C.[376] Note that the feed enters the column continuously, and the outlet
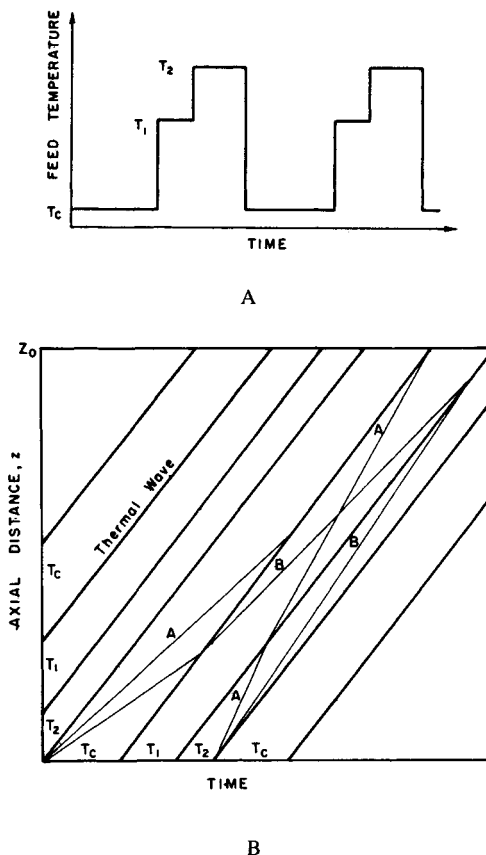
FIGURE 4-23. Multicomponent CZA. (A) Feed temperature; (B) solute movement diagram for linear isotherms. (From Wankat, P. C., *Ind. Eng. Chem. Fundam.*, 14, 96, 1975. With permission.)

products exit as peaks which are considerably concentrated. These results are shown at the cyclic steady state which was usually reached after the fourth cycle of operation. A direct mode system like this will require more energy than the traveling wave mode. In large-scale systems slow radial heat transfer might force one to build the column as the tubes of a shell-and-tube heat exchanger. Currently, this direct mode system does represent the best CZA fractionation.

D. Chromatothermography

Chromatothermography was developed as a gas chromatography method for continuously fractionating several solutes.[746,771,773,993,1107,1119,1120,1123] Chromatothermography uses a furnace which moves along the column. This furnace develops both radial and axial temperature gradients. The axial gradient can move at any desired velocity. Each solute will focus at the temperature where its velocity is equal to the velocity of the furnace. Thus, if a dilute feed continuously enters the column the solutes will be fractionated and separated. The solute movement theory with nonlinear isotherms has been applied to chromatothermography.[993] Small-scale gas chromatothermography systems were commercially available in the U.S.S.R. for a period.[746] Current interest in the method appears to be quite low, although specialty applications as an analytical method have been reported.[771,1107]

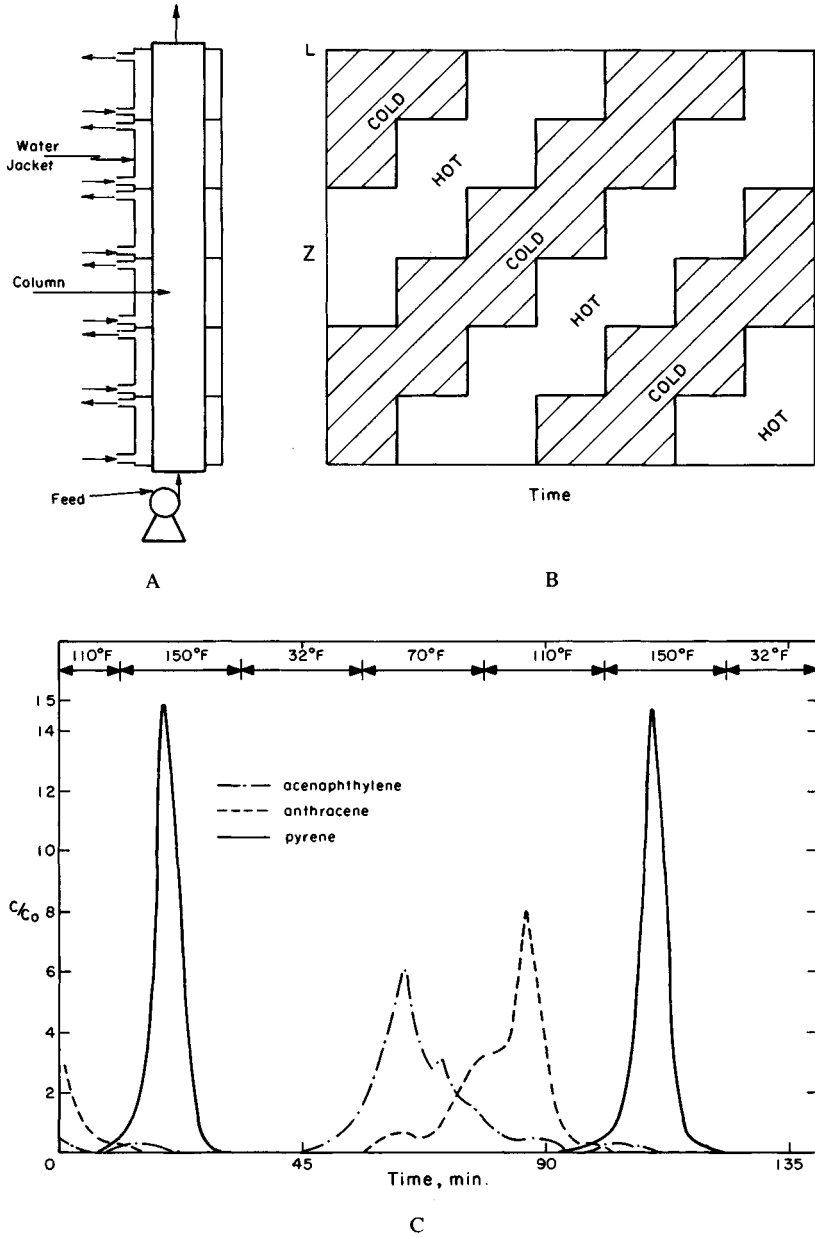The forced traveling wave CZA system[376] is obviously quite similar to chromatother-

FIGURE 4-24.   Forced traveling wave, multicomponent CZA. (A) Column system; (B) theoretical temperature profile; (C) separation of 3 solute system in 18-section column. Solvent is 2-propanol and adsorbent is polyvinyl pyrrolidone resin. Temperatures shown are jacket temperatures of the last section in the column. (From Foo, S. C. et al., *Ind. Eng. Chem. Fundam.*, 19, 86, 1980. With permission.)

mography. The CZA system would be easier to scale-up. Traveling wave CZA systems would be even easier to scale-up and would have lower energy requirements, but the thermal wave velocity may be too high or too low. There is more interest in the CZA-type systems for industrial gas separations than in trying to scale-up chromatothermography.

Chromatographic distillation[1121,1122] has some similarities with chromatothermography in that a temperature gradient is often employed. However, chromatographic distillation usually

uses inert packings and thus is really a distillation operated like a chromatography. The separation obtained depends on the volatility of the compound. Analytical applications have been reported.

V. THEORIES FOR CYCLIC SEPARATIONS

The most commonly used theory for PSA, PP, and CZA has been the local equilibrium or solute movement theory. This theory is simple enough to allow simple analytical or graphical solutions. Thus this theory is very useful for visualizing the separation and as a conceptual tool in developing new cycles. The applications of this theory are outlined in Table 4-1.

The major drawbacks of the local equilibrium theory are it does not include dispersion or rate limitations. Thus it is inadequate for design or when the separation is based on kinetics instead of equilibrium. A variety of more detailed models have been applied to cyclic separations and are outlined in Table 4-2. These theories can be classified as either continuous contact or staged-type models. The continuous contact models treat the column as a continuum and solve the partial differential equations which result. Numerical integrations may first simplify the equations to ordinary differential equations or may numerically integrate the complete set of equations. Frequency response methods are an alternate method of solving the equations after making some limiting assumptions. They have been used for extensive studies of the optimum operating conditions of direct, thermal parametric pumps.

Staged and cell theories divide the column into a number of discrete stages or cells. Equilibrium staged models assume that each stage is at equilibrium; thus, they are not appropriate when the separation is based on kinetics instead of equilibrium. The equilibrium staged models are certainly appropriate for staged systems such as extraction, but are less useful for column systems where an HETP or number of stages must be measured. These models have been used to develop a useful graphical analogy between distillation and PP.[448,449,451,454,455] Mixing cell models also divide the column into sections, but they do not assume equilibrium. One modification, the STOP-GO algorithm,[962] has been used for extensive simulations and comparisons with experimental PP results. The STOP-GO method transfers all of the fluid from one cell to the next during the GO period. During the STOP the resulting ordinary differential equations are solved for mass transfer. In the limit of long times this model reduces to an equilibrium staged model with discrete transfer steps.[1038]

Usually, all of the detailed models will give approximately the same results if the parameters are adjusted accordingly. Several models have been compared and the relationships between parameters developed for PP.[338]

VI. THE FUTURE FOR CYCLIC SEPARATIONS

Obviously, pressure swing and vacuum swing adsorption are now and will remain popular separation methods for gases. I expect that the current trends towards systems with higher productivity or higher recoveries will continue. These two trends represent lower capital and lower operating costs, but they are not always compatible. The goal is to achieve both simultaneously. I also expect that PSA, VSA, or pressure-swing chromatography will be used for fractionation of gases.

Parametric pumping has not fulfilled its initial, perhaps oversold, promise. Except for a few special applications such as Sirotherm, I doubt that parametric pumping of liquid systems will have much large-scale application. For gases, systems combining aspects of PSA and PP[581] may be used on a large scale.

Cycling zone adsorption with focusing may well be used for large-scale separation of gases. Application to liquid separations is likely to be limited to specialized circumstances where the chemicals used for the traveling wave already occur in the manufacturing process.

Chapter 5

LARGE-SCALE CHROMATOGRAPHIC SEPARATIONS IN FIXED BEDS

I. INTRODUCTION

Chromatography was first developed as a separation method, and large-scale liquid chromatographs were in use before the development of either gas-liquid (GLC) or high-performance liquid chromatography (HPLC). For example preparative ion-exchange chromatography (IEC) was used in the Manhatten project[53,937] and is used commercially for separating rare earth metals.[53,401,431,543,882] In the late 1940s, carotene, xanthophyll, and chlorophyll were commercially separated on an activated carbon column using gradient elution and backwash.[898] The Arosorb process developed by Sun Oil Co. was used commercially in the early 1950s to separate aromatics from alkyl hydrocarbons.[319,471,908] The Arosorb process is a crude, but very large-scale example of liquid chromatography (LC) using silica gel. They found that large-diameter columns could be packed to be as efficient as small-diameter columns.[471] Large-scale applications of size-exclusion chromatography (SEC) quickly followed the initial development of the method.[306,348,548,549] The pharmaceutical applications of SEC remain quite common. After GLC was invented,[542] several attempts were made as early as 1956[362] to utilize GLC on a large scale.[275,362,868,984]

Analytical applications of chromatography were extremely successful and advances in detectors, columns, and packings occurred and continue to occur rapidly.[705] Chromatography created a revolution in analytical chemistry. Complex mixtures which could not be analyzed by other means could be analyzed rapidly by chromatography. These analytical successes led to very high hopes for large-scale chromatography. When some early systems showed significantly lower efficiencies than expected, and chromatography did not prove to be a panacea for all separation problems, the method fell into disfavor.

Currently, there is a resurgence of interest in large-scale chromatography. The resurgence of interest has occurred due to the development of improved systems and because of increased need. Improved packing methods have increased the efficiency of large-scale systems so that for small pulse inputs, the large-diameter columns are more efficient than analytical columns. This reduces the column size needed for a given separation. Improved control methods have made batch processing much easier to automate and thus have reduced operating costs. The rapid development of biotechnology and genetic engineering has led to many new processes where large-scale chromatography might be one of the preferred separation methods.

This chapter covers elution and displacement chromatography in fixed beds. First, the basic operating scheme will be presented and then design considerations which are applicable to all types of chromatography will be discussed. Then, a section each will be devoted to liquid chromatograph, size exclusion chromatography (SEC), gas chromatography (GC) and on-off chromatography (ion exchange and affinity). Other operating configurations which may be applicable to the same separation problems are covered in Chapters 6 to 8. The chromatographic reactor,[628,883,884,891] which is being used in at least one fairly large-scale system,[891] is beyond the scope of this book. Because of the thousands of papers published,[272] no attempt will be made to be inclusive.

II. BASIC OPERATING METHOD

We will first consider chromatography with migration of solutes down the bed. On-off chromatography, where sorption is so strong that the solutes do not move, is considered in
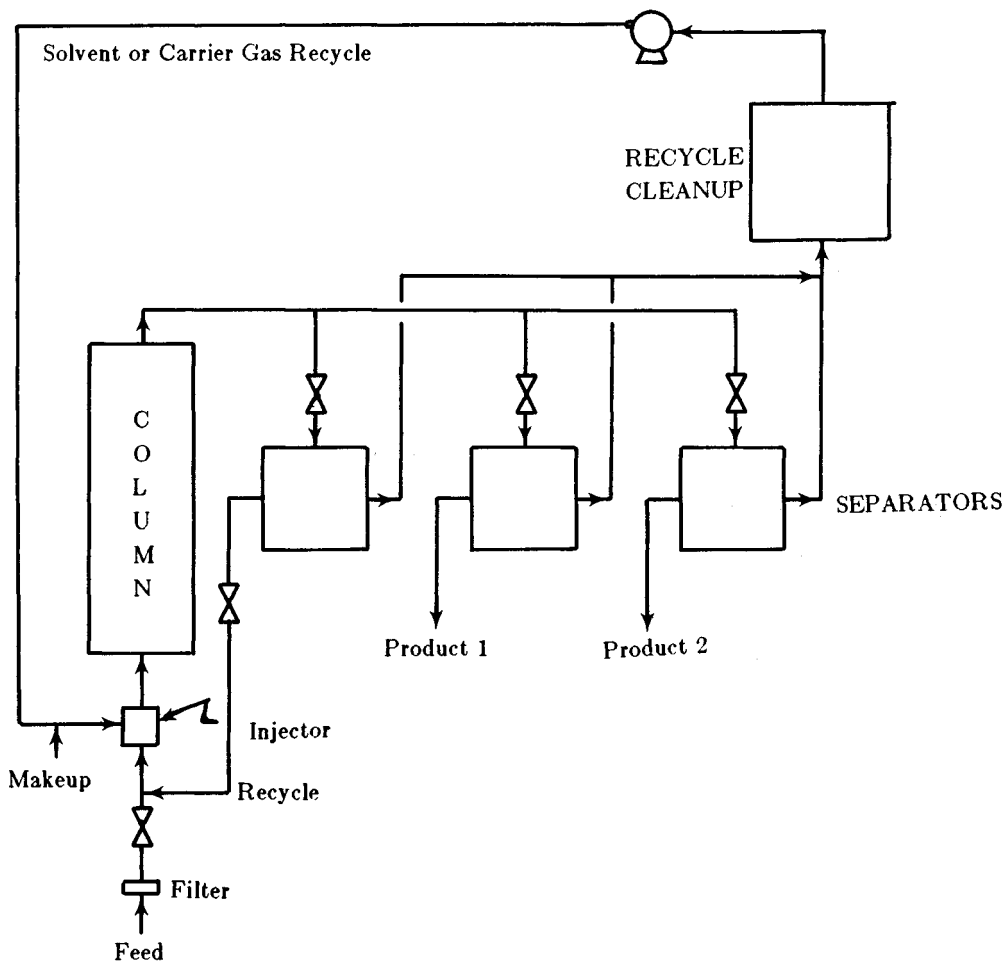
FIGURE 5-1.   Schematic of system for large-scale chromatographic separation.

Chapter 5, Sections IV.C and VIII. The basic method for separating a mixture by large-scale chromatography is essentially the same as in an analytical chromatograph. A pulse of feed is added to the column and then pushed through with solvent or carrier gas. This was illustrated with the solute movement theory in Figure 2-5 for solutes with linear isotherms and in Figures 2-15 and 2-16 for coupled solutes. The solute which spends the least amount of time in the stationary phase moves faster and exits the column first. This is true whether the separation mechanism is based on adsorption (GSC or LSC), partition (GLC or LLC), or size exclusion (SEC).

Large-scale elution chromatography differs from analytical systems in several respects. The goal of analytical chromatography is to rapidly obtain a high-resolution separation of a small sample. In large-scale chromatography the goal is to separate large amounts of material. Complete resolution is not required. The details of operating large-scale and analytical chromatographs differ because they have different goals.

A. Chromatographic System

The entire *system* for a chromatographic separation consists of considerably more than just the chromatographic column. A representative, large-scale chromatography system is shown schematically in Figure 5-1. The feed must be filtered or the column packing will

serve as a filter and will clog. The feed is often mixed with a recycle of partially separated material (see Chapter 5, Section IV.A). The total feed is then injected onto the column or into the line with the solvent or carrier gas. The feed injection system should be designed to produce a sharp square wave. The feed pulse is followed by solvent or desorbent in a liquid system and by a carrier gas in a gas system. In some cases, a backflush is used for heavy solutes (see Chapter 5, Section IV.C).

The feed and solvent or carrier gas enter into the column. The distribution system should be designed so that the entering fluid is evenly distributed across the cross section of the column. The column needs to be carefully packed to prevent channeling and to have a high efficiency (low HETP or high N). The packing is held by frits at both ends. The distributor at the top is also designed to have uniform flow with a minimum of mixing.

Once the separated material leaves the column, it is sent to different product separators using a rotary valve or manifold system. The system is controlled automatically based either on time or concentration measurements (UV, RI, OD, conductivity, etc.). The controller also automatically injects the next feed pulse. The distance of travel from the top of the column to the valve which isolates each product should be minimized to reduce mixing.

The products are sent to separators which recover the purified solutes from the solvent or carrier gas. In gas chromatography (GC) the separators are usually condensers (cold traps). In liquid chromatography, vacuum evaporation, distillation, extraction, or crystallization can be used. In large-scale chromatography, a complete separation to two adjoining solutes is often not obtained. Instead, a cut containing both components is recycled (see Chapter 5, Section IV.A).

If the carrier gas or solvent is to be reused, it is then sent to a purification section where the last traces of the solutes are removed. Purification is usually done by adsorption. The carrier gas or solvent is then recycled. In many cases, recovery and reuse of the carrier gas or solvent is required to make the process economical. The exception is when water is the solvent.

Although the chromatographic column is the heart of the process, it may not control either the capital or the operating expenses. Often, the separators control the operating costs unless the chromatographic packing has a very short life and must be frequently replaced. If carrier gas or solvent is not reused, make-up expenses may be the highest operating cost. With expensive packings such as affinity chromatography packings or bonded reverse-phase packings, the packing costs may control capital costs. With cheaper sorbents, the separators may control capital charges. Since all parts of the system can be important to the cost of the separation, the entire system must be optimized. Thus, a more expensive column system which reduces the separator costs may be the least expensive overall system. In general, the higher the solute concentrations leaving the column, the cheaper the separator and recovery costs.

The separation achieved in the chromatograph is readily predicted using the theories discussed in Chapter 2. A qualitative feel for the separation can be obtained from the solute movement theory such as in Figure 2-5. For linear systems, the staged (Chapter 2, Section VI.A) and rate models (Chapter 2, Section VI.B), which include zone spreading, are easy to use. Applications of the linear theory of chromatography were reviewed in Chapter 2, Section VI and are cited in reviews of preparative chromatography.[133,363,401,402,405,422,626,761,762,787,930,1020,1022,1109] Unfortunately, most large-scale chromatographic systems operate at fairly high concentrations where the equilibrium isotherms are nonlinear and may be coupled. The local equilibrium theory can be used for qualitative predictions (see Figures 2-15 and 2-16). For favorable (Langmuir type) isotherms, a sharp leading shock wave followed by a long diffuse tail are predicted (Figure 2-15). The opposite behavior is predicted and observed in GLC. A good approximation to the actual behavior of a nonlinear solute can be obtained by assuming the shock wave forms a constant pattern

wave (see Chapter 2, Section VII.A) and the diffuse wave is controlled by the isotherm effect. Thus, the local equilibrium calculation can be used for the diffuse wave. With a large N, the shock wave can be approximated as step function and the diffuse wave as an exponential.[401]

B. Problems with Elution Chromatography

At first glance, a chromatograph looks like a miraculous device. A pulse of complex mixture is inserted into a column filled with a suitable packing, and a series of separated compounds leave the product end. This seems simpler than the continuous countercurrent systems such as distillation, which are commonly used for commercial separation. With continuous distillation, four columns will be required to completely separate a five-component mixture. A single chromatographic column can do the same separation, although at least five, and probably more, separators would be needed in the process shown in Figure 5-1. Chromatographs have almost completely replaced distillation as an analytical tool, but have made little in-roads into large-scale processing. Elution chromatography has not replaced a significant number of continuous countercurrent separators because of problems inherent in the operating method.

First of all, chromatography uses a mass separating agent. This agent, the solvent or carrier gas, must later be removed. Thus, the entire system will usually contain more steps than a separation process which uses an energy separating agent (e.g., distillation or crystallization). For analytical purposes, the mass separating does not have to be removed or recovered, and this difference is unimportant. In large-scale application, the mass separating agent must be removed and usually must be recovered. Thus, large-scale chromatography immediately becomes more complex than analytical chromatography.

Second, elution chromatography is inherently a batch process. This is not a major problem when the entire plant is batch. However, the long-term trend has been towards continuous plants. Thus, either the batch chromatograph must be integrated into the continuous plant with suitable holding tanks, or columns in parallel can be used to approximate continuous operation. Both methods make the system more complex and expensive.

Third, an elution chromatograph is a thermodynamically inefficient system. These inefficiencies can be explained by considering the concentration profiles shown schematically in Figure 5-2 at three different times.[1057] A feed with three solutes with linear isotherms is illustrated, but the basic priniciples apply to other cases. Between feed pulses, no solutes are fed into the column. This results in the regions marked 1, where no solute is present. Since no solute is present, no useful separation is being done. The sorbent and solvent required to fill these regions is being ''stored'' for future use in a rather expensive storage vessel. In the region marked 2, all solutes are present at the feed concentration, while in the regions marked 4 two solutes are present at the feed concentration; in region 3 one solute is present at its feed concentration. No useful separations are occurring in these regions. In region M, previously separated solutes are remixing. This obviously increases entropy, but may be advantageous from a practical standpoint, since it allows more frequent feed pulses. The regions where useful separation is occurring are S, 3' and 3". In region S, solutes are being separated from each other. In region 3', solute is being removed from the sorbent. Region 3" is the leading edge of a solute wave where solvent or desorbent is removed from the solute. With nonlinear isotherms or when the sorption effect is important, very skewed peaks may result.[158] There will still be regions which are not producing useful separation at any given time. Some of the regions shown in Figure 5-2 may not occur in a particular operation.

The inefficiencies can also be looked at from a thermodynamical viewpoint. As soon as they are introduced, solutes separate. If zone spreading is ignored, an infinitesimal pulse will separate immediately. In large-scale applications, the pulses are large and the separated
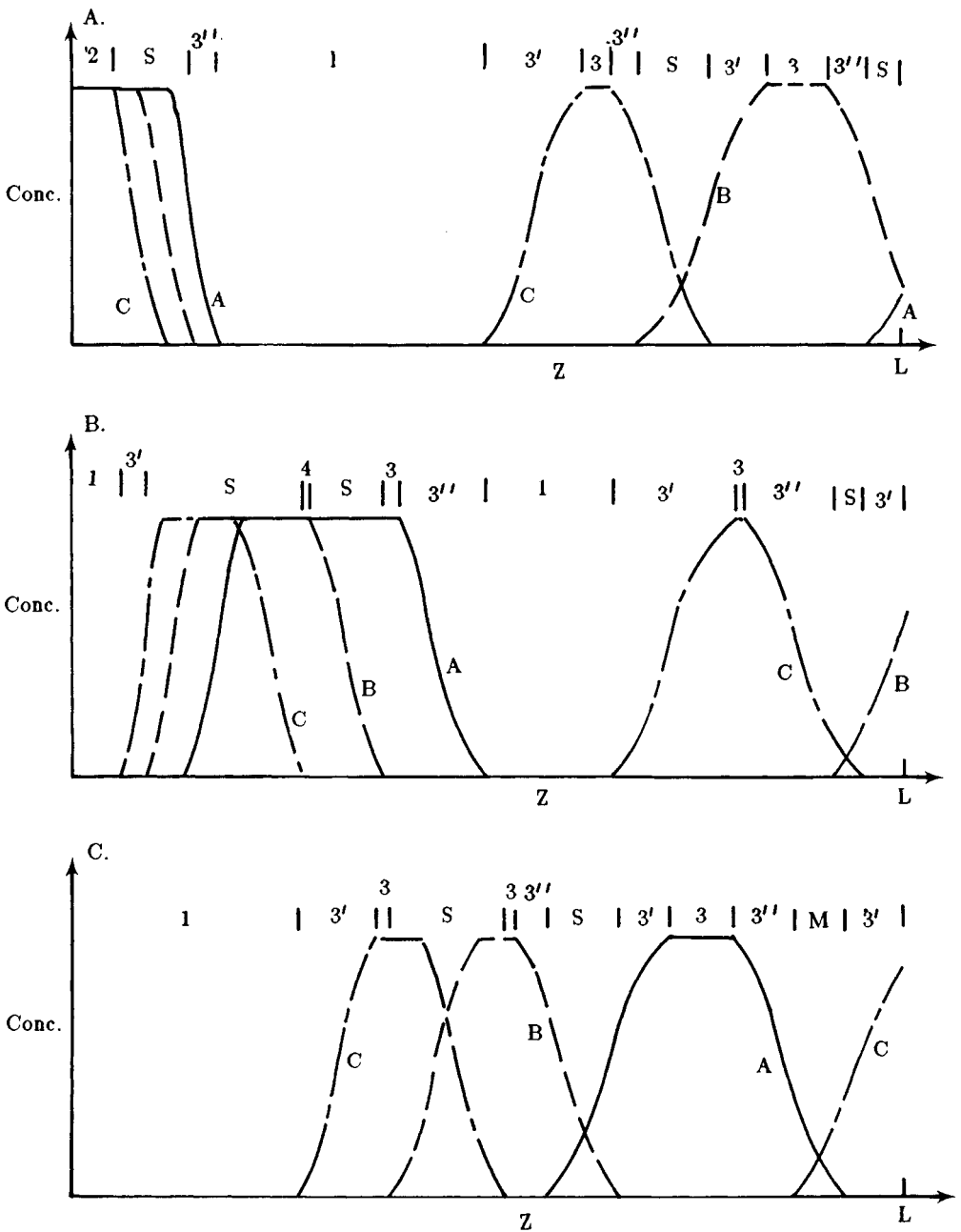
FIGURE 5-2. Schematic of concentration profiles inside a preparative elution chromatography column.[1057] (A) —— (B) ------- (C) — · — ·.

B and C are remixed with A, which enters later during the pulse. This mixing increases entropy. The zone spreading and dilution of peaks also increases entropy since the solutes are mixed with solvent. Thus, in Figure 5-2A, most of solute C in the center of the diagram is pure. Further travel of this peak down the column causes more dilution and hence, an entropy increase.

What can be done to reduce the size of the inefficient regions? The ultimate solution may be to use a completely different operating method such as countercurrent or simulated
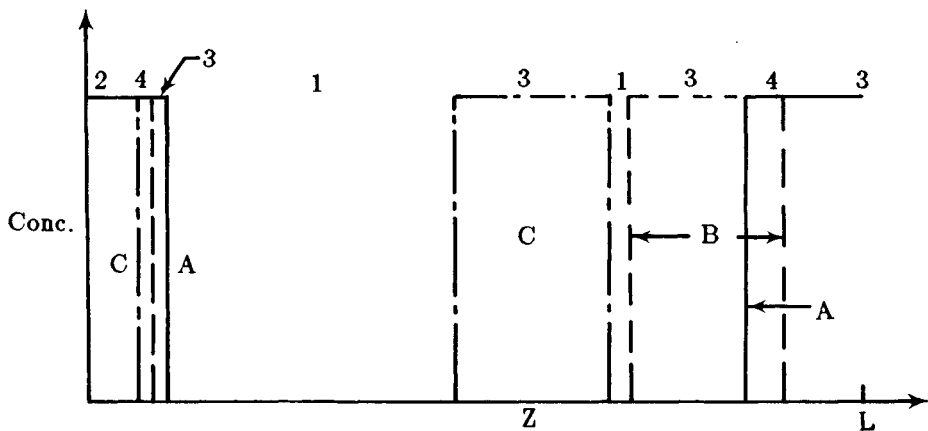
FIGURE 5-3. Schematic of concentration profiles inside an ideal preparative elution chromatography column.[1057] Infinite number of stages (no zone spreading). Same key as Figure 2.

countercurrent (Chapter 6) or a process which is a hybrid between elution chromatography and simulated countercurrent (see Chapter 7). Although these methods are more efficient, they are also more complex.

Suppose we want to use an elution chromatograph. What can be done to increase efficiency? Decreasing dispersion and increasing the mass transfer rate (decreasing HETP) will help. This can be done by decreasing the particle diameter (see Chapter 5, Section III.C) or increasing the diffusivity by using a less viscous solvent or carrier gas. When HETP decreases and N increases, there will be less zone spreading and the sizes of zones S, 3′, and 3″ will decrease. This allows one to use larger feed pulses and to input the next feed pulse sooner. These steps decrease the size of region I. However, even with infinite N, there is a limit to how much the inefficient regions can be decreased. This is illustrated in Figure 5-3 which is drawn with no zone spreading and thus is the solute movement theory solution.[1057] Since there is no zone spreading, each solute remains at its feed concentration, and regions S, 3′, and 3″ all become vertical lines. However, regions 1, 2, 3, and 4 still remain. Region I can be reduced in size (that is the next feed pulse can be input sooner), but regions 3 and 4 will grow in size, since part of regions 3′ and 3″ are converted into these regions. The net result is some decrease in the inefficient regions and some increase in feed capacity. For the ideal linear chromatograph, the best we can do with three components and still achieve complete separation is to feed one third of the time. This requires $K_B = 0.5(K_A + K_c)$ so that the AB and BC resolutions are the same. In general, the feed period will be significantly less than one third of the time.

In practice, zones S, 3′ and 3″ are not vertical, since dispersion, finite mass transfer rates, and nonlinear isotherms all cause zone spreading. When high product purity is required, a long column may be needed to completely separate the products. This will dilute the products, use more sorbent, and make the separation more expensive. An alternative is to only partially separate material and recycle the fraction which is incompletely separated. This recycle reduces the size of region I and is usually beneficial (see Chapter 5, Section IV. A).

The mixing region, M, can be eliminated by withdrawing products as soon as they are separated. Column-switching procedures are discussed in Chapter 7, Section II). Column switching can be very helpful when one solute is strongly sorbed and moves very slowly.

If the selectivity between components A and B is close to 1.0, a fairly long column will be required. If component C moves quite slowly, it will be easy to separate from component B, but component C will take a long time to exit from the column. This delays the input of the next feed pulse. This "general elution problem" can be alleviated in several ways.

One approach is to do the separation in several steps so that only components A and B are present when they are separated. Various column-switching procedures are a second approach (see Chapter 7, Section II). A third approach is to use programming of flow rate, temperature, or solvent composition to hustle component C out of the column faster (see Chapter 5, Section IV.B). Programming helps, but with this technique, the column usually has to be reconditioned before the next feed pulse can be added.

Displacement chromatography (see Chapter 2, Section IV.D and Chapter 5, Section IV.B) uses a strongly adsorbed displacer to push all solutes out of the column. Between the solutes, zones S, 3' and 3" will be quite small. Removal of the displacer from the column will result in a long tail because of the nonlinear isotherm. Thus, zone 3' will be quite long for the displacer. Zones 1, 2, and 3 still exist, although they may be smaller than in elution chromatography. Thus, displacement chromatography is also an inefficient process.

The different methods of increasing column efficiency or feed throughput can all help. However, they all tend to make the chromatographic system more complex.

A fourth general problem delaying the use of chromatography in large-scale applications is its unfamiliarity and lack of standardized design procedures. Engineers are naturally hesitant to use an unfamiliar technique, particularly when there have been failures in the past. This problem should disappear as large-scale chromatography becomes more common and as companies develop standardized equipment.

The final problem is economics. Because of all the reasons cited, chromatography can be a fairly expensive separation process. Since chromatography must compete with other separation methods, chromatography will only be used where it has economic or other advantages.

III. GENERAL DESIGN CONSIDERATIONS

The different types of chromatography all share many similar design requirements.

A. Sorbent and Solvent or Carrier Gas Requirements
The choice of the sorbent and solvent is of critical importance. The following are designable.

1. High selectivity, α_{21}. For linear isotherms, Equation 2-126 relates resolution to selectivity. When the selectivity is close to 1, the resolution will be small or a large number of stages will be required. As α_{21} increases, the number of stages required for a given resolution drops markedly. Alternately, very large samples can be applied if the selectivity is large.[1078]

    The relative value of α_{21} can be used to classify the separation. If α_{21} is greater than 1.5 or 2.0, the separation is fairly easy and recycle is used for a middle cut to prevent excessive tailing. Although always desirable, in very large-scale liquid systems, selectivities at least this high are very important to reduce sorbent and desorbent requirements. If the selectivity is too low, a research program to find ways to increase the selectivity may be necessary. The selectivity can be changed by modifying the sorbent, and in liquid systems by adjusting the solvent.[422] In HPLC systems, selectivities <1.5 are often used. In GLC systems, a high selectivity is desirable, but temperature stability is probably more important (see Chapter 5, Section VII) and α_{21} values less than 1.1 can be run. If α_{21} is very close to 1.0, the separation should be done in two steps and will be significantly more expensive.

    Specialized separations can be done with small selectivities, but operation is more difficult. Usually, all non-key components will be removed first. Special methods of shaving part of a peak or recycling entire peaks may be necessary to achieve the desired purity. These methods make the separation more expensive, and such operations have been limited to small volume operations.

2.   High capacity sorbent. To avoid programming, the value of k' should be in the range from 4 to 6. High capacity reduces the amount of sorbent needed, while a modest k' makes regeneration easy. In on-off chromatography the condition on k' does not hold, since the sorbed solute is removed by changing the solvent properties.
3.   Tightly sieved, preferably spherical packing. The particle size should be such that 30 d_p is less than the column diameter to minimize wall effects.[271] Regardless of the average particle size, the particles should be tightly sieved and spherical since this makes packing easier and will give the lowest HETP for a given pressure drop. Particle size effects are discussed in Chapter 5, Section III.C).
4.   Rigid, nonfriable, chemically stable sorbent. A long life and resistance to poisoning and fouling are highly desirable. The sorbent should be clean, be without impurities, and be reasonably priced. The bulk cost of the more expensive chromatographic packings should plummet as large-scale use becomes more common. Soft gel packings can be used when their large pore size is required, but the resulting slow flow rates will require larger-diameter systems (see Chapter 5, Section VI).
5.   Appropriate solvent. In addition to giving a high selectivity, the solvent in liquid systems must dissolve the solutes. In large-scale separations, the production of pure components will be optimized if the adsorption of solvent is intermediate between that of the two key components.[215] The solvent or carrier gas should be easy to separate from the solutes and easy to purify and recycle. The solvent or carrier gas should have a low viscosity, as this reduces pressure drop and increases diffusivities which reduces the HETP. A noncorrosive, nontoxic and noncarcinogenic solvent or carrier gas which is cheap and readily available is desired. In foods and pharmaceuticals, solvents must meet Food and Drug Administration requirements.
6.   Chemical programming. If chemical programming is to be used, the added chemical should have the same properties as a desirable solvent. In addition, the gradient former should be easy to remove so the sorbent can be reconditioned for the next feed pulse.

This list is a wish list. Usually some tradeoffs have to be made in the desirable properties. For relatively small installations, it is desirable to use off-the-shelf sorbents even if the column length or the time between feed pulses must be increased. A large number of such sorbents are commercially available for many different types of chromatography.[549,1076] For large installations, a considerable amount of money can be saved by having a better sorbent and development work on sorbent improvement becomes important.

B. Column Design and Packing Procedures

An absolutely even plug flow is desired, since the solute will move at the same velocity across the entire cross-section and bands will remain narrow. Axial mixing destroys separations and needs to be minimized both inside the packed section and in the distributors, valves, piping. etc.

A properly designed column will minimize dead volumes. The sorbent should be firmly held at both top and bottom by screens, mesh supports, or frits. The inlet fluid should not disturb the packing. The distribution system at both ends should be designed to given even plug flow. Improperly designed distribution systems can drastically increase HETP.[158] Several header designs have been used, but the most common types are

1.   Distribution with separate lines running to a chamber above or below the support. This design can give very even distribution with modest pressure drops in the supports. It is easy to scale up to very large sizes, but will be fairly expensive in smaller-scale equipment. (See Chapter 5, Section VI for a more detailed discussion.)

2.   Fairly thick frits with a high pressure drop. If the pressure drop in the frits is comparable to the pressure drop in the packed section, an even plug flow will result. This approach is easy to implement in small sizes, but may be difficult to scale up to large sizes. It also increases the overall pressure drop.
3.   A combination of a distribution system and a frit. The distribution system can be combined with the frit support and serves to spread the fluid to different parts of the frit. The frit tends to given an even plug flow.
4.   Conical end pieces filled with sorbent or inert packing. This approach spreads the fluid out, but flow paths are not the same length.

The distribution systems (items #1 and #3) seem to be preferable for soft gel packings and for large-diameter systems. Frits with high pressure drops seem to be preferred for rigid packings in fairly small-diameter systems.

The feed pulse should be input as a square wave. In very small preparative systems, a syringe can be used (less than a 500-$\mu\ell$ sample).[402] For injections up to 10 to 20 mℓ, a sample injection valve with a sample loop is satisfactory.[52] For the larger systems likely to be used commercially, a separate feed line with its own pump and isolated by a valve is satisfactory. GLC systems have special requirements, since the feed must be vaporized (see Chapter 5, Section VII).

The column should be constructed of material which is not attacked by the fluid. In small sizes, glass, plastic, and stainless steel are popular since they are suitable for a variety of applications. Glass and plastic systems are restricted to lower pressures. Very large systems are often constructed of carbon steel, particularly for hydrocarbon separations. The column should be constructed to code requirements as a pressure vessel. As the diameter increases, the maximum allowable pressure decreases. This may limit the use of small-diameter packing in large systems, unless the column length is also scaled down.

It is often desirable to have a jacketed column. This is particularly true with biologicals where the temperature should be low (0 to 5°C) to prevent degradation. The feed and solvent streams should be precooled or preheated before entering a cold or hot column.

The system should be designed so that the packing can be cleaned and, if necessary, replaced. Periodic backflush will help clean frits and remove trapped air. Provisions should be made for occasional chemical cleaning such as a caustic wash to regenerate the packing. The manufacturer's instructions should be followed for any chemical cleaning, since most packings are stable over limited pH ranges.

Proper packing can spell the difference between success and failure. Packing the column properly must be given the highest priority and cannot be left to untrained personnel. A well-packed column will have no voids at top or bottom. The bed permeability will be constant and a uniform plug flow will result.

Many packing procedures have been developed, although several are either patented or proprietary. Columns with baffles have been used,[984] but baffles do not appear to be helpful with current packing technology. On a small scale, slurry packing of liquid systems seems to reliably give tightly packed columns with low HETP.[363,405,593,930,1022] Unfortunately, the current slurry methods are difficult to use on a large scale. Tamping[363,371,405,592,930,1022] has also been used, but does not appear to be as reproducible as slurry packing or compression systems. Results can be improved by flowing liquid at high pressure after packing and then repacking the voids.[363,405,892,930,1022] Controlled vibration can give good results and has been applied to a large-scale liquid chromatography system.[892] Controlled vibrations and shocks have been used to successfully pack large systems.[158] Axial compression systems use a hydraulic ram to compress the packing.[351,428,429,567,1022] This system reliably obtains low HETP, and the column is easy to unpack and repack. Fairly large liquid chromatography systems have been constructed using this patented system.[351] Modest compression is also

useful in SEC.[343,612] Radial compression of a flexible column has also proven to be a good liquid chromatography packing technique.[567,663,1022,1065] The flexible wall becomes indented by the particles and any "wall effect" is reduced. This method has been scaled up to 2-ft diameter columns.[1065] The column must be packed with no void spaces between the packing and the support or retention screens. Packing procedures which constantly apply a pressure or which pack under a pressure higher than the operating pressure, are useful in preventing void formation during operation.

All columns should be tested after they are packed. This can be done quite conveniently by feeding in a small pulse of solute and determining the HETP from Equation 2-99 under dilute conditions where equilibrium is linear. This test removes concentration effects and measures flow and mass transfer effects. Columns with high HETP values should be emptied and repacked. Double peaks for a single component are another sign that packing is not homogeneous.

It is convenient if the column can be emptied and repacked easily. This is essential if the installation will be used for many different separations and different sorbents must be used. It is also useful if the packing becomes fouled and all or part of the packing must be replaced. Fouling is frequent with biological systems. An alternative solution is to use a guard column for fouling feeds. Wehr[1077] has an excellent review of column care for HPLC columns treating biological samples.

C. Particle Diameter Effects

What diameter particles should be used in large-scale chromatographic columns? There does not appear to be a consensus on the answer, although authors agree that the packing should be larger than the very small 1- to 3-μm packings used in analytical liquid chromatography, and smaller than the 20- to 40-mesh packings often used in large adsorbers.[626,1020] I lean towards particles at the smaller end of this wide range, and will explain my reasons in this section. The argument is similar to that used for adsorption (Chapter 3, Section II.D).

First, consider migrational chromatography for a linear system. Large-scale systems are usually operated at linear velocities where the mass transfer rates (C items in the Van Deemter Equation 2-117) control the plate height. When pore diffusion controls, as is often the case, this means plate height H is directly proportional to d_p^2 and the number of plates is

$$N = \frac{L}{H} \, \alpha \, \frac{L}{d_p^2} \tag{5-1}$$

Equation 3-1 shows that for rigid particles, the pressure drop is also proportional to L/d_p^2. Thus, if we keep L/d_p^2 constant, different columns will have the same pressure drop and the same N. The number of stages required will be set by the packing selectivity and the desired resolution. Since the width of a zone is $w = 4\sqrt{N}$, the relative zone spreading is constant. That is

$$\frac{4\sqrt{N}}{N} = \frac{\text{zone width in column}}{\text{column length}} = \frac{\text{period of zone}}{\text{breakthrough time}} = \text{constant} \tag{5-2}$$

The resolution will be the same for different columns as long as L/d_p^2 is constant. The breakthrough time is proportional $1/L$, since the solute velocity is unaffected by changing d_p. Therefore, we should scale so that

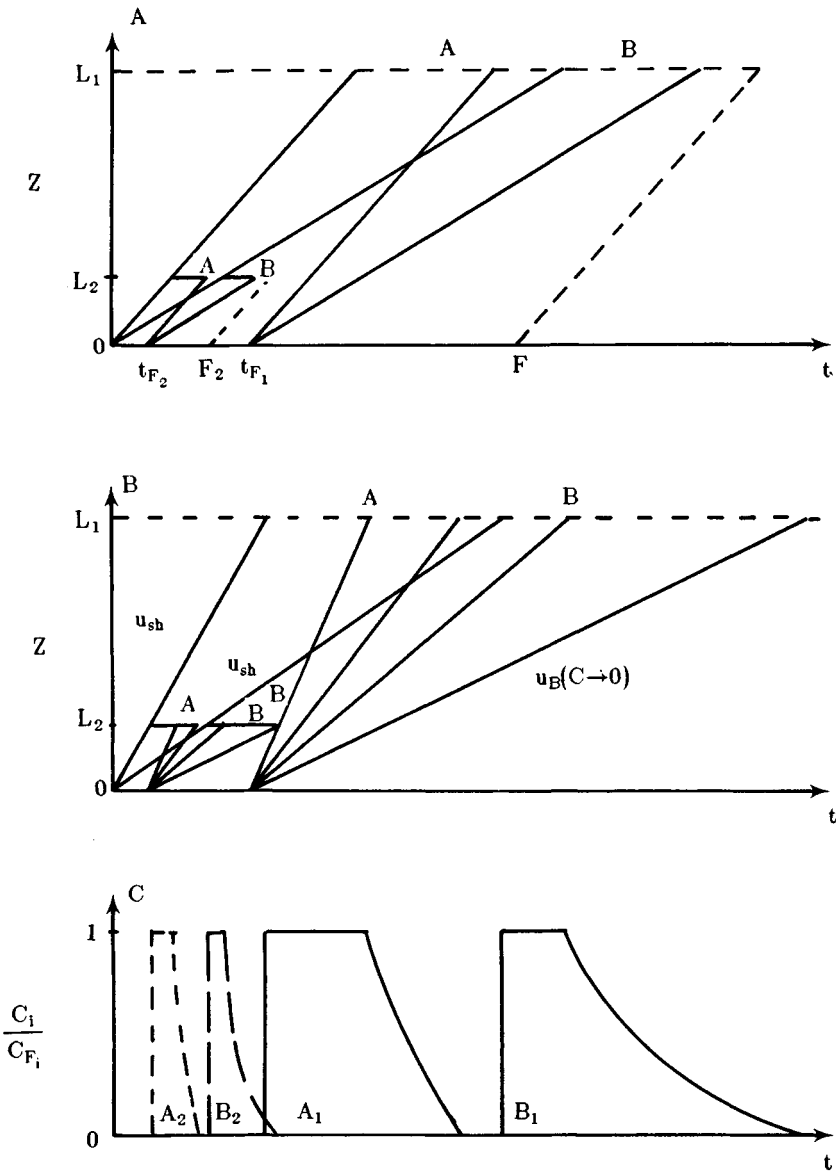$$\frac{t_{cycle}}{L} = \text{constant} \quad \text{and} \quad \frac{t_F}{L} = \text{constant} \tag{5-3}$$

FIGURE 5-4. Effect of scaling so that L/d_p^2 = constant and t_F/L = constant; d_{p2} = $d_{p1}/2$. (A) Solute movement diagram for linear isotherms; dotted line is next pulse; (B) solute movement diagram for noninteracting nonlinear, favorable isotherms; (C) outlet concentration profiles predicted by (B); solid line is for d_{p1}, while dotted line is for d_{p2}.

The solute movement diagram comparing the operation of two linear systems with d_{p2} = $d_{p1}/2$ is shown in Figure 5-4A. Column 2 is one fourth as long as column 1. Column 2 feeds for one fourth the time per cycle as column 1, but the cycles are one fourth as long. Therefore, the throughput is constant. The resolution, Equation 2-125, is the same for both cases. This is true whether we look at the solute movement diagram which ignores zone spreading, or include zone spreading. The conclusion is if L/d_p^2 is constant and Equation 5-3 is satisfied, we will have the same throughput with the same resolution. Of course, the column with the smaller-diameter packing will have less packing and will cycle faster. Practical design considerations are discussed later.

The same conclusion is valid for nonlinear systems. The solute movement diagram for favorable, nonlinear, noninteracting solutes is shown in Figure 5-4B. Each solute has a leading shock front and a diffuse tail as shown in Figure 5-4C. For unfavorable isotherms such as those observed in GLC, the locations of the shock waves and the diffuse tails will be reversed. In Figure 5-4C, the resolutions are the same for cases 1 and 2. This occurs since both the retention times and the zone spreading caused by the diffuse wave are proportional to L, and the change in L divides out in the resolution equation. Although the resolutions between peaks are the same, the actual time is naturally less for the shorter system. Thus, design and operation must be done more accurately.

Finite mass transfer rates and axial dispersion will cause the shocks to become constant patterns. Equation 2-140 shows that this pattern width is proportional to $1/k_M a_p$. When pore diffusion controls, the zone width is proportional to d_p^2. The equation for resolution is then

$$R = \frac{2(t_{R_B} - t_{R_A})}{(w_A + w_B)} = \frac{2L\left(\dfrac{1}{u_{shB}} - \dfrac{1}{u_{shA}}\right)}{(w_p + w_d)_A + (w_p + w_d)_B} \tag{5-4}$$

where w_p is the width of the constant pattern and w_d is the width of the diffuse wave. Since the diffuse wave is controlled by the isotherm effect, w_d is proportional to L, but not to d_p. Then

$$R = \frac{2L\left(\dfrac{1}{u_{shB}} - \dfrac{1}{u_{shA}}\right)}{(k_{Ap}d_p^2 + k_{Ad}L) + (k_{Bp}d_p^2 + k_{Bd}L)} = \frac{2\dfrac{L}{d_p^2}\left(\dfrac{1}{u_{shB}} - \dfrac{1}{u_{shA}}\right)}{k_{Ap} + k_{Bp} + \dfrac{L}{d_p^2}(k_{Ad} + k_{Bd})} \tag{5-5}$$

where k_{Ap}, k_{Bp}, k_{Ad}, and k_{Bd} are proportionality constants. Since L/d_p^2 is constant, the resolutions are the same for cases 1 and 2. The throughputs and pressure drops are also the same, but case 2 requires only one fourth as much packing material.

If the solutes interact, the patterns are more complex as is illustrated in Figure 2-16. However, one still gets shock (constant pattern) waves where the pattern width is proportional to d_p^2, and diffuse waves where the zone spreading is proportional to L. Scaling by L/d_p^2 again keeps resolution, throughput, and pressure drop constant, but the column with smaller particles will be significantly shorter and will use much less resin.

GLC is a special case. In GLC, the sorption and isotherm effects tend to cancel each other (see Chapter 5, Section VII) and mass transfer effects are much less important. Thus, the scaling proposed here may not be appropriate for GLC. SEC is also a special case when large molecules are totally excluded. There is no transfer of these molecules into the pores, and the scaling by keeping L/d_p^2 constant may again be inappropriate.

As one gets to smaller and smaller particles, the exact scaling by L/d_p^2 must eventually break down. With very small particles, pore diffusion will not control, and other zone spreading processes which are not inversely proportional to d_p^2 become important. When $d_p < 10$ μm, kinetic effects can be important.[517] Analytical columns packed with 1-μm-diameter packing showed no C-term (mass transfer limitations) at all.[1019] Thus, in this extreme limit, the scaling factor breaks down. Practical design considerations probably become important before these theoretical limits are reached.

On-off chromatography (Chapter 5, Sections IV.C and VIII) is operated more like adsorption than elution chromatography. The arguments of Chapter 3, Section II.D thus apply, and the conclusion is the same: we should scale so that L/d_p^2 is constant. This assumes that the packing does not become fouled or rapidly lose its effectiveness. An example of the

increase in production capacity which is possible with short, fat columns is given by Janson and Hedman.[549]

The practical design considerations are similar to those discussed in Chapter 3, Section II.D. If we scale as L/d_p^2, the columns will be short and fat, cycling will be more rapid and the particles will be small.

1. Column design. Proper distribution is more important when the columns are short and fat. Since this has been achieved with size exclusion and ion-exchange columns,[544,549,800] similar designs should work for other types of chromatography. The ratio (dead volume) to (column volume) needs to be kept low. This means careful design of head spaces, distributors, valves, and piping to keep the dead volume small. This requirement of keeping deal volume small is probably the most important design limitation on reducing the chromatograph size. In general, the smaller the column, the more careful the designer has to be, since height serves as a safety factor by providing more time between peaks.
2. Operation. Cycles will be shorter and thus, valves must cycle faster. Since very short adsorption cycles are used commercially,[558] this problem can be solved. However, the accuracy required increases, and timing may become a critical problem. A second operational problem is suspended material in the feed. Since the small-diameter packings will easily clog, efficient filters will be required For the initial chromatographic steps, the use of batch or fluidized beds may be preferred.
3. Packing material. The small-diameter particles must be tightly sieved and carefully packed. Wall effects will be less important for small-diameter packings than for larger diameters.[271] Large amounts of small-diameter particles may not be readily available at reasonable prices. If the price per kilogram increases more rapidly than $1/d_p^2$, the scaling suggested here will not be economical. Actual price increases appear to be significantly less than this. Once there is a market for large quantities of small-diameter packings, the prices will drop. The packing must have a long life; otherwise, this technique is not useful as a large number of short cycles will be impossible.

In summary, I recommend that relatively small-diameter particles be packed in short columns which operate with rapid cycles. The 10-μm particles recommended for preparative-scale[1020] (approximately 1-in I.D.) liquid systems may be somewhat small at the current time but seem to be a reasonable goal as we learn more about designing large-scale liquid chromatography systems.

D. Auxiliary Equipment

All the auxiliary equipment must be designed with chromatography in mind. From the point where the feed pulse is added, to the point where the product is isolated, all dead volumes and mixing must be minimized. Thus, fittings and values should minimize dead volume. Pipe diameters should be minimized and piping distances should be as short as possible. Once the products have been isolated, normal design procedures can be used.

Feed and solvent or carrier gas need to be filtered. The chromatographic packing is an efficient, but very expensive filter. A combination of off-line and on-line filtration is useful. All filters should be cleaned or replaced on a regular maintenance schedule. If dirty feeds must be handled without filtration, expanded or fluidized beds will be preferable to fixed beds (see Chapter 6). In liquid systems, the feed and solvent also need to be degassed. This can be done by heating and/or pulling a vacuum on the liquid. Systems which are not degassed may develop gas bubbles in the column and inactivate part of the packing. Very strongly adsorbed materials should be preseparated. This can be done in a separate step or with a guard column.

Solvent or carrier gas must be purified and all solute removed before reuse. It takes very little solute in the solvent or carrier gas to contaminate a high-purity product. For gas systems, the normal separators (cold types) do not remove enough solute to allow recycling the carrier gas. A separate clean-up by adsorption or some other approach is required.

Since temperature affects distribution coefficients, the column temperature should be controlled. In gas systems, an oven is normally used, while liquid systems can be insulated or jacketed. Streams entering the column should be at the same temperature as the column to prevent temperature gradients inside the column. This may require preheating or precooling the feed and solvent or carrier gas. In gas systems, pressure regulators and flow meters need to be jacketed also.

Pumps and compressors should have minimum oscillations since oscillations cause varying velocities. Any pumps handling partially separated material should have a minimal volume to prevent mixing. Many commercially available pumping systems are satisfactory.

The entire system should be automated. Automatic control quickly pays for itself and better control can be obtained than with manual operation. If timers are used for control, flow rates must be kept constant. In this case, constant-volume pumps are better than constant-pressure pumps. A pressure sensor or relief valve can control for inadvertent pressure increases. When timers are used, product concentrations need to be checked periodically. Changes in the feed composition or in the sorbent may require adjustments on the timers. If it can be used, concentration is often a more satisfactory control variable than time. Concentration measurement is usually more expensive, but it does not rely on the assumption that everything can be held constant. Rapid on-line measurements such as conductivity, UV, and refractive index are convenient for control, but since the response could be due to several components, the reason for the recorder response also needs to be checked. The measurement system has to be modified for the high concentrations observed in large-scale systems. A complete but rapid analysis, such as a fast, automated, analytical chromatograph is useful. Products and feed compositions should be analyzed periodically (a column receiving a feed which is different than it was designed for will not perform as expected). Both time-controlled[158] and concentration-controlled[171] systems can be computer controlled.

IV. OPERATING METHODS

A variety of operating methods are used in large-scale chromatography. In this section we will look at these methods in a general sense, while in the following sections we will look at each type of chromatography separately.

A. Elution Chromatography and Recycle

The most common operating method is elution, either with or without recycle. The equipment for this is illustrated in Figure 5-1 and the concentration profiles in the bed are shown in Figure 5-2. The solute movement theory for elution is shown in Figure 2-5. A feed pulse is usually followed by nonadsorbed or weakly adsorbed solvent or carrier gas; however, results will be optimized if the solvent is adsorbed an amount intermediate between the key components.[215] Then, after a sufficient time interval, another feed pulse is added. In large-scale operation, we desire to process as much feed per hour as possible. Therefore, large-volume feed pulses of fairly high concentration should be used.[73,76,156,276,277,279,285,286,363,400-402,405,407,466,524,548,549,864,871,872,904,930,1006,1007,1022] The concentration of solutes in the feed pulse should be below the solubility limit in liquid systems. It is desirable to avoid excessively high viscosities and to avoid "overflooding" in liquid-liquid chromatography (LLC) and GLC. A stationary liquid phase will swell in volume as solutes dissolve in it. If the stationary liquid phase swells past the pores (overflooding), the stationary phase will be swept down the column. In GLC, the latest recommendation is a solute weight fraction in the feed from 0.15 to 0.5.[904]
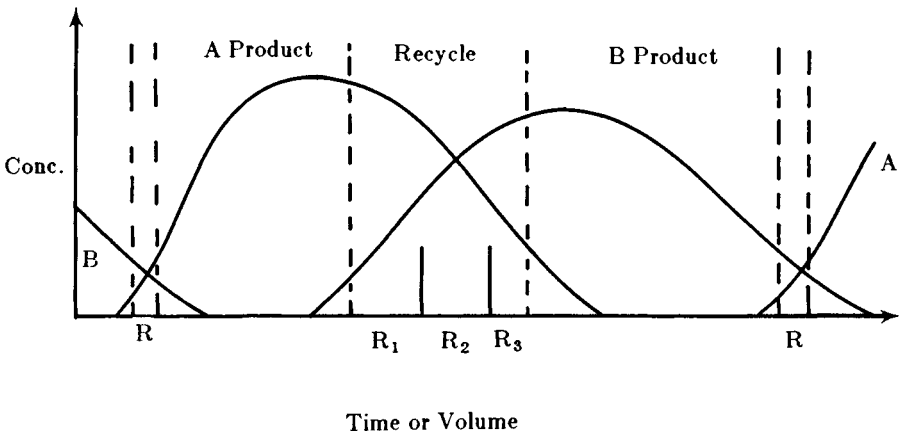
FIGURE 5-5.   Chromatogram of recycle system for nonlinear two-component system.

Several authors have done calculations below the concentration limit where isotherms are linear.[76,133,285,286,524,761,762,787,874,1109] However, in large-scale chromatography, unlike analytical chromatography, there is no reason why operation should be restricted to concentrations below the linear limit. Throughput will be much greater when higher feed concentrations are used and, in one example, was ten times larger for nonlinear operation.[400-402]

The simplest way to take off product is to make a single cut between each component. Unfortunately, in both linear and nonlinear elution chromatography, the peaks spread because of zone spreading or isotherm effects. In order to achieve high purities, the two peaks must be quite well separated. This implies either long columns, or short feed pulses, or both, and reduces the feed throughput. This problem can be resolved with displacement chromatography (see Chapter 5, Section IV.B) or with recycle. When rather poor resolution of the peaks is obtained, the overlapping portion of the peaks can be collected separately and recycled.[73,158,276,277,279,466,864,871,872,1007] This is shown for a nonlinear system with Langmuir-type isotherms in Figure 5-5. The principles for recycle are the same for linear systems and for GLC. For a single feed pulse, three fractions are taken: A product, recycle, and B product. With multiple feed pulses, as shown in Figure 5-5, an additional recycle between two feed pulses is taken. Fast cycling of feed pulses with some solute always exiting the column is usually desirable. With additional components, an additional recycle might be taken between each pair of adjacent components. However, since operation is usually set by the most difficult separation, other component pairs may be adequately separated without recycle. Very strongly sorbed components should be removed first in a separate column. In all cases, much larger sample volumes can be used with recycle.

Recycle operation has usually collected the recycle stream as a single mixed fraction. This can be input before, with, or after the feed. Since the recycle stream is somewhat diluted, it is possible to mix the recycle with a concentrated feed to obtain a net feed of the desired concentration. A relatively large amount of material should be recycled. If the recovery ratio r is defined as the ratio of the mass material recovered to the mass of total feed (fresh feed plus recycle), then the optimum r is around 0.5 to 0.6.[276,279] This result was obtained for linear isotherms, but seems reasonable for nonlinear isotherms also.

The usual recycle arrangement loses some separation which has already been obtained, since streams of different concentration are mixed together. Better results can be obtained by subdividing the cycle into fractions which are recycled separately.[73] Thus, in Figure 5-5, the recycle stream could be subdivided into three fractions. Fraction R1 has a higher concentration of solute A and can injected before the next feed pulse or mixed with the first portion of the fresh feed. Fraction R2 has roughly the same proportion of A and B as the

feed and can be mixed with the fresh feed or be mixed with the second portion of fresh feed. Fraction R3 has a higher ratio of B to A than the feed and should be input at the tail end of the fresh feed. This procedure should increase productivity, but is more complicated and requires more separators. The economics of a particular situation dictate whether a simple recycle or a segmented recycle should be used.

Many times, only one component of a complex mixture is desired. The chromatograph can then be operated to purify only this one component.[158,864] Feed pulses are input so that the weakly sorbed impurity overlaps with the strongly sorbed (slow moving) impurity from the previous pulse. Recycle is used to increase the recóvery of the desired product.

For a difficult, small-volume separation, recycle may be used to achieve the desired separation. If the peak can be recycled without mixing, each pass through the column will increase the separation of components. For example, a 50-ft column can be simulated with a 10-ft column and five recycles. Since no additional feed is added during each recycle, the production rate will be quite small. This procedure is more commonly used in analytical chromatography,[697,930] but can be used on a preparative scale. It is particularly useful in SEC, since very long columns may be required for fractionation.

Other methods employing column switching and moving the feed location with and without recycle are covered in Chapter 7. Column switching can serve the same purpose as recycle and may be used instead of recycle.

B. Programming and Displacement Chromatography

Very strongly sorbed components move very slowly in the column and require a long time to exit. This means that peaks will be very wide, a long time between feed pulses will be required, and throughput will be low. One way to increase throughput is to change a thermodynamic variable so that the equilibrium constant, k_i in Equation 2-29, decreases. This variation of elution conditions is known as programming, or gradient elution, and is commonly used in analytical chromatography.[660,930] Programming, or changing the elution conditions, is also commonly used with backflushing and on-off chromatography (see Chapter 5, Section IV.C).

The purpose of programming is usually to decrease k_i and thus increase the solute velocity, Equation 2-30. This can be done by changing temperature, polarity, ionic strength, pH, or adding chemicals. When the thermodynamic condition of the fluid is changed, the solute comes out faster and in reduced elution volume. Thus, a concentration of the solute is obtained. Once the solute has exited, the column needs to be returned to its original state. The solute velocity can also be increased by increasing the fluid velocity, v. Flow programming decreases the time the solute is in the column, but does not change the elution volume. This technique has been used in preparative-scale GC.[564]

Increases in temperature decrease equilibrium constants. This effect is usually larger in gas systems, and temperature programming is quite common in analytical GC and has been used in preparative-scale columns.[564] Usually, the entire column is heated in an oven. Since heat transfer rates are low, it is difficult to heat large columns rapidly. Thus, temperature programming has not been popular in large scale GC. Decreases in the overall column pressure and vacuum operation are used to help purge PSA and VSA columns (see Chapter 4, Section I.) and similar procedures might be useful in large-scale GC.

A large number of variables can be changed in liquid systems to decrease equilibrium constants.[660,930,931] Increases in solvent polarity help remove polar compounds. Changes in pH are useful for weak acids or bases and for removal of proteins. Changes in ionic strength will also often remove proteins. Compounds which complex with the solute will often help remove the solute. Also, 6 M urea will remove most biological compounds, although it is likely to denature them. The programming can be done in steps, or as a gradient, and several thermodynamic variables can be varied simultaneously. A gradient or series of steps can
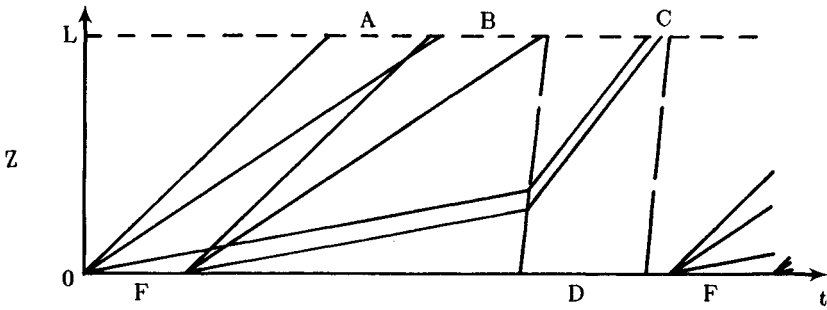
FIGURE 5-6. Solute movement theory for programming in linear chromatographic system. Programming agent not adsorbed.

remove a series of compounds one at a time, and thus increase the separating power of the system. Unfortunately, these schemes increase the complexity of the operation and make recycling of solvents and other chemicals more difficult. Considerable amounts of solvent may be required to recondition the column, particularly if the chemical added is nonlinearly adsorbed and a diffuse tail forms when the chemical is removed. These procedures have been used with biological systems (see Chapter 5, Section IV.C and VII) where solvent recycle is often not employed.

The solute movement theory can be used to study programming operations. For linear systems, if the added material changes k_i of the solutes, but itself either does not adsorb or its adsorption is unaffected by the solutes, then the system is uncoupled, and calculations are easy. This is essentially the case for dilute liquid systems when temperature is varied (see Figure 2-12). The addition of complexing agents, changing salt concentration, or changing pH can also result in an uncoupled system if the added chemicals are not sorbed. The solute movement diagram for such a system is shown in Figure 5-6 for a system with linear isotherms. The column length is set by the difficult A-B separation. Slowly moving component C is removed by adding a step change of a chemical which reduces k_c. If the chemical does not absorb, it will move at a velocity given by Equation 2-30 with $k_i = 0$. In this case, the chemical is easily washed out of the column and the next feed pulse can be quickly added. Note that the concentration of component C increases when it is eluted from the column. The concentration change can be calculated from a macroscopic mass balance. The procedure is analogous to that used for temperature changes, Equations 2-42 to 2-46. In actual practice, zone spreading can be superimposed onto Figure 5-6. Flow reversal (backwashing) is also used in these cases. If the system is coupled, the calculation becomes more difficult.

If the desorbent wave moves at a velocity in between the solute wave velocities,

$$u_s(c_h, c_{desorbent}) > u_{desorbent} > u_s(c_F, c_{desorbent} = 0) \tag{5-6}$$

then focusing (see Chapter 4, Sections IV.B and C) occurs. The result is a *large* increase in concentration, which forms a shock wave which moves ahead of the desorbent wave. When a gradient or series of steps in desorbent concentration is input, Equation 5-6 will be satisfied for different solutes at different desorbent concentrations. This is the basis for chromatofocusing[397a,590,848] and is similar to the multicomponent cycling zone adsorption (CZA) system (see Chapter 4, Section IV.C and Figure 4-20). Chromatofocusing may have major applications in large-scale chromatography, particularly for biologicals.[397a]

Displacement chromatography can be considered as type of programming where the feed pulse is followed by a displacer which is more strongly adsorbed than the solutes. The solutes and the displacer are coupled. If adsorption is strong enough, a series of shock waves

moving at the same velocity are generated (see Chapter 2, Section IV.D.1 and Figure 2-15). The beauty of displacement chromatography is when adsorption is strong enough, the solutes will be concentrated into sharp, narrow bands of pure solute in solvent without tailing. In a well-packed column, very little overlap of the peaks will occur, and recycle is probably not required.[518,565,795] The problems with displacement development are that an appropriate displacer must be found, optimum conditions may be difficult to establish,[1021] and the column must be regenerated with a solvent which is not adsorbed or is less strongly adsorbed than all the solutes. Tailing of the strongly adsorbed desorbent occurs and a considerable volume of solvent may be required.[385] This takes time, and the desorbent/solvent must be separated before reuse. Unfortunately, not all of the researchers who have studied displacement development have considered the entire cycle. Nonexhaustive studies by Carra and co-workers[215,742a,941a] and in our laboratory indicate that with a single solvent, the optimum solvent has a selectivity between the two key components. This, of course, is no longer displacement chromatography.

When the affinities of the species for the resin are very close, pure bands are not created.[280] Instead, a stationary distribution of components occurs in the band, but pure components do not result. This is usually the case when separating isotopes. By taking appropriate cuts, regions concentrated in each species can be obtained. Further concentration can be obtained by recycling the cuts with another displacement development.

C. Backflush and On-Off Chromatography

Although chromatography was first developed as a unidirectional flow system, researchers soon realized that reversing the flow direction (backflush or counter-flow regeneration) can have advantages. When some solutes have much lower velocities than the others, they may be easier to remove if the flow is reversed. This is illustrated in Figure 5-7A without programming, and in Figure 5-7B with programming. In both cases, the distance the solute travels is considerably less when backflushing is used. Note that concentration occurs during the regeneration with programming. Backflushing is also useful with column switching (see Chapter 7, Section II).

The second advantage of backflushing occurs with nonlinear isotherms. The diffuse tail of the pulse input will recompress. Thus, the amount of dispersion can be minimized. However, a price is paid for this. When the flow is reversed, the shock wave at the former leading edge becomes a diffuse wave and spreads out directly proportional to the distance traveled after the flow reversal. This is illustrated in Figure 5-7C for a Langmuir-type isotherm. Since the zone spreading in a diffuse wave is proportional to the distance traveled, strongly adsorbed solute may have considerably less zone spreading if it is backflushed out of a column.

A third benefit of backflushing is the solute which is removed never reaches the downstream end of the column. Thus, the product leaving this end of the column (Figures 5-7A and B) will not be contaminated with solute C. This is important if solute C is nonlinearly adsorbed and has a very steep slope (high K_C) at low concentrations. In this case, component C is very difficult to completely remove from the sorbent and tends to slowly leach out of the sorbent. With normal elution chromatography, it is difficult to produce A and B uncontaminated with C, but with backflushing this is less of a problem. This same principle is used in counter-flow regenerated adsorbers discussed in Chapters 3 and 4.

Backflushing or the use of counter-flow desorption can be the best way to operate in some circumstances. For the separation of an adsorbed gas from a nonadsorbed gas using a nonadsorbed carrier gas,[407] the use of reverse flow regeneration was significantly better than either co-flow desorption or a countercurrent moving bed system. In this case, the selectivity is infinite, so care is required in extrapolating to more typical chromatographic separation problems. However, backflush should definitely be considered when the selectivity is quite
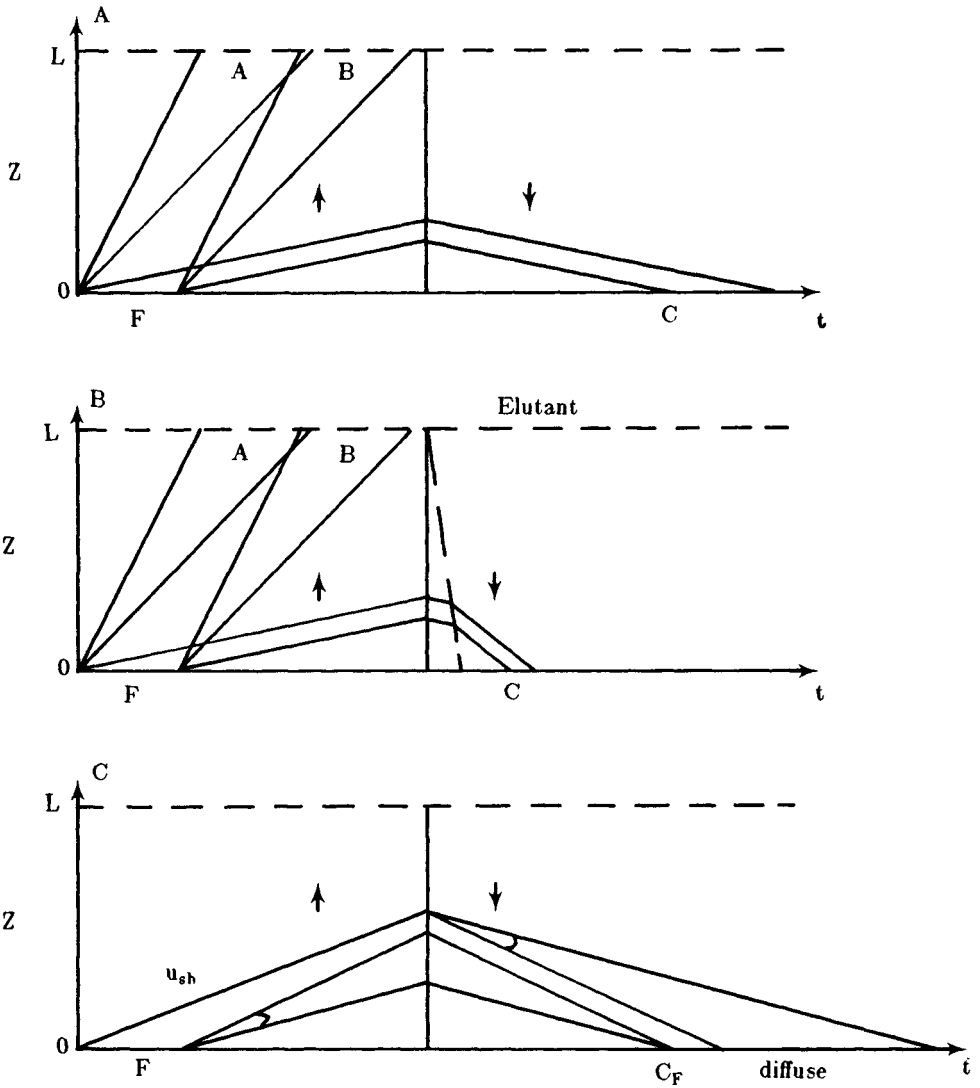
FIGURE 5-7. Solute movement diagram for backflush systems. (A) Linear system without programming; (B) linear system with programming; (C) Langmuir isotherm without programming.

large. One very common situation where selectivity is very high, is when there are strongly adsorbed impurities. In this case, it is often advantageous to remove the strongly adsorbed species first in a heavily loaded column. The precolumn is then washed to remove desired species and backflushed with a strong desorbent to remove the impurities. Removing the strongly adsorbed materials increases the throughput in the column doing the difficult separation.

What I call on-off chromatography* is a case where once the desired solute has sorbed onto a site, it is so strongly held that it does not move until the thermodynamic conditions are changed. Material is fed into the column until the column is almost saturated and then nonadsorbed material is washed out. Elution is often done in a counter-flow direction to avoid contaminating the product end of the column. Elution may be done with a gradient

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* Most users just call this chromatography and don't distinguish it from elution chromatography which has quite different operating principles.

or in series of steps to remove one component at a time. Ion exchange chromatography and affinity chromatography are often operated as on-off systems (see Chapter 5, Section VIII).

In on-off chromatography, the equilibrium isotherm during the ''on'' step is a Langmuir shape which rises very steeply and then rapidly levels off to a saturation value when all sites have been filled. This can often be approximated as a step function as shown in Figure 5-8A. During the ''off'' step the thermodynamic conditions are changed so that sorption is nonexistent or very weak. The solute movement diagram for on-off chromatography is shown in Figure 5-8B. The impurities, A, move rapidly through the column while the strongly adsorbed solute C moves in a shock wave with velocity given by Equation 2-35. Essentially, solute C moves until it finds an open site where it sorbs and then stays there. Any impurity which is weakly sorbed is displaced by strongly sorbed solute C. After the feed pulse, the impurity is washed out of the column. During the wash step, solute C in the intrastitial and interstitial spaces moves up to the shock wave front where it is sorbed. Once all of the C has been sorbed, the front stops moving since nothing desorbs. During the counter-flow elution step, solute C desorbs once the elutant wave reaches the sorbent. A concentrated wave of product C results. If the desorbent is partially adsorbed and the desorbent wave moves slower than the fluid, then a shock wave of solute can move ahead of the desorbent wave. This result is similar to the same phenomenon shown for cycling zone adsorption in Figure 4-20C. With very dilute feed solutions, concentration factors of several thousand can be obtained. The elutant is the washed out of the column either co- or counter-flow, and the next feed pulse can be added.

On-off chromatography can be considered as a limiting case of nonlinear, programmed chromatography with backflush. However, the operating procedure is really closer to adsorption. In many cases, the separation of different adsorbed components is by selective elution, not by different rates of migration in the column. The zone spreading which occurs is due to mass transfer rate limitations and results in constant pattern formation around the shock wave. The resulting mass transfer zone (MTZ) can be quite large when large molecules with low diffusivities are being adsorbed. The methods used for adsorption to get higher bed use (see Chapter 3, Section II.C) can also be used with on-off chromatography. On-off chromatography both separates and concentrates, which makes it different from conventional elution chromatography.

V. LIQUID CHROMATOGRAPHY

Large-scale LC has recently become a hot area of commercial interest. More than six companies are selling standardized columns or complete systems up to or beyond 1 m in diameter[2,14,15,351,371,528,681,894,1012,1065,1083] and many more companies are selling preparative columns up to 1 in. in diameter.[402,717] In addition, several very large (up to 4.0 m in diameter) chromatographic columns have been custom built in the sugar industry[482,490] and a large-scale pilot plant has been operated for xylenes and ethylbenzene separation.[892] This interest indicates that many companies think the time is ripe for greatly increased use of large-scale LC.

It is useful to loosely classify LC systems based on size. The chemist's or biochemist's preparative-scale systems are roughly 1-in. I.D. or smaller. These systems have been in use for years and have been extensively reviewed elsewhere.[133,363,401,402,405,761,762,787,930,1020,1022,1077] Somewhat larger systems are designed for semiworks and production scale of fine chemicals or pharmaceuticals. These columns range in internal diameter from several inches to a few feet. They are usually designed to use standard packings, and will probably be sold in standard sizes. This size range includes low-pressure systems which are relatively inexpensive, but require high selectivities for good resolution, and HPLC systems which are designed for small-diameter packings and higher pressures.

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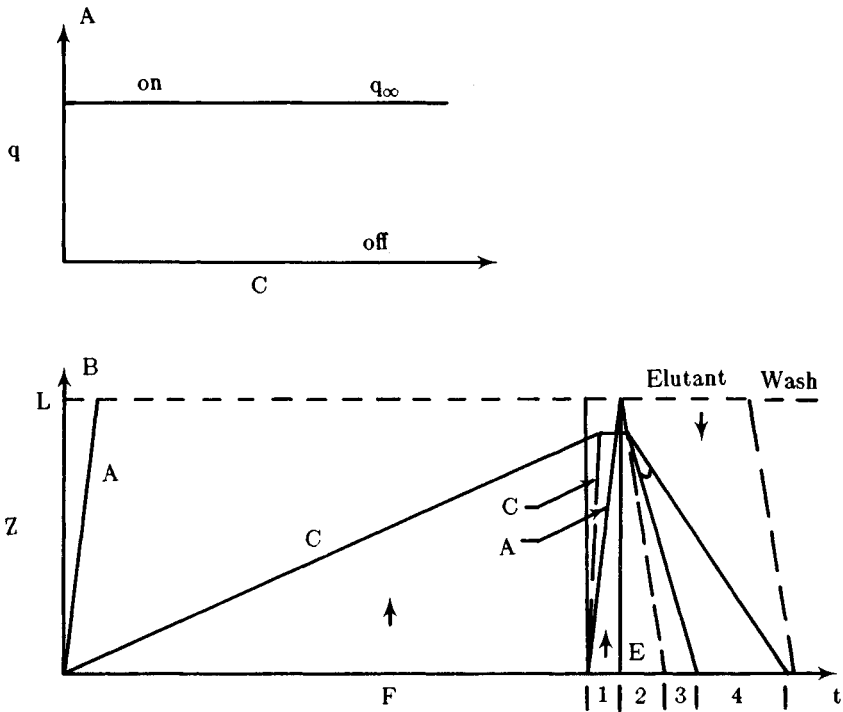
FIGURE 5-8. On-off chromatography. (A) Idealized equilibrium isotherm; (B) solute movement diagram: 1, wash; 2, clean solution; 3, concentrated product; 4, diffuse wave.

Since the major use of the lower-pressure systems has been for size exclusion, ion exchange, and affinity chromatographies, the emphasis in this section will be on HPLC systems. An alternative design for the low-pressure systems is the steady-state rotating, two-dimensional chromatographs as discussed in Chapter 8, Section II. Procedures for increasing the efficiency and capacity of both the low- and high-pressure systems are discussed in Chapter 7. The third size range is quite large-scale, custom-designed systems, which may be up to several meters in diameter. In this size range, the chromatographic systems must compete with commercial, simulated moving-bed techniques (see Chapter 6, Section V.B.2).

The medium-scale systems are still quite new and most of the information is in the manufacturer's literature.[2,14,15,351,528,681,796,894,1012,1065,1083,1116] Commercially available systems include empty, axially compressed columns[70,351,567,1116] up to 30 cm in diameter, radially compressed, prepacked columns up to 20 cm in diameter,[1065] stainless steel columns up to 6-in. I.D. which are available empty or prepacked,[346,1083] and modular stainless steel columns up to 6-in. I.D. which are available empty or prepacked.[528] Glass and plastic columns, with or without adjustable plungers for low-pressure operation, are available in sizes up to 1.2 m.[2,14,681,800] Packaged systems including pumps, valves, detector, and controls, but not the separators to recover solute from solvent, are available.[351,1065,1083,1116] These systems are capable of operation with solvent gradients. Separators are not included since the type and design of the separator will be different for different solutes and solvents.

Costs for columns and systems vary considerably. Table 5-1 lists some of the quoted prices. Glass columns are the cheapest, but they are not suitable for high-pressure operation and need to be protected in a plant. The glass and plastic columns are limited in pressure drop, and thus cannot use very small-diameter packings. They have been used extensively for size exclusion desalting, ion exchange chromatography, affinity chromatography and for relatively simple liquid adsorption or partition chromatography separations. For more difficult

Table 5-1
COSTS FOR LARGE-SCALE LIQUID CHROMATOGRAPHY

Size	Cost	Material	Company	Comments
Empty Columns				
15-cm I.D. by 120 cm	$517	Glass	Ace Glass[2]	
15-cm I.D. by 240 cm	$572	Glass	Ace Glass[2]	
18-cm I.D., length 76 to 97 cm	$2600	Glass	Amicon[14,15]	Adjustable plunger
25-cm I.D., 75- to 100-cm length	$3800	Acrylic	Amicon[14,15]	Adjustable plunger
4.8-cm I.D. by 50 cm	$950	316 S.S.	Whatman[1083]	
2-in. I.D. by 50 cm	$1700	S.S.	H.P. Chemicals[528]	Modular design
6-in. I.D. by 100 cm	$5700	S.S.	H.P. Chemical[528]	Modular design
20-cm I.D. by 100 cm	$5500	S.S.	YMC Inc.[1116]	
Complete Systems				
6-in. I.D. by 6 ft	$87,500	S.S.	Whatman[40,1083]	Silica gel
6-in. I.D. by 6 ft	$96,500	S.S.	Whatman[40,1083]	Reversed phase
20-cm I.D. (three cols.)	$100,000	S.S.	Waters[40,1065]	Radially compressed
20-cm I.D. (one col.)	$65—95,000	S.S.	Waters[42,1065]	Radially compressed
15-cm I.D. by 2 m	$130,000		Elf[41,351]	Axially compressed
4 cols. 10-cm I.D., lengths 10, 50, and 100 cm	$75,000	S.S.	YMC[1116]	Silica gel

Note: All costs are from the cited sources as of the listed date. Since costs change, they should be used as a rough guide only. For current costs, obtain a quotation from the manufacturer.

separations, HPLC systems are used. These use smaller-diameter particles with roughly the same column length to achieve a large number of plates. The pressure required is also increased significantly and the columns are usually made of stainless steel. These HPLC systems are thus significantly more expensive.

Complete systems are more expensive and are also listed in Table 5-1. Since these columns and systems are all of different sizes, have different numbers of theoretical plates, and have very different special features, these costs should not be used to directly compare systems. A chromatographic system should be rated on performance (that is capacity of feed for a given product purity), not on nominal equipment size. Most manufacturers have facilities available to try pilot separations of samples.

Examples of large-scale HPLC chromatograms have been published by the manufacturers[351,681,796,1065,1083] and very recently pilot plant results have been published by other users.[70,209,370,887,889,902,916] The results show that a properly designed and packed large-diameter column will give better separation than a smaller-diameter column. Examples of the separations which can be obtained are shown in Figures 5-9 to 5-11. Preparative performance of an Instruments SA Chromatopac Prep-100 instrument for purification of a red dye are shown in Figure 5-9.[70] This system is an axially compressed column which is 8.0 cm I.D. and a maximum of 1 m long. The column was packed with two 2 kg of a C-18 silica with particle diameters from 25 to 44 μm. A total of 1350 mℓ of feed was added to the column. The dye was concentrated at the head of the column, since water could not elute it. The dye was eluted with 4 ℓ of methanol and water (7.5:92.5) and was more concentrated than in the feed. The impurities were removed with 1.9 ℓ of a 50:50 methanol-water mixture. Final flush was done with 4 ℓ of methanol. Since fractions 5 and 6 contain most of the dye, a center cut was used for the purified dye. The Elf system for axial compression is quite similar, but columns up to 30 cm I.D. and 120-cm long are available.[796]

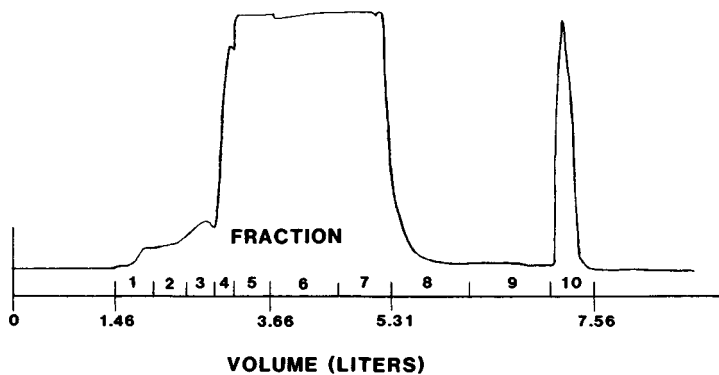Purification of cefonicid using a Waters Kilo-prep system where the columns are radially

FIGURE 5-9. Purification of D & C Red No. 33 with axially compressed chromatograph. (From Bailey, J. E., *J. Chromatogr.*, 314, 379, 1984. With permission.)
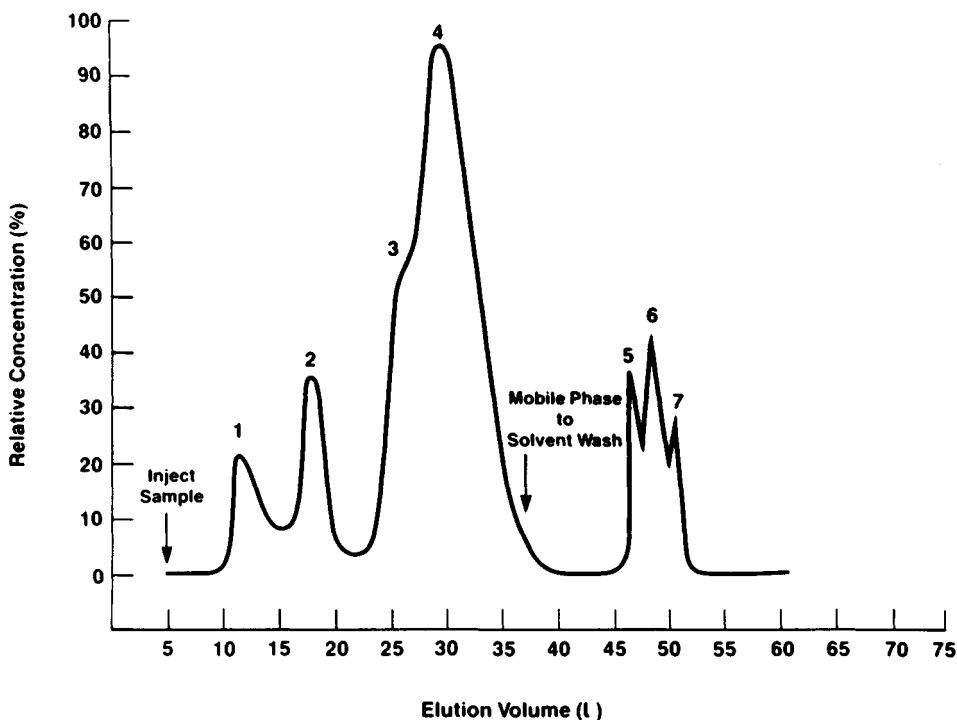

FIGURE 5-10. Purification of cefonicid by liquid chromatography. (From Cantwell, A. M., Calderone, R., and Sienko, M., *J. Chromatogr.*, 316, 133, 1984. With permission.)

compressed is shown in Figure 5-10.[209] Three 60-cm by 20-cm I.D. columns with approximately 8.8 kg of 55 to 105 μm C-18 silica per column were used for this separation. Injection was 270 g and water was the solvent. Note that the early compounds are well separated and could be removed earlier (see Chapter 7, Section II), but impurity peak 3 is barely separated from the cefonicid. A cut between peaks 3 and 4 will give greater than 93% purity of cefonicid. Higher purity could be obtained by recycling material of intermediate composition. Then 4 ℓ of methanol wash was used to rapidly elute most of the strongly adsorbed material. Although a small amount of silica appeared in the product, the weight loss of the packing was negligible and no decline in resolution was observed with re-
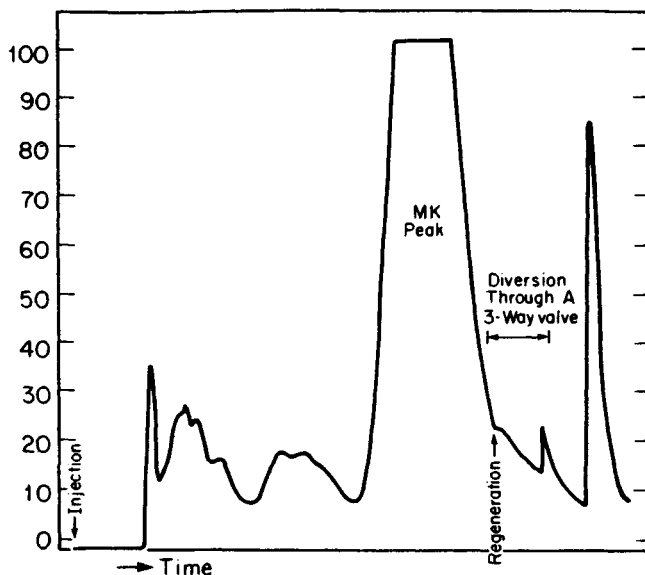
FIGURE 5-11.   Large-scale chromatographic separation of semisynthetic antibiotic (MK) in 15-cm I.D. column. (From Shih, C. K., Snavely, C. M., Molnar, T. E., Meyer, J. L., Caldwell, W. B., and Paul, E. L., *Chem. Eng. Prog.*, 79(10), 53, 1983. With permission.)

peated injections. Other applications of the Waters system have been reported.[191,338a,478,730a,887,1056,1065] The use of column switching is recommended[887] (see Chapter 7, Section II).

The separations shown in Figures 5-9 and 5-10 used columns developed by companies specializing in chromatography. Obviously, it is not necessary to buy a readymade column or system. A report on the development of a 15-cm I.D. chromatographic separator has been published by a group from Merck.[902] The complete development of the chromatographic system for the separation of a semisynthetic antibiotic (MK) is presented. In phase I of the study, 22 different preparative-scale reversed-phase C_{18} packings from 5 manufacturers were tried in an 1-cm I.D. column. The performance of the packings varied markedly from supplier to supplier and for some suppliers, from batch to batch.[371,902] Perhaps this is not surprising, since a reversed-phase packing is not a simple chemical. The performance of the packing will depend on the pore structure of the silica gel used and the details of the derivatization. Apparently, the buyer must beware and should do a use test as a major criterion before accepting a new batch of chromatographic packing. Once a suitable packing had been selected, phase 2, the scale-up and development of a large-scale system, was started. The system used a 15-cm I.D. by 20-cm-long guard column followed by the 15-cm I.D. by 40-cm-long main column. Details of the proprietary distributor and collector in the column were unfortunately not given. Feed pulses were 1.5 to 2.0 ℓ/min for 3 to 4 min with total organic solids of 40 to 80 g/ℓ and 8 g/ℓ of the desired solute, MK. Elution was with water, and regeneration following the MK peak used methanol, methanol and water, and pure water. The operation was completely automated. The results of one run are shown in Figure 5-11.[902] The final MK product had to be treated for silica contamination, since silica was leached from the packing. Apparently, no attempt was made to recycle either water or methanol. Some problems were experienced with deterioration of the packing material, and the authors noted the importance of manufacturing stable, selective, chromatographic packings with a long life.

The results shown in Figures 5-10 and 5-11 are fairly typical for pharmaceutical separations. Complete resolution is often not obtained. A wash or programming step is required to remove strongly adsorbed materials, and a large number of undesired species are present. Higher throughputs could be achieved with recycle or by using the methods discussed in Chapter 7. Higher throughputs could probably also be achieved by adsorbing the strongly adsorbed materials first in a guard column, which operated as an adsorber, or on-off chromatograph. This column could be heavily loaded before it was counter-flow regenerated with methanol. The chromatography column separating the desired compound could then receive multiple pulses of the pretreated feed without requiring a methanol wash. An occasional methanol wash would be useful to help retain capacity.

These examples illustrate that standard, reverse-phase packings can be used in relatively large-scale HPLC systems to separate complex feeds containing very similar compounds. Although reports on commercial production use are scarce,[887] many pharmaceutical companies are either using large-scale HPLC for production, or are extensively studying this possibility.

Liquid-liquid chromatography (LLC) has been used to a lesser extent than adsorption or bonded-phase systems. In LLC, the stationary phase is a viscous liquid coated on an inert porous solid.[930] These packings will be cheaper than using a bonded-phase packing, but bleeding may be a problem. LLC has the advantage that a large variety of stationary phases can be used. Preparative -scale LLC has been extensively studied in the nuclear industry for recovery and purification of uranium, plutonium, americuium, and neptunium.[164,350,683] In that industry, the technique is called extraction chromatography. A major advantage of extraction chromatography is that standard solvents such as tri-*n*-butyl phosphate (TBP) can be used to impregnate the inert supports. Thus, the huge literature on extraction can be tapped, and the amount of preliminary work to find a good stationary phase is drastically reduced. Extraction chromatography is more convenient in that extraction and sharper separations are achieved. Preparative-scale studies have been reported for separation of plutonium-irradiated targets using a 6.2-cm I.D. column,[164] for both uranium and plutonium purification with a 12-cm I.D. column,[360] and for recovery of neptunium, plutonium, and americium with 15-cm and 6-cm I.D. columns.[683]

Adsorption chromatography can also be used for large-scale applications. Molecular sieve zeolites have been used in a preparative scale (5-cm I.D. column) for recovery of ^{137}Cs from radioactive wastes.[1671] Large-scale liquid adsorption chromatography with recycle using zeolite has also been suggested for separation of dimethylnaphthalene isomers.[479] The very large-scale systems discussed below used adsorption. Zeolite molecular sieves have been used on a very large scale in simulated moving bed systems (see Chapter 6, Section V.B.2). The zeolites are expensive compared to other common adsorbents, but they are very cheap compared to reversed-phase chromatographic packings. The zeolites can be chemically modified to increase selectivity. Unfortunately, pore sizes are not large enough for many molecules of biological interest.

In very large-scale systems, the amount of packing used becomes very large. Unless one is lucky and a packing with a large selectivity (greater than 2.0) is readily available, a sorbent/solvent development program is needed. Several very large-scale chromatographic systems have been reported including the historical examples.[53,319,401,471,543,898,908,937] and more recent examples.[492,889,892] The Arosorb process developed by Sun Oil Co. in the early 1950s was a simple large-scale LSC system using elution.[319,471,908] Silica gel beds from 3 to 10 ft in diameter and from 15- to 25-ft high were used. Crude xylenes were used to desorb the adsorbed benzene and toluene. This system was used commercially, but has been discontinued since other separations became more economical.[319]

The recent examples are of considerable interest. Pilot plant studies for the purification of *p*-xylene and ethylbenzene from a mixed xylenes plus ethylbenzene feed were used to
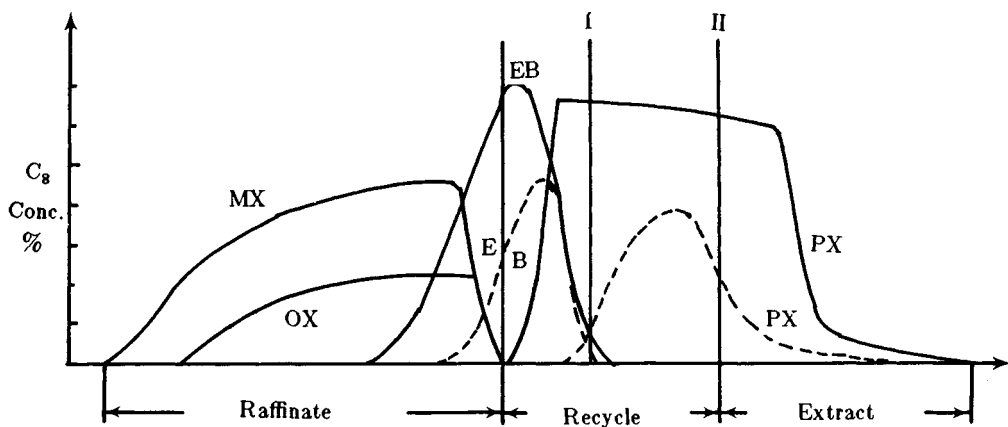
FIGURE 5-12. Pilot-plant scale chromatogram for purification of *p*-xylene.[892] EB = ethylbenzene, MX = metaxylene, OX = orthoxylene, PX = *p*-xylene. ———, Process with recycle; ------- process without recycle; I, cut design without recycle; II, cut design with recycle. (From *Ind. Eng. Chem. Product Res. Devel.*, 21, 656, 1982. With permission.)

design a proposed large-scale system.[889,890,892] One of the proposed systems would produce 70,000 tons/year of *p*-xylene. The adsorbent was specially prepared (and unspecified) and had a selectivity from 6 to 8. A charge of 270 tons of adsorbent would be required. A pilot plant chromatogram is shown in Figure 5-12.[892] The dotted lines show the results for ethylbenzene and *p*-xylene without recycle, while the solid lines show the concentration with recycle. The recycle operations can produce more *p*-xylene, particularly when the fresh feed has a higher concentration of *p*-xylene. In addition, the recycle operation is less sensitive to deterioration of the sorbent. Instead of recycle, additional small columns can be used to further purify partially separated material[890] (see Chapter 7, Section II). The *p*-xylene was recovered from the unspecified desorbent by distillation. The desorbent should have a selectivity for the adsorbent in between that of ethylbenzene and *p*-xylene.[890] The process may have advantages when both *p*-xylene and ethylbenzene are desired, since the competing simulated moving-bed process (Chapter 6, Section IV.B.2) would require two columns.

Quite large-scale chromatographs are used in the sugar industry for enriching fructose (see Chapter 6, Section V.B.2) for a competing process), and for recovery of sucrose from cane molasses,[482] and the separation of fructose from glucose.[490] The mechanism for separation of sucrose from molasses is ion exclusion chromatography, but the operation is similar to other liquid chromatographs. Commercial systems range from 0.5 to 4.0 m in diameter and from 2.0 to 12.0 m high. One plant for Amino Gmbh will process 60,000 metric tons/year of molasses feed in seven 3.6-m-diameter by 12-m-high columns. Typical results are shown in Figure 5-13.[482] Note that considerable overlap of the peaks is allowable and that two separate recycle streams are used. Water is used as elutant, so no attempt is made to recycle the water. All of the very large-scale systems have used packings such as zeolites, activated carbon, or ion exchange resins which are much cheaper than reversed-phase chromatographic packings.

Note that there are qualitative differences between the operation of the very large-scale systems and the HPLC systems. In the very large-scale systems, throughput is of primary importance. Sloppy separations with large recycle streams are allowed. Adsorbents with high selectivities are used and the separations are fairly simple. Every effort is made to avoid dilution and to keep the downstream separation as simple as possible. Thus, gradients and additional eluants were not used. In the HPLC systems, particularly for pharmaceutical applications, purity is much more important and cost is less important. Thus, less effort was
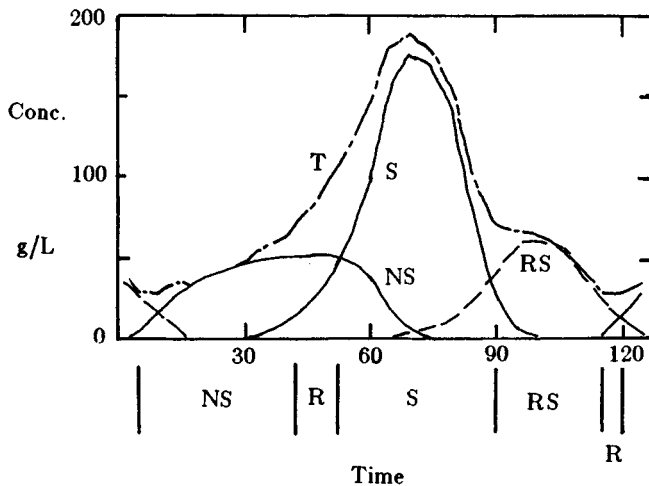
FIGURE 5-13. Purification of cane molasses by large-scale liquid chromatograph.[482] Key: NS = nonsugars; R = recycle; RS = reducing sugars; S = sucrose; T = total concentration. (From *Chem. Eng.*, Jan. 24, 1983. With permission.)

made to fully utilize the column and gradients are often used to elute strongly adsorbed material.

VI. SIZE EXCLUSION CHROMATOGRAPHY (SEC)

SEC (also known as gel permeation chromatography or gel filtration) is a liquid chromatographic technique, but it is based on a different mechanism than adsorption or partition chromatography. In SEC, a packing with a controlled size distribution of pores is used. Small molecules can diffuse into all of the pores, while large molecules are excluded from the pores. Molecules of intermediate size are excluded from a fraction of the pores. Since only the volume outside the particles is available to large molecules, the large molecules travel quickly through the column and exit first. Small molecules have the entire liquid volume available and thus take longest to exit from the column. Intermediate-size molecules exit somewhere in between. Thus, in the ideal case, the separation mechanism is the exclusion of molecules from some fraction of the pores based on the size of the molecule in solution. Solutes which are hydrated or associate in solution will appear larger and exit sooner than otherwise expected. Many secondary effects can occur,[311,781] but size exclusion is the dominant mechanism. Details of the phenomena occuring during SEC are covered in standard references.[53,197,311,549,781,1109]

In the ideal case where adsorption and ion exchange are absent and only size exclusion is occurring, the solute movement theory is easy to apply to SEC. The solute velocity is given by Equation 2-30 with the adsorption equilibrium constant $k_i = 0$. The parameter which distinguishes different species is the fraction of volume of pores a species can penetrate, K_{Di}. Equation 2-3 can be used to determine K_{Di}. The solute movement diagram will consist of straight lines and will look like Figure 2-5. The range of possible solute velocities ranges from

$$u_{large} = v \qquad (5-7)$$

for large molecules where $K_{Di} = 0$ to

$$u_{small} = \frac{v}{1 + \frac{1 - \alpha}{\alpha}\,\epsilon}$$

(5-8)

for small molecules where $K_{Di} = 1.0$. This range is quite limited when compared to adsorption or partition chromatography, where the range can essentially be infinite. The advantage of a restricted ranged of solute velocities is that even the slowest species (small molecules) must exit by the total void volume of the column unless adsorption or ion exchange occurs. Thus, the next feed pulse can be added quickly and capacities are fairly high. Also, the method is relatively insensitive to composition and mild elution conditions can be used. The disadvantage of SEC is it is difficult to fractionate molecules which are close to the same size. Thus, the major large-scale uses of SEC have been for desalting where small molecules such as salts are removed from large molecules such as proteins.

The linear chromatographic theories (see Chapter 2, Section VI) can be applied to SEC. The van Deemter Equation 2-117 and modified forms of the van Deemter equation, Equations 2-122 and 2-124, are applicable to SEC. The mass transfer (C) terms in these equations are inversely proportional to the diffusivity of the solute. When large molecules are fractionated, the mass transfer resistances for diffusion into the pores will be high. This problem will be common for any type of chromatography fractionating large molecules. The use of small particles will greatly decrease the HETP, but it also increases the pressure drop or reduces the allowable flow velocities. In desalting operations, the large molecules do not enter the pores and the C terms disappear in the HETP equations for these large molecules. The scaling procedure described in Chapter 5, Section III.C, is thus less useful for desalting. Since the diffusivities are high for the small molecules which do enter the pores, the HETP can be small for these molecules also. Thus, in desalting, a fairly rigid gel with low HETPs can be used.

A variety of size-exclusion media are commercially available.[306,549,663a,827,1076,1109] Rigid aerogels such as controlled-pore glass or porous silica are the easiest to use since high velocities can be used with low pressure drops. Unfortunately, nonspecific adsorption can be a considerable problem, particularly for biochemicals. To a large extent, nonspecific adsorption can be eliminated by using coated or derivatized silicas,[827] but they are more expensive. Cross-linked dextran gels (Sephadex), polyacrylamide gels (Biogel P), and various agarose based gels (Biogel A, Sepharose, and Ultrogel) are hydrophilic and usually have a minimal interaction with biochemicals.[305,549] However, when these gels are made with the large pore sizes necessary to fractionate large molecules, the gels are soft. This sharply limits the flow rates and even the height of packing which can be used. This is the major problem for large-scale SEC fractionation. Special column designs have been developed for these soft gels.[549] For desalting, much smaller pore sizes are required and the Sephadex and Biogel P gels are much stronger and less compressible. New gels which are stronger and compatible with proteins are being developed.[162,549,827,1003] Column design and operation for the rigid aerogels and for desalting can be similar to LC columns.[14,275,276,306,801]

Scale up requires that the ratio of pulse size to column volume be kept constant.[228,470,549] In addition, the ratio of sample band width to bed height should be kept constant.[549] With stacked columns, keeping the bed height constant and increasing the diameter is suggested.[470,549] For single columns, keeping the column diameter times superficial velocity constant and keeping the length to diameter ratio constant has been suggested.[228] This latter procedure will lead to larger volume systems and probably is not necessary.

Commercial desalting or group separation by SEC has been practiced for many years;[293,306,348,548,549,1109] SEC was used commercially for removing lactose and salts from protein found in whey[307,348,548,549,659] (see also Chapter 7, Section V and Chapter 8, Section III). However, ultrafiltration proved to be more economical, and this application has ceased.
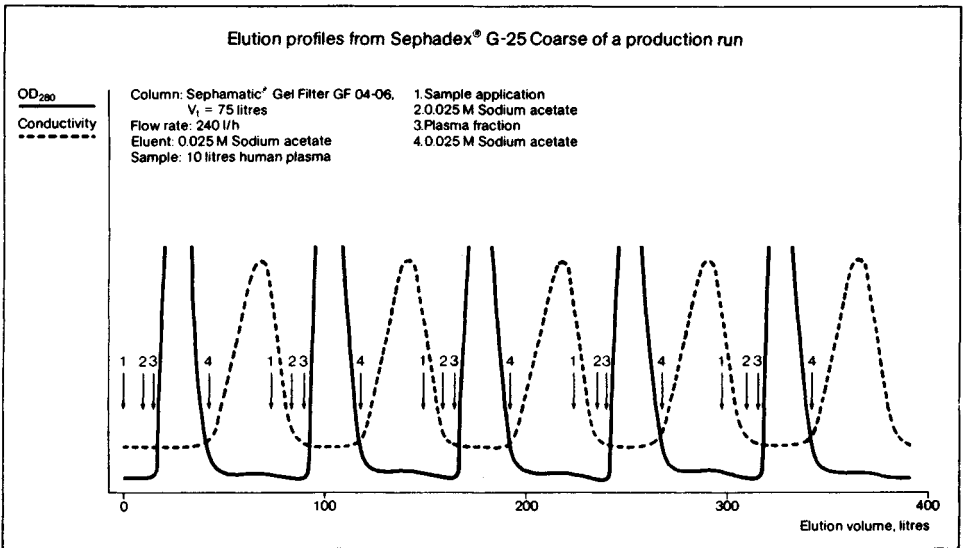
FIGURE 5-14. Desalting of human blood plasma on Sephadex G-25.[296] Column is a Sephamatic gel filter GF 04-06. Total volume, 75 ℓ; flow rate, 240 ℓ/hr. Eluent is 0.025 M of sodium acetate. Sample is 10 ℓ of human plasma. 1, Sample application; 2, 0.025 M of sodium acetate; 3. plasma fraction; 4, 0.025 sodium acetate.

Desalting is currently in commercial use for the purification of plasma proteins,[293,294,296,549] as one step in other protein purification procedures,[294,296,306,549,1109] in the food industry,[306] and as one step in some human interferon purification procedures.[1086] When several different types of chromatography are connected (see Chapter 7, Section II), SEC is useful to change solvents or buffers between systems. The equipment and operating procedures for desalting applications are similar to those used in low-pressure LC.[14,295,306,545,549,801,803] SEC with gels operates at relatively low pressure. Columns made of acrylic plastic, glass, and stainless steel are commercially available in diameters up to 1.2 m.[14,47,549,800,801] The columns may be equipped with a floating head so that different amounts of gel can be used.[14] Slight compression of the gel is advantageous, since it gives sharper, quicker separations.[343,612] This occurs because the compression results in more uniform packing, reduces α and may slightly reduce ϵ. Slurry packing with gravity or pressurized flow or hydraulic compression can be used for packing columns. Columns should be pulse tested to determine the HETP. With this procedure, an HETP of 0.06 cm was obtained for sodium chloride with Sephadex G-10 in an 80-cm-diameter column.[545] For desalting, the typical pulse size is 25 to 30% of the column volume.[306] Upward flow is used to minimize gel compaction. The flow rate depends on the gel type, particle diameter, and column configuration. The smaller the pores in the gel, the larger the particle size, and the smaller the column, the higher the linear velocity can be. However, coarse gels have considerably more zone spreading and dilution than fine gels. For processing biological samples, care must be taken to remove suspended material by centrifugation and/or filtration. When not in use, the column can be maintained free from microbial contamination by storing with 0.01 M sodium hydroxide solution.[295] For pharmaceutical products, special care is required to keep the entire chromatographic system sterile.[294,295]

An example of the desalting of human serum albumin is shown in Figure 5-14.[296] Repeated sample injections are shown. Note that injection occurs before the salts are totally out of the column. Production rate could be increased by using larger samples and recycling overlap. However, since blood plasma procedures usually work on a batch basis and use the column

only part time,[293-295] the SEC production rate is probably not a limiting factor. Chromatographic procedures appear to be economical for relatively small blood banks (approximately 500 ℓ/week or less), but Cohn ethanol fractionation is cheaper on a larger scale.

Preparative-scale SEC with more rigid Sephacryl S-200 on a 25-cm I.D. by 80-cm column and with Ultrogel AcA 34 in a 20-ℓ column gave higher flow rates than Sephadex columns.[876] TSK gels from Toyo Soda are also rigid and have good flow properties.[1003] These gels are probably being used in larger-scale applications.

The separation of synthetic and natural polymers by SEC is common laboratory practice, but commercial separations have been uncommon. The reviews in the literature[1014,1109] discuss fairly modest diameter columns. When rigid gels can be employed, the columns and operating procedures will be similar to other LC systems.[1014,1109] When polymers are being fractionated, the selectivity between two polymers of similar size will be very close to 1.0. Thus, very long columns may be needed.[1014,1109] The larger-diameter preparative columns (up to 10 cm[1014]) were easier to pack than analytical columns and the preparative columns gave lower HETP when tested with dilute pulses. The separation becomes poorer with more concentrated samples because of viscosity increases, hydrodynamic radius changes and restricted diffusion in pores.[1014] To increase throughput, larger sample volumes should be used instead of higher concentrations.[1014,1109]

In the pharmaceutical industry, some commercial fractionation of biomolecules is done with soft xerogels,[294-296,545,549,802] but all of it is for relatively small molecules. In the last step of albumin purification, both salts and contaminating proteins are removed by SEC.[294,296] Insulin is also commercially purified by SEC[549,802] using Sephadex G-50 Superfine Special Grade. These gels are somewhat compressible and do not have good flow properties. Since the gel is too compressible, tall, large-diameter columns cannot be used. Special[14,294,544,545,548,549,800,802,803] arrangements of short, fat columns in series have been developed. In this way, the gel can be supported while a long separation distance is obtained. One of the commercial distribution and withdrawal systems has six pipes arranged in a hexagonal pattern.[544,800] The six inlets or exits flow into or out of a thin mixing chamber below or above the nylon mesh support screen. The use of more inlets and outlets gives better results at the price of increased complexity.[544] An alternate commercial design[14] uses stacked columns which have adjustable lengths and uses a combination of flow distributor and frit. Sizes up to 44 cm in diameter with length variable from 18 to 20 cm (L to diameter = 18:44) are available. Upflow is used since the flow and gravity forces partially cancel each other. The use of a segmented system also provides flexibility if the same equipment is used for many separation problems. These short, fat columns are also used for ion exchange and affinity chromatography of biologicals (see Chapter 5, Section VIII).

For insulin manufacture, six 37-cm-diameter by 15-cm-high columns are used in series[802] (note the ratio of length to diameter is 15:37). A seventh column is kept as a reserve in case the packing on one of the columns needs to be regenerated or replaced. Flow rates for insulin manufacture are 7.4 mℓ/cm² (8.0 L/hr).[802] Even lower flow rates would have to be used if softer gels were used for larger molecules. These low flow rates make large-scale fractionation of most proteins impracticable with current SEC gels.

Clearly, a breakthrough in SEC media is required for increased use of large-scale SEC fractionation of proteins and other large biomolecules. What is needed is a chemically stable, rigid material with large, controlled-distribution pores which is hydrophilic, biocompatible, and relatively inexpensive. Coated silicas[827] and TSK gels[1003] seem to meet all these criteria except cost. Such a media would also have considerable use for affinity chromatography, ion exchange, and liquid chromatographic separations of large biomolecules.

VII. GAS CHROMATOGRAPHY SYSTEMS

There has been considerable interest in both preparative-scale[275,874,1018,1124] and commer-

cial-scale[43-45,158-161,276,277,279,352,532,794,864,868,873,874,984,1006,1007] GLC for many years. This interest has followed a roller coaster. Considerable early interest following the pioneering analytical studies of James and Martin[542] died out when large-scale GLC proved to be more difficult than it first appeared. A second wave of interest is now in progress with much of the work appearing from either the group at ELF[43-45,158-161,352,532,864,1006,1007] (this work was recently extensively reviewed),[158] or Conder's group at the University College of Swansea.[276-279,904] Other studies of large-scale GLC have included the use of moving beds (Chapter 6, Section II.B.2), the use of simulated moving beds, (Chapter 6, Section V.B.4), and the use of rotating systems (Chapter 8, Section II). The unique advantages and disadvantages of GLC will ultimately determine where it is used commercially.

Large-scale GLC uses a system very similar to the process shown in Figure 5-1. The feed and recycle streams need to be vaporized either before or in the injector. The separators are usually condensers or cold traps running at quite low temperatures. The separators are usually simpler than the separation systems required in liquid systems if solvent is to be recycled. The cleanup of the carrier gas is usually by adsorption. The processes discussed in Chapters 3 and 4 can be used for cleanup.

The separation mechanism in GLC tends to be quite different than in liquid systems. First, since separation is based on absorption into a liquid coating, the isotherm shape in GLC is the "unfavorable" isotherm shape shown in Figure 2-2B. With this type of isotherm, the location of shock and diffuse waves is reversed from where it occurs with favorable isotherms (see Chapter 2, Section IV.A.2). Thus, when a pulse is input, the leading edge is a diffuse wave and the tailing edge is a shock. In addition to the isotherm effect, there will be sorption effect in the usual case where a fairly concentrated feed is injected (see Chapter 2, Section IV.C.). The sorption effect produces a shock at the front of the wave and a diffuse wave at the rear. To a large extent, the isotherm and sorption effects can be made to cancel each other out, resulting in quite sharp peaks. This cancellation appears to be unique to GLC and does not occur in GSC with a "favorable" isotherm where the isotherm and sorption effects reinforce each other. Because of this cancellation, the particle diameter scaling discussed in Chapter 5, Section III.C will be less useful for GLC. In GLC, the isotherm and sorption effects are both temperature dependent. The optimum temperature, known as the Valentin temperature, occurs where the isotherm and sorption effect balance. This optimum temperature can be calculated from[864]

$$p_A^o \;=\; p_{out}\,\frac{3}{4}\,\frac{(p_{in}/p_{out})^4 \;-\; 1}{(p_{in}/p_{out})^3 \;-\; 1} \tag{5-9}$$

where p_A^o is the vapor pressure of species A, and p_{in} and p_{out} are the gas inlet and outlet pressures. Equation 5-9 gives different temperatures for each component. Typically, the Valentin temperature is about 15°C above the boiling point of the main component. This assumes that this temperature is not too high for the stationary phase.

A second difference between GLC and adsorption chromatography systems is the stationary phase is a liquid coating on an inert porous solid. We would like this liquid coating to stay put. If the temperature is too high, the stationary phase will slowly vaporize, which causes both a slow deterioration in the column and contamination of the products. As a rule of thumb,[1006] pick a temperature so that less than half of the stationary phase is gone in 2 years. This is about 50 to 80°C less than the maximum operating temperature of the stationary phase.[864] This requirement is much more severe than in analytical chromatography because the large-scale column is designed to stay on stream continuously. The stationary phase must be chosen to have a high enough operating temperature. A high selectivity is also desirable, but probably less important.[864,1006] Since separation is essentially based on relative volatility, it is often difficult to obtain a high selectivity. If the relative volatility is greater

than 1.2, distillation is recommended instead of GLC.[158] The solid support should be inert or deactivated to prevent undesirable tailing due to adsorption. To have long stationary phase life, the entering streams should be deoxygenated.[158] Incidentally, measuring parts per million contamination of the products with the stationary phase may be fairly difficult. The measurement certainly cannot be done with an analytical GLC using the same stationary phase.

Another difficulty with a liquid stationary phase is "overflooding". When solute dissolves in the stationary phase, the liquid expands. If the expansion is too great, the liquid will overflow the pores of the inert solid and be pushed down the column. This overflooding can rapidly destroy the column. To prevent overflooding, the feed in input as a mixture with carrier gas, and the concentration of solutes is controlled. Suggested maximum concentrations to use vary from about 0.3 mol fraction,[864] to between 0.2 and 0.5 mol fraction[277] to 0.15 and 0.5 weight fraction.[278] As long as overflooding does not occur, larger concentrations are an advantage, since product concentrations are higher. This makes condensation easier and throughput will be increased. When overflooding becomes a problem, throughput can be increased by increasing the injection period instead of the concentration. Stationary phase loadings of 10 to 20 wt% are used to help prevent overflooding.[158]

A possible solution to the problems involved in using a stationary liquid phase is to use a "bonded" liquid phase.[335] These phases have been recently developed for analytical GLC. They have lower HETP values, but also lower capacity. Apparently, they have not been tried in large-scale GLC systems.

Operating pressures and temperatures are related. Raising the average pressure increases the mass of gas which can be fed, but it does not change the capacity of the stationary phase without overflooding (see below). Raising the pressure will raise the boiling points of the solutes and the Valentin temperature, but it makes product condensation easier. Operation at fairly high outlet pressure is advantageous as long as the Valentin temperature is not too high for decomposition of the feed or loss of stationary phase. Vacuum operation should probably be avoided. One advantage of GLC is the residence time is quit short compared to vacuum distillation, and thermally sensitive compounds can often be processed.

As in all types of chromatography, the column-packing procedures is absolutely critical. All columns should be tested with a dilute pulse after they are packed. The commercially used procedures are proprietary[43-45,158-161,352] and provide columns with HETP < 1 mm in columns up to 400 mm in diameter. Particle sizes used commercially are as small as 60 to 180 mesh.[159]

The carrier gas needs to be recycled. The HETP is lowest for the carrier gas which has the highest solute diffusivity (see Chapter 2, Section VI.C). This criterion favors hydrogen as the carrier gas and hydrogen is used commercially.[43-45,158-161,352,532,864,1006,1007] Conder's group[277,278,904] worries about the safety of hydrogen and uses nitrogen or helium which have higher HETPs, but are safer. In my opinion, the widespread use of hydrogen in many industries shows that with care, it can be used safely.

A column length between 1 and 3 m has been suggested.[158] The optimum length depends on $\alpha_{2,1}$, k' and the HETP.

Special care is needed in the design of the condensers for recovery of the products. If cooling is too rapid, a fog will form, since diffusion of vapor to the wall is much slower than the rate the gas is cooled. Removal of the resulting small droplets is difficult, although mesh screens help. Useful hints on condenser design are given elsewhere.[277,278,864,904,1007]

The evaporator-injector design also needs special care. A short residence time is desired to minimize thermal degradation. At the same time, complete vaporization of feed is required or the separation deteriorates badly.[904] Spraying the liquid into the carrier gas in the vaporization chamber,[864] or continuous operation of a vaporizer which services several columns operating in parallel[904] is suggested.

Automatic operation is very desirable. If timers are used for control great care must be

taken that gas flow rates and temperatures are constant. This includes thermostating pressure regulators. There will be a start-up period since several hours may be required to heat a large column to its operating temperature.

Several industrial applications of large-scale GLC have been recently discussed in the literature. An excellent review of Elf's system is available.[158] A 100,000 ton/year GLC plant has been built for separating normal paraffins from isoparaffins, cycloparaffins, and aromatics using molecular sieves as the packing.[532] This example represents an easy separation compared to the other examples which represent difficult separations. A system for purifying perfume ingredients and flavor chemicals manufactured from terpene chemicals went on stream in October 1979 at the Glidden division plant of the SCM Corp. in Jacksonville. Fla.[45,158,159,161] The 100-metric ton/year plant produces products with purities about 99% using a 400-mm I.D. column. The industrial (400-mm I.D.) column had lower HETP and produced higher-purity product than either the pilot plant (125 mm I.D.) or laboratory (40-mm I.D.) columns.[159] Economics and energy use for the plant were reported.[158,159] GLC is suggested for systems with relative volatilities less than 1.1, while distillation or vacuum distillation is preferred when the relative volatility is greater than 1.2.[158,159] It is interesting that the suggested relative volatility where GLC is recommended has steadily dropped over the years.[158,159,275,864] This may be due partly to advances in vacuum distillation, but probably reflects a more thorough evaluation of the economics of large-scale GLC. A large number of compounds have been successfully separated on pilot plant and small commercial scales.[158,160,161,352,513,864,1007] The successful separation include a variety of fragrance and flavor chemicals, pharmaceutical products, and organic chemicals. For calculation examples and comparison of results, the separation of α and β pinene has been used.[158,161,275,278,864,867,904] For difficult separations, heart and side cutting, recycle and two-step procedures are used.[158,160,513,864,1007] Chromatograms of the pilot-plant scale results are available elsewhere.[158,160,864,1007] Results from the commercial-scale (40.0-cm I.D. by 1.5 m long) column are given in Table 5-2.[158] Note that the recycle streams are close to the feed concentrations.

Experience in the U.S.S.R. with large-scale GLC has included the purification of 120 tons/year of thiophene, production of 1200 tons/year of 99.8% pure toluene in a 1.2-m diameter column and production of 92% pure commercial indole in a two-step process from a 4% feed.[873] The major problem reported was finding mixtures where large-scale GLC is economical.[873] This is an interesting conclusion, particularly since it was from a Communist country.

Supercritical fluids have been extensively explored for difficult separations, particularly on an analytical scale.[413,790,878] Large-scale, supercritical chromatography is an intriguing idea because recovery of the carrier, probably CO_2, would usually be very simple.[794] Dropping the pressure or changing the temperature will cause the solutes to drop out. The major cost for recycle would be recompressing the carrier. For biochemical systems, supercritical chromatography is of considerable interest.[413] Solubility and density can be almost as large as in liquid systems. The diffusivity is roughly an order of magnitude larger, while the viscosity is over an order of magnitude smaller. The result is significantly lower Δp and HETP values. Selectivities can be varied considerably by adding modifiers to the supercritical fluid, and various programming techniques can be used. In addition, CO_2 is completely acceptable to the FDA. No large-scale applications have been reported yet, although research is in progress and an 80-mm I.D. prototype column has been constructed.[226]

It is interesting to compare large-scale GLC and LC. A very large number of stationary phases are available for GLC, and thus one can probably quickly find a system with a reasonable selectivity. However, in a longer-term development program, larger selectivities can probably be attained with adsorption. Also programming is a much more powerful tool with liquid systems than with gas systems. The recovery of liquid products from the carrier gas is usually fairly easy in GLC. Separation of the product from a solvent will usually be

Table 5-2
COMMERCIAL GLC SEPARATIONS IN 40-CM I.D. BY 1.5-M LONG COLUMN[158]

Concentrations (%)

Products	Feedstock	Product	Reject	Recycle	Operating conditions
Linalol	95	99.3	61.6	95.2	Temperature: 180°C;
Fenchol	4.4	0.2	37	4.8	flow rate: 60 m³/hr;
Other compounds	0.6	0.5	1.4	0.0	carrier gas: H₂;
					outlet pressure:
					atmospheric;
					passified support;
					feedstock: 16.4 kg/hr;
					product: 11.7 kg/hr
Thenylamine	94.5	99.3	71.8	94.1	Carrier gas: H₂; outlet
Light compounds	0.8	0.35	2.5	0.7	pressure: atmospheric;
Heavy impurity	4.7	0.35	25.7	5.2	feedstock: 7.6 kg/hr;
					product: 6.1 kg/hr
Trifluoromethylbromobenzene		(1) (2)			Carrier gas: H₂; outlet
Light impurities	4.0	0.6 8.1	1.4	1.4	pressure: atmospheric;
1,3	91.0	98.9 1.9	22.2	92.2	feedstock: 8.9 kg/hr;
1,4	5.0	0.5 90.0	36.4	6.4	product 1: 7.4 kg/hr;
					product 2: 0.2 kg/hr

From Bonmati, R., Chapelet-Letourneax, G., and Guichon, G., *Separ. Sci. Technol.*, 19, 113, 1984. With permission.

more difficult, but in many LC applications, particularly when water is the solvent, the solvent is not reused. The design and operation of a GLC system appears to be more difficult than the design and operation of a LC system. More information is available on packing large-scale LC systems, and there are more suppliers. GLC has the unique advantage that sorption and isotherm effects can partially cancel each other. On the other hand, lower HETP can be obtained in LC systems. Finally, there are many chemicals, particularly those from biotechnology, which cannot be vaporized and thus, large-scale GLC is not feasible. I think that both large-scale GLC and LC will be used, but I am willing to bet that large-scale LC systems become much more common.

VIII. ON-OFF CHROMATOGRAPHY: BIOSPECIFIC AFFINITY AND ION-EXCHANGE CHROMATOGRAPHY

In on-off chromatography, the desired solute(s) are very strongly adsorbed under the conditions (T, pH, ionic strength, etc.) used for the feed step. Most of the undesired species are either weakly adsorbed or not adsorbed. After the column is loaded, any remaining nonadsorbed species are washed out. The conditions of operation are changed and the adsorbed species are eluted, usually with flow reversal. Continuous or stepwise gradients can be used to elute different adsorbed solutes one by one. The eluants are then washed from the column for the next cycle. The method differs from elution and displacement chromatography since the adsorbed solutes do not migrate through the column and the separation of adsorbed species is done by changing the elution conditions. The method can be applied to any sorption or partition process with very high selectivities between retained and unretained components. it has been most commonly used with biospecific affinity chromatography and IEC. General details of the process and application of solute movement theory (Figure 5-8) were discussed in Section IV.C.

A. Ion-Exchange Chromatography

IEC can be operated as elution, displacement, or on-off procedures. Elution and displacement operations will be similar to the liquid adsorption chromatography applications (Section V). On-off procedures are used when conditions can be set so that mainly the desired species are strongly sorbed and can then be eluted separately. Applications for hydrometallurgical solutions and wastes have been reported.[431] A semicommercial IEC is being used by Asahi Chemical in Japan to produce 500 kg/month of rare earths.[46] Kilogram quantities of promethium,[1084] americium,[1085] and [244]curium[193] have been purified by large-scale, on-off, IEC. Following the feed and wash steps, the desired ions were eluted with a buffered chelating agent such as diethylenetriamine pentaacetic acid (DTPA). An extensive review of ion-exchange applications in nuclear chemical engineering has recently been published.[882]

Commercial purification of antibiotics[548] and proteins[129,294,295,545,548,549,803] are often done by on-off IEC. Proteins are zwitterions and the net charge can be changed by changing the pH. Since the proteins are held at multiple sites, they effectively do not desorb until conditions are changed. Thus, it is often easy to sorb the desired protein and then remove the proteins one by one using gradient elution or displacement.[795] The resulting separations is still somewhat nonspecific. Further separation can be obtained by sending the solution to an ion-exchange column of opposite charge. Usually, basic proteins (isoelectric point above 7.0) are adsorbed on cationic exchangers at a pH less than the isoelectric point, and acidic proteins are adsorbed on anionic exchangers at pH above the isoelectric point. This procedure keeps the pH near neutral and helps to prevent denaturation. A typical feed would be pretreated by centrifugation, filtration, precipitations, etc. and then would be chromatographed in an anion column and then perhaps a cation column. The preliminary ion exchange may be done batch using a centrifuge (see Chapter 8, Section III), since suspended solids will be less of a problem. Desalting and final cleanup are done by SEC and the purified protein is concentrated by ultrafiltration.

The ion exchange of proteins requires ion exchangers which are hydrophilic, have large pores, and have no nonspecifc adsorption. Currently, most commercial ion-exchange processes for proteins use modified agaroses and celluloses. Unfortunately, these packings are soft and the same precautions used for soft SEC gels must be used[295,545,549,803] (see Section VI). Short, fat columns are commercially available for these applications.[14,47,549,800] However, unlike SEC, a long column is not required. Once a solute is sorbed, there is no further zone spreading. The only zone spreading which occurs is due to mass transfer resistances which cause the shock wave shown in Figure 5-8B to spread out. Thus, excellent separations can be obtained in short columns with high flow rates. Better ion-exchange packings for protein separations are being developed,[828] and will greatly increase the feed rates which can be used.

Commercially, human blood proteins, insulin, antithrombin, egg-white lysozyme, growth hormones, antigens, monoclonal antibodies, enzymes, and other biochemicals are purified using IEC as one step of the process.[293,349,803] An example of anion exchange chromatography for desalted human plasma is shown in Figure 5-15.[803] The column used was 15-cm high and 37 cm in diameter (16-ℓ volume). The sample applied was 42 ℓ, which illustrates the large dilute samples which can be applied in on-off systems. Stepwise gradient elution was used as shown in Figure 5-15. After the residual proteins have been removed, the column must be re-equilibrated with 0.025 M sodium acetate pH 5.2 before the next pulse is added. Other examples are readily available.[129,294-296,349,470,545,549,803]

Columns can be scaled up by keeping the weight of protein per unit cross-sectional area constant.[470] Height is usually kept constant, and short, fat columns are used with gels.

A different flow design has been used by AMF in the Zetaprep system for IEC.[67,68] Since a long flow path is not required, an annular cylindrical geometry with radial flow from the outside to an empty inner tube is used. This results in a low velocity in the outer portion
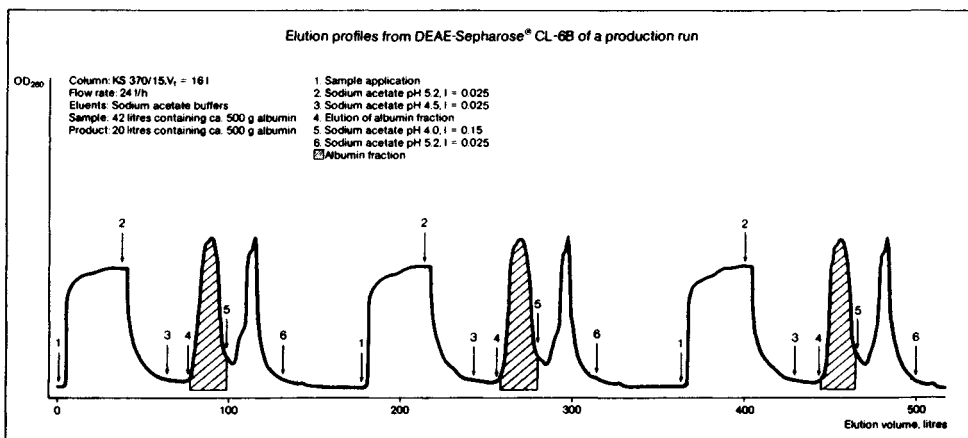
FIGURE 5-15.   Elution profile of desalted human plasma in 0.025 M sodium acetate pH 5.2 on DEAE-Sepharose CL-6B.[803] Flow rate 23.6 ℓ/hr. (1) Wash with 0.025 M of sodium acetate pH 5.2. Peak is mainly IgG; (2) elute with 0.025 M of sodium acetate pH 4.5. Peak is albumin; (3) elute with 0.15 M of sodium acetate pH 4.0. Peak contains residual proteins.

of the packing and a high velocity in the inner portion. Capacity is increased by making the cylinders longer and then by adding more tubes. Thus, the system is modular.

B. Biospecific Affinity Chromatography

In biospecific affinity chromatography the biochemical in solution has a specific affinity or molecular recognition of a compound attached to an inert matrix. Since the sorption is based on a specific affinity, selectivities can be extremely high and solute can be removed from extremely dilute solutions. In affinity chromatography a liquid such as an inhibitor or substrate analog which has a specific affinity for the desired enzyme is covalently attached to an inert solid matrix.[1,290,457,503,547,669,769,888,997,1088] The enzyme is eluted by changing pH, ionic strength, polarity, etc. or by adding an inhibitor to the elutant. Operation usually uses an on-off approach, although if dissociation constants are not very small, elution chromatography is used. Batch adsorption followed by column elution is also used for purification of crude mixtures.[503] In immunosorbent chromatography, monoclonal antibodies are used as the selective ligand.[230,457,520,1088] Both of these methods require a significant effort to develop a suitable sorbent and to find the appropriate conditions for sorption and elution. However, the extreme power of the technique has revolutionized laboratory separations in biochemistry.

Affinity chromatography systems can be divided into specific and general ligands. Monoclonal antibodies and specific inhibitors will produce sorbents which are specific for only one antigen or enzyme. The specific systems have great promise for one-step separations, but they tend to be quite expensive. A very large number of specific systems have been developed for laboratory applications.[1,230,290,520,669,769,888,997,1088] Possible large-scale applications of monoclonal antibodies are extensively reviewed by Chase.[230] A commercially available monoclonal antibody system is used for interferon purification.[547] General ligands will attract a group of compounds with similar chemical groups. Examples of general ligands include concanavalin A,[1,769] lectin,[1] anthraquinone dyes such as Cibacron or Procion dyes,[1,298,457,614,668,670,769,888] NAD,[1,769] and heparin.[349,366] The dyes have received the most attention, since they are very cheap and can do difficult separations. The chemistry of the interaction between protein and dye is not simple, and include both ionic and hydrophobic interactions. Hydrophobic chromatography[896] can be considered as a form of general ligand system.

The acceptance of large-scale applications of biospecific affinity methods has been slow, but is steadily increasing. An up-to-date review is available.[503] Several lectins are commercially purified by affinity chromatography[503,549,803] and some details of the operation are given.[503] Plasma proteins have been purified commercially by affinity chromatography.[349,503,547] These include the purification of plasminogen on Lysine-Sepharose 4B and of antithrombin III on Heparin-Sepharose CL6B. The plasminogen was eluted with ϵ-aminocaproic acid, which is an inhibitor. The ϵ-aminocaproic acid was then removed by SEC or ultrafiltration.[349] The Heparin-Sepharose column was used over 50 times for 1000-ℓ preparations.[349] This long life was achieved by first removing fibrinogen and lipoproteins which might foul the packing. Operation at 5°C for 3 years showed no problem with bacterial growth. IEC was used after the affinity column for removal of proteins which had been ionically held to the Heparin-Sepharose column. Heparin-Sepharose columns are also used commercially for large-scale purification of restriction endonucleases.[503]

Interferons have been commercially purified on columns with Cibacron Blue F3GA.[396] Either sodium chloride or ethylene glycol, or both, are used to remove the interferon. Exact procedures, yields, and purification factors depend on the type of interferon being purified. Yields ranged for 33 to 100%, while single-step purification factors ranged from 15 to 1000 times. Equipment sizes were not given. Reduction of ligand concentration can be useful since the interferon can be removed entirely by a salt gradient. Other interferon separations have been reviewed[503,547] and include the use of commercially available columns using monoclonal antibodies.[547] Cibacron Blue columns are also used commercially for bovine serum albumin final purification.[503]

Immunoadsorbent chromatography is used for commercial purification of antitetanus antibodies from placental blood plasma.[503] Columns up to 7.5 ℓ are used to process 250 to 400 ℓ per night of 4% normal human placental globulins. A porous silica particle coated with DEAE-dextran has tetanus toxoid attached. After 21 cycles during 5 months of operation, no change in behavior of the columns was observed. Flow rates as high as 100 to 400 mℓ/cm^2/hr were used. These flow rates are more than an order of magnitude greater than those used with soft agarose gels.

Details of experimental systems have been reported. For example, a 12-cm I.D. system was used for the purification of galactose-specific lectin using galactose coupled to Sepharose 6B.[359] A 15-cm I.D. column was used for purification of β-galactosidase on p-aminophenyl-β:D-galactopyranoside coupled to Sepharose 4B.[853] A Sepharose 4B-Procion Red H-3B column was used for purification of 3-hydroxybutyrate-dehydrogenase (3-HBDH).[298] the results obtained with a 1.8 ℓ column (13.6 by 12.4 cm) at a flow rate of 1 ℓ/hr are shown in Figure 5-16.[298] Since the 3-HBDH is eluted with salt, ionic effects are probably involved in the binding. Many smaller-scale preparative examples have been reported.[549]

Currently, the best inert supports with large pores have been cross-linked agarose gels, which are quite soft. Thus, short, fat columns were used in most of the above examples (see Section VI for an equipment description). Increased flow rates can be obtained with new cross-linking procedures.[547] High performance affinity chromatography with ligands attached to silica is starting to be used on an analytical scale,[631] and to a much leser extent on a large scale.[503] Large-pore silicas must be used or capacity will be very low.[925] HPLC equipment would be advantageous since high flow rates are used. This was illustrated for the purification of antitetanus antibodies.

Adsorption isotherms in biospecifc affinity chromatography have a sharp Langmuir or Freundlich shape[61,230,231,444,573,1042] which can often be approximated by a step function as shown in Figure 5-8A. The solute movement theory then looks like Figure 5-8B. A shock wave occurs during the adsorption step. Quantitative results, including zone spreading, can be obtained from staged models,[1042] constant pattern models,[61,573,1101] the Thomas solution,[231] or batch models of the adsorption step.[443,444] The typical behavior is a constant pattern shock
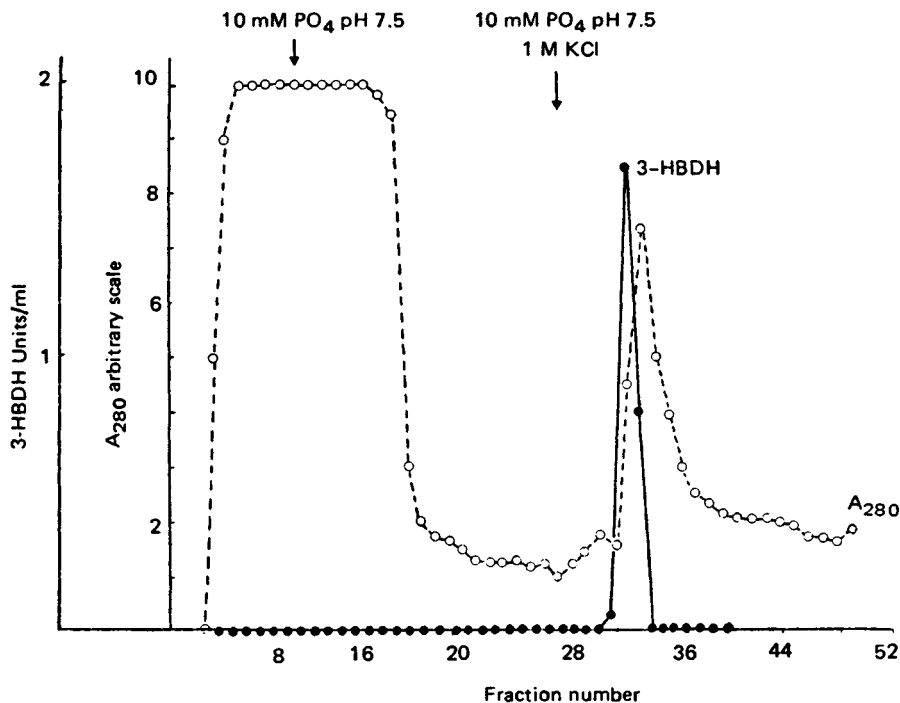
FIGURE 5-16.   Purification of 3-hydroxybutyrate dehydrogenase by affinity chromatography. (From Darbyshire, J., in *Topics in Enzyme and Fermentation Biotechnology* Section 5, Wiseman, A., Ed., Ellis Horwood, Chichester, 1981, Chap. 3. With permission.)

which may be fairly spread because of low diffusivities. In practice,[803] about one half of the sorbent capacity is used and the rest is left for zone spreading and as a safety margin. The methods discussed in Chapter 3, Sections II.C and D for adsorption could be used to achieve higher bed utilizations. In particular, use of small-diameter particles in short beds which are rapidly cycled would be very advantageous for affinity systems when the packing has a long life. Also, two beds in series is an appropriate solution for the problem of low bed utilization with long mass transfer zones (see Chapter 3, Section II.C). The ratio of feed concentration to the value of the dissociation constant should be as large as possible to have sharp breakthrough curves.[231] If the feed concentration is very low, very broad breakthrough curves can result; thus, concentration of the sample before affinity chromatography may be advantageous. The theory of scale-up of the loading step on columns is straightforward, since biospecific affinity chromatography can be considered a special case of adsorption.[61]

The desorption, or off part of the cycle, is very important. When the separation is based only on affinity, elution with inhibitor will remove the protein. When ion exchange and/or hydrophobic interactions are involved, elution can be done with salts, pH changes, and/or ethylene glycol. The elution step has been studied with the same theories applied to the loading step.[230,443,444,1042] Very large increases in concentration of the desired species can be obtained. Counter-flow elution will usually have the advantages of producing higher product concentrations and requiring less elutant. Rather extensive amounts of elutant may be required if diffusion or kinetic rates are low.[230] The presence of multiple binding sites will make elution more difficult. One possible method to use less elutant is to use a sequential approach. First, add one bed volume of elutant. Then, have a delay period to allow time for desorption. Quickly elute the void volume and repeat the delay step. This would be continued until sufficient desorption had occurred.

Although the theory of scale up is straightforward, the practice and economics of large-scale systems are not. The major problems are cost of the affinity matrix[204,230,503,546] and life of the packing.[546] The packing is expensive since the ligands are often very expensive, the support matrices are expensive, the chemical coupling procedure may be expensive, and the development of the coupling procedure is expensive. Large-scale use should cut the cost considerably. The use of general ligands which are applicable to many separations problems will also help cut costs. The lifespan of the packing can have an enormous impact on the cost of the product. Increasing the number of runs which could be made on the adsorbent from 1 to 10 to 100 decreased the projected separation cost per milligram of fibronectin from $3.75 to $0.46 to $0.30.[546] Short resin life can occur due to fouling of the adsorbent by very tightly adsorbed products and due to loss of ligand from chemical cleavage.[230,632] Fouling can be controlled by careful precleaning of the feed, by using guard columns, by optimizing regeneration procedures, and by using biospecific affinity chromatography for final polishing when most other contaminants have been removed. Chemical cleavage of ligand can be partially controlled by controlling pH and other conditions during operation and storage. However, the best way to control the ligand loss problem is improved attachment chemistry which has been optimized for long sorbent life. The observed long life of Heparin-Sepharose in large-scale purification of antithrombin III[349] and of the silica-based packing used for antitetanus antibody purification[503] show that lifespan problems can be solved in large-scale applications. As these problems are solved, biospecific affinity chromatography should become a more common large-scale separation method.

IX. THE FUTURE OF LARGE-SCALE CHROMATOGRAPHY

Large-scale chromatographic processing, particularly of liquid systems, is in a period of rapid growth. I expect this growth will continue since major applications in biotechnology are just opening up. Hopefully, this time around, users and potential users will realize that chromatography is not a miracle separation method which is best for all problems. Chromatography must compete not only with other separation methods such as distillation and crystallization, but also with other methods for operating sorption systems (see Chapters 6 to 8). Properly designed large-scale chromatographic systems applied to the right problems will become common and accepted separation techniques.

Detailed economic comparisons and rules of thumb are needed to determine when chromatography is a good method, which type of chromatography to use, and what operating method to employ. Some of the rules are fairly well known, such as one should use distillation if there is no thermal degradation, no azeotropes, and the relative volatility is not too small. The comparison between chromatography and separation methods other than distillation has not been well codified. Many separations can be done by several different types of chromatography. Decision methods are needed to decide which to use and how to couple several units together. The user has to make similar decisions on the operating method to use. When they can be used, on-off procedures give excellent separations with high flow rates. Thus, on-off procedures would be my first choice; however, they require very high K values for the desired species under "on" conditions and an easy switch of "off" conditions. When on-off procedures are not applicable, I think that the elution and displacement procedures discussed in this chapter will be used for fairly modest-scale systems. For large-scale binary separations, simulated countercurrent or truly countercurrent systems will often have an advantage (see Chapter 6). For intermediate-size separations and for large-scale separations producing several products, the moving port or hybrid systems may have an advantage (see Chapter 7).

Currently, there is little standardization of design methods and hardware. We are in a period where many companies are entering the chromatography business. This leads to many

different types of hardware, although eventually a few designs will dominate. There should be a good market for both turn-key units and for empty columns. The need to design and build your own column for large-scale applications is rapidly disappearing. Large-scale GLC is both more difficult, and probably has a smaller market than large-scale LC. Thus, many more companies will vie in the LC market. This is good news for the user of large-scale LC equipment as he can look forward to rapid development and competitive prices.

Applications of all types of LC in biotechnology will probably be widespread, but all areas are hampered by deficiencies in current packing materials. The packing material for separation of large biomolecules needs to have large pores, be hydrophilic, have minimal nonspecific adsorption, not react and be catalytically inert, satisfy government agency (FDA) requirements, have a long life, and have good flow properties. For good flow properties, rigid spherical particles available in small diameters are desirable. For SEC, a variety of pore-size distributions are needed. For other types of chromatography, the packing material should be very stable. Finally, this wonder support should be widely available and inexpensive. Progress is being made, but it is doubtful the last criterion will be satisfied. Improved packings will also be useful for the other methods of operating sorption separators.

Chapter 6

COUNTERCURRENT SYSTEMS: MOVING BEDS AND SIMULATED MOVING BEDS

I. INTRODUCTION

We saw in Chapters 3 and 5 that batch, fixed bed processes can be quite simple, but they tend to be inefficient and use more sorbent and desorbent than necessary. One obvious way to improve the efficiency and to obtain a continuous process is to move the solid countercurrent to the fluid. Countercurrent flow keeps the mass transfer zone (MTZ) stationary inside the column. Thus, the packing height can be equal to the MTZ instead of two to three times the MTZ, as is common in packed beds (see Figure 3-5). Thus, less sorbent is required. Also, all the solid leaving the adsorber and entering the regenerator can be saturated with adsorbate. Thus, a more concentrated adsorbate stream can be produced and less energy or less desorbent per kilogram of adsorbate will be required. Countercurrent flow has been shown to be superior to other cascade designs[646,673] in many situations. Thus, the goal of considerable research and development has been to obtain countercurrent motion of the solid and the fluid with minimal axial mixing. This has been done by:

1. Flowing the solid
2. Holding the solid rigidly and moving the equipment
3. Using a fixed bed which simulates countercurrent motion by switching valves

Solids movement has been obtained both continuously and intermittently. Both fluidized beds and dense moving beds of solid have been used to obtain continuous countercurrent contact. These methods can work well and are used commercially for solvent recovery, wastewater treatment, and ion exchange, where equilibrium tends to be quite favorable and a large number of transfer units are not required. Intermittent or pulsed flow systems operate as a packed or fluidized bed for much of the cycle, and then a pulse of liquid plus solid is moved. A variety of designs have been developed and are commonly used for large-scale water treatment and ion exchange separations.

The idea of simulating countercurrent motion can be traced back to at least the 1840s when the Shank's system for leaching was employed in England. Various "merry-go-round" systems have been commonly employed for recovery of one solute. Simulated moving bed systems have been a big commercial success for fractionation of two solutes since a very large number of transfer units can be obtained.

II. CONTINUOUS FLOW OF SOLIDS

Both fluidized beds and dense moving bed systems have been used. Often, both methods are used in the same process. The equipment tends to be similar for both single solute recovery and for fractionation of two solutes. We will look first at single solute recovery and then extend these ideas to fractionation.

A. Single Solute Recovery

The solute movement theory developed in Chapter 2 is easily applied to continuous moving bed systems in columns.[1051,1052] Consider the countercurrent system shown in Figure 6-1.
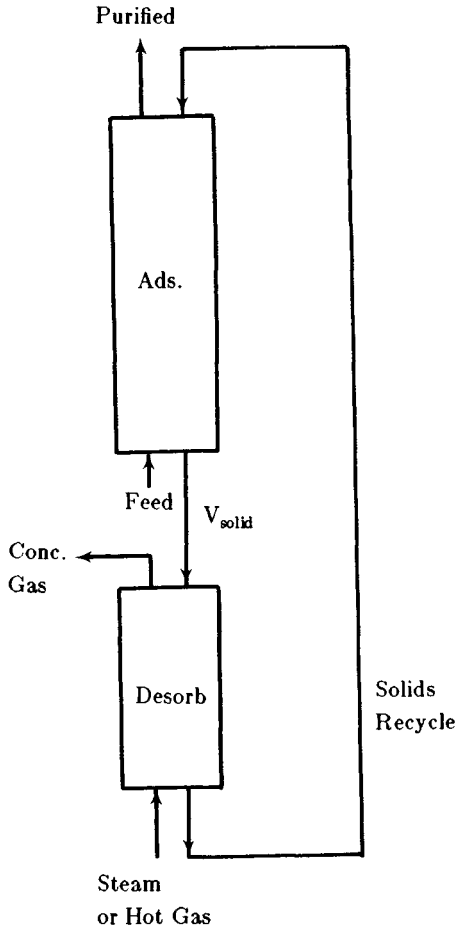
FIGURE 6-1.   Schematic of countercurrent column.

The solute wave velocities calculated with Equations 2-28 or 2-30 were with respect to a stationary solid. Thus, the appropriate fluid velocity to use in the countercurrent system is

$$v = \frac{v_{super}}{\alpha} + v_{solid} \qquad (6\text{-}1)$$

where v_{super} is the superficial fluid velocty and v_{solid} is the solids velocity. Now u_s calculated from Equations 2-28 or 2-30 is the solute velocty with respect to the solid. If the fluid is flowing up and the solids are flowing down, the solute velocity an observer will see is

$$u_{s,cc} = u_s - v_{solid} \qquad (6\text{-}2)$$

In the adsorber, we wish to have the desired adsorbate exit with the solid at the bottom of the column. Thus, we want

$$u_{s,cc} < 0 \quad \text{or} \quad |u_s| < |v_{solid}| \qquad (6\text{-}3)$$

For nonlinear isotherms, Equation 6-3 should be satisfied for all concentrations. If the equilibrium isotherm is known, this allows us to put limits on v_{super}/v_{solid}. For linear isotherms combining Equations 6-1, 6-3, and 2-30 show that solute will exit with the solid if

$$\frac{v_{super}}{v_{solid}} < (1 - \alpha)\epsilon\, K_{d_i} + (1 - \alpha)(1 - \epsilon)\, \rho_s\, k_i \qquad (6\text{-}4)$$

The physical interpretation of Equation 6-4 is if more solute inside the pores and adsorbed on the solid is carried down with the solid than is carried up with the mobile fluid, then solute exits with the solid. Since Equations 6-3 and 6-4 do not include axial mixing and dispersion effects, they represent an upper ideal limit for v_{super}/v_{solid}. In practice, smaller values of v_{super} need to be used.

1. Single Fluidized Beds

The single fluidized bed is the simplest type of continuous solids flow device. If the bed is fairly deep and is very lightly fluidized (expanded), it will act as a moving bed (see Chapter 6, Section II.A.3). If the bed is strongly fluidized, it will act as a single equilibrium stage or close to one equilibrium stage. Both types of fluidized beds can process feeds containing suspended solids. Most of the studies of single fluidized bed systems have been batch operations. The solution for the time-dependent mass balance for a single equilibrium stage with linear equilibrium is[620]

$$\frac{q_\infty - q}{q_\infty - q_0} \exp\left[\frac{-k\, v_0\, t}{\rho_s(1 - \epsilon')\, L_m}\right] \qquad (6\text{-}5)$$

where L_m and ϵ' are the bed length and porosity between particles under expanded conditions. This result would also be applicable to stirred tanks which have been used for ion exchange[816] and powdered activated carbon.[687,990] Under normal fluidizing conditions, the approach to saturation is fairly slow. Also, unless equilibrium is very favorable, a single equilibrium stage is not sufficient. Deeper beds with less strong fluidization, and hence less mixing, can have more than one equilibrium contact. These systems have been successfully modeled with plug flow of the fluid and mixing stages for the solid.[609,610,716]

A large number of batch studies have been aimed at understanding the heat and mass transfer phenomena in a fluidized bed.[6,25,143,398,577,609,610,620,716,738,767,821,847,924,929,1072,1074,1108,1117] Initially, the transfer rate is high and is controlled by the fluid-phase film coefficient. Then the internal particle diffusion becomes important. For the same particle size and fluid velocity, transfer rates in a fluidized bed are lower than in a fixed bed, since the relative velocity between fluid and solid is lower. Under these conditions, the pressure drop in the fluidized bed will be lower. For Reynolds number, $Re = vd_p\, \rho_f/\mu$ between 2 and approximately 2000 the modified Snowden-Turner correlation[821,929] is a good fit to the data for liquid fluidized and fixed beds when the external liquid film resistance controls.

$$Sh_m = \frac{0.86}{\epsilon'}\, Re^{1/2}\, Sc^{1/3} \qquad (6\text{-}6)$$

where the Sherwood number for mass transfer is $Sh_m = k_L\, d_p/D_M$ and the Schmidt number is $Sc = \mu/D_M\rho$. This predicts that the external mass transfer coefficient, k_L, is proportional to $d_p^{-1/2}$. Thus, particle diameter has less effect than in fixed beds with internal diffusion controlling. Fixed beds will have higher k_L than fluidized beds since external porosity is lower in fixed beds. Below $Re = 2$, a partial alignment of the bed occurs and k_L is lower than predicted by the Snowden-Turner correlation. Fortunately, the likely operating range
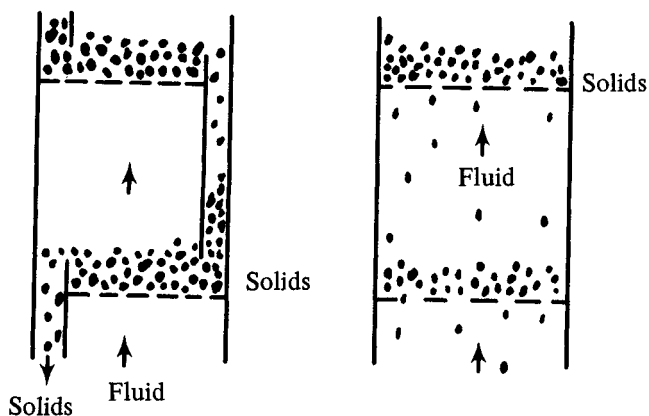
FIGURE 6-2.   Schematic of fluidized bed systems: (A) with down-
comers; (B) without downcomers.

for a liquid fluidized bed is $2 < Re < 25$. Batch fluidized beds have been used commercially
for ion exchange in a few instances.[424] The large variety of models which have been applied
to fluidized bed adsorbers are referenced by McKay.[716]

Fluidized and semifluidized beds of active carbon have been extensively studied for
wastewater treatment[6,22,24,25,398,577,702,716,831,1069-1072,1074] and other separations.[148, 492,494,893] Both
batch and continuous operation are used. These beds have the advantage of not clogging
when there are suspended solids in the feed. The values of $k_L a$ in the fluidized bed were
approximately half those in fixed beds. More transfer units can be obtained by using a deeper
bed.[494,495]

Fluidized beds of active carbon with bacterial growth have also been studied.[22-24,1033,1070]
(See also Chapter 3, Section IV.B.) The bacterial growth is advantageous because it can
bioregenerate the carbon; however, the growth can clog packed beds. Fluidized beds have
the advantage of not clogging, and carbon can easily be removed if it needs to be regenerated
to remove nonbiodegradable adsorbates. This process is very complex and careful meas-
urements are needed for the existing models.[22,23,1033]

2. Multistaged Fluidized Beds

The usual way to obtain more separation with fluidized beds has been to have several
stages of shallow fluidized beds. This can be done with downcomers as shown in Figure 6-
2A or without downcomers as shown in Figure 6-2B. Systems with downcomers have used
sieve or bubble cap plates while systems without downcomers used perforated plates with
larger holes. Early commercial units with downcomers were used for water softening,[494] air
drying,[289,357,358,620] NO$_2$ adsorption,[357] SO$_2$ adsorption, and solvent recovery[65,620,863,985] and
the systems are currently used commercially for solvent recovery.[47,578,1004]

Many of the commercial gas systems were very similar, regardless of the purpose of the
unit. Solvent recovery by activated carbon (see also Chapter 3, Section III.C) is a good
example since new designs[47,1004] are quite similar to older designs,[48,65,165,863] although *major*
advances in the activated carbon have been made. A typical unit is shown schematically in
Figure 6-3.[47] Since solvent concentration in the inlet air stream is usually kept to about one
fourth to one half of the lower explosion limit, the inlet solvent concentration is usually
quite low and the air flow rate is quite high. A staged fluidized bed activated carbon adsorber
is ideal for this situation. Since the activated carbon generally shows very high adsorption
of solvents at low concentrations, only a few shallow (2 to 3 in. of solid) stages are needed.
Thus, the pressure drop through the system is modest. This is important, since the blower
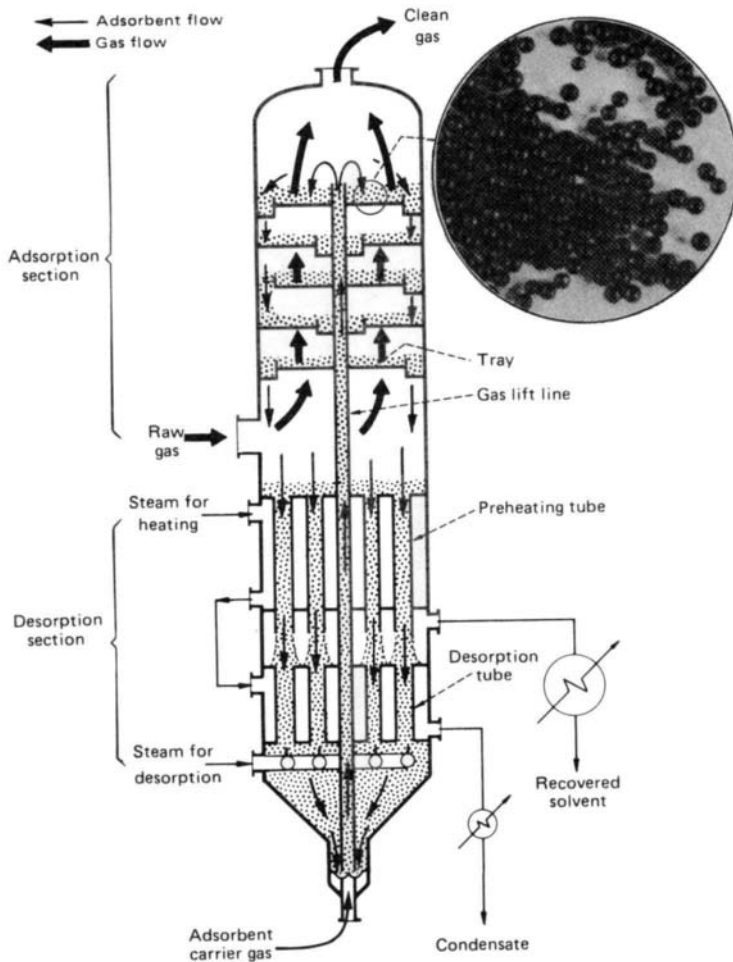
FIGURE 6-3. System for activated carbon recovery of solvent using a staged flui-dized bed for adsorption and a moving bed for regeneration. (From *Chem. Eng.*, 39, 1977. With permission.)

represents a major operating expense. Since steam flow rates in the regenerator are much lower, a dense moving bed is usually used there. The steam/solvent mixture is condensed and then separated in a settler or in a distillation column if solvent and water are miscible.

The continuous activated carbon solvent recovery plants have been used for recovery of many different solvents.[65,165,1004] The continuous units are smaller than fixed bed units and require less carbon. In large sizes, the continuous systems are claimed to be less expensive.[65,165,1004] A detailed economic analysis between fixed bed and continuous plants has not been reported in the open literature. However, it is interesting to note that plants have been built in Japan for air flow rates as low as 350 cfm.[1004] The moving bed solvent recovery systems should use significantly less steam for regeneration than fixed bed systems since the shell of the regenerator is always hot and only the carbon and adsorbate need to be heated. In addition, all the carbon is saturated with solvent when it enters the moving bed regenerator; thus, the energy use per kilogram of adsorbate recovered should be less than in a fixed bed.

The apparatus shown in Figure 6-3 can be modified in many ways. The stripper and adsorber can be in separate shells if desired. Either unit can be above the other. In addition to direct steam heating, indirect heating can be used by building a heat exchanger into the

regenerator[1004] (this idea was used earlier in hypersorbers — see Chapter 6, Section II.B.1). In some cases,[65,863] a side stream of up to 10% of the carbon was regenerated with super-heated steam to prevent a slow loss of activity.[48,65] If the solvent is miscible with water, regeneration can be done by a combination of indirect heating and a hot nitrogen gas purge.[1004] Although not usually done, separate drying and cooling sections could be included.

Tray efficiencies are important for design. Commercial efficiencies of approximately 90% were reported[65] with beds 2 to 3 in. deep when not fluidized. A laboratory study[1011] showed E_{MG} values varying from 0.2 to 0.8, but apparently had quite a bit of by-passing of gas. The downcomers need to be designed to prevent by-passing, but, with one exception,[358] details of commercial design procedures are not given. To prevent stratification based on size and to achieve high efficiencies, uniform particle sizes are very desirable. The use of small-diameter particles with their higher mass transfer rates when pore diffusion becomes important (which it will on the lower stages where the solid is more heavily loaded)[1118] will also increase stage efficiency. Bed dynamics, residence time distributions, and heat and mass transfer characteristics are reviewed elsewhere.[620,820]

Attrition losses are a major concern. When nonspherical activated carbon[48,65] or silica gel[358] was used, the initial loss rate may be quite high (up to 10%),[358] but this soon levels off to a lower rate. The initial high losses appear to be due to a smoothing of the sharp edges on the adsorbent.[65,358] Losses can be limited by reducing the impingement of particles on metal surfaces and having the adsorbent drop as short a distance as possible. Reducing the gas velocity and using spherical particles[358] also help lower the attrition rates. Attrition problems were never solved in the earlier units and they were eventually shut down.[578] Recent designs incorporate these ideas and use small, hard spherical beads which flow well and appear to have solved the attrition problem.[578,1004]

Other staged fluidized bed designs have been studied. A 0.8-m-diameter commercial system without downcomers was built in Japan for acetone recovery,[985] but this equipment appears to have a much more restricted range of gas flow rates than systems with downcomers. A four-stage pilot plant system incorporating centrifugal separators on each stage worked well, but was quite complex.[972]

Stable fluidization of liquid systems in staged fluidized beds has proven to be more difficult. The early commercial Dorr-Oliver Hydro-Softener used an ejector to transfer a slurry of solid from stage to stage.[494] Operation in a fluidized bed with downcomers is possible,[998] but weir height and downcomer design were critical to avoid liquid upflow in the downcomers. Stage efficiencies were also low (0.15 to 0.35). Higher stage efficiencies could be obtained by pulsing the fluid with a bellows attachment,[458] but the range of stable fluidization was not large. The fluidization is very sensitive to changes in sorbent density as exchange or adsorption occurs.[647] Another method used commercial ore dressing jigs.[494,967] The jigging action keeps the solid evenly fluidized and flow from one stage to another was not a problem.[967] These jigs are commercially available, but apparently were never adapted to adsorption or ion exchange on a large scale. A Russian solution[650] claimed to give stable fluidization of viscous oils was to build downcomers with a 140° bend. The development of intermittent operation has solved the problem of stable fluidization of liquids (see Chapter 6, Section III).

Staged theories for these fluidized bed systems are essentially the same as for other staged unit operations.[169,586,707,990,1017] For isothermal systems with equilibrium stages, use of a McCabe-Thiele diagram is straightforward.[492,494,620,990,998] The typical analysis uses a single porosity model for the adsorber and lumps the solute contained with the fluid inside the pore with the solute adsorbed on the solid. The two types of porosities can be included separately if we consider the staged system as a three-phase contactor as shown in Figure 6-4A.[1049] The solid, L, kilograms of dry adsorbent per hour, and the fluid in the pores, W, moles fluid per hour, move co-currently and flow countercurrent to the fluid outside the pores, V moles per hour. A mass balance for Figure 6-4A is
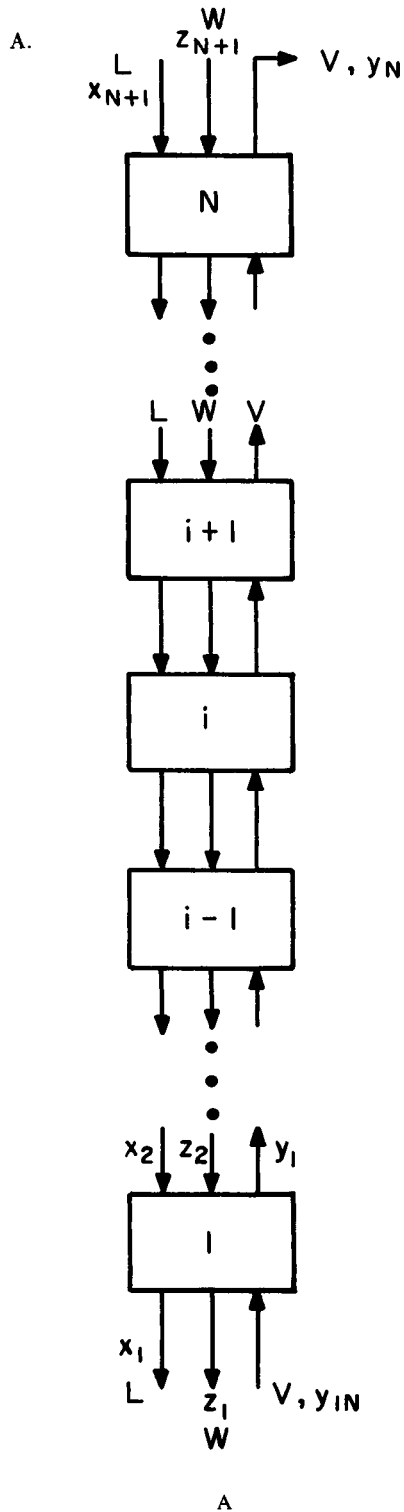
FIGURE 6-4.   Three-phase staged system (solid L, fluid in pores W, and fluid outside pores V). (A) Cascade system; (B) McCabe-Thiele diagram.

B.
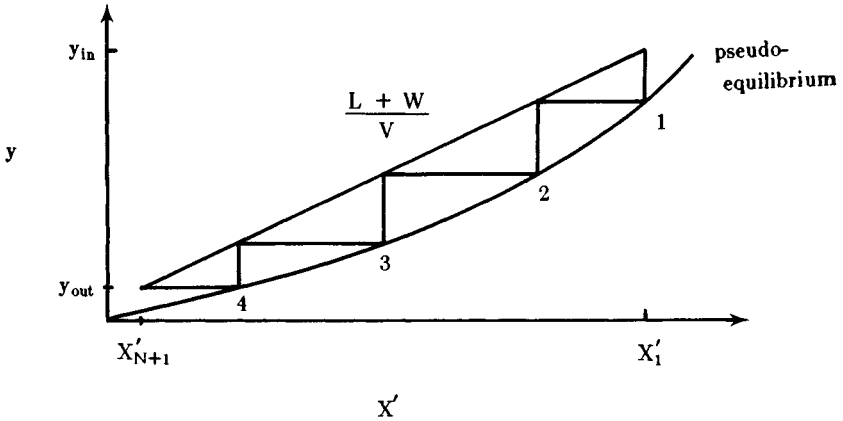
FIGURE 6-4B

$$L_{N+1} x_{N+1} + W_{N+1} z_{N+1} + V_{i-1} y_{i-1} = L_i x_i + W_i z_i + V_N y_N \qquad (6\text{-}7)$$

where z and y are mole fractions of solute in the fluid inside and outside the pores, respectively, and x is the moles solute per kilogram of adsorbent. If flow rates are constant and phases L and W are in equilibrium, we can rearrange Equation 6-7 into the operating equation:

$$y_{i-1} = \frac{(L + W)}{V} x_i' - \frac{L + W}{V} x_{N+1}' + y_N \qquad (6\text{-}8)$$

where x' is the weighted average composition of the downward moving phases.

$$x_i' = \frac{L x_i + W z_i}{L + W} = \frac{\dfrac{L}{W} x_i + z_i}{\dfrac{L}{W} + 1} \qquad (6\text{-}9)$$

On a McCabe-Thiele-type plot of y vs. x' (Figure 6-4B), Equation 6-8 plots as a straight line of slope $(L + W)/V$ and a y intercept $[-(L + W)x_{N+1}'/V + y_N]$.

For an equilibrium stage, we also need to know the equilibrium relationships for y and z and for x and z. For adsorption of small molecules, $y = z$ at equilibrium (fluid inside the pores is the same composition as fluid outside the particles), and the x, z relationship is the equilibrium isotherm. The pseudo-equilibrium curve, y vs. x', is easily plotted by picking an arbitrary $z = y$, calculating x from the isotherm, and determining x' from Equation 6-9. The resulting McCabe-Thiele diagram for the adsorber is shown in Figure 6-4B. In the regenerator, mass transfer will be in the opposite direction and the operating line will be under the pseudo-equilibrium curve. For concentrated systems, the entire problem can be stated in terms of mass or mole ratio units to make the flow rates constant. Nonequilibrium stages can also be stepped off, but a different McCabe-Thiele diagram is required.[1049]

For very dilute systems, the equilibrium expressions become linear

$$y = K_1 x + b_1 \qquad y = K_2 z + b_2 \tag{6-10}$$

and the Kremser equation can be used.[1049] Then, the solution is

$$N = \frac{\ln\left[(1 - \beta)\left(\dfrac{y - y_{N+1}^*}{y_N - y_{N+1}^*}\right) + \beta\right]}{\ln\left(\dfrac{1}{\beta}\right)} \tag{6-11}$$

where

$$\beta = \frac{V}{\dfrac{W}{K_2} + \dfrac{L}{K_1}} \tag{6-12}$$

and y_{N+1}^* is a hypothetical concentration in equilibrium with the entering W and L phases.

$$y_{N+1}^* = \frac{\dfrac{L}{K_1}(K_1 x_{N+1} + b_1) + \dfrac{W}{K_2}(K_2 z_{N+1} + b_2)}{\dfrac{W}{K_2} + \dfrac{L}{K_1}} \tag{6-13}$$

Comparison of Equation 6-12 with the McCabe-Thiele diagram shows that β is the ratio of the slope of the equilibrium line to the slope of the operating line.

The equilibrium expressions in Equation 6-10 can be compared to Equation 2-29. For the usual linear adsorption given by Equation 2-29, we have

$$b_1 = b_2 = 0, \quad K_1 = 1/k_i\bar{\rho}_f, \quad K_2 = 1/K_{d_i} \tag{6-14a,b,c}$$

The molar fluid density, $\bar{\rho}_f$, appears in Equation 6-14b since c in Equation 2-29 and y in Equation 6-10 have different units. Thus, β becomes

$$\beta = \frac{V}{Lk_i\bar{\rho}_f + WK_{d_i}} \tag{6-15}$$

The amount of liquid entrained is

$$W = \frac{L}{\rho_s} \frac{\epsilon}{(1 - \epsilon)} \bar{\rho}_f \tag{6-16}$$

For a low pressure gas system where $\bar{\rho}_f$ is quite small, W may be negligible, and these results reduce to the usual form of the Kremser equation.[169,494,586] When W is negligible, the McCabe-Thiele diagram shown in Figure 6-4B reduces to a standard McCabe-Thiele diagram.[492,494,998]

To have complete removal of solute means $y_N \simeq 0$. In order for this to be true, the operating line slope must be greater than or equal to the slope of the equilibrium line in Figure 6-4B. For linear equilibrium, this is $\beta \leq 1$. In terms of porosities and linear flow rates, the rates V, W, and L are

$$V = v_{super} A_c \bar{\rho}_f \tag{6-17}$$

$$L = v_{solid} A_c (1 - \alpha)(1 - \epsilon)\rho_s \qquad (6\text{-}18)$$

$$W = \frac{L}{\rho_s}\left(\frac{\epsilon}{1 - \epsilon}\right)\bar{\rho}_f = v_{solid} A_c (1 - \alpha)\epsilon \, \bar{\rho}_f \qquad (6\text{-}19)$$

Substituting Equations 6-17 to 6-19 into 6-15 with the requirement that $\beta \leq 1$, we find that the condition for complete removal of solute is Equation 6-4. Thus, the staged theory and the solute movement theory agree qualitatively.

Most gas systems will be nonisothermal. In this case, several different approaches can be taken. The first is to assume the outlet temperature and use an approximate energy balance to relate temperature to the sorbate concentration.[358] From this, a psuedo-equilibrium curve is constructed and stages are stepped off on a McCabe-Thiele diagram. An alternate approach is to do trial-and-error mass and energy balances for each stage. The calculation is essentially the same as absorption calculations.[990] A third, and probably the preferred approach, is to write the equations in matrix form and solve them as a simulation problem on a computer using any method appropriate for absorbers.[488,586] Convergence will be faster if units are used where the flow rates are approximately constant (for some liquid systems volume units are appropriate). Major advantages of the matrix approach are it is easy to program and can be extended to multicomponent problems.

The staged design approach can also be applied to continuous contact moving bed systems even though this is not physically realistic if the height equivalent to a theoretical plate (HETP) is known. When highly purified product streams are produced, the staged solutions for continuous beds can be significantly in error.[865] The main advantage of using the staged analysis is existing methods and computer programs can be used. This may be particularly valuable for multicomponent problems.

3. Dense Moving Bed Systems for Single Solute Recovery

Dense moving beds with continuous flow have been used for the regenerator section of solvent recovery[1004] and ion exchange[492,494,893] systems. Since fluid flow rates are usually significantly lower in the regenerator, the higher capacity of a fluidized bed is not required. The longer residence time in the dense moving bed is an advantage. The regenerator can also be designed to have a heat exchanger for indirect heating of the solids[863,1004] (see also Chapter 6, Section II.B.1).

The simplest type of dense moving bed is simply an empty tube with some type of mechanism to control the solids flow rate. This can be a rotating valve,[126,492,494] an oscillating tray,[126,127] a solids recirculation device (bucket elevator,[65,863] ejector,[494,648] or air lift[126,1004]), or a tube with variable outlet level.[410] In all cases, a plug flow of solids is desired to minimize the HETP and, at least for small units, can be very closely approximated.[555] In small units, a straight or cone-shaped bottom may be sufficient to prevent gross channeling. In larger units, as many as 52 withdrawal points have been used.[863] An alternative is to have baffles[494] which can be part of the shell-and-tube heat exchanger used for indirect heating.[863,1004]

Very low Sherwood numbers have been observed in moving beds.[1113] This was interpreted as being evidence of a significant amount of gas channeling. With downward solids flow, channeling is a major problem at higher velocities.[650] Since higher velocities are desired to increase the film mass transfer coefficient, this creates a problem when the film resistance is controlling. Upward solids flow and downwards liquid flow is used commercially for the regenerator in the Himsley ion exchange system,[509,922] and appears to eliminate the channeling problem.

For small molecules, the MTZ will be short and can be kept entirely within a short moving bed.[554] For molasses color and other large molecules, the MTZ will be longer since diffusivities are low.[554] Thus, longer columns will be required. The big questions with this simple
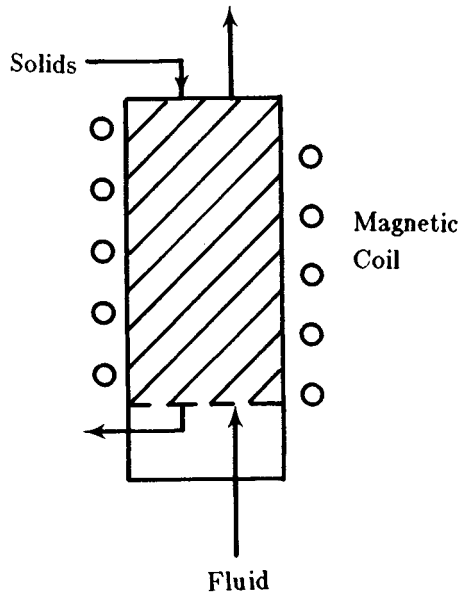
FIGURE 6-5. Magnetically stabilized moving bed.

type of moving bed are will it scale up and what are the limiting fluid velocities? The major problem with scale up is evenly withdrawing solid from the bottom of the system to keep plug flow in the column.

Expanded beds are beds which are operated slightly above the point of incipient fluidization. Sorbent can be added at the top and removed at the bottom. This type of design is used for water treatment with activated carbon[702,831,941,1069,1071] and has been tried for ion exchange.[893] Since loaded activated carbon is heavier, there is some desirable stratification. Because there will be more axial movement than in a dense moving bed,[555] the expanded bed design may be less suited when a large number of transfer units are required. However, semifluidized beds where the bed expansion is limited have pressure drops between those of fluidized beds and packed beds, and breakthrough curves are very similar to a packed bed.[702] The use of a very tightly sieved particle size appears to be very important. A similar arrangement was used with micromagnetic resins for dealkalization of hard alkaline water[148] where the semifluidized regeneration had approximately four equilibrium contacts. The system was considerably smaller than a conventional continuous ion exchange plant, but even smaller and simpler systems were possible with pipe reactors (see Chapter 6, Section II.A.4).

Magnetically stabilized moving beds[60,674,857-861] stabilize a fluidized bed of magnetic particles with an electromagnetic field. This is illustrated in Figure 6-5. The magnetization tends to collapse voids. At high magnetizations, the solids become locked and flow in a rod-like pattern except at the two ends of the column where material must be added and removed.[859-861] Removal can be facilitated with a magnetic distributor-downcomer.[550] Rod-like movement is exactly the behavior required for adsorption separations requiring many stages; thus, this method should be of particular interest for fractionation. This development is a continuation of Exxon's long-standing interest in fluidization (e.g., see Reference 430). The research has included development of magnetic adsorbents. Many of the details are still proprietary, and most of the currently published material is on the hydrodynamics of the system.[60,859-861] Since the bed is actually rigid and will not pass suspended solids, clean feeds are required. The magnetically stabilized moving bed can use very small particle sizes which will reduce mass transfer resistances. When pore diffusion controls, this could result
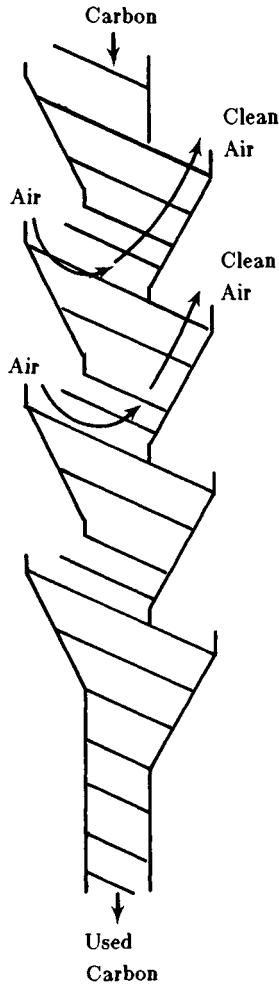
FIGURE 6-6.   Cross-flow, panel bed activated carbon adsorber. (From
Lovett, W. O. and Cunniff, F. T., *Chem. Eng. Prog.*, 70(5), 43, 1974.
With permission.)

in much shorter mass transfer zones, smaller systems, and lower costs. This might be
particularly advantageous for removal of large molecules from liquid systems, where mass
transfer can be quite slow.

Another alternate which has been used commercially for activated carbon odor control is
the panel bed adsorber shown schematically in Figure 6-6.[571,667,789] The air flows essentially
in a cross-flow pattern with an effective width of about 4 in. A large number of these panels
can be operated parallel to each other to treat large air flow rates. The carbon is then sent
to a furnace for regeneration. The cross-flow pattern reduces the pressure drop, but is less
efficient in carbon utilization than countercurrent flow. When treating large volumes of air
with very small quantities of solute, the energy for operating the blower can become the
controlling cost, and a cross-flow design makes sense. The same reasoning is true in cooling
towers where cross-flow designs are used.

Other continuous moving bed contactors have been developed. One example is a zigzag
channel[822,939] with a thin flow of solids which had cross-flow contact of fluid and solid on
each stage, but countercurrent contact from stage to stage. Thus, this device has advantages
of both types of cascades, but has a fairly low solids capacity and possibly excessive attrition.
A complex moving bed developed at Oak Ridge for uranium or water purification used a
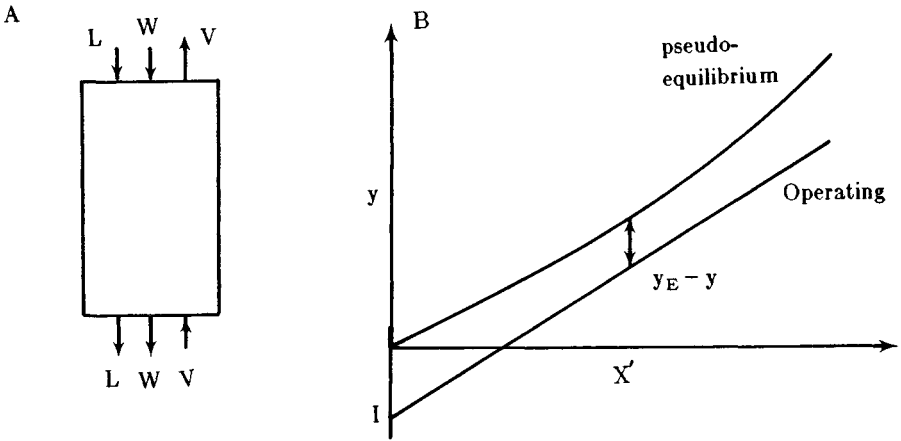
FIGURE 6-7. Continuous system — analysis as a three-phase system. (A) Schematic of column; (B) operating and equilibrium lines when phases L and W are in equilibrium; point I is y intersection, $[y_{out} - L + W/V \, x'_{in}]$.

hydraulic ram section to move the solids.[57,432,433] An attempt was made to commercialize this design, but was not successful. Many other solid-fluid contacting devices have been developed for leaching and could be easily adapted to continuous sorption separation. However, this equipment does not appear to be economical in this application.

The continuous contact moving bed sorption systems can be designed using the transfer unit approach commonly used for other unit operations.[165,586,707,990,1017] The usual approach treats the solid and fluid in the pores as a single phase. The internal and external pores can be included if we consider the adsorber as three phases with W, fluid in the pores, and L, solid, flowing co-currently.[1060] This approach is the brother of the staged three-phase approach discussed in Section II.A.2). The adsorber is shown schematically in Figure 6-7A. We have a series transfer system where solute must transfer from phase V through W to L. The rate expressions can be written as

$$-\frac{V}{A_c}\frac{dy}{dh} = K_{VW}\, a_I(y_E - y) \qquad (6\text{-}20)$$

$$-\frac{L}{A_c}\frac{dx}{dh} = K_{LW}\, a_{II}(x - x_E) \qquad (6\text{-}21)$$

where a_I, a_{II} are the interfacial areas per unit volume between phases V and W, and W and L, respectively, and y_E and x_E are in equilibrium with bulk phase concentration z. This bulk phase concentration must satisfy the mass balance.

$$y = \frac{L}{V}\, x + \frac{W}{V}\, z + y_{out} - \frac{L}{V}\, x_{in} - \frac{W}{V}\, z_{in} \qquad (6\text{-}22)$$

If $(V/A_c\, K_{VW}\, a_I)$ is constant, Equation 6-20 can be integrated to

$$h = \left(\frac{V}{A_c K_{VW}\, a_I}\right)\left(\int_{y_{out}}^{y_{in}} \frac{dy}{(y_E - y)}\right) = (\text{HTU}_{VW})(\text{NTU}_{VW}) \qquad (6\text{-}23)$$

Similarly, if $(L/A_c K_{LW}\, a_{II})$ is constant

$$h = \left(\frac{L}{A_c K_{LW}\, a_{II}}\right)\left(\int_{x_{in}}^{x_{out}} \frac{dx}{x_E - x}\right) = (\text{HTU}_{LW})(\text{NTU}_{LW}) \qquad (6\text{-}24)$$

Equating Equations 6-23 and 6-24 relates the NTU and HTU.

$$\frac{\text{NTU}_{\text{LW}}}{\text{NTU}_{\text{VW}}} = \frac{\text{HTU}_{\text{VW}}}{\text{HTU}_{\text{LW}}} \tag{6-25}$$

The NTU values are usually found by calculating $y_E - y$ (or $x_E - x$) as the distance from the operating line (Equation 6-22) to the equilibrium curve. In a three-phase system, there will be a family of operating lines and determining the column height is a trial-and-error procedure.[952] For adsorption, the mass transfer from the fluid in the pores to the solid is usually *not* controlling and Equation 6-23 would be used for design. If the co-currently flowing L and W phases are in equilibrium, the analysis simplifies considerably. Defining

$$x' = \frac{Lx + Wz}{L + W} \tag{6-26}$$

The operating line is

$$y = \frac{L + W}{V} x' + \left[y_{\text{out}} - \frac{(L + W)}{V} x'_{\text{in}} \right] \tag{6-27}$$

which is a straight line on a plot of y vs. x'. This is shown in Figure 6-7B for a regenerator where transfer is from the solid to the fluid. The distance $y_E - y$ is found from the pseudo-equilibrium curve (y, x, and z in equilibrium) and the operating line. Note that Equation 6-26 is similar to Equation 6-9, Equation 6-27 is similar to Equation 6-8, and Figures 6-7B and 6-4B are related.

If equilibrium is linear,

$$y = K_1 x + b_1 \tag{6-28a}$$

$$x = K_3 z + b_3 \tag{6-28b}$$

and phases L and W are in equilibrium, a three-phase form of the Colburn equation is easily derived.[1060]

$$\text{NTU}_{\text{VL}} = \frac{1}{1 - \mathscr{F}} \ln\left\{ (1 - \mathscr{F}) \left[\frac{y_{\text{in}} - (K_1 x_{\text{in}} + b_1)}{y_{\text{out}} - (K_1 x_{\text{in}} + b_1)} \right] + \mathscr{F} \right\} \tag{6-29}$$

where

$$\mathscr{F} = \frac{K_1}{\left(\dfrac{W}{K_3 V} + \dfrac{L}{V} \right)} \tag{6-30}$$

If $\mathscr{F} > 1.0$, the solute tends to move up the column with phase V, while if $\mathscr{F} < 1.0$ the solute moves down the column with phases W and L. If the amount of fluid in the pores, W, is negligible, Equation 6-29 reduces to the two-phase Colburn equation and the results obtained from Figure 6-7B and Equations 6-23 or 6-24 reduce to the two-phase results. When the fluid in the pores is not negligible, the three-phase analysis includes pore volume and amount sorbed separately.

Other theories for continuous contact moving bed systems have been developed.[313,572,653,808,834,865,866,909,1113] Kasten and Amundsen[572] modeled the changing conditions
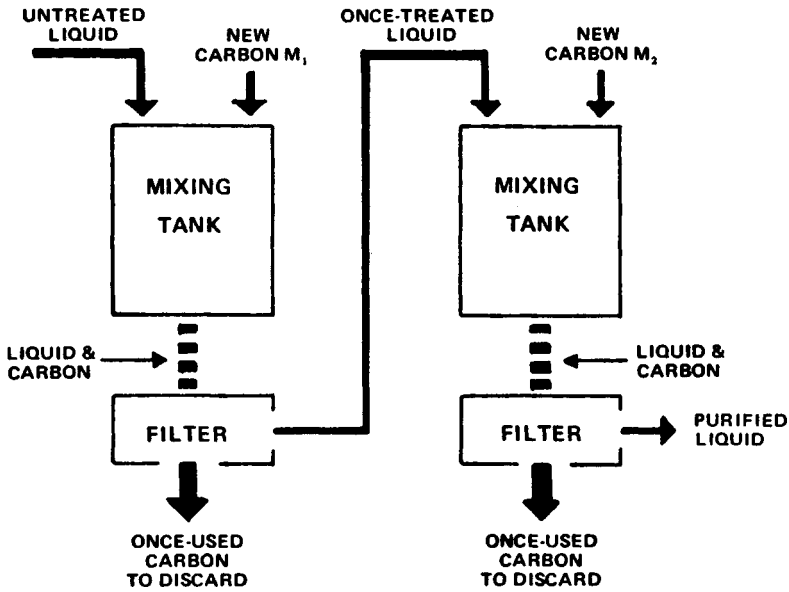
FIGURE 6-8. Two-step divided carbon treatment system for intermittent operation. (From Perrich, J. R., Ed., *Activated Carbon Adsorption for Wastewater Treatment*, CRC Press, Boca Raton, Fla., 1981. With permission.)

inside the solid. Their model was restricted to isothermal systems with linear equilibrium. This model was used as the basis of a computer solution,[808] and was extended to adsorption with nonlinear isotherms.[909] Simpler analytical solutions can be obtained with linear equilibrium and linear transfer models.[865,866,1113] More complex phenomena, such as nonlinear isotherms, can be included in numerical models[653] and in asymptotic solutions.[834]

4. Staged Systems: CSTRs and Pipe Reactors

When equilibrium is quite favorable, one or two equilibrium contacts may be sufficient for separation. In this case, some type of CSTR or co-current flow pipe reactor followed by the solid-fluid separation step can be advantageous. These systems include contact filtration, "resin-in-pulp", and magnetic resin systems.

Contact filtration consists of adding the sorbent directly to the liquid being processed in a stirred tank and then separating the sorbent and liquid by sedimentation or filtration.[137,291,483,493,526,679,687,688,926,928,990] This method is commonly used for treatment of wastewater with either powdered activated carbon or granular activated carbon. The used carbon may be discarded or reactivated. Contact filtration has also been used for treating oils with clay.[493,687,688,990] Batch or continuous single-stage, continuous countercurrent cascades, continuous cross-flow cascades, and divided carbon addition for intermittent operation have all been used. Treybal[990] has an extensive section detailing the calculational methods, power requirements, and mass transfer characteristics of these stirred tank systems. For most wastewater treatment applications, equilibrium is very favorable and one, two, or at most, three stages, are needed. Dosage treatment charts for systems following Freundlich isotherms are available.[137,527,990]

Since wastewater feeds may be intermittent, systems which can easily be started up and shut down are advantageous. Single-stage batch and two-step divided carbon treatment systems meet this requirement. The two-step divided treatment process shown in Figure 6-8[527] uses less carbon than a single stage. The system is designed for intermittent operation. When the charge has been treated, the entire system is drained until the next charge. If

operated continuously, the system shown in Figure 6-8 becomes a continuous cross-flow system which will require more carbon than a continuous countercurrent system. The two-step system has higher capital expenses than a single stage, but uses less carbon.

A continuous, two-stage countercurrent process with two mixing tanks and two filters will use the least amount of carbon. However, handling and filtering the carbon can cause operating problems. A method[928] which is easier to operate, but less efficient, is to pass the impure feed directly to a filter containing the carbon. Since the residence time will be very short, the solution can be recycled through the filter several times.

Powdered activated carbon has also been added directly to activated sludge tanks for wastewater treatment.[49,55,264,291,345] If desired, the carbon and sludge can be recoverd on a filter, dried, and sent to a furnace where the sludge is pyrolyzed and the carbon is reactivated.[345] These methods can be used to design smaller water treatment plants[345] or to control spills.[55]

Large countercurrent, stirred tank systems with screens to recover the sorbent are used commercially in uranium processing by ion exchange[816,882] and gold and silver recovery on activated carbon.[344,468,637,755] These systems require several stages and thus the sorbent must be recovered by screens on every stage. The stirred tank systems can process slurries with up to 50% solids, which is a major advantage when handling ore slimes. The filtration step can be entirely by-passed. This results in major capital savings and increased recovery since metal is not lost in the filter cake. The carbon-in-pulp process is particularly useful for very high clay content ores which are slimy.[344] To prevent clogging of the screens, they can be swept with air.[637,755]

A different type of stirred contactor contained in an elbow has been used commercially for streptomycin recovery from whole broth[108] and for Novobiocin recovery.[121] A merry-go-round arrangement with three fluidized beds in series was used.[121] When a fluidized bed was depleted, it was removed from the merry-go-round and regenerated with downward flow as a fixed bed. The use of the fluidized beds avoided the expensive filtration of mycelium and the loss of antibiotic in the filter cake. Several production plants have been based on this technology.[120] The system was modeled as well-mixed stages with lumped parameter mass transfer. The model fitted both laboratory and production units with a scale-up factor of 4000.[121]

Several alternative stirred tank systems have been devised. These include a system with solids recovery using a liquid cyclone,[534] and compact designs where a series of mixer-settlers were contained in a single shell.[647,920] The compact device was capable of long residence times, but suffered from low resin holdup and considerable backmixing.

If the stirred tanks can be assumed to be equilibrium stages or have a known stage efficiency, the standard staged design procedures are very easy to use.[137,527,691,816,990] Unfortunately, the sorber and the solid-liquid separator (or screen) have very different requirements. Large particles make solid-liquid separation easier (or make the screen less likely to bind). If a slurry is being processed, the sorbent particles must be large so that they will be retained while the suspended solids in the feed are passed. These large particles have low mass transfer rates and equilibrium is not achieved. The stage efficiency in one large-scale system was 65%.[755]

Alternate continuous contacting systems have been developed by CSIRO in Australia using magnetic solids.[19,145,146,148-151,154,170,264,324,325,812,963] Very small magnetic ion exchange particles have very high mass transfer rates when the liquid is stirred and the flocs have broken apart, but when not stirred the particles floculate and settle rapidly. For example, 65- to 125-μm particles of a weakly basic resin with 20% Fe_2O_3, required 120 sec to settle when not magnetized, but only 18 sec when magnetized.[145] Methods for making the resins are reviewed by Clemence et al.[264] One scheme to use these resins was a fluidized bed followed by a dense moving bed regenerator.[19,148,170] An interesting alternative when equi-
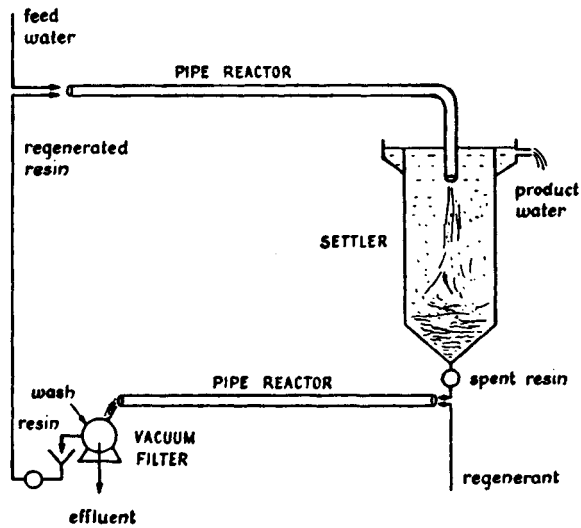
FIGURE 6-9. Pipe reactor system for magnetic ion exchange resins. (From *J. Chem. Tech. Biotechnol.*, 29, 273, 1979. With permission.)

librium is very favorable, such as in dealkalization of water, is shown in Figure 6-9.[145,812] The raw water and resin are contacted co-currently at high velocities in a pipe reactor to give one equilibrium contact. The highly turbulent flow keeps the resin particles separated. The slurry is then separated in a settler where the resin flocculates and rapidly settles. Resin is regenerated in another pipe reactor and recycled. Several units could be cascaded if more than one equilibrium stage is required, but this would make the process more complex.

Stirred multistage contactors similar to liquid-liquid extractors were also developed for the magnetic resins.[154,963-966] The stages were separated by perforated plates with fairly large holes. At low rpm the stirrer "shovels" resin through the holes, while at higher rpm the mixing aids fluidization.[963] The presence of the stirring provides much higher turn-down ratios than are normally achieved. Continuous countercurrent flow of the resin and liquid was achieved in several pilot scale units and in fairly large-diameter demonstration units (160 cm[963] and 330 cm[964]). These systems were used for continuous Sirotherm demonstration units (Chapter 4, Section III.E). The continuous plant used significantly less resin than a batch plant.

It would also be quite interesting to develop magnetic adsorbents and apply this method to adsorption problems such as wastewater treatment or product recovery. A start in this direction is the use of very small (less than 1 μm) magnetic particles with immobilized affinity chromatography (see Chapter 5, Section VIII) for rapid recovery of biological products from crude homogenates.[547] The use of very small adsorbent particles would be advantageous whenever pore diffusion controls mass transfer rates.

5. Slurry Adsorption

Another method for obtaining countercurrent motion between solid and fluid is to slurry the solid in a liquid and then flow the fluid and slurry countercurrent to each other in any standard contacting device. Since the slurry can be pumped, very small particles can be used. In addition, attrition should not be a problem, and the good heat transfer characteristics of the liquid will prevent an undesirable temperature buildup. The disadvantages of this approach are that equilibrium capacity of the adsorbent may be lower if the solvent competes with the solute for adsorption sites, and additional mass transfer resistances have been added.

In most cases, slurry adsorption has been applied to treat gas streams, but liquid streams can also be treated.

Although the phenomenon of slurry adsorption was first explored in 1910[372] and processes were patented in 1958,[698-700] it does not appear to have been commercialized. Equilibrium properties[372,570,624,720,733,751] and rates[372,570,720,733,751] of slurry adsorbents have been fairly extensively studied (more references are cited in these references). If the liquid does not penetrate into the pores or is not adsorbed, then the adsorption of gas *at equilibrium* is unchanged by the presence of the liquid. An example of this is the sorption of ethylene gas on 4 Å zeolite molecular sieve slurried in benzene. If the liquid competes for sites, then considerably less solute will be adsorbed. This is true even if the liquid is only weakly adsorbed, since its concentration is much greater than the solute concentration. Since the gas-liquid, liquid-film, and pore-diffusion resistances can all be important, an extra resistance has been added and rates will be slower than normal adsorption.

A slurry adsorption process[393] would consist of a slurry adsorber and a desorber using either a staged or continuous contractors. Although chemical desorption could be used, thermal desorption or thermal desorption plus depressurization would be more likely. One advantage of the slurry system is it can easily be adjusted for changing conditions by changing the mass of solid in the slurry. It appears that slurry adsorption can only be economical when the liquid does not compete for adsorption sites. This case was explored[393] and the author concluded that slurry adsorption had advantages, but no analysis of economics was presented.

A different system for moving the adsorbent countercurrent to the liquid is to add a flotation agent to a finely dispersed solid and then float the adsorbent with air bubbles.[740,1080] Unfortunately, many common flotation agents adsorb and decrease the capacity of the adsorbent, and the total system capacity is probably low. This method does not appear to have been commercialized, but was operated on a pilot-plant scale with both columns and flotation cells.

It appears to me that slurry adsorption could have advantages in special cases, but I doubt it will ever become a common separation method. It would probably be fruitful to look at separations being done by absorption to see if the addition of solid adsorbent would be helpful. Addition of a solid might be helpful if one species is controlling the absorption, because its solubility in the solvent is fairly low. A specific adsorbent could increase the slurry capacity for this solute and thus make the absorber smaller. Adding a solid might also be useful for handling surges or plant upsets.

B. Continuous Solids Flow Fractionation Systems

Systems with a continuous flow of solids have been used for fractionation of two solutes. Several cascade designs have been used, but most are variants of the basic cascades shown in Figures 6-10A and 6-10B.[125,492,569,865,967] In the adsorption cascade, Figure 6-10A, heat and steam are used for desorption and no carrier gas, solvent, or desorbent is used. Zones I and II adsorb solute B, while solute A moves up the column. Thus, zone I keeps B from the A product, while zone II keeps A from the B product. In zone III, solute B is desorbed with steam and external heating. Zone IV cools the solid with external cooling so that the solid can be returned to zone I.

In the chromatography system shown in Figure 6-10B, a desorbent, solvent, or carrier gas is used for desorption. In addition, zone III may also be heated to aid in desorption. Zone I removes B from the A product, zone II removes A from the B product, and zone III desorbs solute B. The purpose of zone IV is to recover desorbent for recycle. Zone IV is optional, but when it can be used it reduces the amount of makeup desorbent required and makes the A product more concentrated. In a generalized sense, both zones III and IV are producing reflux for zones I and II, which are doing the desired separation.
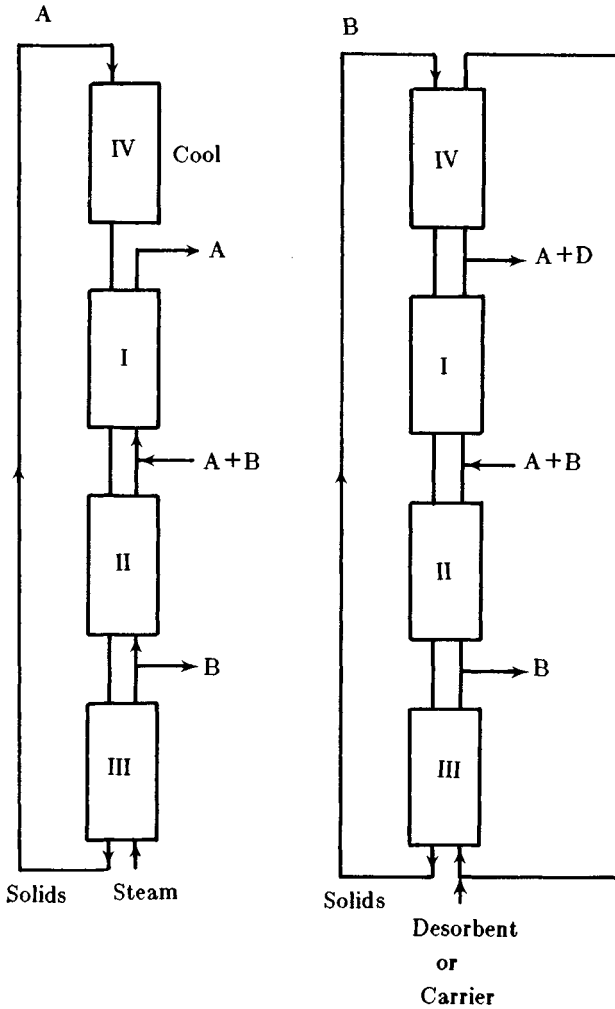
FIGURE 6-10. Cascades for fractionation: (A) adsorption; (B) chromatography.

The solute movement theory can be applied to both cascades. In both systems, we want solute A to move up in zones I and II

$$u_{Acc_1}, u_{Acc_2} > 0 \qquad (6-31a)$$

solute B to move down in zones I and II and up in zone III

$$u_{Bcc_1}, u_{Bcc_2} < 0 < u_{Bcc_3} \qquad (6-31b)$$

and in the chromatography system, Figure 6-10B, solute A should move down in zone IV.

$$u_{Acc_4} < 0 \qquad (6-31c)$$

The solute velocities in the countercurrent system are calculated using Equations 6-1, 6-2, and 2-28 or 2-30. Equation 6-31 should be satisfied for all concentrations in a given zone. For highly nonlinear systems, this may be difficult. In the adsorption system, the gas flow

rate in zone III is usually quite low. Thus, fairly high temperatures are required to desorb the solute and thus make $u_{B_{cc_3}} > 0$. In the chromatography system, the fluid flow rate can be high in zone III and high temperatures are not required; however, high temperatures or a desorbent which competes for adsorption sites will help desorb solute B in zone III. If zone IV in the chromatography system is used to purify desorbent or carrier for recycle, Equation 6-31c must be satisfied. Equation 6-31c is very difficult to satisfy if solute A is very weakly adsorbed, and optional zone IV may not be useful. Cooling of zone IV may increase adsorption and help Equation 6-31c to be satisfied.

Equation 6-31 can be used to determine ranges of fluid velocities and product flow rates for each of the zones.[1051,1052] Since the solute movement theory ignores dispersion effects, the ranges are optimistic. Equation 6-31 does serve to help the designer set reasonable initial conditions for more detailed design calculations.

1. Fractionation by Continuous Adsorption

The one example of large-scale commercial fractionation by adsorption is "hypersorption". Hypersorption was developed by the Union Oil Company of California in the late 1940s and early 1950s and was used commercially until the early 1960s. At that time, low-temperature distillation proved to be more economical. Activated carbon was used to separate light hydrocarbons and to produce acetylene. Technically, the systems worked well, although attrition was a problem.

The hypersorption process has been explained in detail in many original articles,[124,125,127,199,386,566,576] books,[487,687,990] and review articles.[79,126,1016] I will use less detail since the process is no longer in use. The basic cascade shown in Figure 6-10A was modified for the apparatus shown in Figure 6-11.[125] The solid passes successively through the cooling (zone IV), adsorption (zone I), rectifying (zone II), and desorption (zone III) sections. The desorption section is done in two parts: a region with steam stripping and a region with external heating. The solid was recycled using a gas lift line. A small slip stream of carbon can be removed and be sent to a separate high-temperature reactivator. Typical sizes and operating conditions[576] for a design rate of 75,000 SCF/hr of feed gas are given in Table 6.1. Alternative designs were also used. For example, columns with sidecuts were designed by contacting gas with carbon which by-passed zone I, and then a pure sidecut stream could be withdrawn. This type of column has the same function as a multicomponent distillation with a rectifying section.

The Hypersorber is a complex, nonisothermal, multicomponent separator. Experimentally determined concentration and temperature profiles for recovery of propane and heavier components from natural gas are shown in Figure 6-12.[125] The concentration profiles are somewhat similar to those observed for multicomponent distillation.[169,488,586] The temperature profile shown in Figure 6-12B is quite complex because of the addition of steam, the external heating and cooling, and the significant heat of adsorption.

The system operated as a dense moving bed. The carbon flow was controlled by oscillating trays with downspouts, a mechanism which was first patented in the 1880s.[967] Movement of the top tray filled the downspouts which then emptied when they were covered by the top tray, but opened by the bottom tray. The carbon movement was essentially vertical. In the cooling and heating sections, the carbon flows in the tubes of a shell-and-tube heat exchanger. In zones I and II, the HETP in commercial units was approximately 10 in.,[124] which implies that there was either significant mass transfer resistances or axial mixing. The commercial systems had the equivalent of approximately six equilibrium contacts in both zones I and II.[124] This was sufficient for the separations which were done commercially. Attrition losses were a problem, but could be reduced if modern spherical carbon beads were used.

Laboratory units showed very high mass transfer rates, and hence, low HTU for exchange

LIFT GAS RETURN

LIFT LINE

CYCLONES

COOLER

TOP PRODUCT

FEED

BOTTOM PRODUCT

STEAM IN

STRIPPER

RECIPROCATING FEED TRAY

SOLIDS FLOW CONTROL VALVE

LIFT LINE
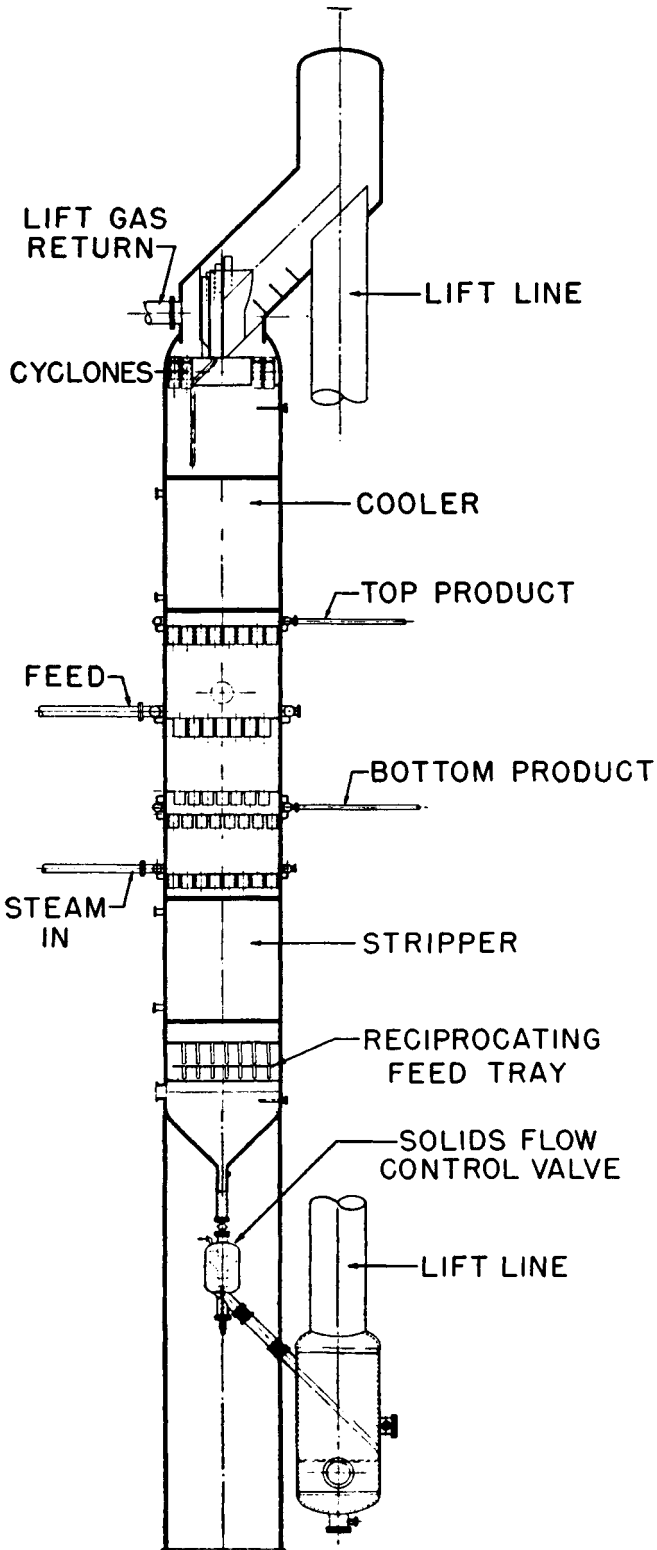
FIGURE 6-11. Hypersorption apparatus. (From Berg, C., *Chem. Eng. Prog.*, 47, 585, 1951. With permission.)

Table 6-1
OPERATING CONDITIONS FOR HYPERSORBER

Carbon flow rate: Maximum is 32,000 lb/hr, Design is 18,000 lb/hr
Design gas flow rate: 75,000 SCF/hr
Pressure: 75 psig
Steam rate: ca. 400 lb/hr
Carbon stripping temperature: 510°F
4.5 ft diameter, 85 ft high
Distance from feed to product: 5 ft
Carbon: 12—60 mesh coconut-shell or fruit-pit
Feed gas: 5.8 vol % ethylene
Product gas (vol %):
   0.1% O_2, 2.9% CO_2, 3.6% C_2H_2, 92.7% C_2H_4, 0.7% C_2H_6
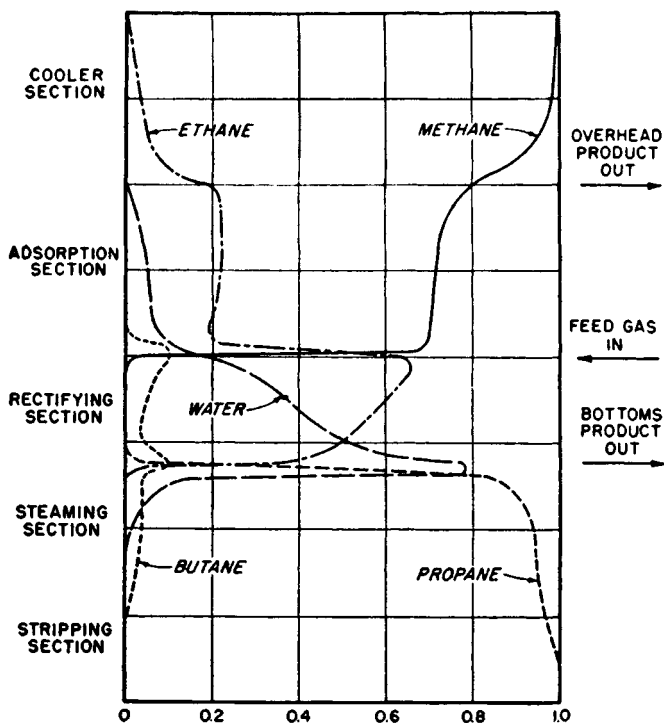
A

FIGURE 6-12.   Concentration and temperature profiles in hypersorber for propane and heavier removal from natural gas. (From Berg, C., *Chem. Eng. Prog.*, 47, 585, 1951. With permission.)

adsorption of ethane and ethylene.[199] When exchange adsorption occurs, the sections are essentially isothermal. In other sections where heat transfer was important, the heat transfer rate was low and apparently occurred mainly due to interparticle conduction.[199] Thus, HTU values for methane-acetylene and methane-carbon dioxide-acetylene separations were significantly higher[566] than for exchange adsorption.

The preferred method for doing calculations for the commercial units was to treat the hypersorber as a staged, multicomponent system.[124,125,576] Then, standard calculation methods developed for multicomponent distillation could be used. This approach does require separate determination of the HETP. Isothermal, binary calculations can be done on a McCabe-Thiele
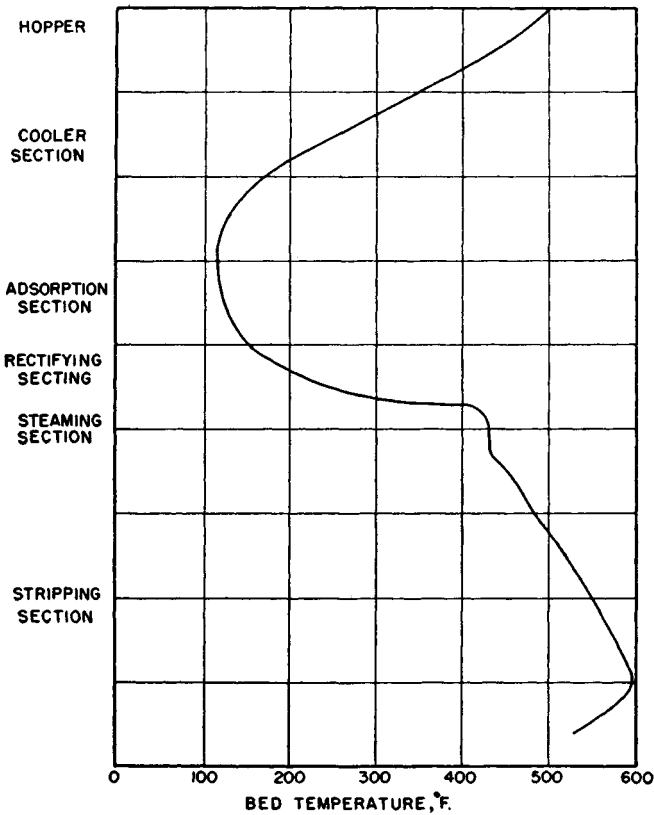
FIGURE 6-12B

diagram.[990] However, considering the temperature profile shown in Figure 6-12B, this method has limited utility. The HTU-NTU mass transfer approach was applied to isothermal laboratory columns[199,566] and good agreement between theory and experiment was observed.

Other designs have been tried for adsorption fractionation, but were not used commercially. A small-scale system using an open tube with vibration at the bottom was tried for separation of ethanol and benzene on activated carbon.[525] With 12 to 18 mesh British sieve size, the H_{OG} was from 10 to 16 in. A pilot scale system similar to the hypersorber except with a staged fluidized bed adsorber (zones I and II), was studied by Esso[361] for light hydrocarbon separations using activated carbon. The stage efficiencies were 96 ± 5% with fluid velocities in the commercial design range. This equipment was apparently never commercialized. A large number of other moving bed devices have been patented.[1025]

Two developments could make these fractionators economic again. One is better adsorbents such as the spherical carbon beads used for activated carbon recovery.[47,1004] The other important development is better methods of moving the solid such as magnetically stabilized fluidized beds.[674,857-861] These developments should reduce attrition and increase the number of contacts which can be obtained. Of course, the competition is now stiffer, since the simulated moving bed is now a well-developed device (see Section V.B). Exchange adsorption separations are an interesting candidate for additional development since the HTU values are low and short bed sections are sufficient.

2. Fractionation by Continuous Chromatography

Several continuous chromatography schemes using variations of the cascade shown in Figure 6-10B have been studied. Although fairly successful on a small scale, the method
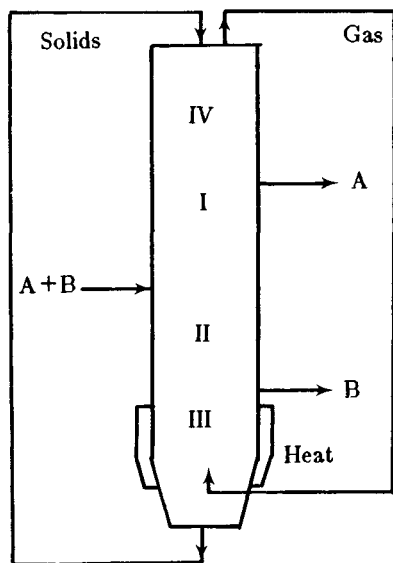
FIGURE 6-13.   Schematic of continuous,
countercurrent GLC system.

apparently has not been commercialized. Most of the studies have been on gas-liquid chromatography (GLC), perhaps because much of the research occurred shortly after the phenomenal analytical success of GLC in the 1950s. This work has been extensively reviewed.[78,79, 829,947,951]

A typical arrangement for continuous countercurrent GLC is shown in Figure 6-13.[79,85,101,374,386,881] The solid coated with the stationary phase flows countercurrent to the gas stream in an empty tube. Zone III is usually heated to help in the removal of the less volatile component, B. A carrier gas is added at the bottom of the column, and in most systems a zone IV is included so that carrier gas could be recycled. Continuous chromatography can be modified to produce three products by adding a side column which acts the same way as a side rectifier in multicomponent distillation.[79,96] The continuous chromatograph has also been studied as a reactor.[11,970,971,1023]

Typical experimental concentration profiles are shown in Figure 6-14[79] for the separation of benzene and cyclohexane on a polyglycol derivative at 20°C. The more strongly sorbed benzene is removed as the bottom product, while cyclohexane exits as the top product. Note that the highest concentration of both solutes is near the feed point. The measured HETP was 0.9 in. (22.9 mm), which is high. Later workers were able to reduce the HETP to 13 mm at low gas flow rates and to 19 mm at high gas flow rates.[813] This compared to an HETP of 5 mm for the same column operating as a fixed bed, pulse chromatograph.[813] The HETP is larger in the moving bed system because of channeling, mixing, higher external porosity, and higher solute concentrations. The latter has an effect because isotherm curvature will cause zone spreading.

Another approach, which was not very successful, is to flow the liquid downwards over a stagnant inert packing.[79,460,814] The operation is essentially a fractionation by absorption. With knitted packing, the HETP was 50 to 300% greater than that observed with continuous GLC.[814]

Few continuous flow, liquid phase, chromatographic fractionation systems have been reported. The countercurrent flow of liquid and solid is more difficult, but was used for uranium purification[57] using a fractionation scheme somewhat different than those shown

FIGURE 6-14.   Concentration for separation of cyclohexane and benzene by continuous GLC. (From Knox, J. H., Ed., *Developments in Chromatography, Part I*, Applied Science Publishers, 1978. With permission.)

in Figure 6-10. Systems with intermittent solids flow have been studied (see Section III.B) and a continuous flow system was simulated in the laboratory,[491] but the actual countercurrent flow was not tried.

The solute movement theory can be applied to continuous chromatography. The result will be conditions for separation in each zone which are the same as for hypersorption, Equation 6-31a to c. Staged theories have been extensively used to model continuous chromatography.[374,492,813,983] Zones I, II, and IV are usually isothermal, and often zone III is close to isothermal, but at a higher temperature. The McCabe-Thiele diagram will be similar to two solvent extraction.[169,586] This is shown in Figure 6-15 for the more volatile of the two solvents. Note that concentration is highest at the feed stage and drops off at the ends. The A does exit at the top of the column. The ratio of L to V would be set so that more strongly component B will have a very low y_{top} and a higher x_{bot}. The graphical approach is useful for understanding the separation. However, the solution is trial-error and is inconvenient when there is a large number of stages. If the system is dilute and the isotherms are linear, the Kremser equation modified for a center feed[169,374,586] is convenient. For more concentrated systems, computer models can be used.[983] The random walk analysis used to study analytical chromatography has been extended to countercurrent chromatography.[885]

What can be seen for the future of continuous countercurrent chromatography? First, the results could be improved by operating the GLC at the optimum temperature and by using hydrogen as the carrier gas (see Chapter 5, Section VII). Second, a better method of controlling solids flow such as magnetic stabilization could serve to reduce HETP values. Once these problems have been solved, the moving bed chromatograph has to compete with moving bed adsorbers, elution chromatography, simulated moving beds, and hybrid methods. My guess is that moving bed chromatographs will remain uncommon.

III. INTERMITTENT SOLIDS FLOW

With intermittent solids flow, the contacting is done in two steps. In the fluid flow step, the solid is either in a packed bed or is fluidized while the fluid flows through the solid. In the solids flow step, a slurry of solids and fluid is pulsed in the countercurrent direction. The net result is countercurrent flow of solid and fluid. Physically, there are several different

▲ cyclohexane

■ benzene

FIGURE 6-14.   Concentration for separation of cyclohexane and benzene by continuous GLC. (From Knox, J. H., Ed., *Developments in Chromatography, Part I*, Applied Science Publishers, 1978. With permission.)

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FIGURE 6-15. McCabe-Thiele Analysis for continuous, countercurrent chromatography.

ways of doing this, several of which have been successfully commercialized. Intermittent flow is used because it allows for stable operation without excessive mixing of the solid.

The development of the separation is easily seen from the solute movement theory for a system with a packed bed during the fluid flow step. For removal of a single solute, there will be at least one sorption and one regeneration section. During the fluid flow step, the movement of solute is given by Equations 2-28 or 2-30. During the solids flow step, we assume that a plug of solids of height l_p is moved downwards into the regenerator. Fresh solids are placed into the sorber. The solute movement diagram for a nonlinear isotherm is shown in Figure 6-16A. The thermodynamic conditions in the regenerator are changed so that removal of the solute is facilitated. Thus, the fluid velocities are much lower in the regenerator and a concentrated product is produced. Note in Figure 6-16A that only a shock wave (constant pattern behavior) occurs in the sorption section, while the regenerator is controlled by a diffuse wave (proportional pattern behavior). If the conditions in the regenerator can be changed enough so that solute equilibrium becomes unfavorable, then a shock wave will occur in the regenerator instead of the diffuse wave. This can be done in water softening by using a high salt concentration in the regenerator, and is desirable, since it gives more complete regeneration using less regenerant.

In normal practice, the height of bed moved, l_p, is much less than the total length of the bed. This is particularly desirable if the MTZ is quite long. The average solids velocity is

$$v_{solids,\ avg} = l_p/t_p \qquad (6\text{-}32)$$

where l_p is the length of solids moved, $l_p < L$, and t_p is the period of fluid flow which can be adjusted to give any desired average solids flow rate. If we control the solids movement so that

A

B

C
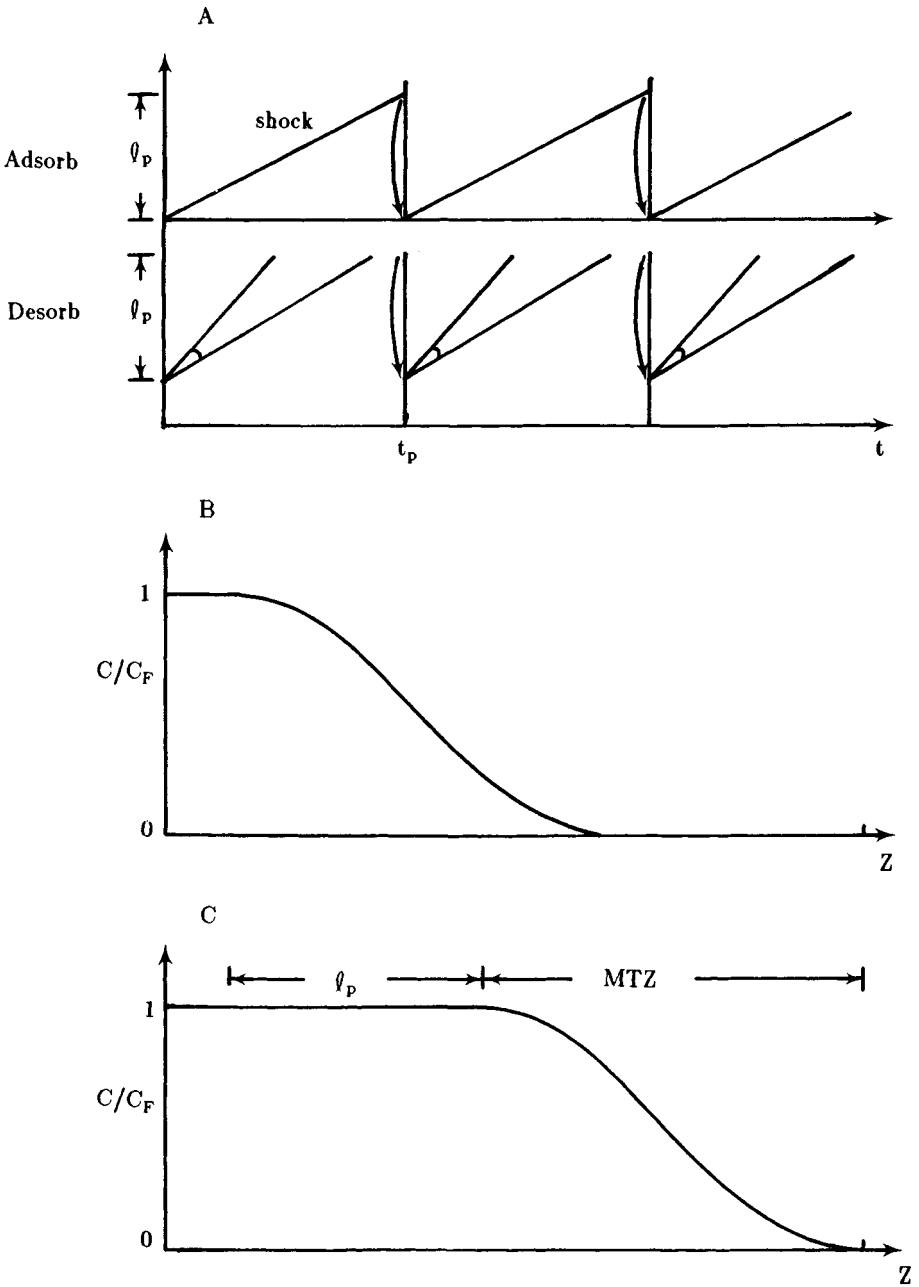
FIGURE 6-16. Intermittent solids movement systems for one solute. (A) Solute movement diagram. Entire bed is removed during each solids movement step, $\ell_p = L$. (B) Mass transfer zone in column at beginning of fluid flow step. $\ell_p < L$; (C) Mass transfer zone in column at end of fluid flow step. $\ell_p < L$.

$$V_{solids,\ avg} = u_{sh} \tag{6-33}$$

the constant wave pattern will be held "stationary" in the bed. (Obviously, it moves back and forth each cycle, but its average position is constant). Now the long MTZ can be kept entirely inside the bed. This situation is shown in Figure 6-16B and C which shows the

MTZ at the beginning and end of the fluid flow step. This is very useful since all the sorbent sent to the regenerator will be fully loaded and a more concentrated solution with less regenerant consumption will be produced. This type of operation is used with intermittent solids flow in activated carbon adsorbers. Operation with small pulses would also be desirable for fractionation.[1051,1052]

In Figure 6-16 we have assumed that the solids slurry can be transferred as a plug without mixing. It is important that new and old parts of the bed do not mix. Any such mixing will increase the length of the MTZ or make fractionation more difficult. In actual operation, both the feed flow rate and concentration fluctuate. Temporary increases in these will increase both u_{shock} and the MTZ. In order to produce a product of desired quality, the effective solids velocity must be increased (Equation 6-32). Since instantaneous adjustment is difficult, a practical bed length would be significantly longer than the minimum length, l_p + MTZ.

Mathematically, an intermittent solids flow system and a simulated moving bed (SMB) system (see Section V) are similar if the solids are assumed to move in plug flow.[380,655,954,1051] In the SMB system, the switching of locations shown in Figure 6-16 is done with valves by changing which parts of the bed are in a given section. Obviously, the two systems are physically very different. The intermittent solids movement system is required if the solids must be sent to a separate furnace or column for regeneration. Otherwise, the choice between intermittent solids movement and a SMB will depend on the importance of mixing, what is commercially available, and an economic evaluation for the specific case.

A. Packed Bed During Fluid Flow Step

Systems with a packed bed during the fluid flow step are commonly used in activated carbon adsorption and in ion exchange. In the activated carbon systems, $l_p <<$ L[13,53,380,493,526,527,553,688,831,941,1082] to keep the MTZ inside the column. The bottom of the column would typically be a cone with a 60° angle connected to a valve and eductor for transferring the slurry.[527,553,941] The solids are dewatered by draining with or without air flow. The carbon is then reactivated with steam, solvent wash, or most commonly, in a high-temperature kiln (see Chapter 3, Section IV.B).

Intermittent solids movement activated carbon and bone char adsorbers have been common for many years in the sugar industry.[53,299,493,687,688] Also, 40-ft-tall carbon beds have been reported[53] for decolorizing sugar solutions. The pulse of carbon is first transferred to a "sweetening off" column where sugar solution from the void spaces is removed with a water wash. After dewatering, the carbon is reactivated in a kiln and then cooled. Before returning the carbon to the adsorber, it is "sweetened on" by filling the voids with clean sugar solution. Since the color forming materials have quite high molecular weights, the diffusion in the carbon pores is very slow. The MTZ is thus quite long and use of a long column with short pulses is appropriate. Many sugar refineries are switching from carbon to resin systems for economic reasons.

Pulsed beds are commonly used for activated carbon treatment of waste-water.[13,527,553,941,1082] Since the MTZ tends to be quite long, a single fixed bed would have low bed utilization and only partly loaded carbon when it is regenerated. A pulsed bed system can completely load the carbon. A typical pulsed bed system is shown schematically in Figure 6-17.[941] Fluid flows upward and carbon is intermittently pulsed downwards in a slurry. The spent carbon is sent to a drain bin and dewatering screen before being regenerated in a furnace.[941] After regeneration and quenching, the regenerated carbon is mixed with fresh makeup carbon and recycled to the adsorbers. Pulsed beds are typically designed so that $20 \, l_p = L$[527,1082] and the results are very close to a truly countercurrent system. Pulsed beds operate at velocities in the range of 5 to 9 gpm/ft^2 which is higher than the 3 to 7 gpm/ft^2 used for beds in series and considerably higher than the 1 to 4 gpm/ft^2 for single beds.[527]

The Asahi system[53,56,163,198,299,332,149,493,622,649,922,928,936,943,1111] does all the steps in a con-

CHARGE CHAMBER
(TYP.)

SCREENED
OVERFLOW

EFFLUENT TAKE-OFF
HEADER

TYPICAL INFLUENT/
EFFLUENT SEPTA

VESSEL CONSTRUCTION
316SS CARBON STEEL
W/RUBBER OR EPOXY
LINING

CARBON BED

NOZZLE (TYP.)

FEED INLET

WATER INLET

INLET HEADER

PULSE TRANSFER
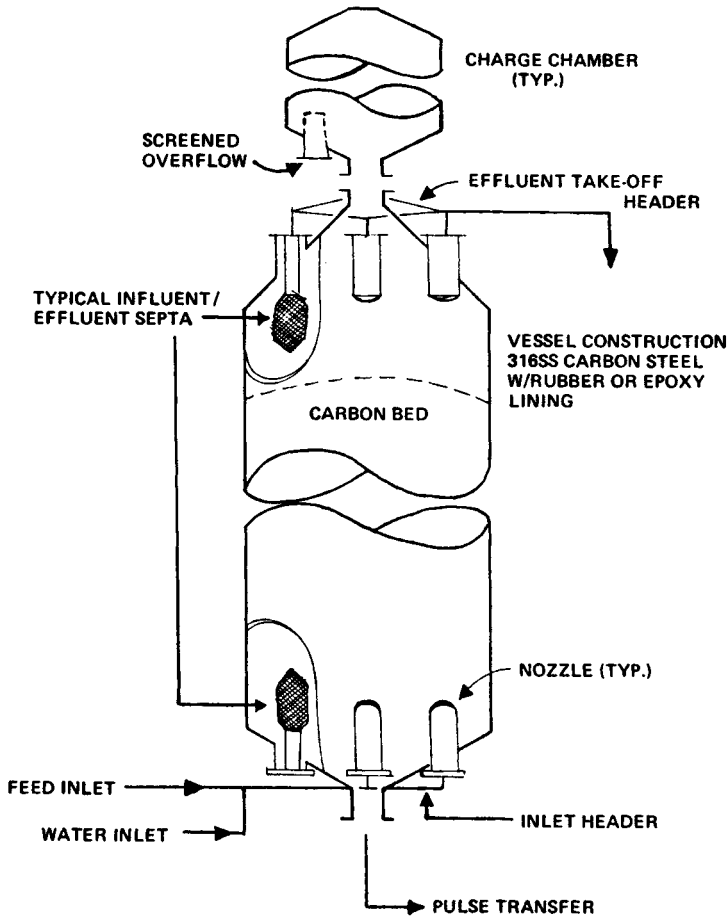
FIGURE 6-17. Typical pulsed bed activated carbon wastewater treatment system. (From Perrich, J. R., Ed., *Activated Carbon Adsorption for Wastewater Treatment*, CRC Press, Boca Raton, Fla., 1981. With permission.)

ventional pressure vessel with a support grid at the bottom and a resin retention grid at the top (Figure 6-18).[56] During the feed step (Figure 6-18A), the upward flowing water pushes the resin against the top grid, forming a densely packed bed. The product water exits at B. The ball at D is held shut by the water flow, preventing addition of resin. While water is being treated, some of the feed water is used to push resin in the cone out at C and into the resin hopper for the next unit. When the fluid flow step is finished, valve A is closed and valve E is opened to reduce the pressure. The resin is no longer held at the top of the unit and drops down into the cone. Ball D drops, allowing fresh resin from the feed hopper to enter. This operation takes less than 1 min. Then valve E is closed and valve A is opened to start the next cycle.

The entire system consists of the loading column, the regeneration column, and a wash column to remove regenerant. The solids circulate in a loop through the three columns. All three columns use the basic operating principle described above. Since flow rates differ in the three columns, their geometries differ. The loading column, where equilibrium is quite favorable, but flow rates are high, is relatively short and fat. The regeneration column has low flow rates, but less favorable equilibrium and thus is tall and narrow. The purpose of the washing column is to displace regenerant fluid in the void volume and thus a fluidized bed is used, but the same solids transfer mechanism is used. For demineralization, mixed resins are used and the flow sheet is modified.[163,936]
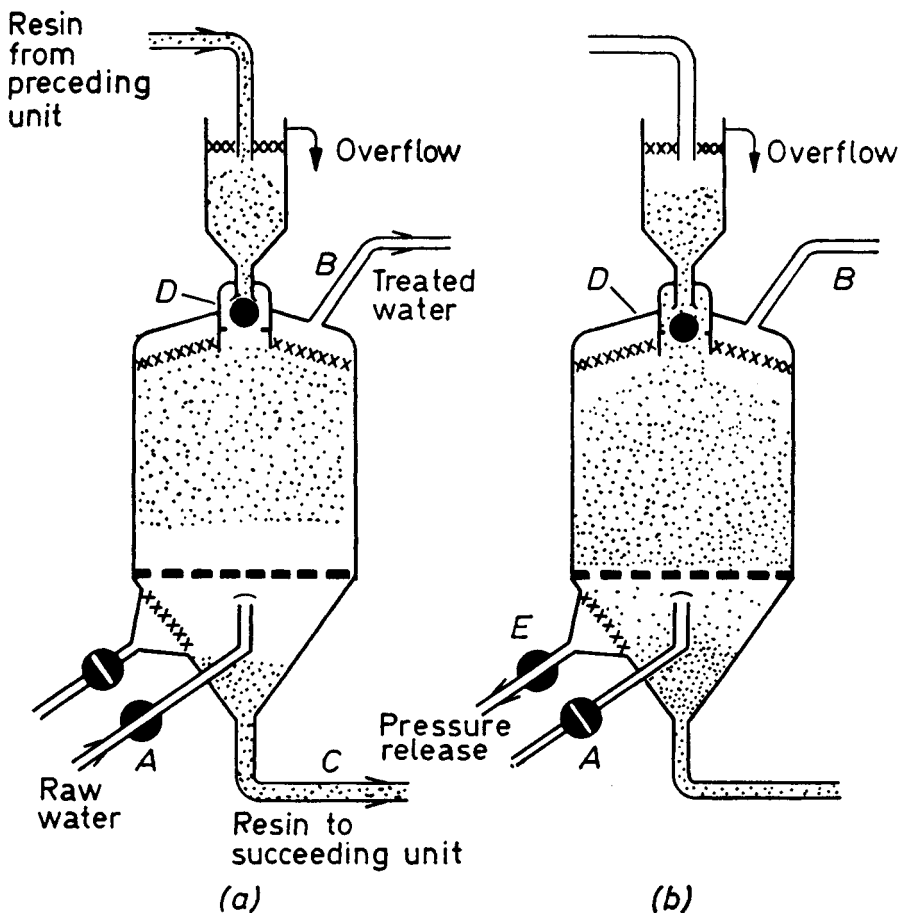
FIGURE 6-18. Asahi system for resin transfer. (A) Fluid flow step and resin transferred to feed hoppers of next unit; (B) addition of new resin.

Problems with the plants have arisen in binding of the outlet strainers and maintenance of the ball valve at D.[922] The functioning of the valve at D is critical for proper operation. The system is gentle on the resin since the only moving part in contact with the resin is valve D. The Asahi system has been extensively used for water softening and demineralization, in sugar refining, and effluent treatment.

The Higgins or Chem-Seps process uses a continuous loop instead of separate vessels.[53,56,57,232,299,332,493,496-501,622,647,855,922,928,943] This system is shown in Figure 6-19. During the fluid flow step, the resin is in a packed bed in the treating and regeneration sections while the resin is fluidized in the backwash section. During the solids movement step, which lasts around 15 to 20 sec, a pulse of water is used to push the resin countercurrent to the liquid flow. During the solids movement, "slippage" occurs in that the liquid moves two to three times faster and further than the solid. The rinse is used to push the solutions back by making a void volume displacement of salt solution. Permutit had a similar system which was commercially available for several years.[419]

This Chem-Seps system has been widely used for water softening, water dealkalization, demineralization, ammonium nitrate recovery, removal of nitrate ion, hydrometallurgical processes, and wastewater treatment. Early plants were plagued by resin attrition. Redesign of the valves in contact with the resin has reduced attrition to less than 25% per year for cation resins and 35% per year for anion resins.[922] Resin replacement represents an operating cost which is small compared to regenerant cost or capital charges.

Valve positions during cycles

Run cycle		Pulse cycle	
Valves open	Valves closed	Valves open	Valves closed
A,WA,IN,EF	B,C,D,PU	B,C,D,PU	A,WA,IN,EF,RI,RE
RI, RE			
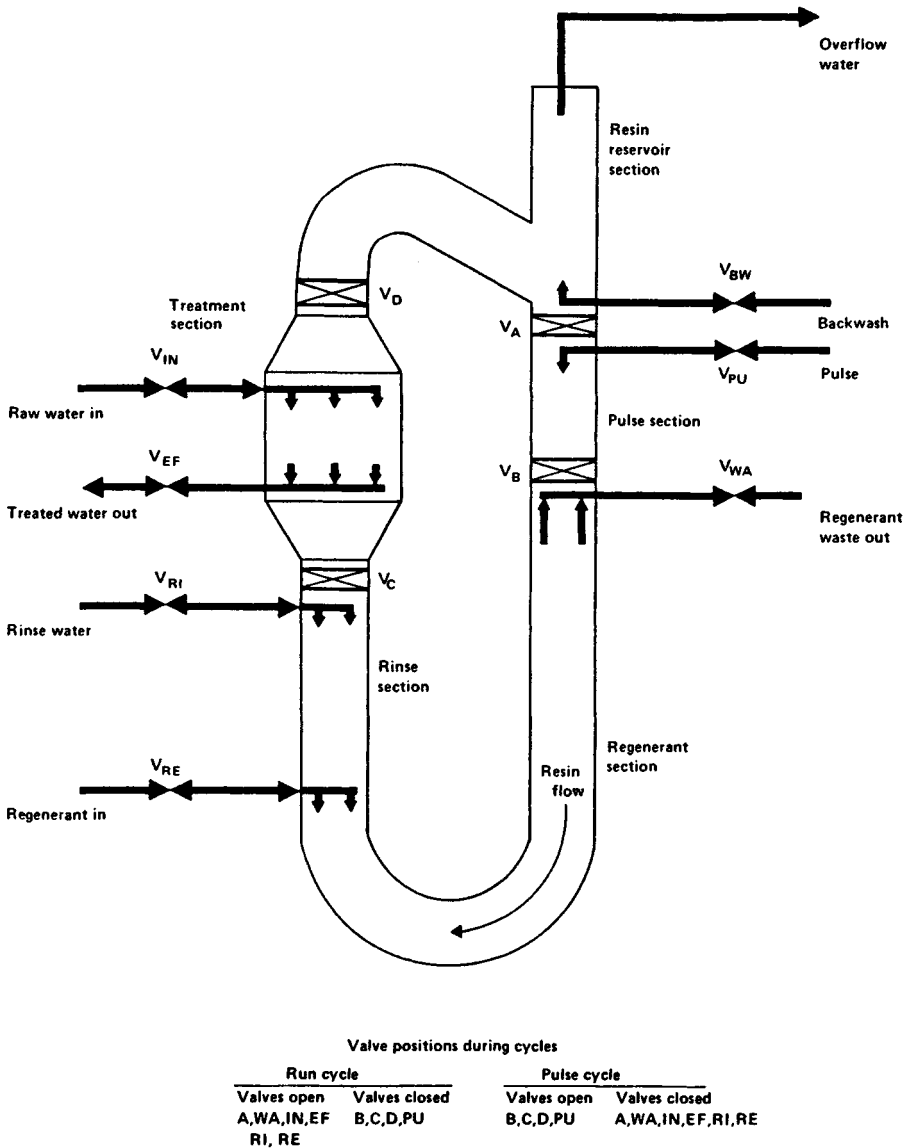
FIGURE 6-19. Chem-Seps semicontinuous ion exchange system. (From Calmon, C. and Gold, H., Eds., *Ion Exchange for Pollution Control*, Vol. 2, CRC Press, Boca Raton, Fla., 1979. With permission.)

A slightly different type of pulsed moving bed ion exchange system has recently been commercialized for recovery of uranium from mine water.[508] This system uses an ordinary column with downward flow of the fluid and a short upward pulse of the resin as a slurry. A solid plug of resin moves up the column and there is no resin mixing. Two columns, each 2.16 m in diameter, were used for loading with a total flow of 204 m^3/hr of water. Resin is transferred once every 3 hr with a resin batch size of 87 ℓ. The influent contained from 3 to 5.9 mg of uranium per liter, while the effluent had to be less than 0.010 mg/ℓ. The single regeneration column has a much lower liquid flow rate and was 0.61 m in diameter. The total bed depth was 4.36 m, which allowed for 15 resin batches in the column at one time. The eluate sent to the mill was 15 g of uranium per liter, which is a 3000-fold increase in concentration. Obviously, this type of equipment could be adapted to other situations.

All of the intermittent solids movement systems with packed solids beds may have some problems with plugging if the feed contains high suspended solids loadings. (Low loadings of suspended solids can be tolerated.) Thus, the feed may need to be filtered. If operation without filtration is desired, one of the fluidized bed designs (see next section) will be preferable.

When first introduced, the continuous ion exchange systems were claimed to have very significant advantages over fixed beds. Much of this advantage was from comparison of the countercurrent moving bed system with a packed bed using co-flow regeneration. When compared with packed beds using counter-flow regeneration, the regenerant usage of packed and continuous systems is very similar. The continuous systems can have lower capital investment, can be more flexible, are often easier to control, and require less floor space than fixed beds. However, the continuous systems must be properly designed and must have good liquid and solids distribution. Otherwise, channeling and resin short-circuiting can drastically decrease the separation. The continuous system also requires more head space than fixed beds. Finally, if the ion exchange system is critical, a second continuous ion exchange system will be needed for standby. Since multiple fixed bed columns are commonly used, the fixed bed system essentially has built-in standby capacity.

The intermittent packed bed systems really consist of a number of batch steps. The most realistic models will treat the problem in this way.[380,437,653,954] However, if $l_p << L$ so that a large number of pulses are required to move solid completely through the bed, the pulsed operation approaches continuous movement asymptotically. Some designers have assumed that operation was close to continuous countercurrent operation and designed the pulsed system as a continuous countercurrent system[163,649,923] since it greatly simplifies the calculations. As l_p/L decreases, this assumption becomes more reasonable.

B. Staged Fluidized Bed During Fluid Flow Step

Fluidized beds which can treat slurry feeds are very desirable in ion exchange treatment of leachates in mineral processing plants. These "resin-in-pulp" plants simplify the solids separations part of the plant (always operationally difficult) and reduce or eliminate losses of product entrained with the solid. The system needs to be designed so that the small particles in the feed slurry are entrained with the fluid, while the larger resin particles move countercurrent to the fluid. Several staged fluidized bed designs have been developed which are capable of doing this. They all work on the principle of intermittently stopping flow, allowing the resin to settle, and then moving the solids downwards as a slurry. Similar devices could be adapted to adsorption.

The basic principle for intermittent resin movement in a fluidized bed was developed by Cloete and Streat[267] in 1963. They first used a system with separate stages connected by piping,[122,267] but later applications of the method used a staged fluidized bed without downcomers.[265,328,379,611,921,922,939,943] Similar designs were independently developed by the U.S. Bureau of Mines[410,411,862,922,943,989] and Liquitech.[766] The three-step operational principle is illustrated in Figure 6-20. The relatively long fluidization period has the fluid passing through and fluidizing each bed (Figure 6-20A). Then, a short period for settling (Figure 6-20B) is followed by reverse flow where the resin is transferred downwards to the next stage (Figure 6-20C). Since velocities are low and no valves close on the resin, the attrition rates are very low. A complete plant consists of a loading column which receives the raw feed and a separate column where resin regeneration and washing are done. As in previous systems, the regeneration column is long and narrow, since flow rates are low and long residence times are required.

The actual operation is time dependent, but a cyclic steady state is soon reached. The nature of the cycles is shown in Figure 6-21[328] which shows concentration profiles in a four-stage contactor once the cyclic steady state has been reached. The concentration on each
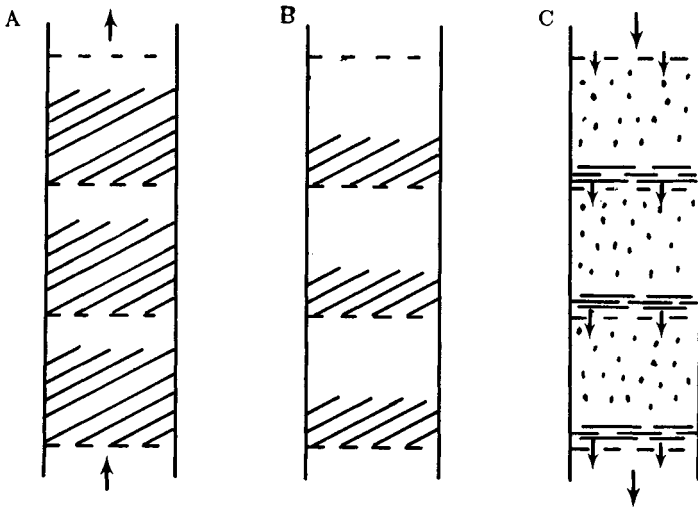
FIGURE 6-20. Principle of operation of intermittent staged fluidized bed. (A) Fluidized bed; (B) stop flow and settle resin; (C) flow reversal and resin transfer.

stage starts and ends at the same value, and then the cycle repeats. Note, that the concentration decreases in steps as you go up the column (stage four is the top stage). To predict the actual profile, a time-dependent model was numerically integrated.[328,379,921] Simpler series of mixed cell models can be solved analytically if the liquid side resistance is controlling.[610,611,924] The mixed cell model which was preferred used N mixing cells for the solid and plug flow of the liquid.[611] It is interesting that the mixed cell models do not give an accurate fit of breakthrough data for single deep fluidized beds,[610,611,924] but they do give a good fit for shallow staged fluidized beds.[611] Models with film diffusion control,[636] pore diffusion control,[435] and a mixed quadratic driving force model[379] required numerical integration, but gave good fits of the data. Simulation of large-scale systems required a variable rate constant for good fits.[379]

Comparison of the intermittent transfer system with continuous resin flow showed that the intermittent transfer system is superior at low fractional conversion and, if operated optimally, was always superior to continuous solids flow.[435,436] This improvement occurs because the average driving force for mass transfer is larger in the intermittent transfer system. Essentially, the complete contents of each stage should be transferred each cycle.[379,435,436,989] The top stage should also be loaded intermittently. For gross predictions, the system can be assumed to be truly countercurrent and steady-state staged models can be used.[435,436,1009]

Current commercial applications of intermittent fluidized bed ion exchange are the South African National Institute of Metallurgy Continuous Ion Exchange (NIMCIX),[265,379,410,922] U.S. Bureau of Mines (USBM),[410,411,826,922,943,989] and Himsley systems.[265,509,922,943] The NIMCIX plant is a direct follow-up of the original Cloete-Streat development. It is in commercial use in South Africa and in the U.S. for U_3O_8 and gold recovery. Attrition losses of resin are less than 1% of resin inventory per month[265] and thus is not critical. Operating experience has shown no major problems.[265] The independently developed USBM contactor, which differs mainly in the plate design, is in commercial use in the U.S.[989] Details of the NIMCIX and USBM plants are available elsewhere.[265,922,943,989]

The most recent design is the Himsley system.[265,299,509,922,943] The loading column is a staged fluidized bed, but transfer of resin is done differently. The resin is transferred sequentially starting at the bottom of the column where a resin transfer tank is filled and used
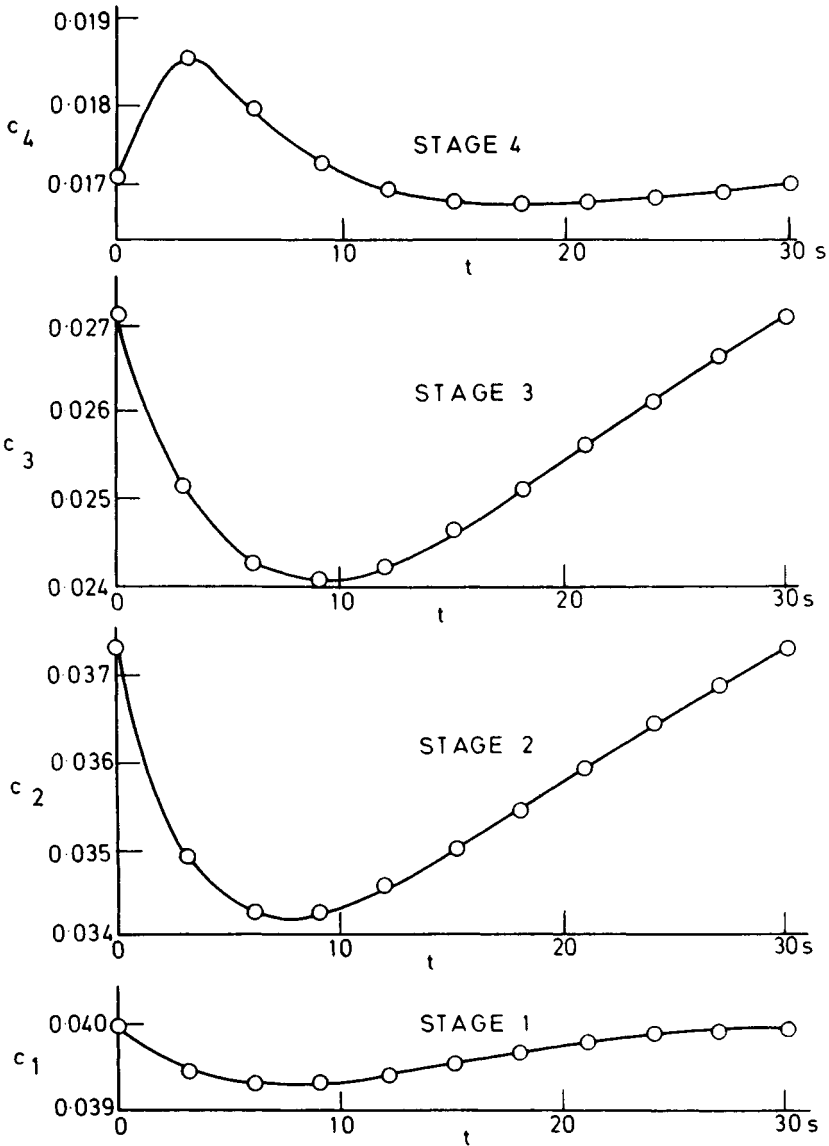
FIGURE 6-21.   Concentration profiles for a four-stage intermittent fluidized bed ion exchanger. (From Dodds, R., Hudson, P. I., Kershenbaum, L., and Streat, M., *Chem. Eng. Sci.*, 28, 1233, 1973. With permission.)

to control the amount of resin moved. The manifold system shown in Figure 6-22[509] is used to pump liquid around from one stage to the stage above. This liquid recirculation locally reverses the flow of fluid. This flow reversal, shown for the third stage, carries resin down to the next stage. Note that the pump and valves work on liquid and not resin. Since flow of feed is continuous throughout the transfer process, mass transfer continues on all stages except the one stage where resin is being transferred. The Himsley process uses a packed bed regenerator with intermittent *upward* flow of solid. This minimizes axial mixing. The resin is rinsed at the top of the regenerator or in a separate vessel. The Himsley system is used in Canada and South Africa for uranium recovery. Feeds with dissolved solids apparently cause no problems. Details of Himsley plant installations are presented elsewhere.[922,943] The
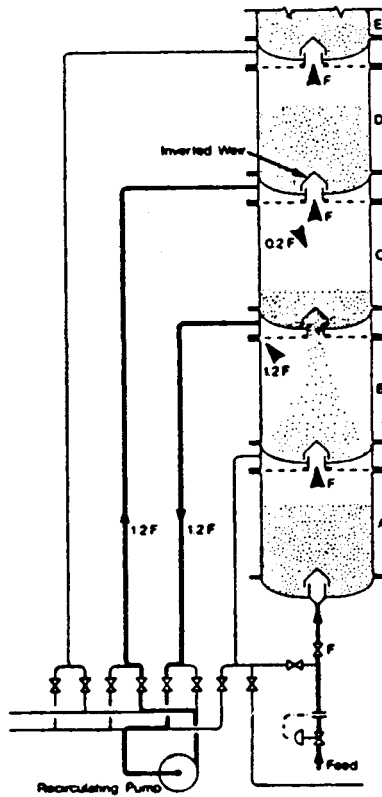
FIGURE 6-22. Resin transfer system for Himsley contactor.

suggested design procedure uses laboratory data from a single three-stage system which is then scaled up to the desired throughputs.[509]

Stages can also be separate instead of being stacked in a column. This can have the advantage of handling higher solids concentrations in the feed. The Porter system[265,922] uses four lines of five fluidized stages each for recovery of uranium. Each stage is on the ground and air lifts are used to transfer resin from one stage to the next. This is an extremely large system and is quite expensive since there is little economy of scale.

The intermittent fluidized bed designs could be applied to fractionation of ions by using a center feed and thus introducing a zone 2 (see Figure 6-10B) into the contactor. Since this would only be feasible when the separation factor is fairly large, and hence, few stages are required, it does not appear to have been done commercially. It has been demonstrated in a small-scale modification of the original Cloete-Streat design.[266]

Particle size requirements for liquid fluidized bed systems are different than they are for packed beds. In fluidized beds, the mass transfer rate increases as particle diameter decreases, but both the fluidizing velocity and the velocity at which particles will be carried from the bed decrease as particle diameter decreases. For ion exchange of dilute solutions, small particles are generally controlled by hydrodynamics and not rate. Thus, for dilute solutions, fairly large particles should be used. For concentrated solutions, mass transfer rate usually controls and small beads are preferred. If the feed contains suspended solids, fairly large resin beads are used so that the solids pass through the column while the beads stay in the column.

C. Miscellaneous Designs

Several designs which do not easily fit into other categories have been tried at various times. A laboratory-staged system with intermittent transfer of both fluid and solids based on the Craig countercurrent distributor was used to separate Li^+ and K^+.[495] This design is not suitable for scale up. Another small-scale device consisting of tubing wrapped around a cylinder has been used for both ion exchange[906,907] and gas adsorption.[906] The apparatus slowly rotated and by screw action moved slugs of solid through the tubing. This device would also be difficult to scale up.

A dense moving bed system with pulse movements of the solids was used for thermally regenerated fractionation by ion exchange.[71] This separation is based on shifts of the equilibrium curve when the temperature is changed and this is somewhat analogous to parametric pumping and the Sirotherm process (see Chapter 4, Section III.E). The system consisted of a cold and a hot column with center feed into the hot column and a recycle line leaving the center of the cold column and being reinjected with the fresh feed. This recycle line allowed for adjustment of the operating line to follow the curvature of the equilibrium curves. Separations of Ca^{++}/K^+ and Na^+/H^+ were obtained, but with rather large internal recycle flows. It should be possible to scale up this system, but no follow-up research has been reported.

IV. MOVING EQUIPMENT SYSTEMS

Another approach to obtaining continuous countercurrent motion of solid and fluid is to form a packed bed and then move the entire packed bed counter to the liquid flow. The two main methods for doing this are moving belt systems and rotating column systems. There was considerable interest in these systems in the 1950s and 1960s, and some commercial, large-scale systems have been built. However, this approach tends to be mechanically quite complex. Advances in the moving bed and simulated moving bed techniques have apparently removed much of the need for moving equipment systems. Of course, a clever inventor might develop a simple moving equipment system which would capture a large market. Because of my pessimism about the future of moving equipment systems and apparent declining interest, this section will be a short overview.

Moving belt systems package the sorbent inside a flexible belt or tube. This belt is then rotated through reservoirs in a direction countercurrent to the fluid flow. A schematic of one way of doing this is shown in Figure 6-23. A variety of modifications of this basic scheme are discussed in the literature.[229,356,494,521,543,568,622,708,748,770] The basic scheme involves running the belt through a feed tank, then past squeeze rollers, and, possibly, a wash to remove nonsorbed material. Then the belt goes through a regeneration tank, excess regenerant is washed out, the belt is squeezed to remove excess wash liquor, and the belt then returns to the feed tank. Usually some type of arrangement such as tight tubes,[356,708] baffles,[748] or seals[568] are used to obtain good contact between liquid and solid and prevent liquid by-passing the belt. The basic flowsheet would be modified depending upon the purpose of the apparatus. Moving belt systems have been used for recovery of ions,[543,568,708,748] purification of biological material on an immunosorbent,[229,521] and for continuous gas chromatography (GC) using a bundle of fibers.[356]

There are several problems with the moving belt technique. The major problem is that mass transfer rates tend to be very low. It is difficult to force high velocity contact of the fluid and the solid, and fluid by-passing is a problem. Newer designs[568] may have partially solved the by-passing problem. The belt adds an additional mass transfer resistance which can be significant. Thus, long residence times and a significant amount of sorbent may be required. In addition, belt wear may be a problem, particularly if strong chemical solutions are involved. Despite these problems, a few commercial plants have been reported. Each

Wash   Regenerant   F

Pressure
Rolls
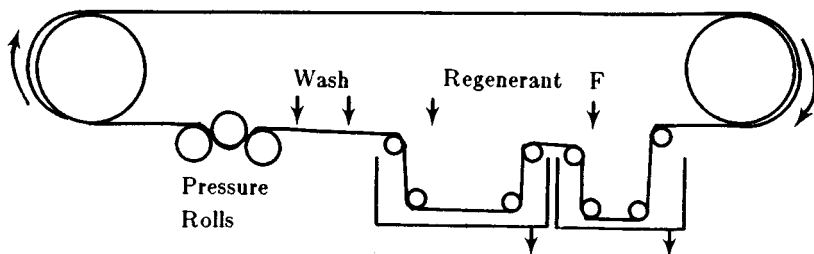
FIGURE 6-23.   Moving belt system.

Carrier

←F

B   A

Elutant
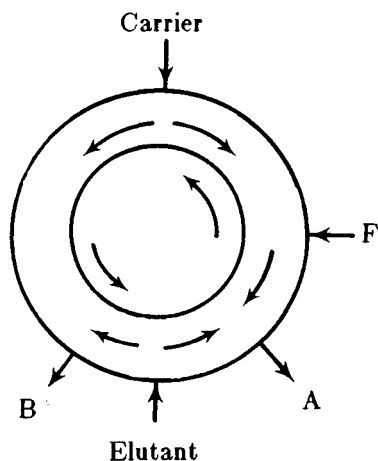
FIGURE   6-24.   Rotating   circular
chromatograph.

plant appears to be custom designed. This points out an additional problem. No standardized design procedure exists as it does now for moving bed and SMB plants. Thus, considerable development work would be required for each application.

The second major approach is to use a column which rotates counter to the fluid. This approach has been used for fractionation of solutes by gas or liquid chromatography (LC).[77-81,88,92,95,97,394,423,675,829,951] The idea is illustrated in Figure 6-24. The sorbent is packed in a circular tube or annulus which rotates. Thus, the adsorbent is moved in a solid body rotation usually counter to the fluid flow. In the scheme shown in Figure 6-24, fluid and solid flow countercurrent in some sections and cocurrent in other sections. This cocurrent flow region was eliminated[77-79,81,95,97,423] by placing a valve between the elutant and the product A port, but this makes the apparatus more complex. In these instruments, different parts of the apparatus could be externally heated or cooled.

Most of the applications of the rotating column equipment have been for gas-liquid chromatography (GLC),[77,80,95,97,423,675] although ion-exchange chromatography,[394] liquid chromatography (LC),[81] and gel permeation chromatography[77,81] have also been studied. In all cases, leakage is a problem which can be overcome, but at the price of making the apparatus more complex. In the circular configuration of Figure 6-24, the length of travel of the solute is limited, the apparatus is quite bulky, and scale up to larger sizes would be difficult. Despite these problems, a few commercial units were sold.[78]

To partially solve the difficulties of the design shown in Figure 6-24, a compact circular chromatograph was designed and built.[78-81,88,92] This is illustrated in Figure 6-25.[79] The fluid
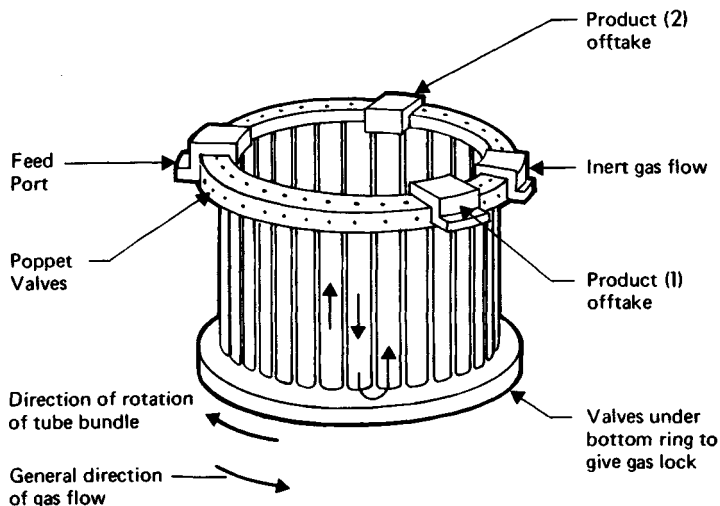
FIGURE 6-25.   Compact rotating circular chromatograph.

is now shunted through a series of columns counter-flow to the direction the tube bundle is rotated. The resulting flow path for the fluid is much longer than it could be in the rotating annulus device. Although each column is a packed bed, the average movement of solid and fluid is countercurrent. This device did considerably improved separating ability, but was plagued by sealing problems. This device was also sold commercially, but production has apparently ceased.[79]

A large number of separations using the two types of rotating circular chromatography have been published.[77-81,88,92,95,97,394,423,675] The interested reader is referred to Barker's excellent reviews,[78,79] which cover all but the ion exchange chromatography.[394] The rotating circular chromatographs are modeled as packed beds. The models used include solute movement theories,[79,92,97] and steady-state film diffusion control.[394,423]

A third approach is to mechanically move the solid with moving baskets on conveyor belts, scraper arms, or screw conveyors. This approach has been used for years in liquid-solid extraction and leaching systems.[269,729,990] Some attempts to adapt mining equipment to adsorption have been made,[494,647,967] but the units have never been widely adopted. The Greerco Countercurrent Contactor, which uses a horizontal paddle agitated conveyor for ion exchange has been applied in pharmaceutical processing.[120] This type of moving equipment might be useful with adsorbents having very poor flow properties.

V. SIMULATED MOVING BED (SMB)

The idea of simulating countercurrent operation can be traced back to at least 1841, when the Shanks system for leaching soda ash was introduced in England.[990] The simulated countercurrent system is still in use for leaching[810,990] and for batch simulation of countercurrent extraction.[877,990] The Shanks or merry-go-round system has also been applied to adsorption and ion exchange for removal of a single component for many years.[586,622,943] The basic idea in all these applications is illustrated in Figure 6-26. The stationary phase (solid or liquid) is held in all the tanks or columns. For the situation shown in Figure 6-26, feed percolates through four of the columns while the fifth is either regenerated, or unloaded and then reloaded with fresh solid or solvent. The feed location is now switched and the column which had been first and is now saturated (or leached out) is regenerated or unloaded. The previously regenerated column becomes the last in the series. This process continues
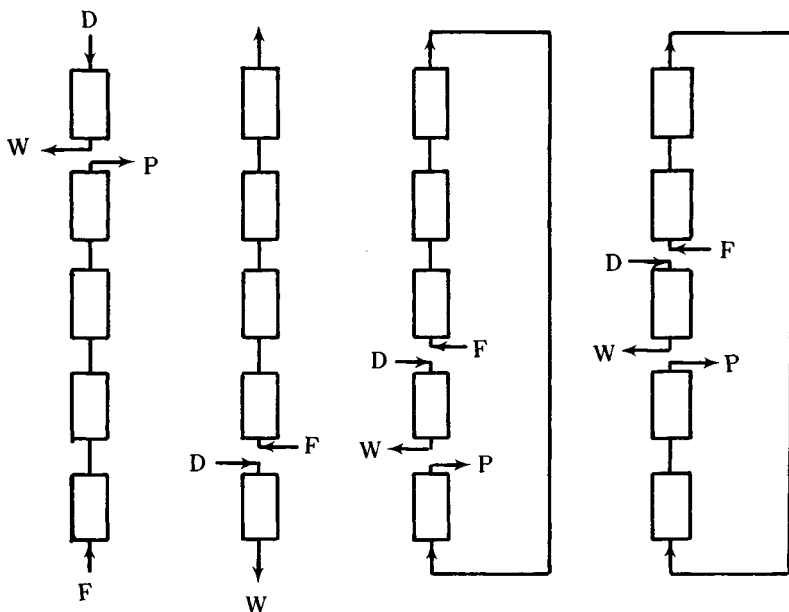
FIGURE 6-26. Simulated moving bed or merry-go-round system.

with the switching going in a loop or merry-go-round. If you fix your eye at the product port, every time a switching occurs you see the solids move downward while fluid flows upward. Thus, the complete operation simulates a simple countercurrent system with a single zone. Since the solids really do not move, this is a simulated countercurrent or SMB system. For adsorption and chromatographic separations, these are really packed bed operations. The use of small particles, short columns, and rapid cycles will be advantageous (see Chapter 3, Section II.D and Chapter 5, Section III.C).

Some obvious modifications are easily made to the basic scheme shown in Figure 6-26. If desorption took longer than one switch period, additional columns could be added. Then two, three or more columns could be desorbing either in a cocurrent or a countercurrent direction at the same time. The cleanest column would be added back to the adsorption series at each switching time. The desorption step could be either thermal or pressure swing or use a desorbent. For fractionation systems, additional zones are added (see Section V.B).

A. Single Solute Simulated Moving Beds

The first application of merry-go-round or SMB techniques for adsorption and ion exchange are difficult to trace. The method has been in use for many years[380,586,622,636,785,865,943,990,1016] and is related to the column switching methods discussed in Chapter 3, Section II.C. The SMB method can be used to keep the MTZ inside the series of adsorption columns and fully saturate the column which is removed for adsorption. This is exactly what the intermittent moving bed accomplishes. Thus, Figure 6-16 can be used to explain the SMB, in addition to the intermittent moving bed. The movement of the MTZ from Figure 6-16B to 6-16C occurs during the flow period while feed is processed. The saturated column of length l_p is then removed from service and a freshly regenerated column is added. This takes us from Figure 6-16C back 6-16B where the process is continued. If the MTZ is short, the use of many segments is not warranted, and simpler column switching methods are used.

Mathematically, the intermittent moving beds and SMBs are the same. Physically, they are different. If the desorption is done thermally, the energy balances will also be different. In the intermittent moving bed, the solid to be regenerated flows into a column which is
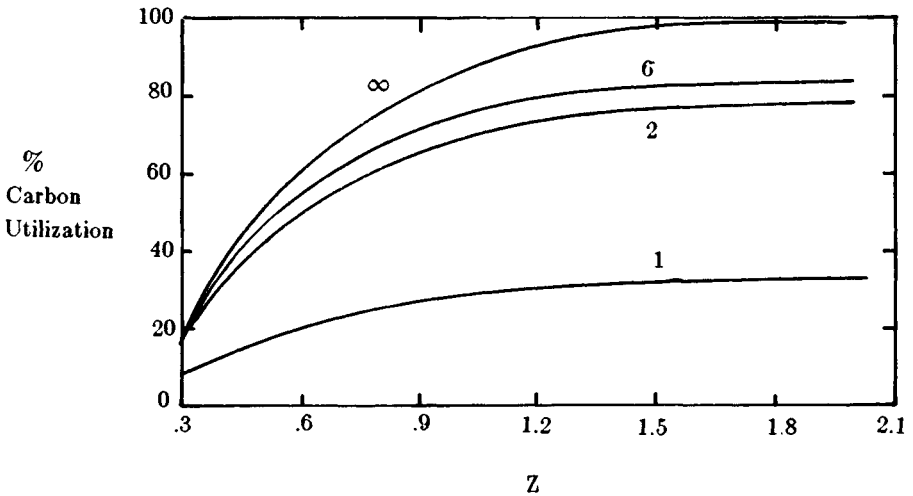
FIGURE 6-27. Percentage of carbon utilization vs. column length for adsorption of two solutes on activated carbon. Parameter is the number of beds in the SMB. (From Liapis, A. I. and Rippin, D. W. T., *AICHE J.*, 25, 455, 1979. With permission.)

always hot. In the SMB, the entire column section is removed to be regenerated and thus both the solid and the column shell must be heated (and later cooled).

The solute movement theory for an intermittent moving bed was shown in Figure 6-16A. This is also applicable to the SMB if the observer fixes himself at the product port. Then, every time columns are switched, the observer sees the solid move downward.

The solute movement diagram can also be used for an observer fixed on the ground. This will be done for fractionation systems. For favorable isotherms such as the Langmuir shape, the MTZ will eventually reach a constant length where the sharpening effects of the isotherm just balance the spreading effects of dispersion and slow mass transfer. If the MTZ is kept inside the series of columns as in Figure 6-16, it always stays the same length and a cyclic steady state is reached. The MTZ travels at the shock velocity, u_{sh}, given by Equation 2-35. To keep the MTZ in the series of columns, the average solids velocity must be less than or equal to u_{sh}. The length of each column segment, l_p is related to the period of flow by Equations 6-32 and 6-33 which were first developed for intermittent solids movement. Since product is always removed before breakthrough of the MTZ, the product is pure. The sorbent is regenerated after the MTZ has passed and thus the sorbent is fully saturated before regeneration. This produces a more concentrated product. Complete regeneration is not essential. The MTZ is of constant length and never leaves the merry-go-round.

How close is this simulation to a truly countercurrent system? Intuitively, as we subdivide the total column length into more and more segments and decrease the period between switches, we should asymptotically approach a truly countercurrent operation. Models of the SMB technique agree with our intuition.[247,591,655,954] The productivity or utilization of the adsorbent shows a large increase going from one to two segments.[655,954] Every additional segment adds a smaller increase to the adsorbent utilization. The exact amount of increase depends upon the parameters used in the model. The results of one such simulation[655] are shown in Figure 6-27 for adsorption of two solutes. The curve marked NP = ∞ corresponds to a continuous countercurrent system. With different parameters, Svedberg[954] found that four active segments for adsorption gives at least 90 to 95% of the utilization of a continuous countercurrent system with a single adsorbed component. Breakthrough occurs earlier with two solutes because of "roll-over" of the less adsorbed solute (see Figure 2-16B) and bed utilization is lower. The time to reach the cyclic steady-state will also depend on the number of solutes and the parameters used in the model.[247,591,655,954]
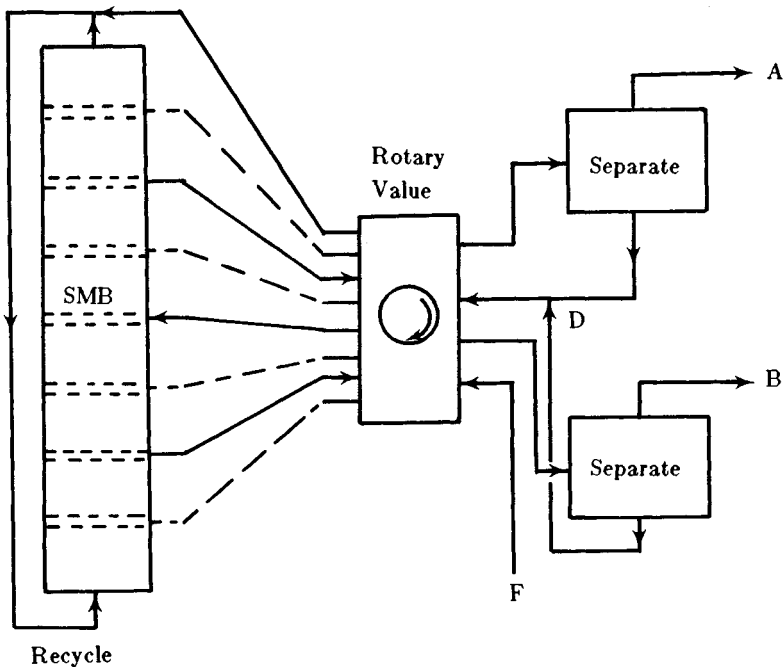
FIGURE 6-28. Simulated moving bed system using rotating value to control fluid distribution. Illustrated with two sections per zone. At time shown the zones are in the order: IV, I, II, and III, starting at the top.

The use of SMB or merry-go-round systems is quite common and often not reported in the literature. Applications in the pharmaceutical industry,[247] for activated carbon adsorption in the chemical industry,[380,522] for ion exchange, particularly uranium purification,[622,943] and for wastewater treatment with activated carbon[291,636,785] have been reported. Usually, from two to five columns are used. Note that the SMB system is overkill if the MTZ is relatively short. Also, countercurrent and simulated countercurrent processes may not be optimum for particular separation problems. When removing a nonlinearly adsorbed component from a nonadsorbed component by GC, a single column with reverse flow regeneration was better than a countercurrent system.[407,778] This is a rather peculiar example, but does serve as a warning that countercurrent or simulated countercurrent operation may not automatically be best.

B. Simulated Moving Bed Fractionation

For SMB fractionation, a modification of one of the cascades shown in Figure 6-10 is used. The chromatographic-type systems, Figure 6-10B, are by far the most common. Each zone shown in Figure 6-10B would consist of one or more sections. With sharp MTZs or when high-purity products are not required, one section per zone is satisfactory. When sharper separations are required, several segments per zone are needed. Early research used essentially the cascade shown in Figure 6-10A for a thermal SMB system.[339,340,487,523] This arrangement simulates the hypersorber (see Chapter 6, Section II.B.1). The cascade shown in Figure 6-10B without zone IV was also used,[200,491] but was not commercialized. Current industrial applications of SMB systems were started by Dr. Donald Broughton and co-workers at Universal Oil Products[3,50,128,135,136,140,172-177,179-182,184-186,315-319,369,584,763-765,938,980] who used the cascade shown in Figure 6-10B. The actual apparatus can use a system with packed segments as shown in Figure 6-28 or a series of individual columns as shown in
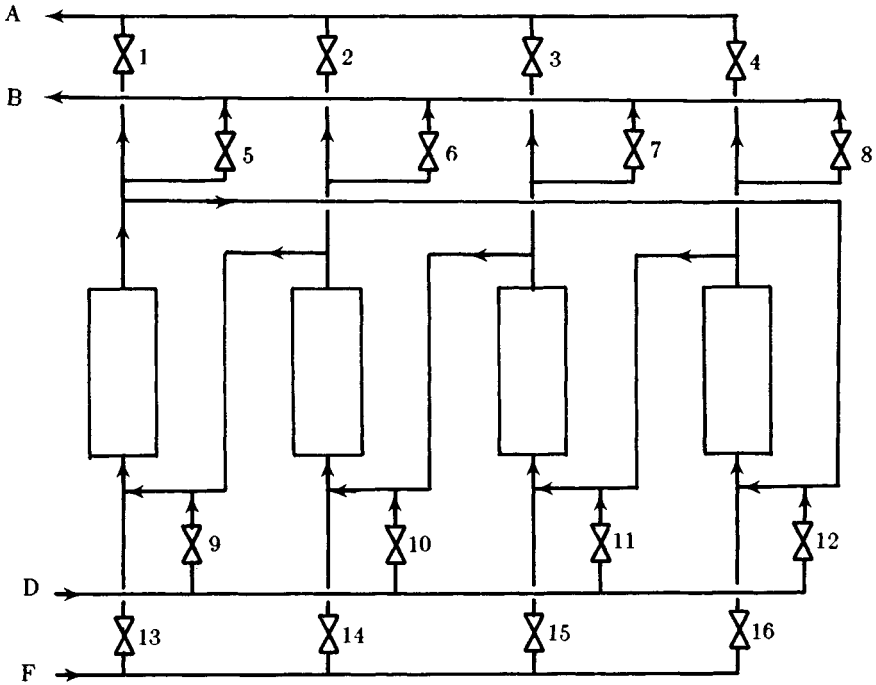
FIGURE 6-29.   Arrangement for SMB with one column per zone and four zones.

Zone	Inlet valve open	Outlet valve open
I	13, 14, 15, or 16	1, 2, 3, or 4
II	None	None
III	9, 10, 11, or 12	5, 6, 7, or 8
IV	None	None

Figure 6-29. In both systems, the amount of fluid recirculated is usually significantly greater than the amount of feed added or products withdrawn.

1. Solute Movement Theory

The solute movement theory can be used to explain how the SMB system works as a fractionator.[1051,1052] The cascade shown in Figure 6-10B is simulated by switching port locations. We want the least adsorbed solute A to move faster than the port movement in zones 1 and 2 and slower in optional zone 4. In this way, solute A is moving up in zones 1 and 2 and down in zone 4 in the simulated cascade. The average velocity of port movement is

$$u_{Port} = 1_{Port}/t_{Port} = v_{solid_{avg}} \qquad (6-34)$$

Then the condition to have A exit in the A product is

$$u_{A_1}, u_{A_2} > u_{Port} > u_{A_4} \qquad (6-35)$$

In practice, $u_{A_1} > u_{A_2}$ since the fluid velocity will be greater in zone 1. To have solute B exit in the B Product, we want B to move down in zones 1 and 2 and up in zone 3 in the simulated cascade. This will occur if

$$u_{B_3} > u_{Port} > u_{B_1}, u_{B_2} \qquad (6-36)$$

Equations 6-35 and 6-36 should be satisfied for all concentrations which occur in a given zone. These equations represent the same condition as Equation 6-31a to c which specified the conditions for fractionation in a moving bed. In the moving bed, the solute velocities were shifted by v_{solid} (Equation 6-2) which in the SMB is u_{Port} (Equation 6-34).

The conditions for separation of A and B in a nonlinear system are

$$u_{A_2}(c \rightarrow 0) > u_{port} \qquad (6\text{-}37)$$

and

$$u_{B_{1sh}}(c_F) < u_{port} \qquad (6\text{-}38)$$

Since feed is introduced between zones I and II, $v_2 < v_1$. Also, the condition for solute A is written for the slowest solute wave (as concentration goes to zero), while the condition for B is for a more rapid shock wave. In order to satisfy both equations, the selectivity must be fairly large; otherwise, the velocities of A and B will not differ enough.

The solute movement diagram can be drawn in two ways. First, it can be drawn from the point of view of an observer sitting at the outlet port. Then every time the valves switch, the observer sees the solid move downward. If there is no mixing, the result[1051,1052] will show a series of downward movements every time the valves switch (as in Figure 6-16), but with an overall upward movement for solute A and a downward movement for solute B in zones 1 and 2.

The second point of view is for an observer fixed on the ground. This observer sees a stationary solid with valves changing the location of product and feed ports. The solute movement diagram for this situation for two independent solutes with linear isotherms is shown in Figure 6-30.[1051,1052] This is shown for the four-zone cascade of Figure 6-10B with two segments in each zone. When the ports shift, the solute waves do not shift, but the solute velocities will change if the solute is shifted into another zone. This occurs since the fluid velocity must be somewhat different in different zones, since there are additions and withdrawals between zones. In addition, the desorbent concentration will vary in the zones. If the desorbent affects equilibrium, this will also change the solute velocities.

In Figure 6-30, both solutes continually move up, but solute B is moving down with respect to the port locations. Thus, solute A overtakes the A product port, while solute B is overtaken by the B product port. Feed is introduced continuously into all the ports marked F, but for simplicity, only one set of solute waves is shown in Figure 6-30. When fluid reaches the top of the cascade, it is recycled to the bottom. In Figure 6-30, we have assumed that this is done without mixing. If Equations 6-35 and 6-36 are satisfied, solute A appears in zones 1, 2, and 4 while solute B appears in zones 1, 2, and 3. Solute A appears in zone 4 since only a portion of the fluid is withdrawn as product. Any A not withdrawn moves slowly in zone 4 and will be placed in zone 1 again after the valves switch location. If zone 4 is not present, all of the fluid is withdrawn as A product. The absence of zone 4 will make the A product more dilute, but in practice, makes the B product purer, since there can be no carryover of A in the recycle stream.

The solute waves are spread out by dispersion and mass transfer in the packed sections. Thus, a tight uniform packing with small-diameter particles is desired (see Chapter 5, Section III.C). To simulate countercurrent motion, each packed section must be close to identical. Mixing in between the packed sections will also reduce the separation. Thus, the collectors and distributors between sections need to be carefully designed. This is true whether the sections are separate columns or segments of a single large column. Mixing in the valves must also be minimized. UOP uses a special rotating valve to simultaneously switch all
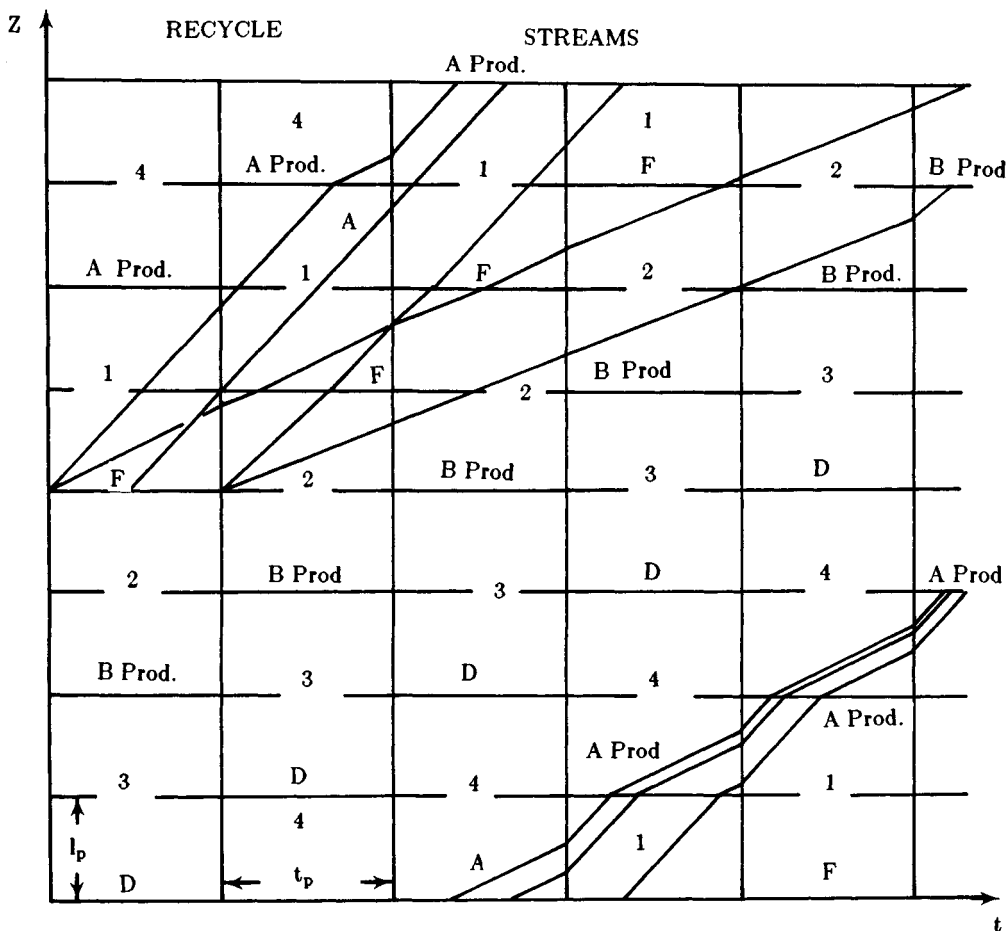
FIGURE 6-30.   Solute movement diagram for fractionation by SMB for two independent solutes with linear isotherms. Two sections per zone.

sections (see Figure 6-28) while others use manifolds of solenoid valves (e.g., Figure 6-29). The more difficult the separation and the higher the desired purities, the more important minimizing these dispersion and mixing effects will be.

The simplest type of SMB would have one column or section per zone. One way this can be done using solenoid valves for the switching is shown in Figure 6-29. Even for this relatively simple arrangement, 16 valves are required. When the valves switch, the column which was zone IV becomes zone I, zone I becomes II, zone II becomes III, and zone III becomes zone IV. More complete separation can be achieved by adding additional columns to some of the zones. For instance, all of component B must be eluted from zone III before the valves switch or B will be carried into zone IV and eventually into zone I and into the A product. With nonlinear isotherms, component B will tail in zone III and the B product will be diluted. If zone III always consists of two or more columns, the MTZ can be retained in zone III, and the column which will become zone IV can be completely eluted. Slightly different arguments can be used to justify the use of two sections in the other zones. When sharp separations are not required, the arrangement in Figure 6-29 is adequate. Equipment similar to Figure 6-29 is used commercially.

It is interesting to compare the SMB to truly countercurrent processes. Both systems are steady state devices for doing a binary separation. Partial separation of additional components

can be done with a side withdrawal. The truly countercurrent system can use side columns similar to side strippers for complete separation of additional components (Sections II.B.1 and II.B.2). This is not an option with the SMB, but the SMB can be modified to do multicomponent separations by operation in a different cycle where it is a batch chromatograph for part of the cycle (see Chapter 7, Section IV). The SMB system is actually a fixed bed system. Thus, flooding should not be a problem, but excessive pressure drop could be. In addition, clogging of the bed by suspended solids in the feed can be a problem. The fixed bed SMB will have a lower external porosity, α, and hence, higher capacity than truly countercurrent systems; however, this is offset by the distribution regions between sections. The actual movement of solids requires means for avoiding axial mixing and may result in excessive attrition. However, truly countercurrent systems do allow for easy solids replacement or external reactivation. Both systems have mechanical difficulties to overcome. In the SMB, these difficulties involve valving and timing, while in a truly countercurrent system, moving the solids in a plug flow is the major problem. Currently, the simulated countercurrent systems are the preferred choice for large-scale separation of liquids.

Another competitor for the SMB is scaled-up elution chromatography (Chapter 5). Elution chromatography is a simpler system which can separate more difficult to separate components than the SMB. If the selectivity, α_{21}, is close to one, it is difficult to simultaneously satisfy Equations 6-35 and 6-36. Numerical calculations show the SMB is more efficient, will tend to require about one half as much desorbent, will produce more concentrated products, and will use about one fourth as much adsorbent.[182,319,865] Elution chromatography is preferable for small-scale applications, particularly if the same system will be used for many different separation problems. Elution chromatography is also preferable if no sorbent with a reasonable selectivity (roughly, greater than 1.3 to 1.5) can be developed. Elution chromatography also has an advantage when one desires to completely fractionate a multicomponent mixture. SMB systems are preferable for large-scale liquid-phase systems dedicated to a single separation where a binary separation is desired (this means either two components are present or only one component of a multicomponent mixture is desired and it is either most strongly or least strongly adsorbed). Since the SMB produces more concentrated products, the downstream processing units will be smaller and cheaper to operate. This is often critical when overall costs of the large-scale system are compared. Only liquid-phase adsorption SMB separations have been commercialized, although size-exclusion and gas-phase separations have been studied. Even for liquid-phase adsorption, the choice between a SMB or elution chromatography or a hybrid system is not clear for intermediate-size systems or large-scale systems where a center cut is required (see also Chapter 7, Section VII).

2. Liquid Adsorption Systems

Liquid-phase SMB is now a fairly common commercial separation. The early work was pioneered by UOP, who now have over 64 large-scale units licensed and operating throughout the world.[179] A schematic of the UOP arrangement for an SMB is shown in Figure 6-28. The Molex process for separating normal paraffins from branched-chain and cyclic hydrocarbons on 5 Å molecular sieves was announced in 1959.[181] Other articles[140,185,584,938] discussed Molex, but without details of the simulated countercurrent separator. Some details of the separator were first given in the patent[184] and in Broughton's[172,173] articles. In 1969, the SMB was applied to the separation of olefins and paraffins in the Olex process[50,174-176,180,183] and to the separation of *para* and *meta* xylene in the Parex process.[3,128,136,174-176,186,315,316,369,980] The Parex process has been extremely popular with many units in operation.[179] The SMB (called Sorbex by UOP) is not limited to hydrocarbons. Fructose and glucose are commercially separated (Sarex) by the UOP Sorbex process.[135,763,764] Fructose-glucose separation has also been extensively studied by other researchers and will

be discussed in more detail later. The latest separation to be commercialized is the separation of *para* or *meta* cymene from an isomer mixture.[179] A large number of other separation problems have been developed at the pilot plant scale. These include *para* and *meta* cresol from an isomer mix, ethylbenzene from C_8 aromatics, butene-1 from a C_4 olefin-paraffin mixture, *p*-diisopropylbenzene from an isomer mixture, β-pinene from a pinene mixture, and *p*-diethylbenzene from an isomer mixture.[182,183,317,318,765] The UOP applications of simulated countercurrent separation are also reviewed in detail elsewhere.[177,179,182,319]

The UOP Sorbex separations all use the cascade shown in Figure 6-10B. Although Broughton[172,186] states that zone 4 is optional, all of the UOP processes appear to include zone 4 to allow recycle of some desorbent and thus reduce the load on the downstream separators. The commercial Sorbex systems use a single column which is divided into packed sections with distributors between each section (see Figure 6-28). The number of sections per zone varies, but is usually more than four. The pilot plant unit used 24 separate columns to simulate countercurrent motion.[317] A specially designed and quite expensive rotary valve is used to control liquid distribution, feed introduction, and product withdrawals from each section. The recirculating liquid flow rate in the system is considerably greater than the feed and product flow rates. The UOP systems have been designed for quite high purities and high recoveries (for *p*-xylene 99.3% purity at up to 99.7% recovery),[319] and thus may be overdesigned for less demanding separations.

Simpler versions of the SMB are also used commercially.[177,531,779] Toray Industries built a SMB (Aromax) for production of 100,000 metric tons/year of 99.5% pure *p*-xylene.[779] This SMB used automatically sequenced on-off valves for switching port locations and was horizontal. A reflux of product *p*-xylene was used to increase *p*-xylene concentration in the extract product. The desorbent was an aromatic. Illinois Water Treatment (IWT) has commercialized an SMB process for separating fructose and dextrose.[531] A 90% fructose corn syrup product is produced while the dextrose product is recycled to the isomerizer. Other applications of the SMB system are being studied.[531]

Practically any adsorbent-desorbent combination can be used. The higher the selectivity, the easier the separation. A selectivity α_{21} of around 2.0 is high enough to encourage a more detailed analysis of the separation.[317] The desorbent or solvent used can also have a large effect on the selectivity, and certainly has a large effect on the cost of downstream separators. The ideal desorbent will be easy to separate from the products and will have a selectivity for the adsorbent in between that of the products. A desorbent with intermediate selectivity will help separate the components without the excessive zone spreading which can occur with nonadsorbed solvents or the difficulty in removing strongly adsorbed desorbents. In a commercial license, a large portion of the price may be paying for sorbent/desorbent development.

The results for a commercial Parex separation using a specially formulated zeolite molecular sieve adsorbent and *p*-diethylbenzene as the desorbent are given in Table 6-2.[319] In this case, *p*-xylene is the most strongly adsorbed component (B in Figures 6-10B and 6-30). The product concentrations vary throughout the cycle, but the cycle repeats itself every time the valves are switched. The results given in Table 6-2 are the average concentrations which are close to what a truly countercurrent system would give. A typical plant for producing *p*-xylene would produce 100,000 metric tons/year of *p*-xylene product.

To some extent, the separations can be customized by changing the combination of adsorbent and desorbent. For example, ethylbenzene can be recovered from the mixed xylenes feed by using a different adsorbent/desorbent combination.[317] In this case, ethylbenzene is the least adsorbed component (A) and the column is operated so that all other components exit with the B product.

The average composition profiles in the column are shown in Figure 6-31 for the separation of fructose from glucose in a pilot plant.[763] The more strongly adsorbed fructose moves

Table 6-2
COMMERCIAL PAREX OPERATION WITH *p*-DEB HEAVY
DESORBENT SEPARATION OF *p*-XYLENE FROM
CRYSTALLIZER MOTHER LIQUOR

(Wt %)	Feed	Extract	Extract after toluene removal	Raffinate	Recovery product (%)
Nonaromatics	0.29	0.00	0.00	0.29	
Toluene	0.45	1.54	0.00	0.28	
Ethylbenzene	12.38	0.34	0.35	14.10	
p-Xylene	11.76	97.94	99.48	0.53	96.7
m-Xylene	62.96	0.09	0.09	70.93	
o-Xylene	12.16	0.09	0.08	13.87	
Total	100.00	100.00	100.00	100.00	
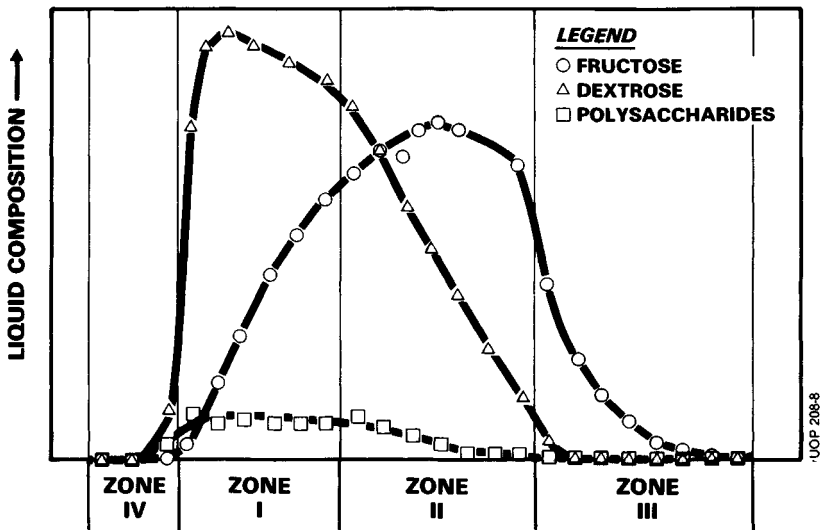
FIGURE 6-31.   Composition profile for separation of fructose and glucose in a pilot plant SMB system.

down the column in zones I and II and up in zone III while glucose moves up the column in zones I and II and down in zone IV. The polysaccharides do not adsorb, and in fact, tend to be excluded from the adsorbent. Thus, most of the polysaccharides exit with the glucose product. Since the polysaccharides are not adsorbed, a small fraction will be carried with the recycled desorbent through zone IV and into zone III where they contaminate the fructose product. On a dry solids basis, the feed was 47.3 wt % fructose, the fructose product was 91 wt % fructose, and 91.5 wt % of the fructose was recovered. Better separations can be obtained in the commercial units. Deionized water was the solvent and a modified molecular sieve zeolite was the adsorbent.

The separation of fructose from glucose is industrially very significant and has been extensively studied. There is a market for fructose-glucose mixtures with fructose concentrations ranging from 42 to 100 wt % (on a dry solids basis). The 42 wt % mixture is the usual product from enzyme isomerization of glucose. Currently, the largest market appears to be for rather modest increases in the fructose concentration (roughly 55 to 60 wt %), but the trend has been towards higher and higher fructose concentrations in the syrup. For partial

Table 6-3
COMPARISON OF PREPARATIVE
CHROMATOGRAPHY AND SMB FOR
SEPARATION OF BENZENE AND NAPHTHALENE
ON ALUMINA IN *N*-HEXANE

Batch	Chromatograph	SMB
Adsorbent loading, g/g ads. hr	0.0241	0.0344
Relative loading	70%	100%
Solvent circulation, mℓ/g solute	265	103
Relative solvent circulation	257%	100%

fructose enrichment, much simpler SMB systems[531,533] are often used commercially. A system with one segment per zone is sufficient to achieve the desired commercial concentrations. The systems use four separate columns which are connected by a manifold using solenoid valves. Zone IV is included to reduce the amount of additional water (the desorbent) required. These simple systems cannot produce as pure a fructose product as the multiple section per zone system, but they are significantly cheaper. The usual sorbent is an ion exchange resin in the calcium form which will complex with the fructose.[192] Most of the polysaccharides can be removed by using a more complex cycle which includes a batch step.[511]

Barker and co-workers[84,91,98,102] developed a slightly different process for separation of fructose and glucose. Their system used separate columns, contained no zone IV, and hence, had no recycle, and could be operated with the purge section (zone III) totally isolated from the remainder of the system. In this configuration, a roughly 50% fructose feed (dry solids basis) produced an 85% pure fructose and a 99.9% pure glucose. With a 68 wt % fructose feed and connecting zones III and II, a 99.9% pure fructose product was obtained.[102] Unfortunately, operating without a zone IV requires additional water for desorption and the fructose product tends to be quite dilute (from 3.4 to 16.3% w/v).

For the rather easy separation of benzene from naphthalene on alumina using *n*-hexane as the solvent, the comparison between batch operation and a three-zone SMB is given in Table 6-3.[968] The SMB clearly uses less desorbent, but since neither system was optimized it is difficult to draw quantitative conclusions.

These studies illustrate the tradeoffs involved in using zone IV. A higher purity with less sorbent can be obtained without zone IV, but significantly more desorbent is required and the product is diluted. Reported commercial application have used SMB systems with a zone IV.

In addition to the solvent movement theory,[10,79,84,90,1051,1052] staged models[90,91,102,177,182,186,260,865] have been used to model SMB operation for liquid systems. The staged models have the advantages of showing zone spreading and being readily extended to complex equilibria. However, they do require an independent estimate of the HETP under the operating conditions in the SMB. This estimate can be obtained from breakthrough curves[186] or by fitting SMB data. For nonlinear equilibria, a numerical solution of the stages model is required. The limiting separation which could be obtained can be determined by ignoring the cyclic nature of the SMB and assuming a truly countercurrent system. Steady-state computer staged models developed for other unit operations can then be used.

3. Size Exclusion Chromatography (SEC)

The simulated moving bed cascade can be used with a variety of unit operations. Extension to size exclusion chromatography (SEC) (see Chapter 5, Section VI) is straightforward. Barker and co-workers[10,79,88-90,103] did this extension of their three-zone system for the partial fractionation of dextran polymers. Continuous SEC desalting could also be done on the same
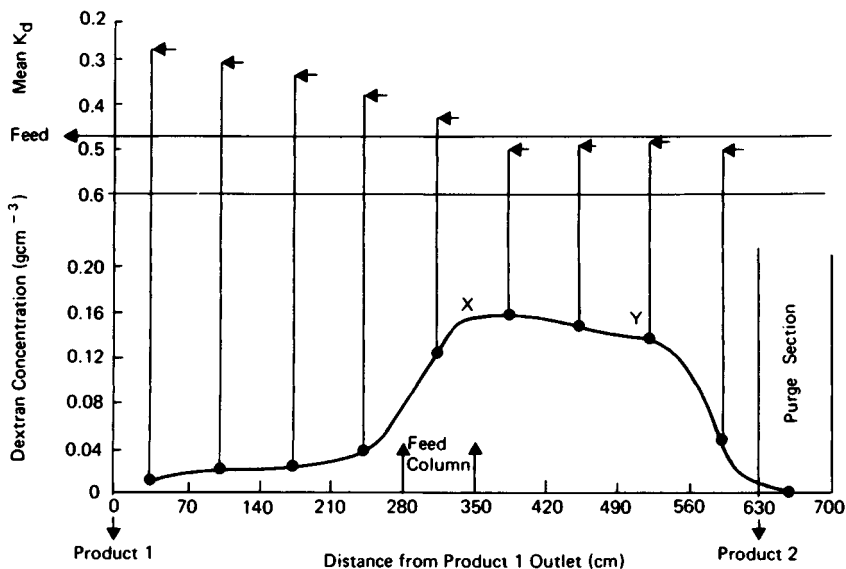
FIGURE 6-32. Dextran concentration and mean K_d values for size exclusion SMB. (From *Ind. Eng. Chem. Process Des. Develop.*, 17, 302, 1978. With permission.)

equipment, and would be an easier separation. The dextran polymers are produced with a molecular weight distribution which is wider than desired. A much tighter distribution is desired for commercial applications. An example of the concentration profile for the SMB fractionation of dextran is shown in Figure 6-32.[89] The top part of Figure 6-32 shows the mean K_D values of the dextran which is an indication of the mean molecular weight. The bottom part shows the dextran concentration along the ten columns. The higher molecular weight (smaller K_D) material is more excluded by the Spherosil XOBO75 packing. Thus, the higher molecular weight material tends to stay with the mobile liquid and exits as product 1. Since the lower molecular weight material (higher K_D) has a higher concentration in the pores, it is carried in the direction of simulated solids movement and exits as product 2. The mean K_D values of the two products were well separated, but the peaks were quite broad and showed considerable overlap.

Later work[10] showed that ultrafiltration was more efficient at removing small molecular weight material (< 12,000 daltons) while the SMB was more efficient for removing large molecular weight material (> 98,000 daltons). The combination of SMB size exclusion followed by ultrafiltration gave the desired molecular weight distribution. A final cleanup with a mixed bed ion exchange column was required to remove silica which dissolved from the Spherosil packing. The SMB used for these studies was a three-zone system with zone 3 isolated from zone 2. Better separations would probably be obtained if zones 2 and 3 were connected so that separate elutant was not used in zone 2.

4. Gas Systems

Application of simulated countercurrent techniques to GLC has been extensively studied by Barker and co-workers.[79,82,83,86,87,93,94,99,100] A three-zone SMB was used with zone 3 completely isolated from zone 2. Thus, separate carrier gas and purge flows are required in zones 2 and 3. The columns were packed with inert particles (chromosorb P) coated with the stationary fluid. Mixtures separated included Arklone P (1,1,2-trichloro-1,2,2-trifluoroethane) from Genklene P (1,1,1 tri-chloroethane) which has a separation factor $\alpha_{21} = 2.9$ at 21°C,[79,82,83,86,87] Arklone P and dichloromethane with $\alpha_{21} = 1.16$,[79,82] and fatty acids and

fatty acid esters.[79,94,99,100] Nitrogen was used as the carrier gas. The temperature trace and composition profiles for the separation of Arkone P from Genklene P in a 12-column system are shown in Figure 6-33.[82] Note that the temperature varies from one column to the next. This occurs because the SMB is not a truly steady state system, but has reached a cyclic steady state. Considerable temperature variation occurs because thermal effects are much more important in gas than in liquid systems. The separation shown in Figure 6-33 is quite easy and much of zones 1 and 2 are not needed. With more difficult separations, the extra length was required.[82,83,86,87,94,99,100]

Better separations were obtained when the feed was vaporized before injection instead of vaporizing the feed inside the column.[82] The temperature in the purge section was fairly low because of desorption. Heating the purge gas or the column would increase desorption and reduce the amount of purge gas required. Staged models were modified to include the heat effects.[83,93]

The separations obtained in the GLC systems could probably be improved or higher throughput could be obtained by connecting zones 3 and 2 together, by using hydrogen or helium as the carrier gas, and by operating at the optimum temperature (see Chapter 5, Section VII). More concentrated products could be obtained by connecting zones 3 and 2 and adding a zone 4.

5. Thermally Regenerated SMB

A thermally regenerated SMB which simulates the cascade shown in Figure 6-10B can also be developed. For dilute systems, no steam or desorbent would be required. Instead, Equations 6-35 and 6-36 would be satisfied by decreases in the equilibrium constant and hence, increases in the solute velocity in the heated zone III. Zone IV would be cooled to adsorb solute A and allow recycling solvent or carrier gas. Operation could be either with each column serving as an heat exchanger (direct mode) or with a heat exchanger heating or cooling the fluid (traveling wave mode) before it enters each adiabatic column. The cascade which is simulated is shown in Figure 6-34A. The feed contains solutes A and B and solvent S. When the port locations are switched, the heat exchangers move with the ports. The heat exchanger between zones II and III cools the recirculating fluid to T_{Feed}. For dilute systems, the solute movement theory is easy to apply to both these modes. The solute movement theory for the system with heat exchangers is shown in Figure 6-34B for a system with one column per zone. The first time period in Figure 6-34B corresponds to Figure 6-34A. There are thermal waves in zone I, III, and IV since these columns were at a different temperature before the ports switched locations. Remember that the simulation of counter-current motion is achieved in Figure 6-34A by switching the ports in the same direction as the fluid flow (upwards). Thus, for example, after the switch, the new zone I is initially cold, but is warmed to T_F by the fluid. The diagrams are drawn for a typical dilute liquid system where

$$u_{th} > u_A(T_h) > u_A(T_F) > u_A(T_c)$$

and Equations 6-35 and 6-36 are satisfied because K values are temperature dependent. As in Figure 6-30, the A and B solute waves are shown for only one feed period. All of the A solute eventually exits in the A product stream and all the B in the B product stream. The advantage of a thermally regenerated SMB is that no additional solvent or carrier gas need be added. The solutes are both concentrated and separated. The disadvantage is not only must the solutes have different adsorption constants, but the constants must be reasonably temperature dependent.

When I first conceived of the thermally regenerated SMB, I thought I had a great new idea. Visions of fame and fortune, or at least one publication, entered my head. However,
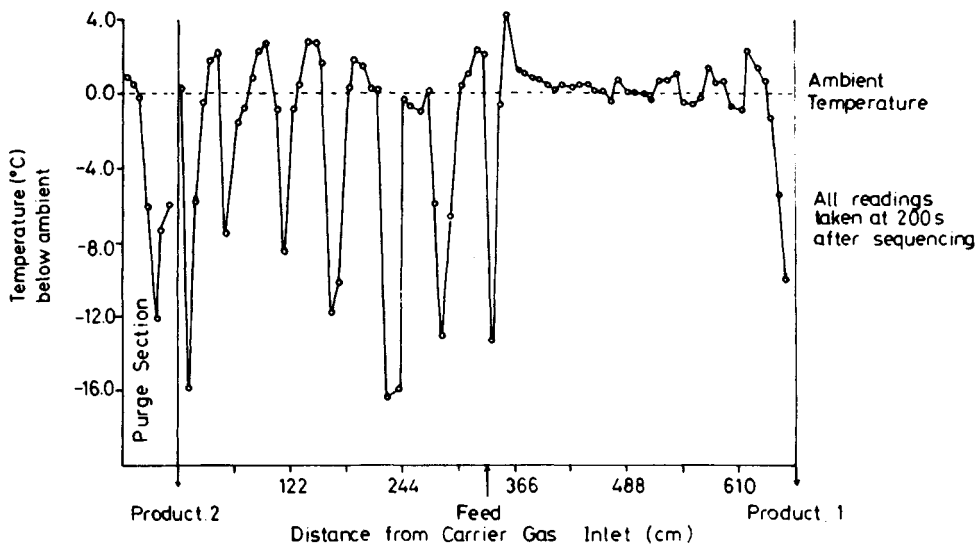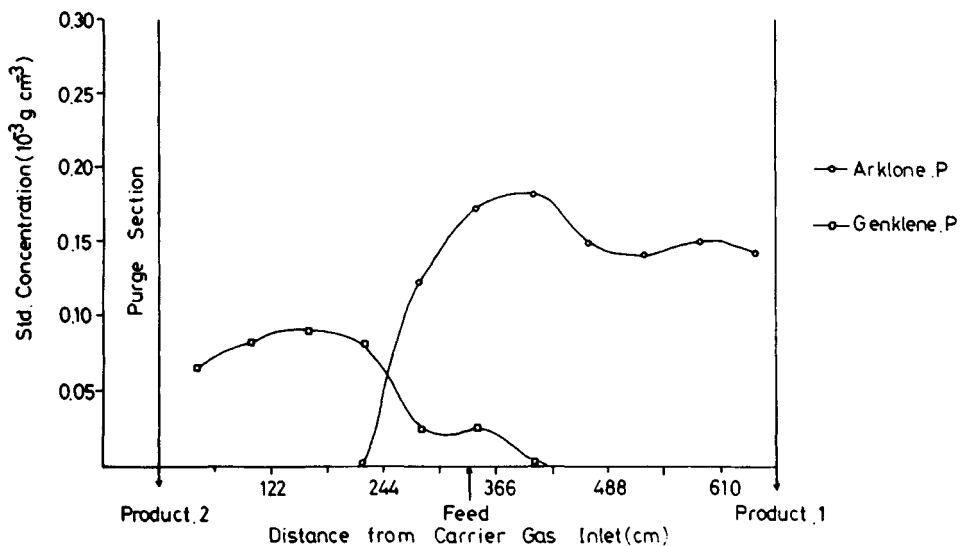
FIGURE 6-33. (A) Temperature and (B) concentration profiles for separation of Arklone P and Genkelene . P by SMB. (From *Chromatographia*, 12, 277, 1979. With permission.)

while doing the literature survey for this book, I realized the thermally regenerated SMB is an old idea.[339,340,487,523] This thermally regenerated SMB system was extensively studied and piloted in the late 1940s and early 1950s for separation of concentrated hydrocarbons, although it was not called a SMB. Extra steam for regeneration of the activated carbon was used and the cascade in Figure 6-10A was simulated. Abandoned for many years, the thermally regenerated SMB may be a useful idea, particularly when the mixture to be separated is a dilute mixture in a carrier or solvent. A variation of this idea for desalination using thermally regenerable ion exchangers has recently been patented.[178] The history of
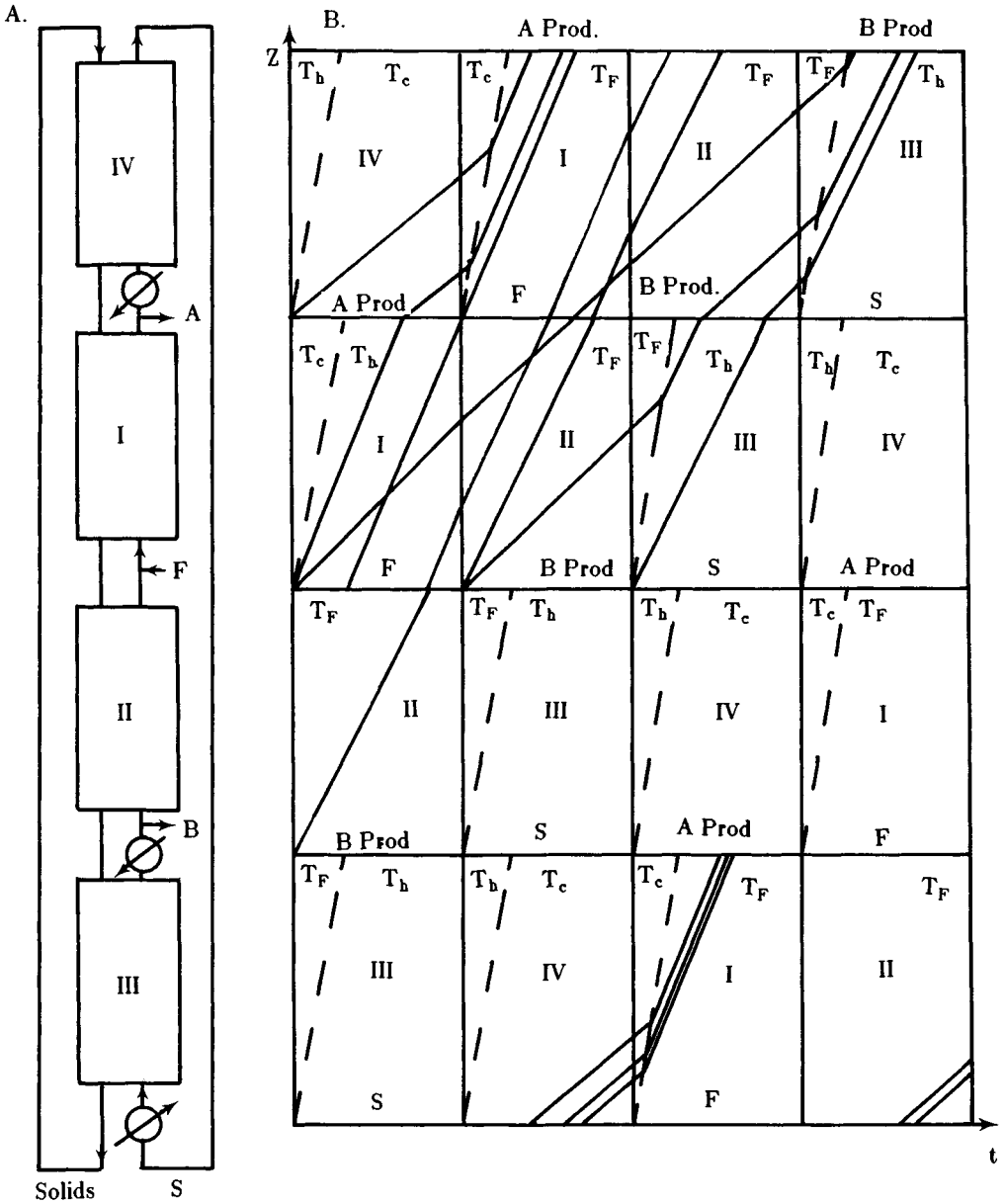
FIGURE 6-34.   Solute movement theory for thermally regenerated, traveling mode SMB. Dilute system with linear isotherms. Two sections per zone. --- Thermal waves. ——— Solute waves (steeper slopes in zones I and II are solute A).

separation processes contains many examples of separation techniques which were finally adopted years after the first unsuccessful use.

VI. THE FUTURE FOR CONTINUOUS COUNTERCURRENT SYSTEMS

Many of the systems discussed in this chapter are commercial systems and will remain commercial systems. Staged fluidized beds with continuous flow are used commercially for solvent recovery from air and could be used for drying gases, particularly when the water

concentration is high. Intermittent movement, staged fluidized beds are useful for liquid systems and are used commercially for ion exchange. They are particularly advantageous when the feed contains suspended solids. Similar systems may be useful for activated carbon treatment of wastes, particularly when the organic loading in the waste is quite high.

Dense moving beds with continuous solids flow work well at low velocities, but at high velocities, fluidization or excessive channeling may occur. Thus, these devices are currently restricted to situations where pore diffusion controls and low fluid flow with long residence time is required. Regeneration of both activated carbon and ion exchange resins is the current commercial application. The magnetically stabilized fluidized beds do not have the same flow rate restriction, and this new technology may be useful at much higher velocities.

Pulsed flow packed bed systems of various types are used commercially for ion exchange and adsorption. These applications will continue.

For easy separations where one equilibrium contact is sufficient, magnetic sorbents in continuous stirred tanks and pipe reactors are very appealing. Commercial ion exchange use of these systems will probably begin soon. If magnetic adsorbents are developed, similar schemes could be commercially interesting for adsorption, particularly where very large flow rates must be treated. Wastewater treatment is one possible example.

Fractionation is difficult to do with moving bed systems unless the separation factor is quite large. The only new method which I expect may find extensive application for fractionation is the magnetically stabilized fluidized bed. Use of SMB will increase. Moving equipment techniques may be used occasionally, but I doubt they will become widely used.

Chapter 7

HYBRID CHROMATOGRAPHIC PROCESSES: COLUMN SWITCHING AND MOVING PORTS

I. INTRODUCTION

In Chapter 5, we saw that column chromatography is a relatively simple, flexible method which can separate multicomponent mixtures in a single column. Unfortunately, the productivity of the packing is low and large amounts of solvent are needed. In Chapter 6, Section V.B, we saw that simulated moving bed (SMB) systems were more efficient separators. Unfortunately, the SMB is a fairly complex binary separator. What we want is the best of both worlds: high productivity and low solvent use in a multicomponent separator. In this chapter, we will discuss column switching, moving feed, and moving port chromatography, which are attempts to achieve high productivity in a multicomponent separator. These methods essentially combine elution development with port movement.

The hybrid processes are generally more complex than scaled-up elution chromatography and less complex than the SMB. For binary separations, their sorbent productivitiy and solvent usage is in between elution chromatography and the SMB. For multicomponent separations, they might have the highest sorbent productivity and the lowest solvent usage, particularly if a center cut is desired. Since high sorbent productivity reduces the size of the chromatograph and low solvent use drastically cuts both the capital and operating costs of downstream separators, the hybrid processes may become the most economical chromatographic process in some situations.

II. COLUMN SWITCHING METHODS

Column switching has been used for years in both gas[303,304,131,439] and liquid[930,326,613,684,658,685] chromatography. Although first developed for analytical applications, it has been adapted to production use.[159,864,873,1065,887] The basic apparatus is illustrated in Figure 7-1A. When a multicomponent mixture is to be separated, fast moving solutes which separate on column A can be withdrawn at product location 1. Solutes which do not completely separate, can be sent to column B to be removed at product location 2. Slowly moving solutes which separate on column A can be removed at a later time at product location 1. Fresh solvent or carrier gas can be inserted into column B as shown in Figure 7-1A, but the system is often operated in a way that does not require this. The two columns can contain the same or different packings, and can be based on totally different types of chromatography.[613,658] If different packings are used, the method is sometimes called "multidimensional chromatography". Obviously, this idea can be extended to several columns which can be hooked together in both series (Figure 7-1B) and parallel arrangements (Figure 7-1C).[930] Fully automated systems have been developed,[159,326,439,613,661,685,728,864,1065,1093] and semipreparative-scale[661] and large-scale[1065] units are commercially available.

The reason why column switching is helpful is easy to see from the solute movment theory. This is illustrated in Figure 7-2 for the equipment shown in Figure 7-1A where columns A and B contain different packings. Solute 1 is removed after column A, while solutes 2 and 3, which are not separated, are sent to column B where they are easily separated. Component 4 is removed from column A. In this application, fresh solvent or carrier gas is added to column B after the 2 + 3 peaks have entered that column. The next feed pulse can be input into column A much sooner than would be possible if a single long column A
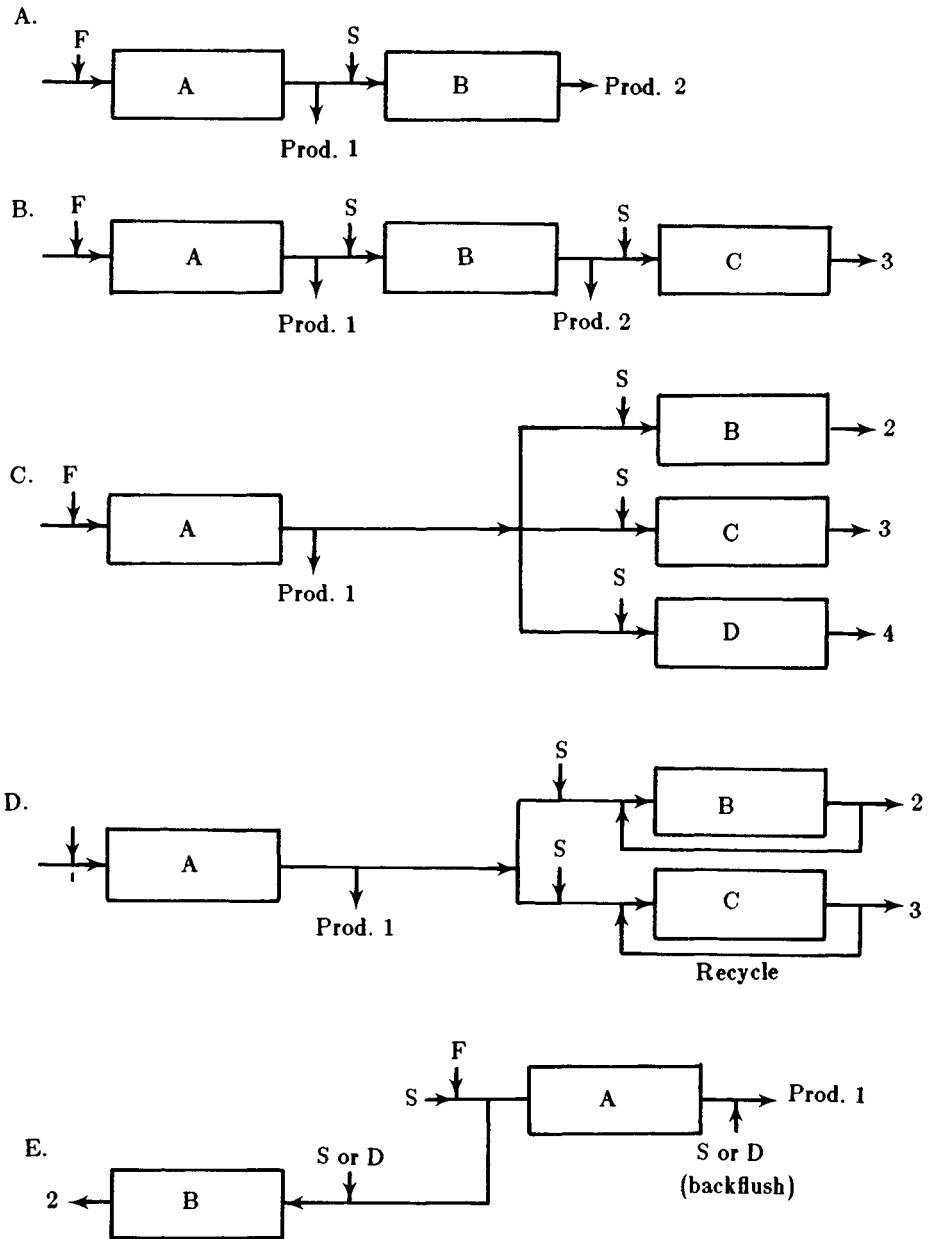
FIGURE 7-1.   Schematic of column switching systems. (A) Basic system; (B) series arrangement; (C) parallel arrangement; (D) parallel arrangement with recycle; (E) for backflush material.

had been used. Thus, the throughput is increased. If one pair of components is very difficult to separate, the use of a precolumn to remove all other components is strongly recommended.[864] Throughput can be further increased by partially separating components and recycling the overlapping peaks. Recycle can be back to the initial column or around a single column, as shown in Figure 7-1D.

The chromatographic theories discussed in Chapter 2, Section VI can be applied to column switching. The use of a single short column to remove solutes 1 and 4 in Figure 7-2 reduces their zone spreading. The valves and piping between the columns do add to the zone spreading of components 2 and 3; however, with properly designed fittings, this effect is small.[329]
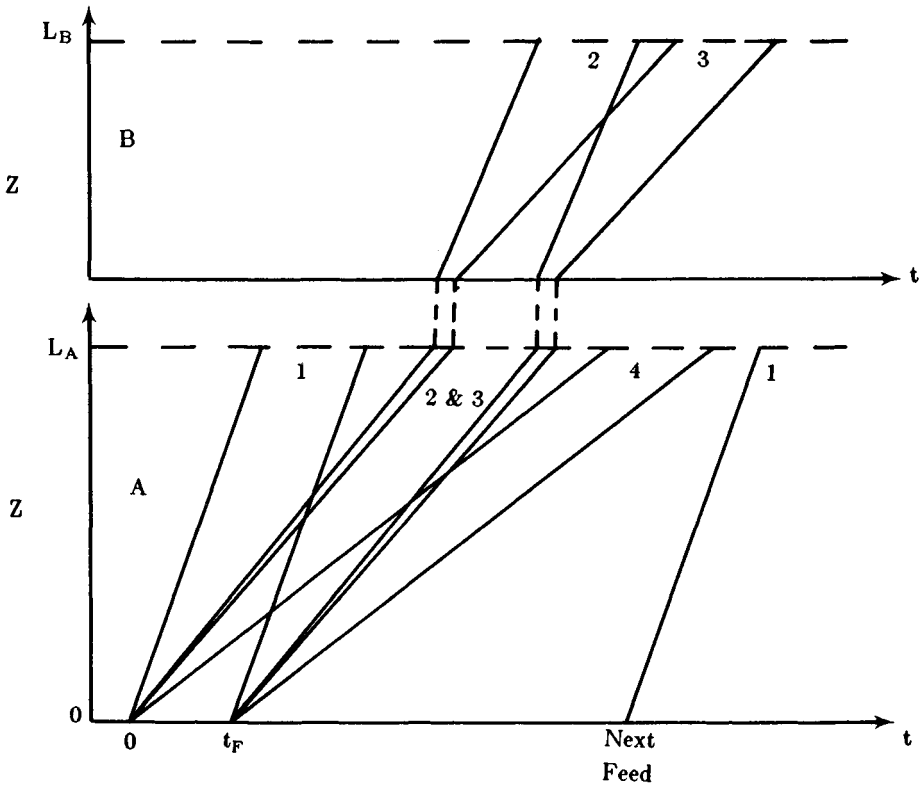
FIGURE 7-2. Solute movement diagram for column switching system of Figure 7-1A. Isotherms are linear.

The column switching systems shown in Figure 7-1C can be used instead of recycle. For example, for a three-component feed, all columns in the parallel arrangement (Figure 7-1C) would usually be packed with the same packing. A heart cut of the first product 1 would be removed after column A. The material which would normally be recycled (see Figure 5-5) is sent to column B. This column gives species 1 and 2 as products. The second product is withdrawn after column A, and recycle material is sent to column C. The products are components 2 and 3. Solute 3 is then recovered from column A, and the recycle from overlap with the next pulse is sent to column D. The use of two or more columns has the advantage that the individual recycle fractions (R1, R2, and R3 in Figure 5-5) can easily be kept separate from each other. Thus, the partial separation will be retained, and this column switching is better than normal recycle. This column switching procedure has been suggested for large-scale xylene and ethylbenzene separation.[890,891] Another use for columns in parallel is to develop a system which will have continuous feed input and product withdrawal.

Several variants of the basic method have been developed. The column switching methods can be employed with backflush.[131,303,728,930,1093] In fact, improving backflush of slowly moving solutes was the original goal in development of column switching methods.[303] An example would be to send rapidly moving solutes to column B in Figure 7-1A, and then to backflush column A to remove the other solutes. The backflushed material can also be sent to another column as shown in Figure 7-1E to separate several slowly moving components. This column could utilize the same or a different packing. Either a solvent or a desorbent can be used for the backflush.

Use of a spatial temperature gradient in a GC column with withdrawal ports between the

steps in temperature has been proposed.[336] Theoretically, this method would have the benefits of thermal programming, but would be simpler and easier to scale up. Column switching with different packings can be used as an alternate to gradient elution.[785] Since column clean-up is not required, the column switching method generally has higher feed throughput. Another proposed alternative is to use a column with layers of different sorbents.[1096] Once separation of components is obtained within the column, each sorbent layer would be eluted with cross flow. This should minimize zone spreading upon elution, but requires several selective sorbents. The column switching methods can also be used with solvent programming or separate desorption steps.

"Box-car chromatography"[932] is a variant of column switching methods. A short pre-column is used to remove both slow moving and fast moving components. The desired components are separated in a long column with several sets of peaks in this column at the same time. Results for the analytical separation of anticonvulsant drug mixtures are given which show roughly a fivefold increase in the rate of analysis.[932] The use of this technique for preparative separations with $\alpha_{21} \le 1.05$ is suggested, but was not demonstrated. A recycle mode of operation was also developed.

Moving withdrawal chromatography[727,1054] is another variant where a series of columns are used such as in Figure 7-1B. Partially separated solutes are removed as soon as they are sufficiently pure. When a stream is removed at an intermediate location, fresh solvent or carrier gas is added to the downstream column. The solute movement diagram for moving withdrawal chromatography is shown in Figure 7-3.[1054] As an illustration of the operation, at time t_1, feed and solvent or carrier gas are added to the bottom of the column, while solute C is withdrawn at ς and fresh solvent or carrier gas is input at ς (above the withdrawal port). Simultaneously, solute B is removed at the top of the column. The solute movement theory predicts a 69.5% increase in throughput for the separation of naphthalene (A), anthracene (B), and pyrene (C) on polyvinylpyrollidone resin compared to normal elution chromatogrpahy at the same resolution.[1054] A staged model, which includes zone spreading, predicts a 39% increase in throughput at the same resolution when compared to normal elution chromatography for the same three components.[727] As is true of all the column switching systems, more improvement will be seen as the components become more spread out. Overlapping peaks can be recycled or be sent to a parallel column switching system. With one very slowly moving component, backflush or gradient elution will be useful.

With higher concentrations, shock and diffuse waves will appear in Figures 7-2 and 7-3. Thus, the theories have to be adjusted, but the basic operating principles will be the same. The characteristic diagram for moving withdrawal of two coupled solutes (see Chapter 2, Section IV.D.1) is shown in Figure 7-4. With coupled solutes, such as ions, the more strongly held solute, B, serves to displace A. Thus, A is concentrated and pure A can be produced. By producing most of the A product while it is concentrated, the moving withdrawal system obtains a more concentrated product than normal elution chromatography (compare Figure 7-4 with Figure 2-16). The B product must tail, but it is also more concentrated than the elution chromatography product. The moving withdrawal system also allows the next pulse to be put in earlier and thus increases throughput. With nonlinear, coupled systems, flow reversal may be useful to recompress the diffuse waves (see Section V).

Figures 5-2 and 5-3 showed the inefficient regions in normal elution chromatography. Column switching methods remove the fast and slow moving components once they have separated. This reduces the size of region 1 and, if desired, of region M. Since there is less sorbent which is doing nothing, the sorbent productivity increases. In the next section, we will look at a method which also reduces the size of regions 2 to 4.
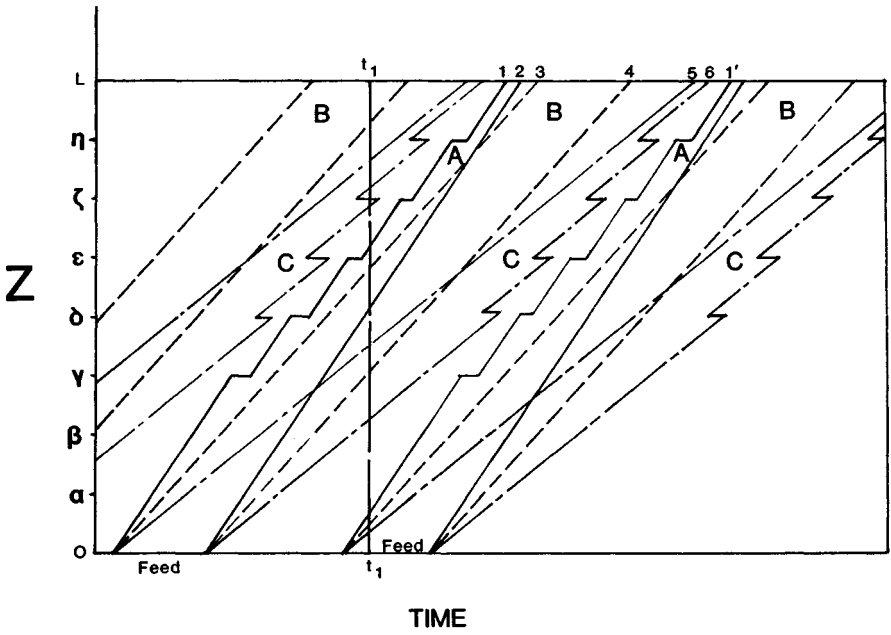
FIGURE 7-3. Solute movement diagram for moving withdrawal chromatography with linear isotherms.[1054] (From *Ind. Eng. Chem. Fundam.*, 23, 256, 1984. With permission.)
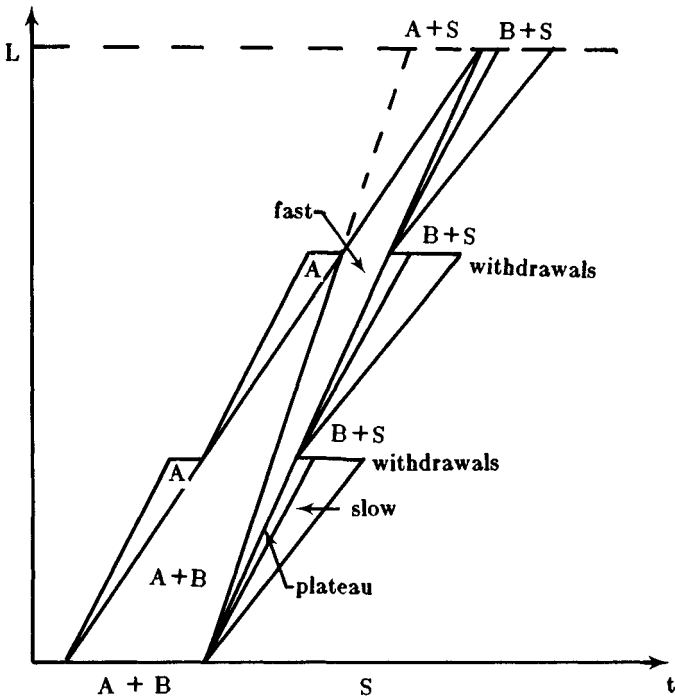
FIGURE 7-4. Solute movement solution for moving withdrawal with coupled nonlinear solutes.
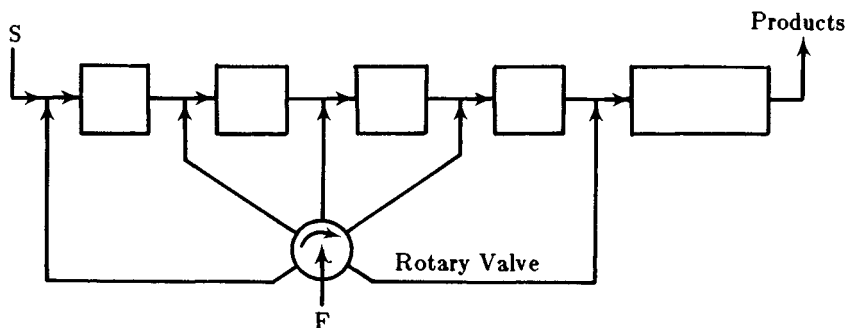
FIGURE 7-5.   Schematic of moving feed chromatography apparatus.

III. MOVING FEED CHROMATOGRAPHY

The inefficient regions near the feed pulse can be reduced by moving the location where feed is introduced. This is done in simulated moving beds and in the method of moving feed chromatography.[709,1045,1061] The system shown in Figure 7-5 has been used to do this experimentally. The solvent or carrier gas is continuously added to the left end of the column. The feed pulse is first added at the left end, and is then progressively moved into the column. For example, if we desired to feed for 20 min total, feed would first be introduced for 4 min into the left end of the column in Figure 7-5. For the next 4 min, feed would be introduced into the second feed port, and for the next 4 min, into the third feed port, and so on. When the 20 min were up, feed would usually be shut off and the column would be eluted. After elution, the next feed step is started. In some cases, such as Figure 7-6, feed can continually be introduced somewhere in the column.

This mode of operation at first seems to be the opposite of what you would want to do. The column is being shortened during the feed pulse. The idea is to follow the separation of the key components so that feed is always added at a point where this separation has not yet occurred. The solute movement theory[709,1045,1061] can be helpful in explaining why this system works. Figure 7-6[709] shows the solute movement diagram for the separation of naphthalene and anthracene. The feed pulse is introduced at $z = 0, 5, 10, 15,$ and 20 cm for 5-min periods or a total of 25 min. The next feed pulse is started at $t = 20$ min. Thus, in this diagram, feed is being introduced into two locations simultaneously for part of each cycle. To construct Figure 7-6, linear isotherms were used and the feed rate was assumed to be small compared to the solvent flow rate so that velocity is constant.

Comparison of Figure 7-6 with the solute movement diagram for normal elution chromatography (e.g., Figures 2-5 or 5-4A) shows that the trailing edge of the slower peak, A, exits much sooner in the moving feed system. This is also illustrated in the experimental data shown in Figure 7-7 where the cobalt chloride exits sooner in the moving feed system. Thus, the next feed pulse can be added earlier, increasing throughput. Since feed is added on top of existing solute, the bands are narrower and more concentrated, which will increase downstream separator costs. In addition, the moving feed system can be designed to have *better* resolution between the N and A peaks than a normal chromatograph. This is also illustrated in Figure 7-7. There will be less zone spreading of the trailing edge of the N peak and the leading edge of the A peak in the moving feed system since they travel a shorter distance in the column. Of course, the intermediate injection ports will increase zone spreading, but in a properly designed system, this can be quite small.
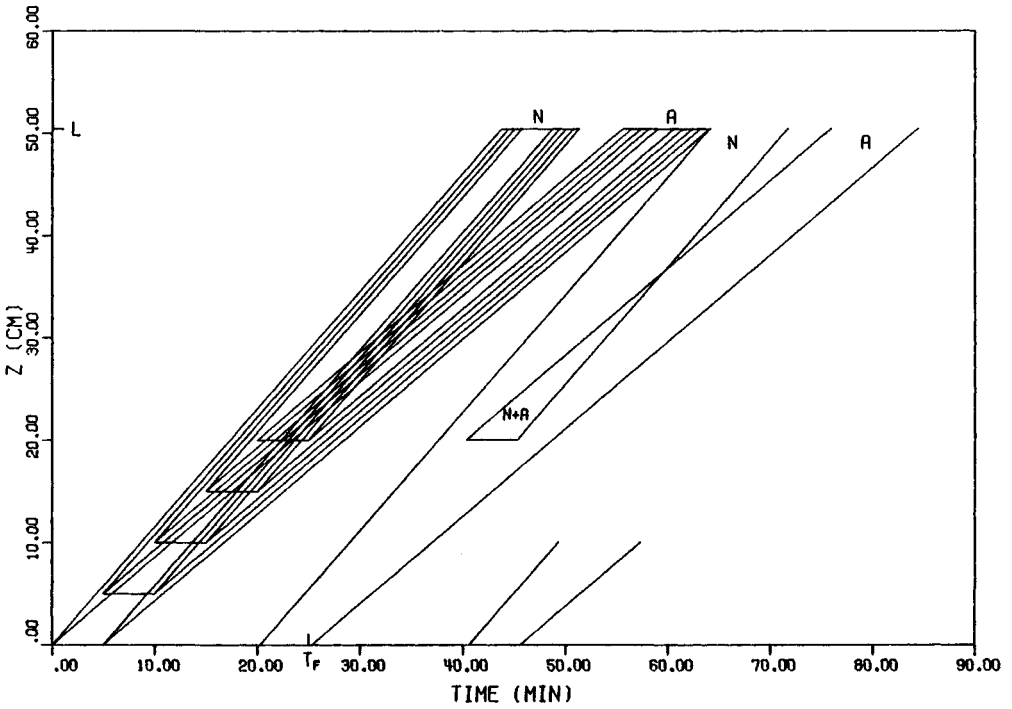
FIGURE 7-6. Solute movement diagram for separation of naphthalene, N, and anthracene, A, by moving feed. (From *Ind. Eng. Chem. Fundam.*, 22, 10, 1983. With permission.)
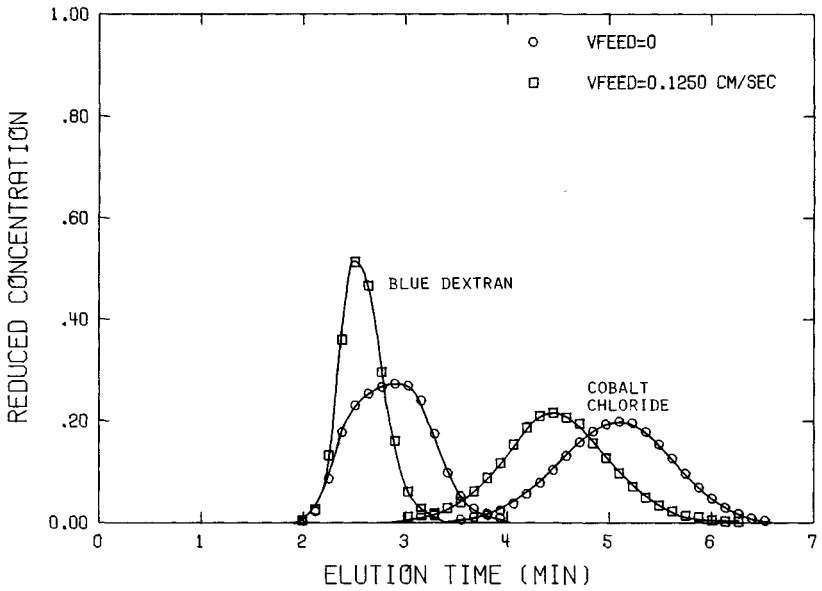
FIGURE 7-7. Separation of Blue Dextran 2000 from cobalt chloride on Sephadex G-25 gel. VFEED = 0 is normal elution chromatography with 18.7-cm long bed. VFEED = 0.1250 is moving feed chromatography with 20 sec of feed injected at 0, 2.5, and 5.0 cm. (From *Ind. Eng. Chem. Process Des. Develop.*, 21, 416, 1982. With permission.)

The movement of the feed port is similar to the movement of ports in simulated moving bed systems (see Chapter 6, Section V.B). We can define an average velocity of the feed port in the same way.

$$u_{port} = l_{port}/t_{port} \qquad (7\text{-}1)$$

The optimum feed port velocity will be between the velocity of the two solutes

$$u_N \geqslant u_{port} \geqslant u_A \qquad (7\text{-}2)$$

With a multisolute system, the feed port movement can be optimized for the key components only. Thus, it will be nonoptimum for other components; however, with a stationary feed $u_{port} = 0$, which is not optimum for any component.

Several variations of the basic design shown in Figure 7-5 are possible. The feed injection point can be moved continuously up the column.[1045] This will further increase the sorbent productivity and reduce the regions of the column where no separation is occurring, but would be difficult to do experimentally. The moving feed method has been adapted to existing ion exchange chromatography columns by drilling a hole in the column wall and inserting a syringe needle into the packing for the intermediate feed points. A nonoptimized moving feed can also be used as an option in a commercial modular liquid chromatography system.[1065]

The moving feed method should be applicable to GC, ion-exchange chromatography, LC, and size exclusion chromatography (SEC). Experimental results have been presented for liquid[18] and size exclusion[1061] systems. The results for a desalting operation by size exclusion are shown in Figure 7-7.[1061] The moving feed system shows better resolution, has more concentrated bands, and the cobalt chloride exits sooner, which will allow the next pulse to be input earlier. The moving feed peaks, particularly Blue Dextran, are not Gaussian. The peaks can be estimated as a sum of Gaussian peaks input at different times and locations, and this sum is not Gaussian.

The resolution obtained for separating naphthalene, anthracene, and pyrene pairs in 2-propanol on a Polyclar AT resin by moving feed liquid chromatography is shown in Figure 7-8.[709] Resolution was defined by Equation 2-125. The system was operated so that the total feed time is inversely proportional to u_{port}. Thus, there is an optimum port velocity or an optimum rate of switching to maximize resolution. At this optimum, the resolution for the moving port system was significantly higher than for a stationary feed with the same feed time. The resolution and throughput for ternary systems was also higher. Depending on the system increases in throughput, up to 300% could be obtained at the same resolution.

The theoretical results shown in Figure 7-8 were obtained by using superposition with the linear dispersion model developed in Chapter 2, Section VI.B. If X(z, V) is the breakthrough solution given in Equation 2-101, the moving feed solution is[709]

$$\frac{c_i}{c_{io}} = [X(L,V) - X(L,V - V_0)] + [X(L - \Delta z_1, V - V_0) - X(L - \Delta z_1, V - V_0 - V_1)]$$

$$+ [X(L - \Delta z_1 - \Delta z_2, V - V_0 - V_1) - X(L - \Delta z_1 - \Delta z_2, V - V_0 - V_1 - V_2)] + \ldots \qquad (7\text{-}3)$$

where V_0, V_1, and V_2 are the feed volumes and Δz_1 and Δz_2 the port distances.

The Peclet number was determined from a stationary feed experiment. The agreement between theory and experiment was quite good. Any linear solution to the breakthrough problem, such as Thomas's J-function solution, could be used in Equation 7-3. The results of a numerical staged model[727] agreed with the linear dispersion model predictions. For the ternary system, naphthalene, anthracene, and pyrene, the staged model predicted that moving
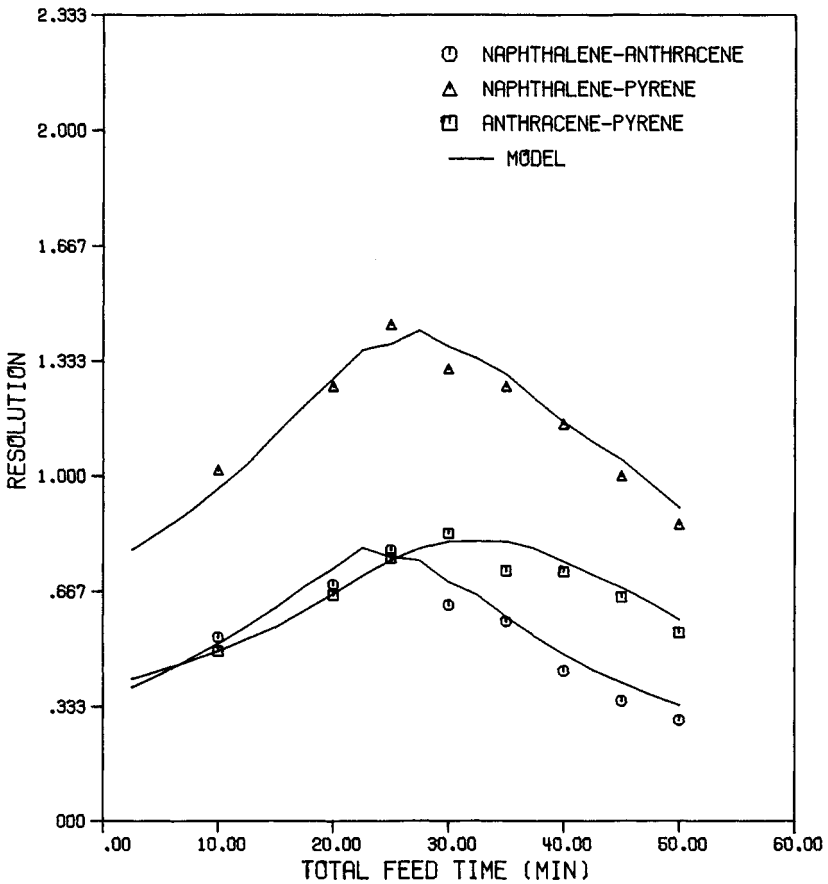
FIGURE 7-8.   Resolution vs. total feed time for moving feed HPLC. (From *Ind. Eng. Chem. Fundam.*, 22, 10, 1983. With permission.)

feed chromatography increased purity by 22% and throughput by 33% when compared to normal chromatography.[727] Changes in velocity were included, but they were small.

The moving feed system shows the most improvement compared to normal preparative chromatography, when the feed flow rate is a small fraction of the solvent flow rate. Then the velocity is approximately constant. This method of operation is often used and may be required to prevent over-flooding the stationary phase. The worst case for the moving feed system is when solvent is stopped and feed is added separately at the same flow rate. Suppose this stop-flow approach is used in the moving feed system shown in Figure 7-5. When feed is added between sections 1 and 2, solvent must be added to section 1. Thus, if the velocity is v in section 1, it will be 2v in all other sections. The effect of this velocity change is easily seen in a solute movement diagram for a system with linear isotherms. This is illustrated for both moving feed and ordinary chromatography in Figure 7-9. Only one intermediate feed is shown and only the fastest solute is plotted to keep the diagram simple. The solute sees a velocity change at the circled locations in the moving feed case. For normal chromatography, the velocity is constant. The band width for normal chromatography is constant, as expected. The band width for moving feed chromatography increases until all solute is out of the high velocity region. If the product is withdrawn at L_1, the moving feed band width is narrower. Thus, when the stop-flow feed procedure is used, the moving feed procedure is advantageous for short columns, but not for long columns. The same conclusion is valid for solutes moving slower than u_{port}. The length of column required depends on how easy it is to separate the two key components.
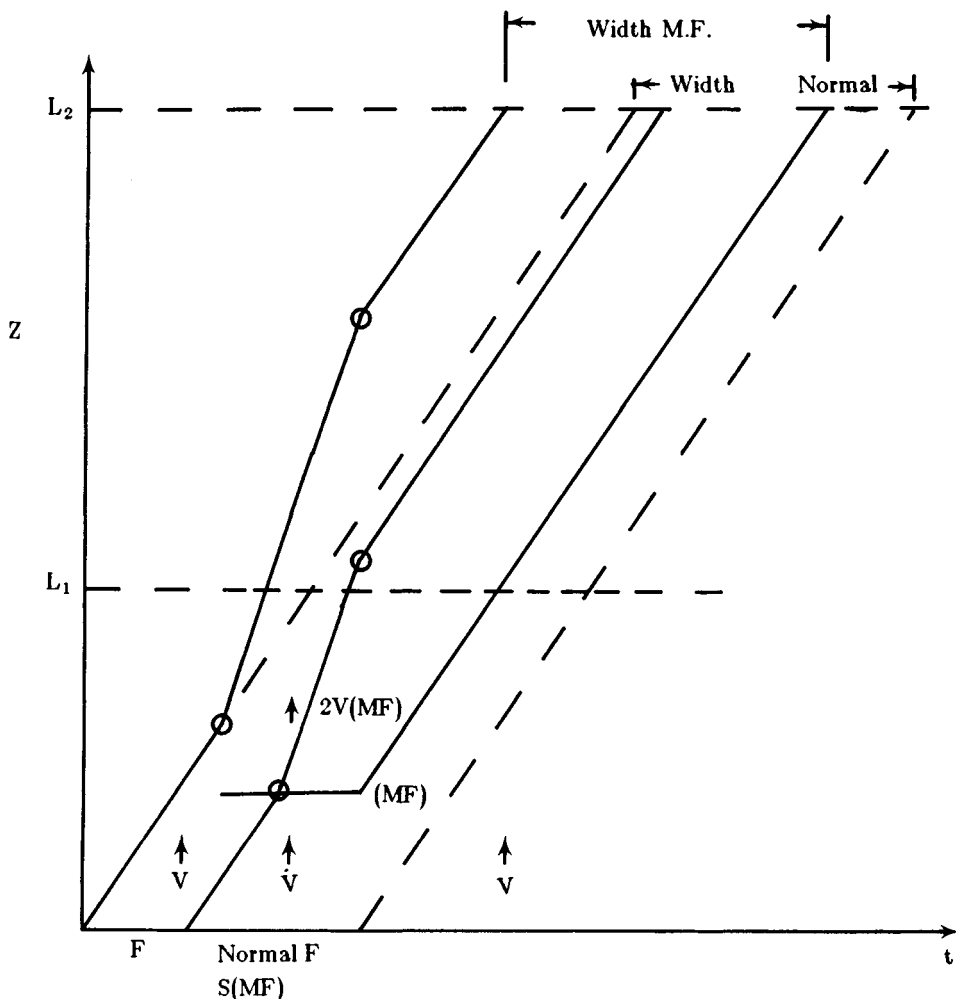
FIGURE 7-9.   Solute movement diagram comparing moving feed and normal chromatography when solvent is stopped while feed is added. Linear isotherms. —— Moving feed case ---- Normal chromatography.

Very recent unpublished results in our laboratory show that for long columns the same results are obtained as with moving feed by feeding at $z = 0$, if all the feed is added at $z = 0$ in the first feed period. This implies that for maximum throughput in large-scale chromatography, solvent should be stopped and feed should be added separately if this is feasible. In many preparative systems where feed is now mixed with solvent, significant increases in throughput can be obtained by changing the mode of feed injection.

The experimental results and theories shown here have been for linear systems. Moving feed can also be applied to nonlinear systems. The throughput should increase compared to normal operation, but resolution or purity may suffer since the moving feed system has higher concentrations in the column. Flow reversal may be useful with nonlinear systems and in this case moving feed chromatography can be combined with two-way chromatography (see Section V).

IV. MOVING PORT CHROMATOGRAPHY

The column switching methods reduce inefficiencies at the product end of the column, while the moving feed method reduces inefficiencies at the feed end. A marriage of these

H

η   14

13

G

ζ   12

11

F

ε   10

9

E

δ   8

7

D

6

γ

5

C

4

β   3

B

2

α   1

A

Feed
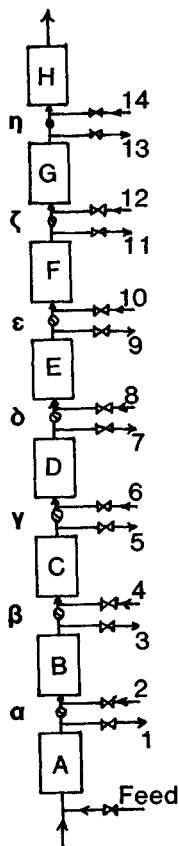
Solvent or Carrier Gas

FIGURE 7-10.   Schematic of moving port chromatography apparatus.
(From *Ind. Eng. Chem. Fundam.*, 23, 256, 1984. With permission.)

two methods should combine these two advantages. Moving port chromatography is a combination of moving withdrawal and moving feed chromatography. A schematic of one way this could be done is shown in Figure 7-10.[1054] The outlet ports, 1, 3, 5, . . . , are used to withdraw products when desired. When product is withdrawn, the entire stream is removed and fresh solvent or carrier gas is added directly above the withdrawal (ports 2, 4, 6 . . .). The inlet ports can also be used for moving feed. We will assume that the feed flow is a small fraction of the solvent or carrier gas flow.

The solute movement diagram is shown in Figure 7-11[1054] assuming that velocity is constant. To illustrate the operation, at time t_1 solvent is added at the bottom of the column and in ports 6 and 14. Feed is added to port 4. Product A (naphthalene) is withdrawn at port 5, product C (pyrene) at port 13, and product B (anthracene) at the top of the column. The solute movement theory predicts a 246% increase in throughput at the same resolution when the moving port system is compared to normal elution chromatography.

A numerical staged model using the STOP-GO algorithm (see Chapter 4, Section V) has been used to predict moving port chromatography separations.[727] Results for good, but not optimized, operating conditions are shown in Figure 7-12.[727] The intermediate withdrawal ports were open when the fastest (N) solute's concentration was 1% of its maximum and closed when the next (A) solute's concentration was 1% of its maximum. The port was reopened when anthracene concentration dropped to 1% of its maximum and remained open to collect pyrene until its concentration dropped to the 1% level. This choice was arbitrary,
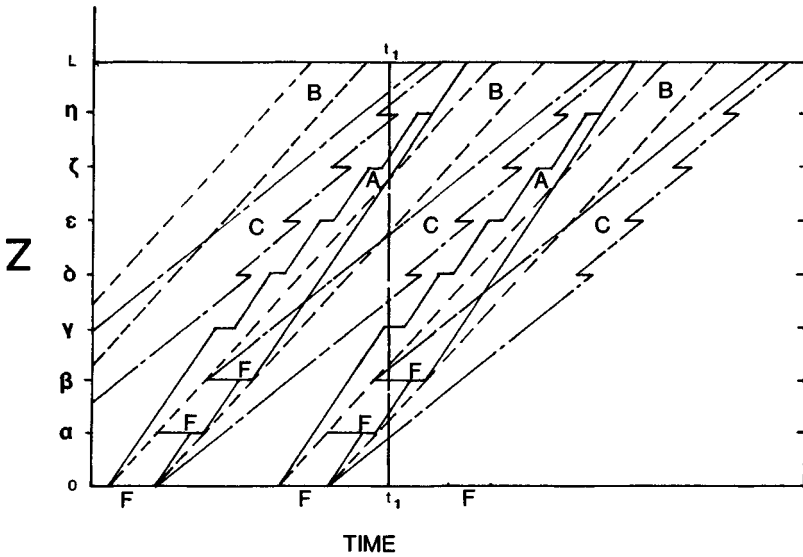
FIGURE 7-11.   Solute movement theory for moving port chromatography for linear isotherms. (From *Ind. Eng. Chem. Fundam.*, 23, 256, 1984. With permission.)

but seemed reasonable for illustration. Obviously, timing is critical and the results could be improved by optimizing the timing. Note the sharp cutoffs shown in Figure 7-12A when the valve is closed or opened. In Figure 7-12B, the anthracene peak is exactly the same as for the moving feed system, but the N and P peaks have been truncated. Better resolution could be obtained by shortening the feed period, increasing column length, or decreasing the particle diameter. Much of the overlapping portions could be recycled, or be sent to a parallel column switching system (Figure 7-1C). The staged model predicted a 22% increase in average purity and a 120% increase in throughput when the moving port chromatograph was compared to normal operation.

No experimental results have been reported yet for the moving port chromatograph. The apparatus is similar to SMB systems and an SMB could probably be converted into a moving port system fairly easily. A comparison between moving port chromatography and a SMB is given in Table 7-1.

For nonlinear competing systems, the theoretical calculations become more difficult, but the basic operating principles should be unchanged. Since flow reversal is often advantageous with nonlinear systms, it may be possible to combine moving port chromatography with backflush or with two-way chromatography (see the next section). The optimum solvent probably has a selectivity in between that of the key components, since this is the case for normal elution chromatography and the SMB.

Moving port chromatography can also be used with solvent, flow, or temperature programming. With a stepwise elution, one possible cycle is

Feed
Wash out weakly adsorbed solutes
Increase desorbent concentration and remove next strongly adsorbed solute
Increase desorbent concentration

.

.

.

Regenerate column
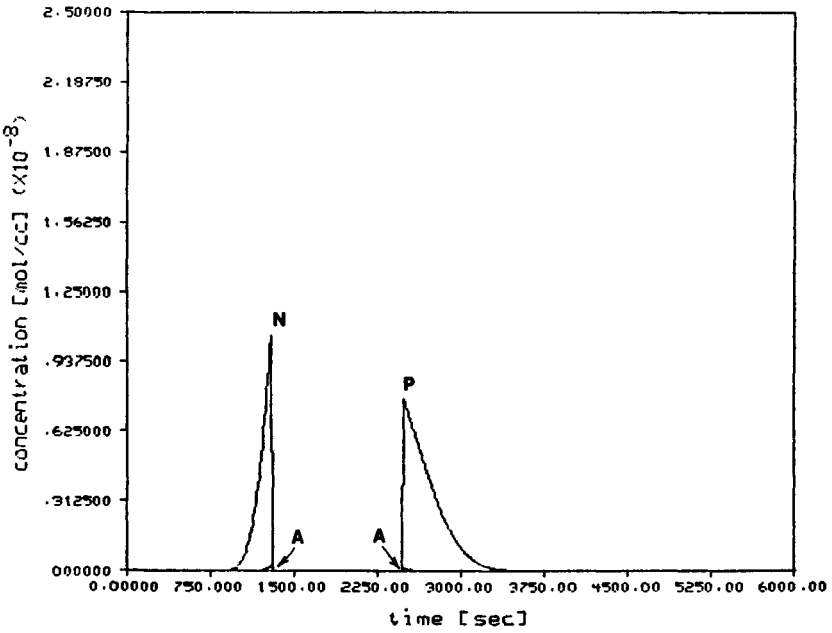
A
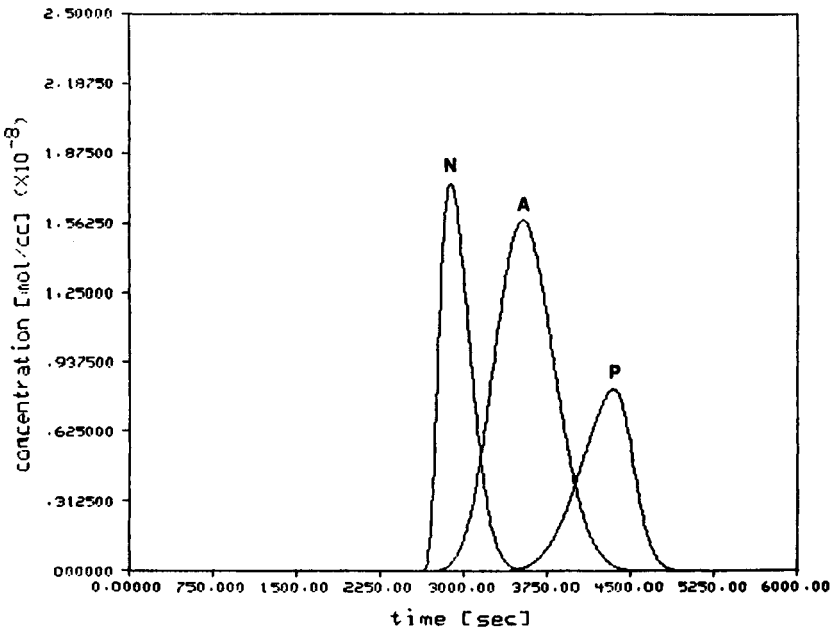
B

FIGURE 7-12. Computer simulation of moving port chromatography. Feed ports at 0, 5, 10, 15, and 20 cm. Withdrawal ports at 25, 30, 35, 40, 45, and 50 cm. Total feed time 25 min/pulse. Napthlalene (N):u_N = 1.15 cm/min, H_N = 0.222 cm. Anthracene (A):u_A = 0.85 cm/min, H_A = 0.311 cm. Pyrene (P):u_P = 0.62 cm/min, H_P = 0.321 cm. (A) Intermediate withdrawal products at 25 cm, (B) final product withdrawal at 50 cm. (From *Chem. Eng. Commun.*, 31, 21, 1984. With permission.)

Table 7-1
COMPARISON OF MOVING PORT CHROMATOGRAPHY AND SMB

Moving port chromatography	SMB
Batch	Pseudo steady state
No recycle	Continuous recycle
Sections near end do not receive feed	All columns receive feed during cycle
For product withdrawals remove everything	For product withdrawals remove only part of fluid
Separate elution step w/o feed	No separate elution step
Multicomponent	Binary separation
Experimental	Commercial
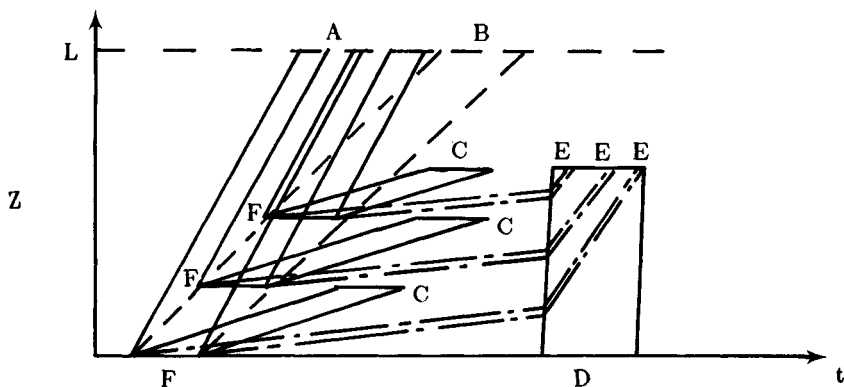
FIGURE 7-13. Solute movement theory for moving port chromatography with desorbent elution. Linear isotherms.

The details of a theory for desorbent elution depends on the chemistry. The desorbent may compete with the solutes for sites, or it may complex with solutes in free solution. When the desorbent complexes with solutes in solution, the solute movement theory may be very simple. Assume that the desorbent does not adsorb. Then the desorbent wave velocity is given by Equation 2-30 with $k_i = 0$. The desorbent waves have constant velocities. What desorbent does, is effectively change the k_i values for the solutes. An example solute movement diagram for a linear system with four solutes is shown in Figure 7-13. A moving feed is used since it is optimal for the A-B-C separation; however, it is not optimal for E. The concentration of E will be less than with normal feed. Moving withdrawal is advantageous for component C, since it allows earlier addition of the desorbent. Moving withdrawal is not particularly advantageous for solute A, so it is not used. Solute E is strongly adsorbed and is removed with desorbent. This could be done either co-currently as shown, or with backflush. Solute E and desorbent are removed at the third withdrawal port instead of being flushed through the entire column, since this allows introduction of the next feed pulse earlier and requires less desorbent. Obviously, the method can be adapted to a variety of situations.

The products from the intermediate withdrawal or the final withdrawal can be partially recycled or sent to parallel column switching systems (Figure 7.1.C). The result will be sort of a "tree" of interconnected column sections. Different sorbents can be employed in the different sections of this modified moving port chromatograph. This combines the multidimensional chromatography ideas of column switching with moving port chromatography. The optimum ways to couple and time such systems are an important area for future research.
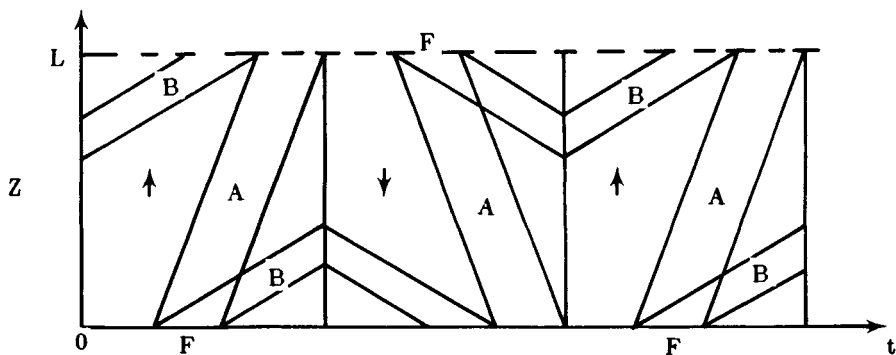
FIGURE 7-14. Solute movement diagram for two-way SEC with feed from both ends. Shown for linear isotherms. (A) = high MW species; (B) = low MW species.

V. TWO-WAY CHROMATOGRAPHY

In two-way chromatography, flow is first up the column and then is reversed. Products are withdrawn from both ends and perhaps, from the middle of the column. Several different modifications of two-way chromatography are possible and will be discussed in this section. This method has advantages, but the equipment and operating procedures can be complex.

Two-way chromatography was applied to SEC for commercial purification of whey proteins in Gotene, Sweden[659] (see Chapter 5, Section VI). The main purpose of the flow reversal appears to have been to keep the nets supporting the gel free of precipated protein, but a 10% increase in capacity was also claimed. This capacity increase may have been due to less clogging of the support nets. The system used alternating feed from both ends. The fast moving, high molecular weight proteins were removed in the same direction as the feed pulse. The slow moving, low molecular weight salts and lactose were backflushed.

Although complete details of the operation were not given, one way this two-way chromatography could be done is illustrated in Figure 7-14. Note that feed is introduced several minutes after the flow direction is reversed. This method certainly could be used for other chromatographic systems, but reasons for increased throughput are not obvious. It would probably have advantages when the strongly adsorbed solute has a nonlinear isotherm.

For nonlinear competing solutes, flow reversal and intermediate withdrawal may be useful. In a very complete article, Bailly and Tondeur[72] developed this idea into the method they called two-way chromatography. The method was illustrated with the system $H^+ - Na^+ - K^+$ on a duolite C20 sulfonated polystyrene ion exchanger in a 3.2-m long column. Most of the theory and results use the least strongly retained ion, H^+, as the eluant. The separation corresponds to the separation done by normal chromatrography in Figure 2-16 and by moving withdrawal chromatography in Figure 7-4.

The simplest version of the process is single feed, simple reversal. This operation is shown schematically in Figure 7-15.[72] At the start of the cycle, the column is saturated with Na^+ and K^+. In step 1, H^+ is used as eluant and Na^+ and K^+ are stored in the right storage tank. Note that the more strongly retained K^+ lags behind the Na^+. Since the K^+ is displaced by less strongly retained H^+, diffuse waves are formed. In step 2, the K^+ product is withdrawn as a sidestream at point B. The K^+ is diluted by H^+, but contains very little Na^+. The column section from B to C is idle during this step. The flow is reversed during step 3, and feed is from the Na^+ and K^+ storage tank. Pure H^+ is stored in the left reservoir. Inside the column, the Na^+ passes through and moves ahead of the K^+. Note that a concentrated Na^+ peak is formed, since K^+ serves as a desorbent. (This can be compared to the desorbent operation shown in Figure 2-15). The Na^+ peak will become very sharp,
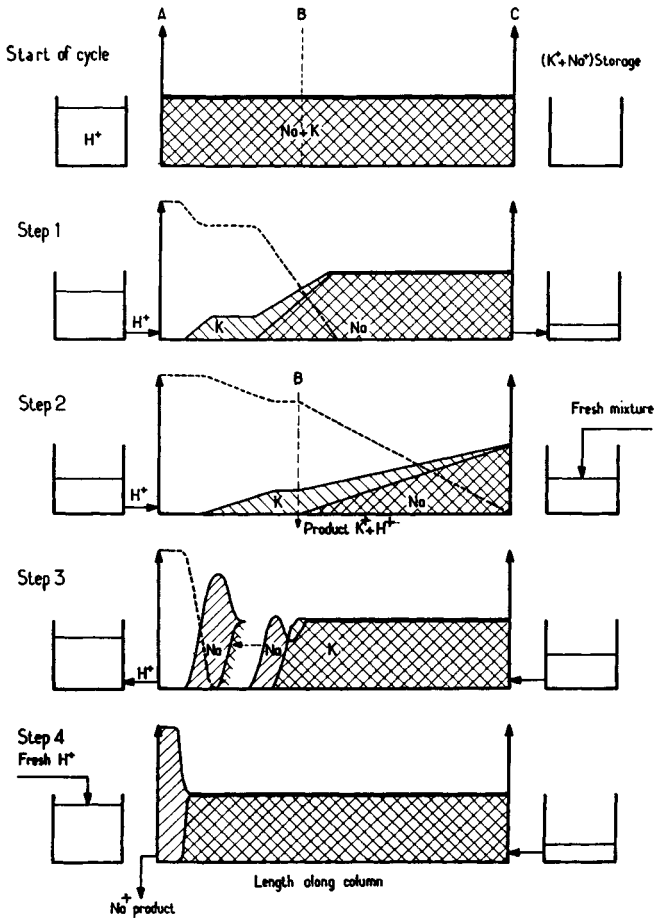
FIGURE 7-15. Schematic of concentration profiles during single feed, simple reversal two-way chromatography for coupled ions. (From *Chem. Eng. Sci.*, 36, 455, 1981. With permission.)

since it is bounded by shock waves. In step 4, essentially pure Na$^+$ product is withdrawn. This step is continued until the column is saturated with Na$^+$ + K$^+$ and we have returned to the start of the cycle.

This cycle takes advantage of the coupling between ions. A flow reversal cycle like this will be much less helpful for linear systems. The local equilibrium model for coupled isotherms was used[72] to analyze the process. The diagrams which result use the principles used for Figures 2-15, 2-16, and 7-4 (see Chapter 2, Section IV.D.1), but are considerably more complex because of the interferences caused by the flow reversal. This analysis agrees with the qualitative description given in Figure 7-15. The theory also qualitatively predicts the experimental results shown in Figure 7-16. During step 2, the K$^+$ product is diluted by H$^+$ (not shown in Figure 7-16A), but contains very little Na$^+$. During step 3, the H$^+$ is pure, and then there is a sharp front between H$^+$ and Na$^+$ (Figure 7-16B). The Na$^+$ peak is almost pure until the K$^+$ and Na$^+$ at the feed concentration breaks through. Some of the K$^+$ tail removed in step 2 can be left in the column, and the Na$^+$ will pass through this. The result will be a less dilute K$^+$ product in Figure 7-16A.

An alternative to the system shown in Figure 7-15 is two-sided feed injection.[72] This process uses an eight-step cycle with feed from both ends of the column, and two sidestream withdrawals. Details are presented in the original paper.[72] The more complex cycle uses
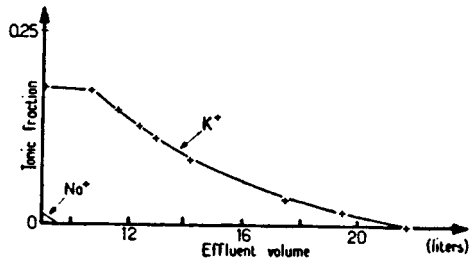
A
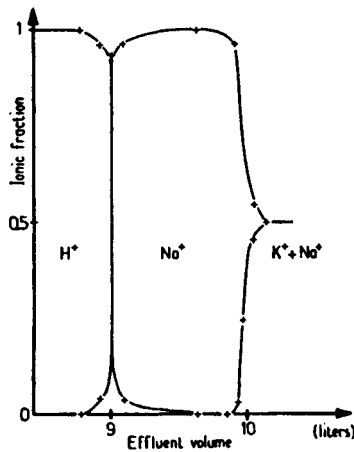
B

FIGURE 7-16. Experimental results for single feed, simple reversal two-way chromatography. (A) Effluent concentration history for sidestream product (step 2); (B) effluent concentration history of Na$^+$ product (steps 3 and 4). (From *Chem. Eng. Sci.*, 36, 455, 1981. With permission.)

less eluant and has a higher sorbent productivity. Single-sided and two-sided feed systems were also developed for the case where the most strongly retained ion, K$^+$, was the eluant and H$^+$ and Na$^+$ were separated.[72] With K$^+$ as the eluant, pure Na$^+$ was produced and H$^+$ was separated from the Na$^+$, but it was diluted with K$^+$.

These coupled ion exchange processes both concentrate and separate. They used less eluant than normal chromatography and the product streams were more concentrated, but the sorbent productivity was lower. Two-way chromatography can be improved by using multiple columns similar to the methods used for pressure swing adsorption (see Chapter 4, Section II). In this way, all parts of the column can be separating at all times.

VI. SIMULATED CO-CURRENT OPERATION

In Chapter 6, Section V.B, we saw that simulated countercurrent operation was often a useful method. Gerhold[414] has developed a system which can be considered either a simulated co-current process or a complex chromatograph with recycle and column switching. This process has been commercialized by Universal Oil Products.[408]

The process is shown schematically in Figure 7-17.[414] There are six columns which are each operated one sixth of the cycle out of phase with the previous column. During step 1,
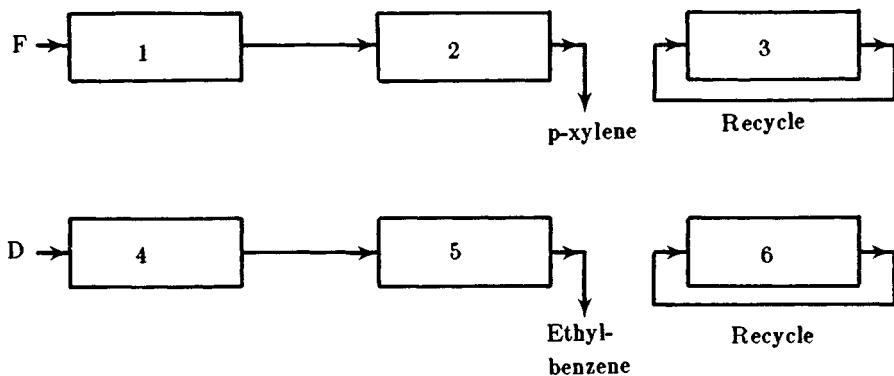
FIGURE 7-17. Gerhold simulated co-current flow process illustrated for separation of *p*-xylene and ethylbenzene. (1) Feed step; (2) removal of *p*-xylene product; (3) pumparound (recycle); (4) desorbent feed; (5) removal of ethylbenzene product; (6) pump-around (recycle).

a mixture of the two solutes to be separated (e.g., *p*-xylene and ethylbenzene) are fed to the first column. The material leaving column 1 goes to column 2 which received feed during the previous time step, and elutes the more strongly adsorbed *p*-xylene (plus desorbent) left from steps 5 and 6. The material from the feed pulse remains in column 1. During step 2, column 1 receives effluent from column 6 which is now receiving feed. During the pump-around, step 3, the peaks move further in column 1 and any left-over dilute *p*-xylene is returned to the front end of this column. Fresh desorbent (e.g., *para*-diethylbenzene) which has a selectivity between *p*-xylene and ethylbenzene is added in step 4. The outlet from column 1 during step 4 is the feed to column 2, which had received desorbent in the previous step. During step 5, column 1 receives effluent from column 6 which is now receiving desorbent. The product from step 5 is ethylbenzene plus desorbent. The pump-around in step 6 serves to recycle unseparated material back to the front of column 1 and leaves an impure *p*-xylene tail, which is then purified in steps 1 and 2. An example for the separation of fructose and glucose using water as the elutant was also given in the patent.[414]

From a chromatographic viewpoint, step 2 is removing the pure trailing edge of the slower moving compound, while step 5 removes the pure leading edge of the faster moving compound. Step 6 is a recycle of unseparated material. Step 3 is a recycle of dilute *p*-xylene desorbent, which serves as an elutant for the main peak. The use of steps 1 and 4 without product allows impure streams to be used as elutant and can be considered a column switching method. The process has feed one sixth of the time and fresh desorbent added one sixth of the time. If flow rates are equal (they were approximately equal for fructose-glucose separation and were unequal for *p*-xylene-ethylbenzene), this represents a 50% dilution of the feed. Thus, fairly minimal dilution of the products occurs. Although the process is difficult to understand, the equipment is fairly simple.

This patent illustrates that there are many clever ways to operate chromatographic columns. It will be interesting to see if this method can be combined with other operating principles such as flow reversal.

VII. THE FUTURE FOR COLUMN SWITCHING AND MOVING PORT METHODS

Column switching methods are a standard operating procedure for analytical and preparative separations. As the large-scale separations of complex biological mixtures becomes common-place, column switching methods will be used more often. A standardized procedure

for selecting sorbents and optimizing the operation for large-scale separations would be most useful.

The moving withdrawal, moving port, SMB, and moving bed systems are more complex. An approximate order of increasing complexity is:

scaled-up	column	moving	moving	simulated	moving
chromatography	switching	withdrawal	port	moving bed	bed

For binary separations, this list is also in the approximate order of increasing sorbent productivity and decreasing solvent use. On a laboratory scale, normal preparative chromatography is by far the simplest process, and since productivity and solvent usage are relatively unimportant, it is the obvious choice. On the very large scale, such as *para-* and *meta*-xylene separation, productivity and solvent use become critical. Here the SMB and the moving bed (if successfully developed for chromatography) often have an advantage for *binary* separations. In some intermediate production range, it is likely that the systems of intermediate complexity, productivity and solvent use, would be most economical. For nonlinear competing solutes, two-way chromatography should also be considered for separation of two solutes.

With three or more solutes, the situation is different. Both the SMB and the moving bed are binary separators. More than one SMB or moving bed system would be required. Thus, the systems with multicomponent separation capacity probably have an advantage. For intermediate- and large-scale systems where a few products are desired, the moving withdrawal and moving port systems are likely to prove most economical. This is particularly true if a center cut is required.

The average velocity of the feed ports can be optimized in the moving feed and moving port systems to minimize zone spreading and dilution of the desired product. If a large number of products are desired, a network of separators is probably useful.

Chapter 8

TWO-DIMENSIONAL AND CENTRIFUGAL OPERATING METHODS

I. INTRODUCTION

The last set of operating techniques we will look at are two-dimensional and centrifugal methods. These have been lumped together for convenience. The two-dimensional methods are an alternate way of doing chromatography or adsorption which produces a steady-state separation. For a while, these machines captured the imagination of many researchers and were produced commercially. Unfortunately, they are mechanically complex and, with a few exceptions, are no longer used. We will first consider the basic idea and compare it with more typical chromatography systems. Then, applications of the basic scheme, other two-dimensional geometries, and regenerated two-dimensional methods will be discussed.

Centrifugal chromatography, the chromatofuge, is an old scheme which keeps resurfacing for specialty applications. The chromatographic packing is placed in a centrifuge, and pulses of feed are added while the centifuge is spinning. Production rates tend to be quite high, and the method has advantages for viscous solutions. Similar centrifugal methods have also been used for adsorption and ion exchange. The chromatofuge is discussed in Section III.

II. TWO-DIMENSIONAL ADSORPTION AND CHROMATOGRAPHY

In this section, we will explore the basic two-dimensional (2D) design and see how it works. The analogy between two-dimensional and one-dimensional (1D) equipment will be used to develop solutions for the 2D system. Applications of the basic 2D chromatographic design and other 2D geometries are discussed. Finally, we will consider regenerated 2D adsorption and chromatography.

A. Basic Two-Dimensional Chromatography Scheme and Analogy with One-Dimensional Systems

The idea for 2D chromatography was first suggested by Martin[694] in 1949. He suggested building an annular column and packing the annular space as shown in Figure 8-1. The entire annulus is then slowly rotated past the feed injection point where feed is added continuously. Solvent or carrier gas is added continuously to the rest of the annulus. Solutes which are weakly adsorbed spend very little time on the stationary phase (actually a rotating phase now), and thus, these solutes exit the column at a small angle of rotation θ. More strongly adsorbed solutes come out at a large angle and so on. Thus, the system is a continuous separator where θ has replaced time. The carrier velocity and angular velocity, ω, are usually set so that all solutes exit in less than one rotation ($\theta < 360°$).

Martin[694] developed his idea for this apparatus by analogy to typical 1D chromatography. The analogy can be made mathematically precise and can then be used to develop other 2D systems.[1046] For a 1D system, the solute mass balance is Equation 2-66

$$\alpha \, \frac{\partial c_i}{\partial t} + K_{di}(1 - \alpha)\epsilon \, \frac{\partial c_i^*}{\partial t} + \rho_s(1 - \alpha)(1 - \epsilon) \, \frac{\partial q_i}{\partial t} +$$

$$\alpha \, v \, \frac{\partial c_i}{\partial z} - \alpha(E_D + D_M) \, \frac{\partial^2 c_i}{\partial z^2} = 0 \qquad (2\text{-}66)$$
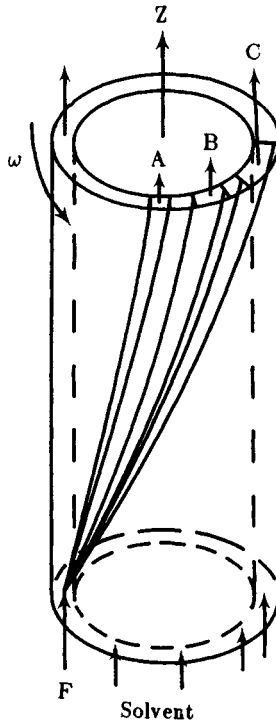
FIGURE 8-1. Rotating annulus, 2D steady-state chromatograph.

the corresponding mass balance in cylindrical coordinates for the steady-state 2D system in Figure 8-1 with a solid rotation of both fluid and solid phases is

$$\alpha \, \omega \, \frac{\partial c_i}{\partial \theta} + K_{di}(1 - \alpha)\epsilon \, \omega \, \frac{\partial c_i^*}{\partial \theta} + \rho_s(1 - \alpha)(1 - \epsilon) \, \omega \, \frac{\partial q_i}{\partial \theta}$$

$$+ \, \alpha \, v \, \frac{\partial c_i}{\partial z} - \alpha(E_D + D_M) \frac{\partial^2 c_i}{\partial z^2} - D_\theta \frac{1}{r^2} \frac{\partial^2 c_i}{\partial \theta^2} = 0 \tag{8-1}$$

The assumptions made in deriving Equation 2-66 have also been made for Equation 8-1. Note that the axial geometries are similar in the 1D and 2D systems, and the cross-sectional area for flow does not change. A comparison of Equations 2-66 and 8-1 show that there is a term-by-term correspondence between the equations, except for the last term in Equation 8-1, which represents dispersion in the θ-direction. If dispersion in the angular direction can be neglected, then Equation 2-66 can be transformed into Equation 8-1 by making the simple transformation

$$t \rightarrow \theta/\omega \tag{8-2}$$

For the analogy between 1 and 2D systems to hold, the equilibrium expression and the other balance equations must also transform. Since equilibrium expressions are usually time independent, they are unaffected by the transformation in Equation 8-2. The solute mass balance on the solid phase, Equation 2-67 is

$$\rho_s(1 - \epsilon)(1 - \alpha) \frac{\partial q_i}{\partial t} + K_{di}\epsilon(1 - \alpha) \frac{\partial c_i^*}{\partial t} = -k_T a_p(c_i^* - c_i) \tag{2-67}$$

while for the steady-state 2D system it is

$$\rho_s(1 - \epsilon)(1 - \alpha) \, \omega \, \frac{\partial q_i}{\partial \theta} + K_{di}\epsilon(1 - \alpha) \, \omega \, \frac{\partial c_i^*}{\partial \theta} = -k_T a_p(c_i^* - c_i) \qquad (8\text{-}3)$$

Equation 2-67 tranforms into Equation 8-3 when Equation 8-2 is used. The energy balance is given by Equation 2-68, while the energy balance for the 2D system is

$$\rho_f \, C_{P_f} \, \alpha \, \omega \, \frac{\partial T}{\partial \theta} + \rho_f \, C_{P_f} \, \epsilon(1 - \alpha) \, \omega \, \frac{\partial T^*}{\partial \theta} +$$

$$\rho_s \, C_{P_s}(1 - \epsilon)(1 - \alpha) \, \omega \, \frac{\partial T_s}{\partial \theta} + \rho_s \, C_{P_f} \, \alpha \, v \, \frac{\partial T}{\partial z} - (E_{DT} + D_T) \, \rho_f \, C_{P_f} \, \alpha \, \frac{\partial^2 T}{\partial z^2} - D_{\theta T} \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} =$$

$$h_w A_w (T_{amb} - T_w) - C_{P_w} \, \omega \left(\frac{W}{A_c}\right) \frac{\partial T_w}{\partial \theta} \qquad (8\text{-}4)$$

If thermal dispersion in the θ-direction can be ignored, there is a term-by-term agreement between Equations 8-4 and 2-68. However, the annulus system has a different wall area A_w for external heat transfer and the weight of wall per length W will be different. Thus, the energy balances transform if angular thermal dispersion is negligible, but the terms for h_w, A_w and W/A_c will be different. The energy balance on the solid phase is

$$\rho_s \, C_{P_s} \, (1 - \epsilon)(1 - \alpha) \, \omega \, \frac{\partial T_s}{\partial \theta} + \rho_f \, C_{P_f}\epsilon(1 - \alpha) \, \omega \, \frac{\partial T^*}{\partial \theta}$$

$$= -h_P \, a_P \, (T^* - T) + (1 - \epsilon)(1 - \alpha) \, \rho_s \, \Delta \, H_{ads} \, \omega \, \frac{\partial q}{\partial \theta} \qquad (8\text{-}5)$$

Equation 2-69 transforms to Equation 8-5 when Equation 8-2 is used. The boundary conditions for the 1D time-dependent and the 2D steady-state systems will also transform.[1046] Thus, the 2D system in Figure 8-1 is analogous to the 1D system if mass and thermal dispersion in the θ-direction are negligible.

Since the systems are analogous, the solutions obtained in Chapter 2 for 1D, time-dependent adsorption and chromatography can be applied directly to the two-dimensional, steady-state system by letting $t \rightarrow \theta/\omega$. There is no need to separately solve the 2D set of equations. This analogy is also true for staged models.[1059] The analogy also holds if the annulus in Figure 8-1 is held stationary, and both the feed injection point and the product collectors are rotated at angular velocity ω.

The solute movement solution for the chromatography system shown in Figure 8-1 is easily derived by the methods used in Chapter 2[1059] or from the analogy. This solution is restricted to systems with negligble dispersion and very rapid mass transfer so that solid and fluid are in equilibrium. The solute velocity now becomes a slope, S_i, and is

$$S_i = \frac{v}{\omega \left[1 + \dfrac{1 - \alpha}{\alpha} \, \epsilon \, K_{di} + \dfrac{1 - \alpha}{\alpha} \, (1 - \epsilon) \, \rho_s \dfrac{\Delta q_i}{\Delta c_i}\right]} \qquad (8\text{-}6)$$

which corresponds to Equation 2-28. Nonlinear systems will have shock and diffuse waves in the same form as 1D columns. For linear isotherms, $q_i = k_i c_i$ and the result is

$$S_i = \frac{v}{\omega \left[1 + \dfrac{1 - \alpha}{\alpha} \, \epsilon \, K_{di} + \dfrac{1 - \alpha}{\alpha} \, (1 - \epsilon) \, \rho_s \, k_i\right]} \qquad (8\text{-}7)$$

The solute movement diagram for the chromatograph in Figure 8-1 is shown in Figure 8-2 for linear isotherms. Since mass transfer rates are finite and dispersion does occur, the
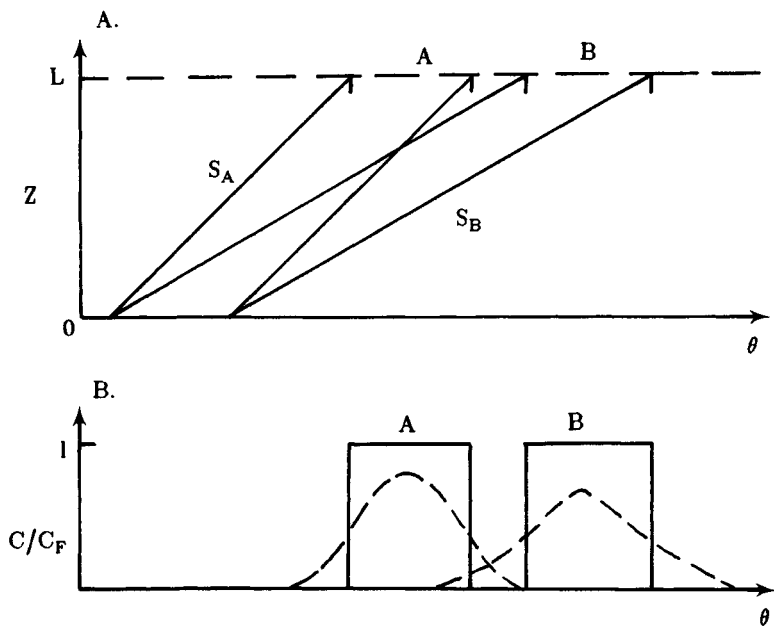
FIGURE 8-2. Solute movement theory for 2D chromatograph with linear isotherms. (A) Solute movement in column; (B) product concentrations. — Predicted ----. Experimentally observed.

experimental results show zone spreading as illustrated in Figure 8-2B. Figures 8-2 and 2-5 should be compared to see the great similarity for 1 and 2D systems.

B. Applications of Two-Dimensional Chromatographs

The rotating annulus design has been tried for almost all types of chromatography. Packed annulus systems for liquid chromatography were first studied by Svensson et al.[955] They had trouble with lateral flow with an annulus system packed with powder. To eliminate this problem, they replaced the annulus with a series of columns arranged in a circle as in a Gatling gun. This "Gatling gun" arrangement is shown in Figure 8-3. The connection between 2D and 1D systems is now very obvious, and angular dispersion is negligible. Each column is eluted individually as a 1D column. The Gatling gun system gave good continuous separation once all the columns were matched and the flow rate to the columns was controlled. This control was necessary so that solute always exited at the same angle θ. An alternate control method is to use computer control and have the computer remember the retention behavior of each column and adjust the timing.[780] The device is then no longer steady state. A third arrangement for the rotating annulus system is to hold the annulus stationary and rotate the feed system and the fraction collector at the same speed.[337] Slight modifications of this have been suggested.[20] A fourth possible arrangement is to use a Gatling gun-type system and rotate the feed and product collectors instead of the columns. This, apparently, has not been tried.

Many other researchers have explored the rotating annulus system adding their own clever touches. The packed annulus has been replaced by a sheet of paper to develop 2D paper chromatography,[935] but this is obviously not a large-scale technique. The Gatling gun arrangement with up to 100 columns was used for continuous GLC to produce purities up to 99.9%.[323,807,973] Separation of α- and β-pinene[973] can be compared to the results obtained in columns (see Chapter 5, Section VII). Prototype industrial systems were built in Italy, but did not prove to be economical. In the U.S., the Rotosorber,[51] which was 8 ft in diameter
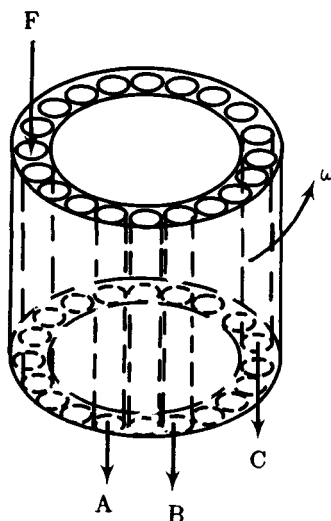
FIGURE 8-3. "Gatling-gun" arrangement with a series of columns for
continuous 2D chromatography.

and 12 ft high, was commercially available for a period. A retention argument, similar to
that used here, was used to predict when solutes would exit.[323,807,973] The linear theory of
chromatography has also been used to analyze the rotating annulus system.[417] The rotating
annulus system has been applied to gel permeation chromatography.[383,384,768] Since the
apparatus could not be pressurized, flow rates were low. This early work and other geometries
are covered in several review papers.[78,79,829,947,951,1055]

The state-of-the-art of the rotating annulus design is the continuous annular chromatograph
(CAC) developed at Oak Ridge National Laboratory.[115-118,207,208,886] This pressurized system
is shown in Figure 8-4.[207] By careful design and construction, these workers were able to
build several slightly different apparatuses which overcame channeling and mechanical
problems. Packing the annulus was claimed to be easier than packing columns, since the
walls of the annulus serve as supports. This may mean increased wall effects for zone
spreading. The equipment is complex and, compared to a chromatographic column, must
be fairly expensive. Although the equipment can be pressurized, even small versions were
limited to 90 psi[207] which limits particle sizes to fairly large diameters. Size-exclusion and
ion-exchange chromatography separations were done. The equipment was also used for
gradient elution chromatography. Typical results are shown in Figure 8-5.[207] In all cases,
excellent separation could be obtained by decreasing the feed rate. Higher capacities were
obtained in a device with a small inner radius (5.1-cm diameter) and an annulus width of
up to 11.43 cm.[115] This arrangement has a cross-sectional area for flow greater than 96%
of an empty column. Angular dispersion was found to be negligible.[117] A 2D staged model[886]
and a more detailed model based on a 1D chromatographic model for nonlinear isotherms
and using the analogy between 1 and 2D systems were used to analyze the system.[117] The
nonlinear model gave reasonable fits to the data when dispersion terms were included.

A variety of other geometries have been used for continuous 2D chromatographs. Rotating
annulus systems with radial flow[476,747] have been used. Either the annulus can rotate, or the
feed and product ports can rotate. Rotating the annulus appeared to be preferable. The 1D
systems analogous to this system are the annular column used for solvent recovery with
activated carbon (Chapter 3, Section III.C.2) and the chromatofuge discussed in Section III.
The theory developed in Section III can easily be tranformed by Equation 8-2 to the radial
flow rotating annulus system.
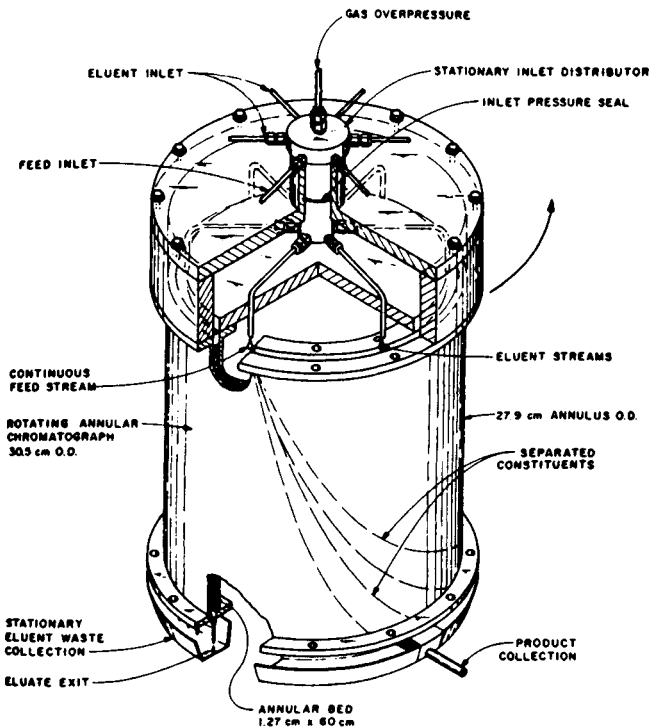
FIGURE 8-4.   Pressurized, continuous annular chromatograph. (From Canon, R. M., Begovich, J. M., and Sisson, W. G., *Sep. Sci. Technol.*, 15, 655, 1980. With permission.)
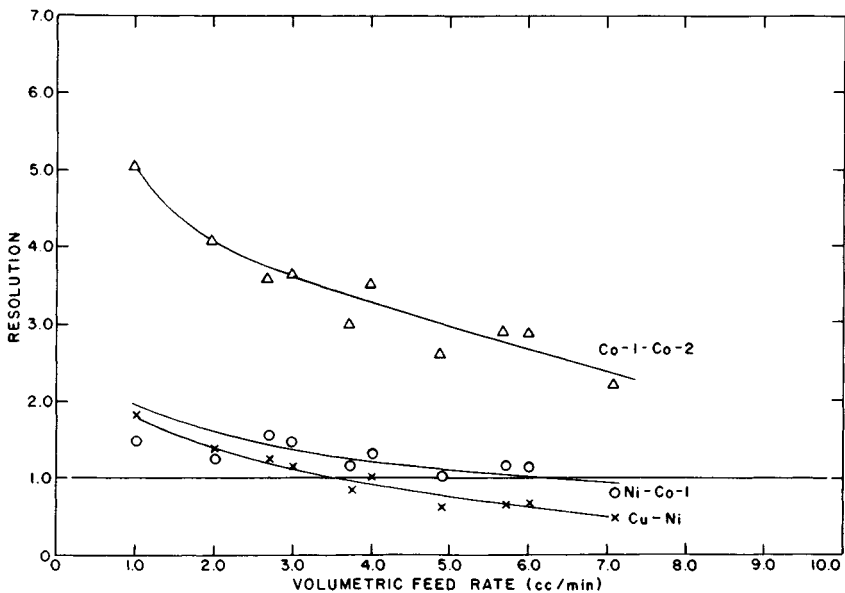
FIGURE 8-5.   Resolution vs. volumetric feed rate for separation of copper, nickel, and cobalt complexes in $(NH_4)_2\ CO_3$ on Dowex 50W-X8 (50 to 60 μm size) on rotating annulus chromatograph shown in Figure 8-4. (From Canon, R. M., Begovich, J. M., and Sisson, W. G., *Sep. Sci. Technol.*, 15, 655, 1980. With permission.)
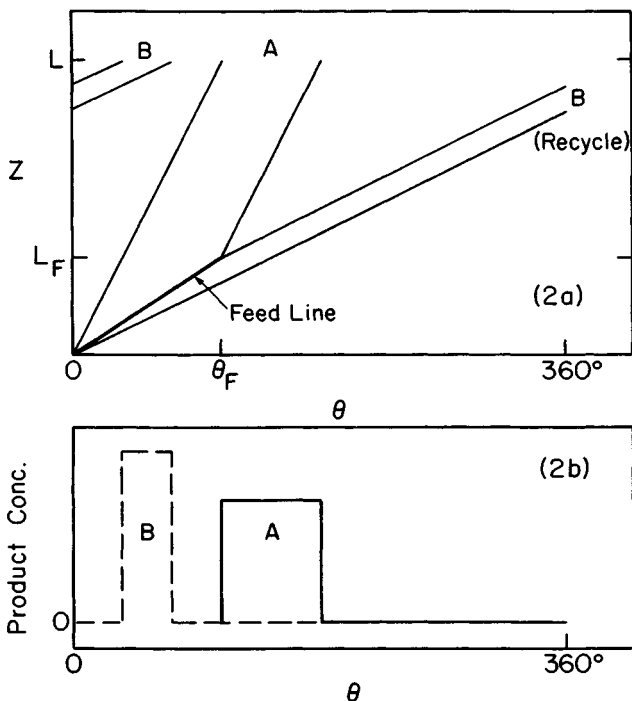
FIGURE 8-6. Slanted feed line system for 2D rotating annulus system. (From Wankat, P. C., *Sep. Sci.*, 12, 553, 1977. With permission.)

Sussman and co-workers[718,948-950] developed a "continuous surface chromatograph" using a rotating flat-plate geometry. The two flat plates are coated with stationary phase and are separated by 0.003 to 0.005 in. Slow rotation of the plates gives a 2D separation, which is similar to the radial flow systems, except this system acts as a gas capillary column. Although preparative in a laboratory sense, the flow rates are too low to consider this a large-scale device.

Rotation is not necessary to obtain 2D flow. Horizontal gas flow and downward liquid flow can be obtained in a rectangular box packed with adsorbent.[994] By injecting feed into one corner, a continuous 2D gas-liquid chromatography (GLC) system resulted. A similar idea was used to develop a continuous 2D thin-layer chromatography system with flow of two solvents fed from different sides of a triangular glass plate.[995] Apparently, neither of these ideas was followed up. A 2D thin layer chromatography column with sequential, instead of simultaneous development, is being studied for analytical separations.[461,462]

The moving feed system discussed in Chapter 7, Section III can be extended* to 2D systems.[1047] The result is the slanted feed line system shown in Figure 8-6[1047] for a rotating annulus system. The separation between two components is optimal when the slope of the feed injection line, S_{Feed}, lies between the slope of the two components.

$$S_A > S_{Feed} > S_B \qquad (8\text{-}8)$$

This is the case in Figure 8-6. The slanted feed line will theoretically increase the feed throughput. Column switching methods (Chapter 7, Section II) and the moving port system (Chapter 7, Section IV) can also be adapted to steady-state 2D operation; however, reduction

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* Actually, the 2D slanted feed system was thought of first, and the moving feed system was then developed from this by analogy.

practice may be difficult in the moving annulus system. Slanted feed and withdrawal lines can also be applied to other 2D geometries and to other 2D separations such as 2D electrophoresis and 2D magnetic methods.[1055] Under certain circumstances, a 2D system with slanted feed and withdrawal lines will become analogous to a continuous countercurrent cascade.[1050]

Also 2D chromatographs have also been developed using a cross-flow, magnetically stabilized, fluidized bed.[908a,908b] The technology is very similar to that used for magnetically stabilized countercurrent moving beds (see Chapter 6, Section II.A.3). Separations of carbon dioxide from helium and of light hydrocarbons were obtained. Exxon appears to be putting significantly more effort into commercializing the countercurrent system than this cross-flow system.

C. Regenerated Two-Dimensional Separators

The 2D chromatographs have a low feed throughput compared to the size of system, the amount of solvent, and the amount of adsorbent used. The throughput can be increased by using a more efficient regeneration scheme and feeding to a larger fraction of the annulus. One way of doing this for single solute systems is shown in Figure 8-7.[165,616] This system for solvent recovery by activated carbon adsorption and steam desorption is in commercial use. The process is similar, but since radial flow is used, not exactly analogous to the solvent recovery systems discussed in Chapter 3, Section III.C. The solvent laden air flows radially inward while the steam flows outward. The rotation of the bed carries the saturated carbon to the desorption region. Since a separate cooling portion is not used, this device would not be applicable if hot carbon is a catalyst for the solvent. A cooling portion could be added, but the equipment would be more complex. In the region where the feed gas is cooling the carbon, less solute is adsorbed. If cooling is fairly rapid, this will have little effect on the total amount of solute adsorbed. The theoretical methods used in Chapter 2 can be adapted to this system by including the effect of changing velocity due to the annular flow.

A similar commercial design uses a packed disc or cylinder which rotates like a wheel.[211,571] As shown in Figure 8-8, inlet gas flows through most of the wheel, while the hot desorbing gas flows countercurrently through the remainder. These devices are used for removing impurities from air,[571] for dehumidifying air,[211] and for solvent concentration.[724] Essentially the same apparatus called the "thermal wheel" is commonly used for recovery of waste heat.[54,212] This equipment is simple and easy to operate automatically. Since heat exchange and dehumidification are easily combined,[211] this type of apparatus is convenient for exchanging air in buildings. The solute movement theory is easily applied to this system and is shown later (Figure 8-9B).

A design for removal of NO_x from hot flue gases using an axial flow rotating annulus system with countercurrent flow of the hot regeneration gas has been proposed.[415] A separate region for cooling the annulus was included. Unfortunately, no experimental or theoretical work was reported.

Rotating bed systems for ion exchange have been developed.[263,494] One system was similar to Figure 8-7, except the steaming section is replaced by a wash section, a regeneration section, and another wash section, to remove the regeneration liquor.[494] The other systems[263] use the geometry shown in Figure 8-1 with successive additions of feed, regenerant, and rinse water. Both rotating tubes and rotating feed pipes have been used.[263] None of these methods appear to have been commercialized.

A renegerated rotating annulus system for single and multiple solute systems can be modeled using solute movement theory. The axial flow rotating annulus geometry, shown in Figure 8-1, is used, except feed enters the entire annulus, or the rotating wheel system shown in Figure 8-8 is used. Changes in temperature are used to regenerate the system. In the traveling wave mode of operation, the feed temperature varies in the θ-direction. The
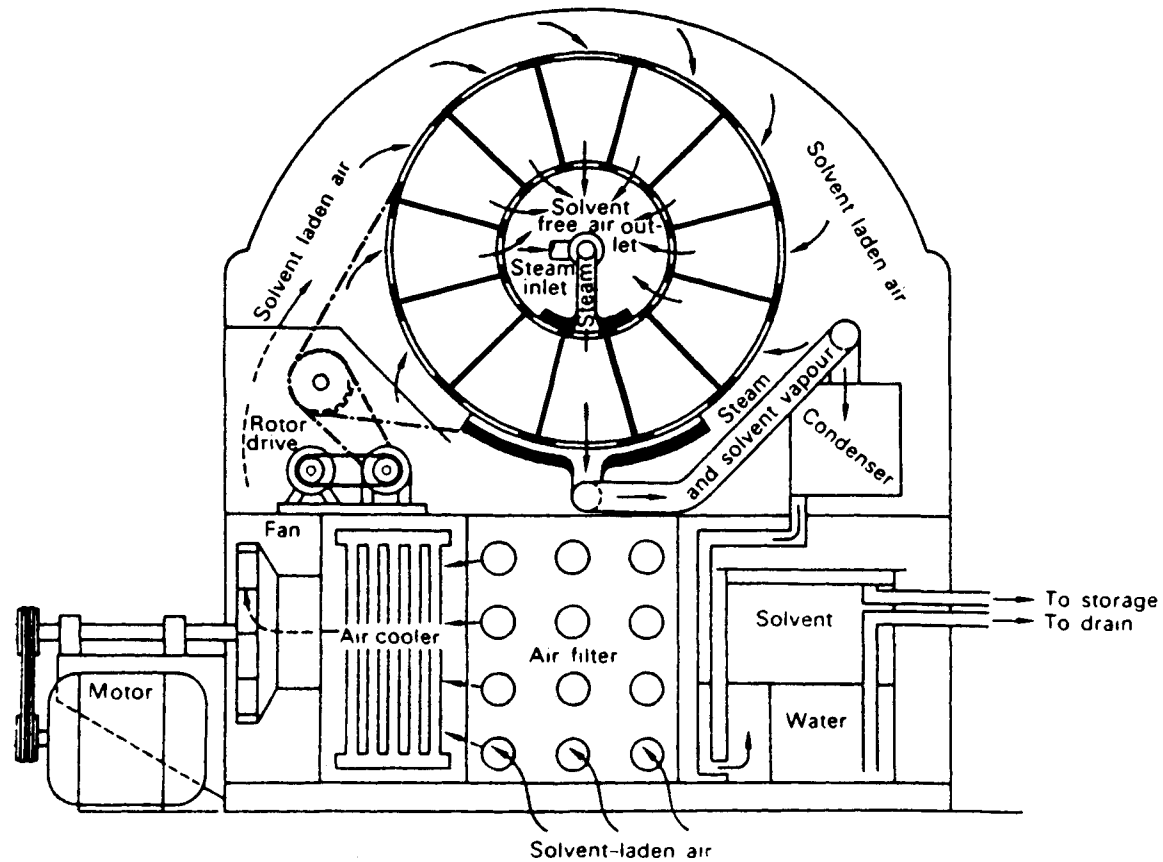
FIGURE 8-7. Rotary bed activated carbon adsorber for solvent recovery. (From Richardson, J. F. and Peacock, D. G., Ed., *Chemical Engineering*, Vol. 3, 2nd ed., Pergamon Press, 1979. With permission.)
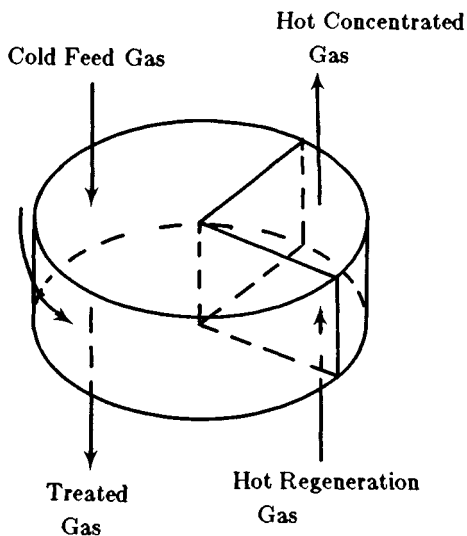
FIGURE 8-8.   Rotating wheel system for thermal regeneration.
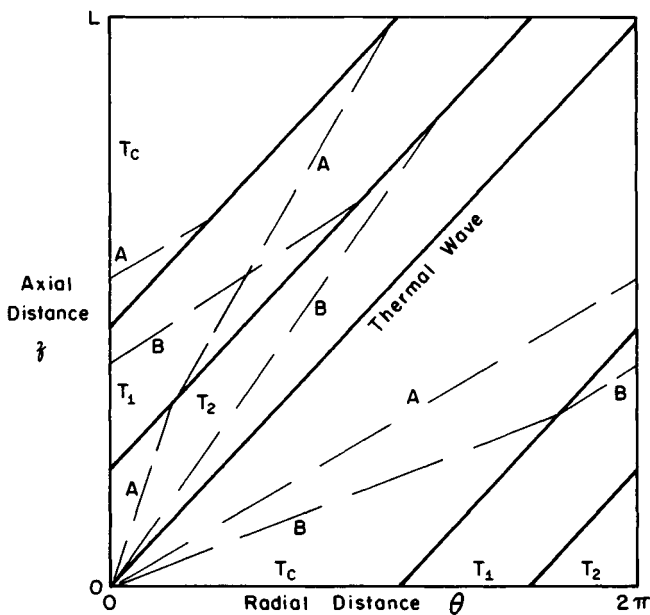
A

FIGURE 8-9.   Solute movement theory solution for regenerated 2D adsorber. (A) Co-current flow system for multicomponent separation. Linear isotherms. (B) countercurrent flow regeneration for rotating wheel system. Nonlinear isotherm. Single solute. (From *Ind. Eng. Chem. Fundam.*, 15, 309, 1976. With permission.)

energy balance, Equation 8-4, can be solved directly or by analogy with the 1D system. If we make the local equilibrium assumptions (see Table 2-1), then the thermal wave travels at a slope of

$$S_{th} = \frac{v}{\omega} \left\{ \frac{\rho_f \, C_{P_f}}{\left[1 + \frac{1-\alpha}{\alpha} \epsilon \right] \rho_f \, C_{P_f} + \frac{(1-\alpha)(1-\epsilon)}{\alpha} C_{P_s} \, \rho_s + \frac{W}{\alpha \, A_c} C_{P_w}} \right\} \qquad (8\text{-}9)$$
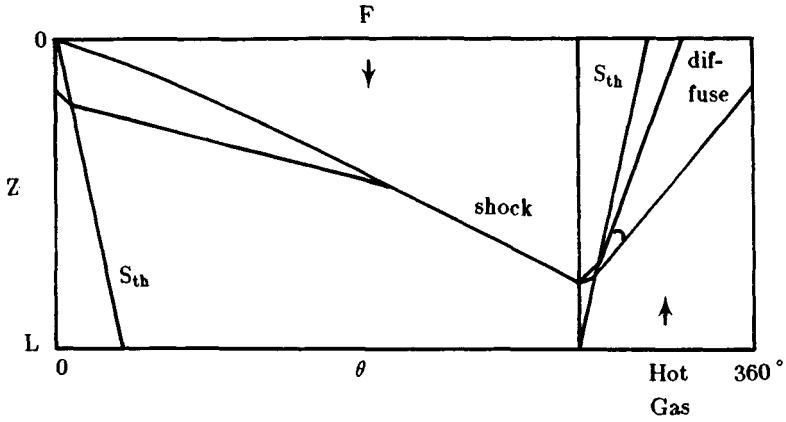
FIGURE 8-9B

which is analogous to Equation 2-41. If the thermal wave slope is in between the slopes of the solute at two different temperatures, focusing occurs (see Chapter 4, Section IV. B and C), and the solute will concentrate at this temperature boundary.

Figure 8-9A[1059] is drawn for the case with linear isotherms where

$$S_A(T_c) < S_{th} < S_A(T_1) < S_A(T_2) \qquad (8\text{-}10a)$$

$$S_B(T_c) < S_B(T_1) < S_{th} < S_B(T_2) \qquad (8\text{-}10b)$$

The feed to the rotating system is at temperature T_c from $\theta = 0$ to $\theta = \theta_1$, at T_1 from θ_1 to θ_2, and at T_2 from θ_2 to 2π. This temperature change propagates through the bed as illustrated in Figure 8-9A. Note that solute A concentrates at the $T_c - T_1$ boundary, while solute B concentrates at the $T_1 - T_2$ boundary. Extension to more solutes is obvious. This co-current flow 2D system is analogous to cycling zone adsorption with focusing. In Chapter 4, Section IV, we explored the analogous situation and noted that with linear isotherms, the local equilibrium theory predicts infinite concentrations at the temperature boundary. If nonlinear isotherms are used, this physically impossible situation does not occur (see Figure 4-20C). Staged models[1059] also do not predict infinite concentrations.

This regenerated 2D adsorber can also be operated in the direct mode by rotating the annulus past external heaters. If these heaters are set at a given slope, the local equilibrium solution looks exactly the same as Figure 8-9A, except the slope of the thermal waves is now arbitrary. This is an advantage, since the natural thermal wave velocity may be too fast or too slow to satisfy Equations 8-10. The direct mode will be more complex and use more energy than the traveling wave mode. A radial flow geometry could also be used.

The solute movement analysis is also easily applied to the rotating wheel system shown in Figure 8-8. Equations 8-6 or 8-7 and 8-9 are valid for both feed and regeneration, except the flow is in the opposite direction during regeneration. This result is shown in Figure 8-9B for removal of a single adsorbate with nonlinear isotherms. With counterflow regeneration, complete regeneration is not required. Note that Figure 8-9B is very similar to Figure 4-15C which was constructed for a recuperative-mode parametric pump. The only difference is θ in Figure 8-9B replaces time in Figure 4-15C.

A variety of other 2D systems which are analogs of the 1D systems studied in Chapters 3 to 7 can be brainstormed.[1046,1047,1050,1055] These include 2D analogs to parametric pump-

ing,[1046] layered chromatography with cross-flow elution,[1046] pressure-swing adsorption,[1046] moving feed chromatography,[1047] and continuous countercurrent separation.[1050] The processes have also been extended to three dimensions.[1037,1050] All of these extensions were done theoretically without experimental backup.

An alternate regenerated 2D system without solid body rotation has been suggested.[1000] A flat rectangular box packed with adsorbent is used. Solvent at temperature T_1 flows for period t_1 in the x direction and and is followed by flow of solvent 2 at temperature T_2 for period t_2 in the y direction. This cycle is then repeated. The solutes will follow different paths which can be predicted from the solute movement theory. Throughput will be low, since feed is input at only one point. No experimental results were presented.[1000]

D. The Future of Two-Dimensional Adsorption and Chromatography

Presently, 2D adsorbers are used commercially for solvent recovery and for removing impurities from air. They will continue to be used in these specialized markets. The situation is somewhat different for the other 2D designs. There is no doubt that they can be made to work and will give sharp separations. However, when compared to 1D columns, the 2D systems are more complex. The throughput rate and the adsorbent productivity can be increased by decreasing the particle diameter or by using a regenerated system, but these methods will also work for 1D systems. The major advantage of 2D systems, steady-state, was originally considered to be very important. However, with recent advances in instrumentation and computer control, batch or cyclic operation is now less of a disadvantage. In my opinion, the steady-state advantage of 2D systems is now a marginal advantage to make 2D systems preferable when compared to the simpler column systems.

If the adsorbent is not the most expensive part of the system, and the most expensive part of the system can be used continuously, 2D adsorbers and chromatographs are likely to have a significant economic advantage. This is analogous to 2D applications in magnetic separations[139,412,1055] where the rotating matrix is cheap, but the stationary magnet is quite expensive. For example, if microwave heating is used for desorption, a 2D system may have an advantage. The microwave oven could be used continuously while the adsorbent was rotated through the oven. As a second example, if the adsorbent must be regenerated in a separate oven, or if the adsorption is irreversible, then 2D (or other moving bed systems) may have an advantage. Finally, 2D systems may have an advantage when using electrosorption or combining chromatography and electrophoresis, since elution is easier.

A detailed comparison of optimized chromatographic systems would be a welcome addition to separation literature. Such a comparison should include equipment and operating costs for the same separation problem. Unfortunately, economic evaluations are not readily available.

III. CENTRIFUGAL CHROMATOGRAPHY AND ADSORPTION — THE CHROMATOFUGE

An alternative to using a column for chromatography or adsorption is to use a centrifuge. This method was developed by Hopf[515] in 1947, who suggested the name chromatofuge. A sprinkling of other investigators have explored the use of the chromatofuge since then.[132,307,353,373,480,481,634,735,743,744] Despite the sparse research activity, the chromatofuge appears to have some advantages for large-scale chromatography.

The basic design shown in Figure 8-10 has varied little since Hopf's original work.[515] The basket of a centifuge is lined with filter paper, felt, or cloth and then packed with sorbent. A second layer of paper or cloth is placed over the inner surface. In operation, feed and solvent are introduced through the central perforated pipe while the basket spins. The velocity of the liquid depends on the rotational speed, not the feed rate, as long as the basket does not flood. The eluted liquid is collected and drained from the bowl. The bowl should

Feed

Feed Basket

Packing Support

Products
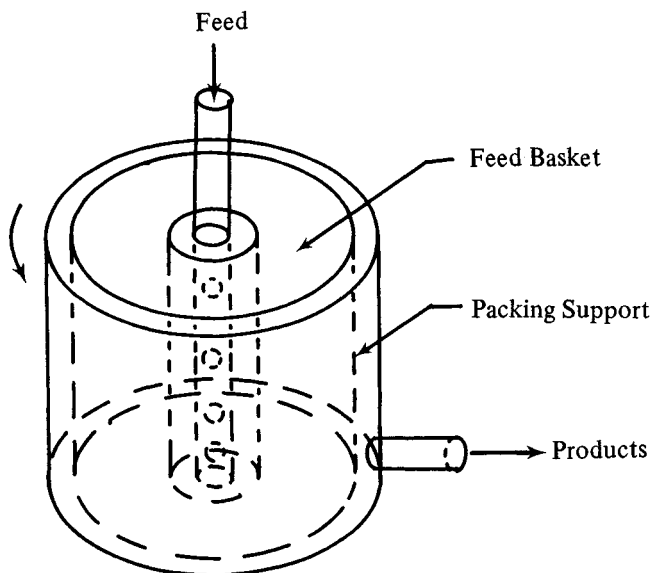
FIGURE 8-10. The chromatofuge.

be designed to drain rapidly and minimize holdup. Hopf's[515] original laboratory apparatus had a 30-cm radius basket and the basket was 10 cm high. His plant-scale system was converted from an existing centrifuge. It had a 125-cm radius basket which was 80 cm high. This is a fairly large-scale system. Large-scale separation of oleic acid from rinolecic acid, alcohol-ketone separation, and purification of crude castor oil were reported.[515]

The chromatofuge is a very flexible system. It is easy to pack. Slurry is poured in while the basket is spinning and then the speed is increased. The column essentially packs itself. If the packing needs to be changed, the top lid can be unbolted and the basket emptied. The chromatofuge has been used with adsorption chromatography, ion exchange chromatography, and size-exclusion chromatography. It has also been applied to liquid adsorption. Gradient elution is easy to use. Dirty feeds which contaminate the first few centimeters of the bed have been used.[515] This packing can be removed and replaced. The chromatofuge is useful for viscous solutions.[307,353,481,743,744] A small-scale analytical system, which is rotating disk, is commercially available,[634] and centrifugal paper chromatography is also used to accelerate the flow of mobile phase.[132] The chromatofuge was also used as a reactor.[515]

Two different operating techniques have been used. In the first, the feed is added to the wet spinning adsorbent. The solutes can then be eluted with the same solvent the feed was dissolved in, or a stronger desorbent can be used. Solvent gradients are easy to use. The sorbent is then reconditioned and the next feed pulse is added. This method is thus analogous to normal chromatographic or adsorption processes.

The second technique was developed for desalting viscous solutions by size exclusion.[306,307,353,481,743,744] In this technique, much of the water is spun out of the gel by rotating at high speed. The centrifuge is slowed down and sample is added at low speed. About 5 to 10 min are allowed for equilibrium within the gel. The centrifuge is then spun at high speed for 10 to 15 min to spin out the high molecular weight products which are excluded. The centrifuge is slowed down and the low molecular weight compounds are washed out with one to two column volumes of water. Fairly long cycle times are required to allow the large molecules time to diffuse into the gel. The salt removal step then takes advantage of the much more rapid diffusion of the small molecules. A chromatogram for separation of proteins and lactose in skim milk was shown by Morr et al.[744] This technique was used
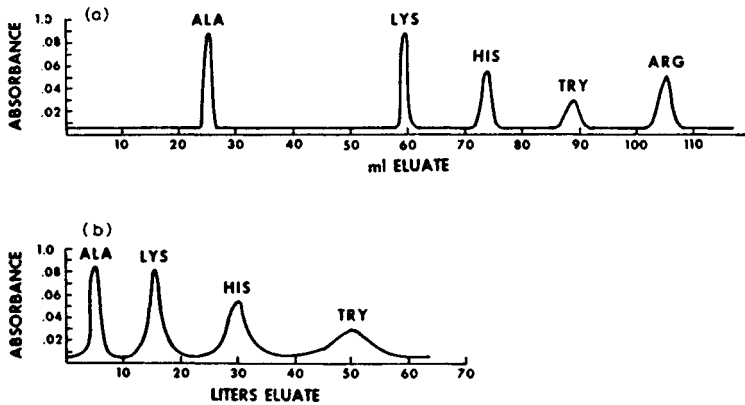
FIGURE 8-11.   Separation of amino acids. (A) Analytical column; (B) chromatofuge. Key: ALA = alanine, LYS = lysine, HIS = histidine, TRY = tryptophan, and ARG = arginine. (From Finley, J. W., Krochta, J. M., and Heftmann, E., *J. Chromatog.*, 157, 435, 1978. With permission.)

commercially for a period for desalting and for separation of protein from lactose in whey in a Stauffer Chemical Co. plant in Rochester, Minn., with a rated capacity of 453,000 kg/day of raw whey.[306,307]

Unfortunately, most of the researchers do not present chromatograms, but give recoveries and purities. The order of elution is always the same as in columns. One reported chromatogram for amino acid separation is shown in Figure 8-11.[373] A 4-in high by 11-in diameter basket centrifuge was packed with Dowex 50 W-X8 resin finer than 400 mesh. Operation was at 1000 rpm (~200 g) and elution was at 1 ℓ/min. Figure 8-11A shows the results from an analytical ion exchange column fed with 50 μg of each amino acid. Then the arginine was removed from the sample for the chromatofuge and 5 g of each amino acid were fed to a chromatofuge. The separation shown in Figure 8-11B for the chromatofuge was excellent and larger samples could probably be added, although nonlinear effects would probably become important. Note that the amino acids exit in the same order in Figures 8-11A and B.

Basket centrifuges have also been used for ion exchange.[292,298,876] One separation was for removal of low concentrations of radioactive caesium and strontium from waste water unto vermiculite.[292] The vermiculite was discarded once it was saturated, but the technique could be used where the sorbent is regenerated. Vermiculite is cheap and has a high capacity for cesium and strontium, but it has poor flow properties which makes its use in columns difficult. In the basket centrifuge, smaller particles could be used while operating at higher flow rates. The result was a much later breakthrough for the centrifuge (compared in terms of bed volumes of water treated). The removal was greater than 96% until 750 bed volumes had been passed. In addition to producing a higher average loading on the vermiculite, the centifuge was easier to unload and if the bed was partially blinded with suspended solids, its flow capacity could be restored by plowing off a thin layer of packing.

Basket centrifuges are commonly used for preliminary adsorption or ion exchange purification of proteins.[298,876] An on-off procedure is used. After sorption, the packing is washed with a suitable buffer solution. Then the proteins are eluted by changing pH and/or ionic strength. This is usually done in the centrifuge, but the sorbent can be packed in a column and then be eluted. The centrifuge has the advantages of very high flow rate and the capability of handling feeds with some suspended solids. Ion exchange celluloses are often employed since they have large pores, and their poor flow properties are not a problem in centrifuges.

Basket centrifuges have also been used for combined adsorption/filtration using a bed of carbon with a thin layer of vermiculite to serve as a filter.[292] This was used for treating an aqueous waste stream containing oil, detergent, and suspended solids to produce clean water in one pass. When the flow rate decreased, a thin layer of vermiculite was plowed off and a new layer was quickly added. This short period without feed could increase the adsorption capacity of the carbon, since it allows time for slowly diffusing molecules to diffuse into the micropores of the carbon. The entire device could be automated. This centrifugal technique appears to be an excellent candidate for a mobile unit for treating waste water.

None of the researchers presented a theory. However, the solute movement theory developed in Chapter 2 is easily adapted to normal elution operation of the chromatofuge. Since the cross sectional area for flow increases, the velocity will decrease. If a liquid continuum exists in the packed region (when the spinning is very rapid this may not be true) the continuity equation becomes

$$\rho_f \, v \, A_c = \text{constant}$$

Since the cross-sectional area for flow is $A_c = 2 \, \pi \, r \, h$ where h is the height of the packing,

$$v = \frac{\text{constant}}{r} \tag{8-11a}$$

where we have assumed that fluid density is constant. The constant in Equation (8-11a) must be $r_0 v_0$, the radius and velocity at the inner surface of the drum. Thus,

$$v = \frac{r_0 \, v_0}{r} \tag{8-11b}$$

The fraction of solute in the mobile phase can be derived by the same steps used to develop Equations 2-26a to 2-26c. Then the solute velocity is

$$u_{s_i} = \frac{v_0 \, r_0/r}{1 + \dfrac{1 - \alpha}{\alpha} \, \epsilon \, K_{d_i} + \dfrac{1 - \alpha}{\alpha} \, (1 - \epsilon) \, \rho_s \, \dfrac{\Delta q_i}{\Delta c_i}} \tag{8-12}$$

Since the solute moves at a velocity of

$$\frac{dr}{dt} = u_{s_i} \tag{8-13}$$

we can insert Equation 8-12 into 8-13 and integrate from r_0 to r and $t = t_0$ to t. The result is

$$t - t_0 = \frac{r^2}{2a} - \frac{r_0^2}{2a} \tag{8-14}$$

where the constant a is

$$a = \frac{v_0 \, r_0}{1 + \dfrac{1 - \alpha}{\alpha} \, \epsilon K_{d_i} + \dfrac{1 - \alpha}{\alpha} \, (1 - \epsilon) \, \rho_s \, \dfrac{\Delta q_i}{\Delta c_i}} \tag{8-15}$$

Equation 8-14 is plotted in Figure 8-12 on a graph of r vs. t for a pulse input for a system
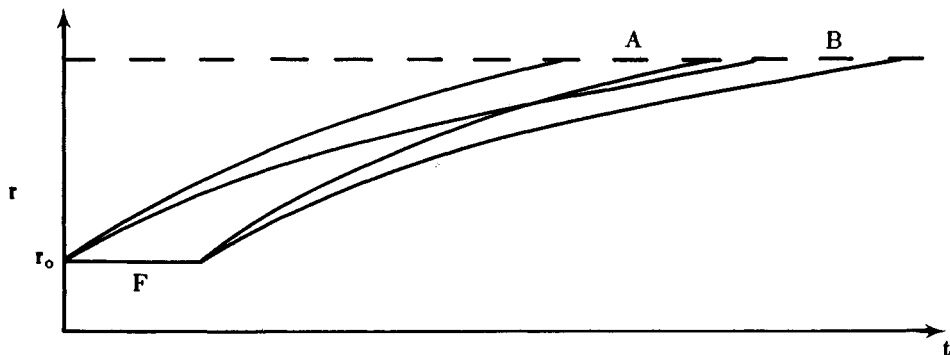
FIGURE 8-12.   Solute movement theory for chromatofuge with linear isotherms.

with linear isotherms. Movement of both solutes slows down as they move radially outward. The extension to nonlinear isotherms is straightforward. The above theory can easily be transformed by Equation 8-2 to the 2D radial flow systems.[476,747]

Centrifugal systems have recently been shown to drastically decrease the size of continuous distillation columns[823] since throughputs and mass transfer rates can be drastically increased. The chromatofuge is unlikely to have such a drastic impact, but it should still be a useful separation device. Since small-diameter rigid packings can be used, the zone spreading effects can be quite small and N quite large (see Chapter 3, Sections II.D and III.C). Then, good resolution of difficult (low selectivity) separations can be obtained, despite the relatively short distance of travel. Since the chromatofuge is easy to pack and unpack, it should be useful where many different separation problems are done on a batch basis. The chromatofuge would also be useful when equipment size must be kept small (e.g., on barge-mounted plants or off-shore). The equipment is not complex and could be easily automated. Also, the chromatofuge works well with viscous solutions which can cause fingering in columns. Another possible application is for liquid adsorption systems where the column is drained before regeneration (see Chapter 3, Sections IV.A and V.B). The centrifugal action would aid drainage. The chromatofuge could also be operated as a cycling zone adsorber (see Chapter 4, Section IV). On the negative side, the chromatofuge is a rotating apparatus and the original equipment and maintenance costs may be high. Since a manufacturer of large-scale equipment is not currently available, the chromatofuge would have to be a do-it-yourself project. However, off-the-shelf equipment or existing surplus equipment could easily be adapted. In my opinion, the chromatofuge has a place as a large-scale chromatography and adsorption system.

APPENDIX A

NOMENCLATURE

a, b	Langmuir equilibrium constants (see Equation 2-14)
a_{io}, B_{io}, β_i, a_{ij}, b_{ij}	Constants in combined Langmuir-Freundlich Equation 2-16)
a_p	Surface area of particles/unit volume
a_I, a_{II}	Interfacial area/volume between phases V and W, and W and L
A_1, A_2, A_{1i}, A_{2i}	Equilibrium constants (see Equation 2-12)
A_c	Cross-sectional area of column
A_w	Area of wall for heat transfer
A, B	Van Deemter equation constants (see Equations 2-117 to 2-119)
b_1, b_2, b_3	Constants in linear equilibrium (see Equations 6-10 and 6-28)
c	Concentration (mol/ℓ)
c	Total equivalents per liter of ions in liquid (see Equations 2-20, 2-21, and 2-23)
c_a, c_b	Concentrations after and before shock
c_{conc}, c_{dilute}	Concentrations in CZA (see Equation 4-11)
c_h	High concentration (see Figure 2-6)
c_i^*	Concentration inside pores
c_i, c_{init}	Initial concentration
c_{imax}	Maximum concentration in pulse
c_l	Low concentration (see Figure 2-6)
c_{RA}, c_{Ri}	Concentration of ion A on resin (see Equations 2-20 and 2-21)
c_S, c_{SM}, c_M	Constants in expansion of Van Deemter Equations 2-121 to 2-124
C, C_M, C_{SM}, C_S	Van Deemter equation constants (see Equations 2-117 to 2-119)
C_{PB}	Bulk heat capacity of solid ($+$ pore fluid) (see Equation 2-77)
C_{P_f}, C_{P_s}, C_{P_w}	Heat capacities of fluid, solid, and wall, respectively
C_{Rtotal}	Total resin capacity (see Equations 2-20, 2-21, and 2-23)
d_f	Film thickness
d_p	Particle diameter
D_M	Molecular diffusivity
D_T	Total effective axial diffusivity (see Equation 2-112)
D_T	Thermal diffusivity
D_θ	Diffusivity in θ direction
$D_{\theta T}$	Thermal diffusivity in θ direction
$erf(u)$	Error function (Equation 2-102)
E_D	Eddy diffusivity
F_i	Pulse of moles of feed (see Equations 2-84 and 2-86)
$f_{(p)}$	Function in Equation 4-14
g	Acceleration due to gravity
G	Mass velocity of gas
ΔG	Free energy change of reaction
h	Height in column
h_p	Heat transfer coefficient for particle (see Equations 2-69 and 8-5)
h_w	Heat transfer coefficient for walls (see Equation 2-68)
H, HETP	Height equivalent to theoretical place (see Equation 2-19)
ΔH	Heat of adsorption
$\Delta H'_{ads}$	Heat of adsorption as function of q'
HTU_{VW}, HTU_{LW}	Height of a transfer unit (see Equation 6-23 and 6-24)

i	Subscript for solute
j	Subscript for stage number
k	Constant in LRC (Equation 2-11)
k_i	Linear equilibrium constant (Equation 2-29)
k_{inert}	Linear equilibrium constant for inerts (Equation 4-3)
k_i'	$k_i V_s / V_m$ relative retention (Equation 2-127)
$\bar{k}_i'$	Average relative retention of two solutes
k_m	Mass transfer resistance in mobile film (Equation 2-120)
k_s	Mass transfer resistance in solid (Equation 2-120)
k_1, k_2	Rate constants (Equation 2-110)
k_A	First order rate constant (Equation 3-11)
$k_{A_i}, k_{A_p}, k_{B_d}, k_{B_p}$	Proportionality constants (Equation 5-5)
k_T	Mass transfer coefficient (Equation 2-67)
K	Constant in BET (Equation 2-8)
K	Permeability (Equations 3-1 to 3-3)
K_A, K_i	Langmuir equilibrium constant (Equations 2-4, 2-7, and 2-13)
K_{AB}, K_{DB}	Equilibrium constants for ion exchange (Equations 2-20, 2-22, and 2-23)
K_d	Fraction of pores available to molecule (Equation 2-3)
K_o	Constant in Arrhenius relationship (Equation 2-5)
K_{LW}, K_{VW}	Mass transfer coefficients (Equations 6-20 and 6-21)
K_1, K_2, K_3	Linear equilibrium constants (Equations 6-10 and 6-28)
l_{port}	Distance between switching ports in SMB
L	Column length
L	Solid flow rate (kilogram of dry adsorbent per hour [Section II.A in chapter 6])
L_{MTZ}	Mass transfer zone length
LUB	Length of unused bed
m	Mass of adsorbent (Equations 2-17, 2-19, 2-132, and 3-11)
m	Constant in LRC (Equation 2-11)
m	Number of zones in CZA (Equation 4-11)
M_s	Mass stationary phase/plate (Equation 2-82)
M_1, M_0	Molecular weights of adsorbed and nonabsorbed species (Equations 4-13 and 4-14)
n	Equilibrium constant (Equation 2-12)
n	Number of components (Equations 2-7 and 2-62)
n	Freundlich equilibrium constant (Equation 2-15)
n	Number of cycles
n_{feed}, n_{purge}	Moles of feed and purge gas, PSA (Equation 4-5)
n_o	Original total number of moles (Equation 2-17)
n_1^s, n_2^s	Number of moles adsorbed (Equation 2-17)
$(n_i^s)_m$	Number of moles for monolayer coverage (Equation 3-18)
N	Number of equilibrium stages in plate models
N	Loading on zeolite (Equation 2-11)
N_o	Maximum loading on zeolite (Equation 2-11)
NTU_{VW}, NTU_{LW}	Number of transfer units (Equations 6-23 and 6-24)
p	Pressure
p_{after}, p_{before}	Pressure after or before pressure change in PSA
$\bar{p}$	Partial pressure of solute
$\bar{p}_v$	Partial pressure of solute during vacuum regeneration

p°	Vapor pressure of pure component
p_H, p_L	High and low pressures
Pe_z	$Lv/(D_M + E_D)$, Peclet number
PSA	Pressure swing adsorption
q, q_i	Amount adsorbed (moles per kilogram)
q_a, q_b	Amount adsorbed after and before shock
$\bar{q}$	Total adsorption (Equations 2-50 to 2-52)
q_i°	Amount adsorbed from pure gas (Equation 2-9)
q_i'	Amount adsorbed and in stagnant fluid for single porosity model (Equations 2-73 to 2-81)
q_{max}	Maximum monolayer coverage (Langmuir Equation 2-6)
q_{mono}	Monolayer coverage (Equation 2-8)
q_{sat}	Bed capacity in equilibrium with feed
Q	Volumetric flow rate of gas (Equation 3-11)
r	Radial coordinate
r_o	Inner radius
R	Gas constant
R	Resolution (Equation 2-125)
R, R_T, R_B	Reflux ratios in parametric pump, R_T is at top and R_B is at bottom of column (Equation 4-10)
Re	Reynolds number, $vd_p\rho_f/\mu$
R_T	Cross-over ratio (Equation, 2-65)
Sc	Schmidt number, $\mu/D_M\rho$
Sh_m	Sherwood number for mass transfer, $k_L d_p/D_M$
S_i	Slope of solute i in two-dimensional system (Equations 8-6 and 8-7)
S_{th}	Slope of thermal wave in 2D system (Equation 8-9)
t_{band}	Period band exits in displacement development (Equation 2-64)
t_{cycle}	Period of cycle (Equation 5-3)
t_F	Period feed is introduced (Equations 2-64 and 5-3)
t_{MTZ}	Time mass transfer zone takes to exit column
t_{port}	Time between switching ports in SMB
t_{Ri}	Retention time (Equation 2-94)
T	Temperature
T^*	Temperature of stagnant fluid
T_{amb}	Ambient temperature
T_c, T_h	Cold and hot temperatures
T_f, T_s, T_w, T_{ref}	Temperatures of fluid, solid, wall, and reference
u_{Acc}, u_{Bcc}	Solute velocity in countercurrent system (Equation 6-2)
u_{large}	Velocity of large molecules (Equation 5-7)
u_{port}	Average velocity of ports in SMB (Equation 6-34) and in moving feed chromatography
u_{small}	Velocity of small molecules (Equation 5-8)
u_s	Solute wave velocity
u_{sh}	Shock wave velocity
u_{Steam}	Velocity of steam wave
u_{th}	Thermal wave velocity
u_{wave}	Wave velocity when fluid velocity changes (Equations 2-55, 2-56, 2-57, and 2-59)
v	Interstitial fluid velocity
v_a, v_b	Velocity after and before wave
v_{in}	Inlet interstitial fluid velocity (Equations 2-53 and 2-54)

v_o	Velocity at inner radius of chromatofuge
$v_{solids,\ avg}$	Average solids velocity with intermittent flow (Equation 6-32)
v_{solid}	Solids velocity
v_{super}	Superficial fluid velocity
V	Volume carrier gas (Equation 2-82)
V	Upward flowing fluid flow rate (moles per hour [Section II. A, Chapter 6])
V	$\epsilon' v A_c t$, elution volume in Equations 2-101 to 2-108
$\overline{V}$	Volume solution to saturate column (Equations 2-101 to 2-108)
V_{col}	Volume empty column (Equation 2-1)
V_e	Elution volume (Equation 2-1)
V_{feed}	Volume of feed gas
V_{feed}, V_{purge}	Volumes of feed and purge gas at column conditions, PSA
V_i	Internal void volume (Equation 2-1)
V_o	External void volume (Equation 2-1)
V_M	Volume mobile phase/plate (Equation 2-82)
V_{purge}	Volume of purge gas
VSA	Vacuum swing adsorption
W	Weight column wall/length column
W	Flow rate fluid in pores (Chapter 6, Section II. A)
w_i	Dimensionless peak width (Equation 2-89)
w_p	Width of constant pattern (Equation 5-4)
w_d	Width of diffuse wave (Equation 5-4)
X	Deviation from peak maximum (Equation 2-96)
X(L, V)	Breakthrough solution (Equations 2-103 to 2-105)
Δx_1	Decrease in mole fraction in liquid (Equations 2-17 and 2-19)
x'	Weighted average mole fraction (Equations 6-9 and 6-26)
x_E, y_E	Mole fraction in equilibrium with bulk concentration, z
y_i, x_i	Mole fractions
y_{in}	Inlet mole fraction
y^*_{n+1}	Hypothetical concentration in Kremser equation (Equation 6-13)
y_{STM}	Mole fraction water in steam (Equations 3-9 and 3-10)
y_{w_b}	Mole fraction water in the bed before regeneration (Equations 3-9 and 3-10)
z	Mole fraction in phase W (fluid in pores)
z	Axial distance
z_{after}, z_{before}	Position of solute wave after and before pressure change in PSA

Greek

α	Interparticle porosity (Equation 2-1)
α_{12}	Separation factor (Equation 2-10)
α_{21}	$k'_2/k'_1 = k_2/k_1$ selectivity (Equation 2-128)
β	Term in Kremser equation (Equation 6-12)
β_A	Ratio inert to adsorbate held in column (Equation 4-3)
ϵ	Intraparticle porosity (Equation 2-1)
ϵ'	Single porosity (Equation 2-75)
γ	Labyrinth factor (Equation 2-115)
γ	Volumetric purge-to-feed ratio $= V_{purge}/V_{feed}$ in PSA
λ	Constant in expansion of D_T (Equation 2-116)
λ_w	Latent heat of water
ν_i	Dimensionless cumulative flow of mobile phase (Equation 2-85)

ρ_B	Bulk density including fluid in pores for single porosity equations (Equations 2-73 to 2-81)
$\bar{\rho}_f$	Molar density of fluid (Equations 2-50, 2-51, 2-52, and 2-53)
ρ_f	Fluid density
ρ_s	Structural solid density
$\sigma, \sigma_t, \sigma_l$	Standard deviation (Equations 2-90, 2-97, and 2-98)
τ	Deviation from center of constant pattern (Equation 2-133)
μ	Viscosity
θ	Angular coordinate
ω	Angular velocity

Other

$\mathcal{F}$	Term in Colburn equation (Equation 6-30)

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