CHAPTER 41
THERMODYNAMICS FUNDAMENTALS

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41.1 INTRODUCTION

Thermodynamics has historically grown out of man's determination—as Sadi Carnot put it—to capture "the motive power of fire." Relative to mechanical engineering, thermodynamics describes the relationship between mechanical work and other forms of energy. There are two facets of contemporary thermodynamics that must be stressed in a review such as this. The first is the equivalence of *work* and *heat* as two possible forms of energy exchange. This facet is encapsulated in the first law of thermodynamics. The second aspect is the irreversibility of all processes (changes) that occur in nature. As summarized by the second law of thermodynamics, irreversibility or entropy generation is what prevents us from extracting the most possible work from various sources; it is also what prevents us from doing the most with the work that is already at our disposal. The objective of this chapter is to review the first and second laws of thermodynamics and their implications in mechanical engineering, particularly with respect to such issues as energy conversion and conservation. The analytical aspects (the formulas) of engineering thermodynamics are reviewed primarily in terms of the behavior of a pure substance, as would be the case of the working fluid in a heat engine or in a refrigeration machine. In the next chapter we review in greater detail the newer field of entropy generation minimization (thermodynamic optimization).

SYMBOLS AND UNITS

c	specific heat of incompressible substance, J/(kg · K)
c_P	specific heat at constant pressure, J/(kg · K)
c_T	constant temperature coefficient, m^3/kg
c_v	specific heat at constant volume, J/(kg · K)
COP	coefficient of performance
E	energy, J
f	specific Helmholtz free energy ($u - Ts$), J/kg
$\overline{F}$	force vector, N

Mechanical Engineers' Handbook, 2nd ed., Edited by Myer Kutz.
ISBN 0-471-13007-9

g	gravitational acceleration, m/sec^2
g	specific Gibbs free energy $(h - Ts)$, J/kg
h	specific enthalpy $(u + Pv)$, J/kg
K	isothermal compressibility, m^2/N
m	mass of closed system, kg
$\dot{m}$	mass flow rate, kg/sec
m_i	mass of component in a mixture, kg
M	mass inventory of control volume, kg
M	molar mass, g/mol or kg/kmol
n	number of moles, mol
N_0	Avogadro's constant
P	pressure
δQ	infinitesimal heat interaction, J
$\dot{Q}$	heat transfer rate, W
$\bar{r}$	position vector, m
R	ideal gas constant, J/(kg · K)
s	specific entropy, J/(kg · K)
S	entropy, J/K
S_{gen}	entropy generation, J/K
$\dot{S}_{\text{gen}}$	entropy generation rate, W/K
T	absolute temperature, K
u	specific internal energy, J/kg
U	internal energy, J
v	specific volume m^3/kg
$\bar{v}$	specific volume of incompressible substance, m^3/kg
V	volume, m^3
V	velocity, m/sec
δW	infinitesimal work interaction, J
$\dot{W}_{\text{lost}}$	rate of lost available work, W
$\dot{W}_{\text{sh}}$	rate of shaft (shear) work transfer, W
x	linear coordinate, m
x	quality of liquid and vapor mixture
Z	vertical coordinate, m
β	coefficient of thermal expansion, 1/K
γ	ratio of specific heats, c_p/c_v
η	"efficiency" ratio
η_{I}	first-law efficiency
η_{II}	second-law efficiency
θ	relative temperature, °C

SUBSCRIPTS

$(\,)_{\text{in}}$	inlet port
$(\,)_{\text{out}}$	outlet port
$(\,)_{\text{rev}}$	reversible path
$(\,)_H$	high-temperature reservoir
$(\,)_L$	low-temperature reservoir
$(\,)_{\text{max}}$	maximum
$(\,)_T$	turbine
$(\,)_C$	compressor
$(\,)_N$	nozzle
$(\,)_D$	diffuser
$(\,)_1$	initial state
$(\,)_2$	final state
$(\,)_0$	reference state

$(\,)_f$	saturated liquid state (f = "fluid")
$(\,)_g$	saturated vapor state (g = "gas")
$(\,)_s$	saturated solid state (s = "solid")
$(\,)_*$	moderately compressed liquid state
$(\,)_+$	slightly superheated vapor state

Definitions

THERMODYNAMIC SYSTEM is the region or the collection of matter in space selected for analysis.

ENVIRONMENT is the thermodynamic system external to the system of interest, that is, external to the region selected for analysis or for discussion.

BOUNDARY is the real or imaginary surface delineating the system of interest. The boundary separates the system from its environment. The boundary is an unambiguously defined surface. The boundary has zero thickness.

CLOSED SYSTEM is the thermodynamic system whose boundary is not penetrated (crossed) by the flow of mass.

OPEN SYSTEM, or flow system, is the thermodynamic system whose boundary is permeable to mass flow. Open systems have their own nomenclature, so that the thermodynamic system is usually referred to as the *control volume*, the boundary of the open system is the *control surface*, and the particular regions of the boundary that are crossed by mass flows are the *inlet* or *outlet ports*.

STATE is the condition (the being) of a thermodynamic system at a particular point in time, as described by an ensemble of quantities called *thermodynamic properties* (e.g., pressure, volume, temperature, energy, enthalpy, entropy). Thermodynamic properties are only those quantities that depend solely on the instantaneous state of the system. Thermodynamic properties do not depend on the "history" of the system between two different states. Quantities that depend on the system evolution (path) between states are not thermodynamic properties (examples of nonproperties are the work, heat, and mass transfer interactions; the entropy transfer interactions; the entropy generation; and the lost available work—see also the definition of *process*).

EXTENSIVE PROPERTIES are properties whose values depend on the size of the system (e.g., mass, volume, energy, enthalpy, entropy).

INTENSIVE PROPERTIES are properties whose values do not depend on the system size (e.g., pressure, temperature). The collection of all intensive properties (or the properties of an infinitesimally small element of the system, including the per-unit-mass properties, such as specific energy and specific entropy) constitutes the *intensive state*.

PHASE is the collection of all system elements that have the same intensive state (e.g., the liquid droplets dispersed in a liquid–vapor mixture have the same intensive state, that is, the same pressure, temperature, specific volume, specific entropy, etc.).

PROCESS is the change of state from one initial state to a final state. In addition to the end states, knowledge of the process implies knowledge of the *interactions* experienced by the system while in communication with its environment (e.g., work transfer, heat transfer, mass transfer, and entropy transfer). To know the process also means to know the *path* (the history, or the succession of states) followed by the system from the initial to the final state.

CYCLE is a special process in which the final state coincides with the initial state.

41.2 THE FIRST LAW OF THERMODYNAMICS FOR CLOSED SYSTEMS

The first law of thermodynamics is a statement that brings together three concepts in thermodynamics: work transfer, heat transfer, and energy change. Of these concepts, only energy change or, simply, energy, is, in general, a thermodynamic property. Before stating the first law and before writing down the *equation* that accounts for this statement, it is necessary to review[1] the concepts of work transfer, heat transfer, and energy change.

Consider the force F_x experienced by a certain system at a point on its boundary. Relative to this system, the infinitesimal *work transfer* interaction between system and environment is

$$\delta W = -F_x dx$$

where the boundary displacement dx is defined as positive in the direction of the force F_x. When the force $\bar{F}$ and the displacement of its point of application $d\bar{r}$ are not collinear, the general definition of infinitesimal work transfer is

$$\delta W = -\bar{F} \cdot d\bar{r}$$

The work transfer interaction is considered positive when the system does work on its environment—in other words, when $\bar{F}$ and $d\bar{r}$ point in opposite directions. This sign convention has its origin in heat engine engineering, since the purpose of heat engines as thermodynamic systems is to deliver work while receiving heat.

In order for a system to experience work transfer, two things must occur: (1) a force must be present on the boundary, and (2) the point of application of this force (hence, the boundary) must move. The mere presence of forces on the boundary, without the displacement or the deformation of the boundary, does not mean work transfer. Likewise, the mere presence of boundary displacement without a force opposing or driving this motion does not mean work transfer. For example, in the free expansion of a gas into an evacuated space, the gas system does not experience work transfer because throughout the expansion the pressure at the imaginary system–environment interface is zero.

If a closed system can interact with its environment only via work transfer (i.e., in the absence of heat transfer δQ discussed later), then it is observed that the work transfer during a change of state from state 1 to state 2 is the same for all processes linking states 1 and 2,

$$-\left(\int_1^2 \delta W\right)_{\delta Q=0} = E_2 - E_1$$

In this special case the work transfer interaction $(W_{1-2})_{\delta Q=0}$ is a property of the system, since its value depends solely on the end states. This thermodynamic property is the *energy change* of the system, $E_2 - E_1$. The statement that preceded the last equation is the first law of thermodynamics for closed systems that do not experience heat transfer.

Heat transfer is, like work transfer, an energy interaction that can take place between a system and its environment. The distinction between δQ and δW is made by the second law of thermodynamics discussed in the next section: Heat transfer is the energy interaction accompanied by entropy transfer, whereas work transfer is the energy interaction taking place in the absence of entropy transfer. The transfer of heat is driven by the *temperature difference* established between the system and its environment.[2] The system temperature is measured by placing the system in thermal communication with a test system called *thermometer.* The result of this measurement is the *relative temperature* θ expressed in degrees Celsius, θ(°C), or Fahrenheit, θ(°F); these alternative temperature readings are related through the conversion formulas

$$\begin{aligned} \theta(°\mathrm{C}) &= \tfrac{5}{9}[\theta(°\mathrm{F}) - 32] \\ \theta(°\mathrm{F}) &= \tfrac{5}{9}\theta(°\mathrm{C}) + 32 \\ 1°\mathrm{F} &= \tfrac{5}{9}°\mathrm{C} \end{aligned}$$

The boundary that prevents the transfer of heat, regardless of the magnitude of the system–environment temperature difference, is termed *adiabatic.* Conversely, the boundary that is the locus of heat transfer even in the limit of vanishingly small system–environment temperature difference is termed *diathermal.*

It is observed that a closed system undergoing a change of state 1 → 2 in the absence of work transfer experiences a heat-transfer interaction whose magnitude depends solely on the end states:

$$\left(\int_1^2 \delta Q\right)_{\delta W=0} = E_2 - E_1$$

In the special case of zero work transfer, the heat-transfer interaction is a thermodynamic property of the system, which is by definition equal to the energy change experienced by the system in going from state 1 to state 2. The last equation is the first law of thermodynamics for closed systems incapable of experiencing work transfer. Note that, unlike work transfer, the heat transfer is considered positive when it increases the energy of the system.

Most thermodynamic systems do not manifest the purely mechanical ($\delta Q = 0$) or purely thermal ($\delta W = 0$) behavior discussed to this point. Most systems manifest a *coupled* mechanical and thermal behavior. The preceding first-law statements can be used to show that the first law of thermodynamics for a process executed by a closed system experiencing both work transfer and heat transfer is

$$\underbrace{\underbrace{\int_1^2 \delta Q}_{\substack{\text{heat}\\ \text{transfer}}} - \underbrace{\int_1^2 \delta W}_{\substack{\text{work}\\ \text{transfer}}}}_{\substack{\text{energy interactions}\\ \text{(nonproperties)}}} = \underbrace{\underbrace{E_2 - E_1}_{\substack{\text{energy}\\ \text{change}}}}_{\text{(property)}}$$

The first law means that the net heat transfer into the system equals the work done by the system on the environment, plus the increase in the energy of the system. The first law of thermodynamics for a cycle or for an integral number of cycles executed by a closed system is

$$\oint \delta Q = \oint \delta W = 0$$

Note that the net change in the thermodynamic property energy is zero during a cycle or an integral number of cycles.

The energy change term $E_2 - E_1$ appearing on the right-hand side of the first law can be replaced by a more general notation that distinguishes between macroscopically identifiable forms of energy storage (kinetic, gravitational) and energy stored internally,

$$\underbrace{E_2 - E_1}_{\substack{\text{energy}\\ \text{change}}} = \underbrace{U_2 - U_1}_{\substack{\text{internal}\\ \text{energy}\\ \text{change}}} + \underbrace{\frac{mV_2^2}{2} - \frac{mV_1^2}{2}}_{\substack{\text{kinetic}\\ \text{energy}\\ \text{change}}} + \underbrace{mgZ_2 - mgZ_1}_{\substack{\text{gravitational}\\ \text{energy}\\ \text{change}}}$$

If the closed system expands or contracts *quasi-statically* (i.e., slowly enough, in mechanical equilibrium internally and with the environment) so that at every point in time the pressure P is uniform throughout the system, then the work transfer term can be calculated as being equal to the work done by all the boundary pressure forces as they move with their respective points of application,

$$\int_1^2 \delta W = \int_1^2 P\, dV$$

The work-transfer integral can be evaluated provided the path of the quasi-static process, $P(V)$, is known; this is another illustration that the work transfer is path-dependent (i.e., not a thermodynamic property).

41.3 THE SECOND LAW OF THERMODYNAMICS FOR CLOSED SYSTEMS

A *temperature reservoir* is a thermodynamic system that experiences only heat-transfer interactions and whose temperature remains constant during such interactions. Consider first a closed system executing a cycle or an integral number of cycles *while in thermal communication with no more than one temperature reservoir*. To state the second law for this case is to observe that the net work transfer during each cycle cannot be positive,

$$\oint \delta W \leq 0$$

In other words, a closed system cannot deliver work during one cycle, while in communication with one temperature reservoir or with no temperature reservoir at all. Examples of such cyclic operation are the vibration of a spring–mass system, or the bouncing of a ball on the pavement: in order for these systems to return to their respective initial heights, that is, in order for them to execute cycles, the environment (e.g., humans) must perform work on them. The limiting case of frictionless cyclic operation is termed *reversible*, because in this limit the system returns to its initial state without intervention (work transfer) from the environment. Therefore, the distinction between reversible and irreversible cycles executed by closed systems in communication with no more than one temperature reservoir is

$$\oint \delta W = 0 \qquad \text{(reversible)}$$

$$\oint \delta W < 0 \qquad \text{(irreversible)}$$

To summarize, the first and second laws for closed systems operating cyclically in contact with no more than one temperature reservoir are (Fig. 41.1)

$$\oint \delta W = \oint \delta Q \leq 0$$

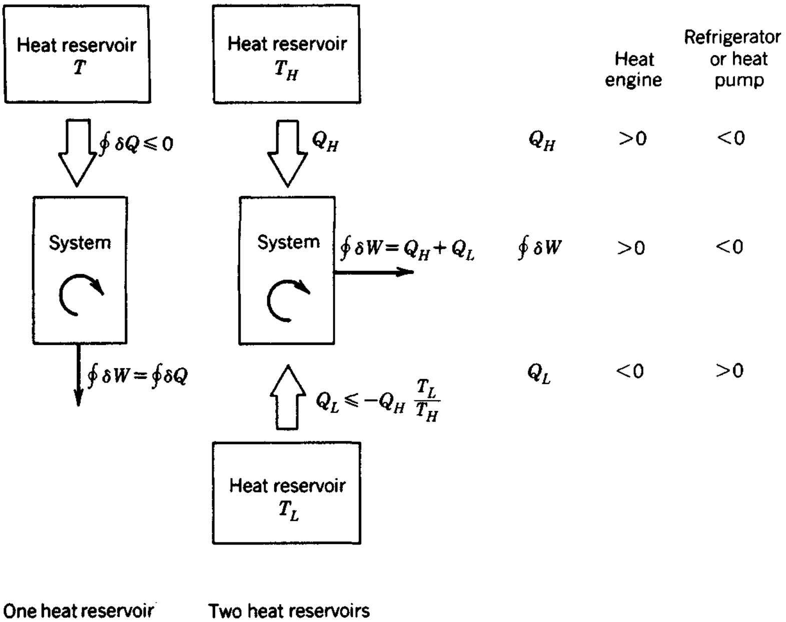


Fig. 41.1 The first and second laws of thermodynamics for a closed system operating cyclically while in communication with one or two heat reservoirs.

This statement of the second law can be used to show that in the case of a closed system executing one or an integral number of cycles *while in communication with two temperature reservoirs*, the following inequality holds (Fig. 41.1)

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \leq 0$$

where H and L denote the high-temperature and the low-temperature reservoirs, respectively. Symbols Q_H and Q_L stand for the value of the cyclic integral $\oint \delta Q$, where δQ is in one case exchanged only with the H reservoir, and in the other with the L reservoir. In the reversible limit, the second law reduces to $T_H/T_L = -Q_H/Q_L$, which serves as definition for the absolute *thermodynamic temperature* scale denoted by symbol T. Absolute temperatures are expressed either in degrees Kelvin, T(K), or in degrees Rankine, T(R); the relationships between absolute and relative temperatures are

$$T(\mathrm{K}) = \theta(^\circ\mathrm{C}) + 273.15\ \mathrm{K} \qquad T(\mathrm{R}) = \theta(^\circ\mathrm{F}) + 459.67\ \mathrm{R}$$

$$1\ \mathrm{K} = 1^\circ\mathrm{C} \qquad 1\ \mathrm{R} = 1^\circ\mathrm{F}$$

A *heat engine* is a special case of a closed system operating cyclically while in thermal communication with two temperature reservoirs, a system that during each cycle intakes heat and delivers work:

$$\oint \delta W = \oint \delta Q = Q_H + Q_L > 0$$

The goodness of the heat engine can be described in terms of the heat engine efficiency or the first-law efficiency

$$\eta_\mathrm{I} = \frac{\oint \delta W}{Q_H} \leq 1 - \frac{T_L}{T_H}$$

Alternatively, the second-law efficiency of the heat engine is defined as[1,3,4]

$$\eta_{\mathrm{II}} = \frac{\oint \delta W}{\left(\oint \delta W\right)_{\text{maximum (reversible case)}}} = \frac{\eta_{\mathrm{I}}}{1 - T_L/T_H}$$

A *refrigerating machine* or a *heat pump* operates cyclically between two temperature reservoirs in such a way that during each cycle it intakes work and delivers net heat to the environment,

$$\oint \delta W = \oint \delta Q = Q_H + Q_L < 0$$

The goodness of such machines can be expressed in terms of a coefficient of performance (COP)

$$\mathrm{COP}_{\text{refrigerator}} = \frac{Q_L}{-\oint \delta W} \le \frac{1}{T_H/T_L - 1}$$

$$\mathrm{COP}_{\text{heat pump}} = \frac{-Q_H}{-\oint \delta W} \le \frac{1}{1 - T_L/T_H}$$

Generalizing the second law for closed systems operating cyclically, one can show that if during each cycle the system experiences any number of heat transfer interactions Q_i with any number of temperature reservoirs whose respective absolute temperatures are T_i, then

$$\sum_i \frac{Q_i}{T_i} \le 0$$

Note that T_i is the absolute temperature of the boundary region crossed by Q_i. Another way to write the second law in this case is

$$\oint \frac{\delta Q}{T} \le 0$$

where, again, T is the temperature of the boundary pierced by δQ. Of special interest is the reversible cycle limit, in which the second law states $(\oint \delta Q/T)_{\text{rev}} = 0$. According to the definition of thermodynamic property, the second law implies that during a reversible process the quantity $\delta Q/T$ is the infinitesimal change in a property of the system: by definition, that property is the *entropy change*

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{rev}} \quad \text{or} \quad S_2 - S_1 = \left(\int_1^2 \frac{\delta Q}{T}\right)_{\text{rev}}$$

Combining this definition with the second-law statement for a cycle, $\oint \delta Q/T \le 0$, yields the second law of thermodynamics for *any process* executed by a closed system,

$$\underbrace{S_2 - S_1}_{\substack{\text{entropy}\\ \text{change}\\ \text{(property)}}} - \underbrace{\int_1^2 \frac{\delta Q}{T}}_{\substack{\text{entropy}\\ \text{transfer}\\ \text{(nonproperty)}}} \ge 0$$

The left-hand side in this inequality is by definition as the *entropy generation* associated with the process,

$$S_{\text{gen}} = S_2 - S_1 - \int_1^2 \frac{\delta Q}{T}$$

The entropy generation is a measure of the inequality sign in the second law and hence a measure of the irreversibility of the process. As shown in the next section and chapter 42, the entropy generation is proportional to the useful work destroyed during the process.[1,3,4] Note again that any heat-transfer interaction (δQ) is accompanied by entropy transfer ($\delta Q/T$), whereas the work transfer δW is not.

41.4 THE LAWS OF THERMODYNAMICS FOR OPEN SYSTEMS

If $\dot{m}$ represents the mass flow rate of working fluid through a port in the control surface, then the principle of *mass conservation* in the control volume reads

$$\underbrace{\sum_{\text{in}} \dot{m} - \sum_{\text{out}} \dot{m}}_{\text{mass transfer}} = \underbrace{\frac{\partial M}{\partial t}}_{\text{mass change}}$$

Subscripts in and out refer to summation over all the inlet and outlet ports, respectively, while M stands for the instantaneous mass inventory of the control volume.

The first law of thermodynamics is more general than the statement encountered earlier for closed systems, because this time we must account for the flow of energy associated with the $\dot{m}$ streams.

$$\underbrace{\sum_{\text{in}} \dot{m}\left(h + \frac{V^2}{2} + gZ\right) - \sum_{\text{out}} \dot{m}\left(h + \frac{V^2}{2} + gZ\right) + \sum_{i} \dot{Q}_i - \dot{W}}_{\text{energy transfer}} = \underbrace{\frac{\partial E}{\partial t}}_{\substack{\text{energy} \\ \text{change}}}$$

On the left-hand side we have the energy transfer interactions: heat, work, and the energy transfer associated with mass flow across the control surface. The specific enthalpy h, fluid velocity V, and height Z are evaluated right at the boundary. On the right-hand side, E is the instantaneous system energy integrated over the control volume.

The second law of thermodynamics for an open system assumes the form

$$\underbrace{\sum_{\text{in}} \dot{m}s - \sum_{\text{out}} \dot{m}s + \sum_{i} \frac{\dot{Q}_i}{T_i}}_{\text{entropy transfer}} \leq \underbrace{\frac{\partial S}{\partial t}}_{\text{entropy change}}$$

The specific entropy s is representative of the thermodynamic state of each stream right at the system boundary. The *entropy generation rate* defined as

$$\dot{S}_{\text{gen}} = \frac{\partial S}{\partial t} + \sum_{\text{out}} \dot{m}s - \sum_{\text{in}} \dot{m}s - \sum_{i} \frac{\dot{Q}_i}{T_i}$$

is a measure of the irreversibility of open system operation. The engineering importance of $\dot{S}_{\text{gen}}$ stems from its proportionality to the rate of one-way destruction of available work. If the following parameters are fixed—all the mass flows ($\dot{m}$), the peripheral conditions (h, s, V, Z), and the heat-transfer interactions (Q_i, T_i) except (Q_0, T_0)— then one can use the first law and the second law to show that the work transfer rate cannot exceed a theoretical maximum:

$$\dot{W} \leq \sum_{\text{in}} \dot{m}\left(h + \frac{V^2}{2} + gZ - T_0 s\right) - \sum_{\text{out}} \dot{m}\left(h + \frac{V^2}{2} + gZ - T_0 s\right) - \frac{\partial}{\partial t}(E - T_0 s)$$

The right-hand side in this inequality is the maximum work transfer rate $\dot{W}_{\text{sh,max}}$, which exists only in the ideal limit of reversible operation. The rate of *lost work*, or exergy (availability) destruction, is defined as

$$\dot{W}_{\text{lost}} = \dot{W}_{\text{max}} - \dot{W}$$

Again, using both laws, one can show that lost work is directly proportional to entropy generation,

$$\dot{W}_{\text{lost}} = T_0 \dot{S}_{\text{gen}}$$

This result is known as the Gouy-Stodola theorem.[1,3] Conservation of useful (available) work in thermodynamic systems can only be achieved based on the systematic minimization of entropy generation in all the components of the system. Engineering applications of entropy generation minimization as a thermodynamic optimization philosophy may be found in Refs. 1, 3, and 4, and in the next chapter.

41.5 RELATIONS AMONG THERMODYNAMIC PROPERTIES

The analytical forms of the first and second laws of thermodynamics contain properties such as internal energy, enthalpy, and entropy, which cannot be measured directly. The values of these properties are derived from measurements that can be carried out in the laboratory (e.g., pressure, volume, temperature, specific heat); the formulas connecting the derived properties to the measurable properties are reviewed in this section. Consider an infinitesimal change of state experienced by a closed system. If kinetic and gravitational energy changes can be neglected, the first law reads

$$\delta Q_{\text{any path}} - \delta W_{\text{any path}} = dU$$

which emphasizes that dU is path-independent. In particular, for a reversible path (rev), the same dU is given by

$$\delta Q_{\text{rev}} - \delta \mathrm{W}_{rev} = dU$$

Note that from the second law for closed systems we have $\delta \mathrm{Q}_{rev} = T\,dS$. Reversibility (or zero entropy generation) also requires internal mechanical equilibrium at each stage during the process; hence, $\delta W_{\text{rev}} = PdV$, as for a quasi-static change in volume. The infinitesimal change in U is therefore

$$T\,dS - P\,dV = dU$$

Note that this formula holds for an infinitesimal change of state along any path (because dU is path-independent); however, $T\,dS$ matches δQ and $P\,dV$ matches δW only if the path is reversible. In general, $\delta Q < T\,dS$ and $\delta W < P\,dV$, as shown in Fig. 41.2. The formula derived above for dU can be written for a unit mass: $Tds - P\,dv = du$. Additional identities implied by this relation are

$$T = \left(\frac{\partial u}{\partial s}\right)_v \qquad -P = \left(\frac{\partial u}{\partial v}\right)_s$$

$$\frac{\partial^2 u}{\partial s\,\partial v} = \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

where the subscript indicates which variable is held constant during partial differentiation. Similar relations and partial derivative identities exist in conjunction with other derived functions such as enthalpy, Gibbs free energy, and Helmholtz free energy:

- Enthalpy (defined as $h = u + Pv$)

$$dh = T\,ds + v\,dP$$

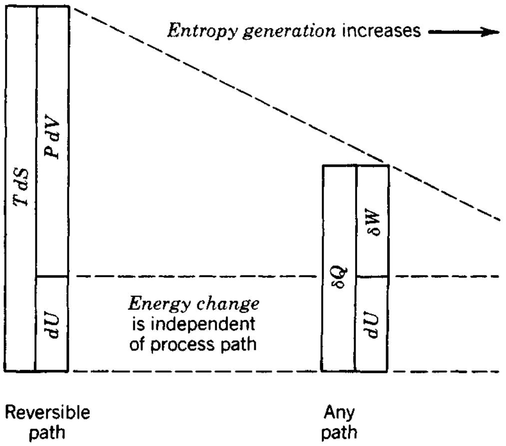


Fig. 41.2 The applicability of the relation $dU = T\,dS - P\,dV$ to any infinitesimal process. (In this drawing, all the quantities are assumed positive.)

$$T = \left(\frac{\partial h}{\partial s}\right)_P \qquad v = \left(\frac{\partial h}{\partial P}\right)_s$$
$$\frac{\partial^2 h}{\partial s \partial P} = \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

- Gibbs free energy (defined as $g = h - Ts$)

$$dg = -s\,dT + v\,dP$$
$$-s = \left(\frac{\partial g}{\partial T}\right)_P \qquad v = \left(\frac{\partial g}{\partial P}\right)_T$$
$$\frac{\partial^2 g}{\partial T \partial P} = -\left(\frac{\partial s}{\partial P}\right)_T = \left(\frac{\partial v}{\partial T}\right)_P$$

- Helmholtz free energy (defined as $f = u - Ts$)

$$df = -s\,dT - P\,dv$$
$$-s = \left(\frac{\partial f}{\partial T}\right)_v \qquad -P = \left(\frac{\partial f}{\partial v}\right)_T$$
$$\frac{\partial^2 f}{\partial T \partial v} = -\left(\frac{\partial s}{\partial v}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_v$$

In addition to the (P, v, T) surface, which can be determined based on measurements, (Fig. 41.3), the following partial derivatives are furnished by special experiments:[1]

- The specific heat at constant volume, $c_v = (\partial u / \partial T)_v$, follows directly from the constant volume $(\delta W = 0)$ heating of a unit mass of pure substance.
- The specific heat at constant pressure, $c_P = (\partial h / \partial T)_P$, is determined during the constant-pressure heating of a unit mass of pure substance.
- The Joule-Thomson coefficient, $\mu = (\partial T / \partial P)_h$, is measured during a throttling process, that is, during the flow of a stream through an adiabatic duct with friction (see the first law for an open system in the steady state).
- The coefficient of thermal expansion, $\beta = (1/v)(\partial v / \partial T)_P$.
- The isothermal compressibility, $K = (-1/v)(\partial v / \partial P)_T$.
- The constant temperature coefficient, $c_T = (\partial h / \partial P)_T$.

Two noteworthy relationships between some of the partial-derivative measurements are

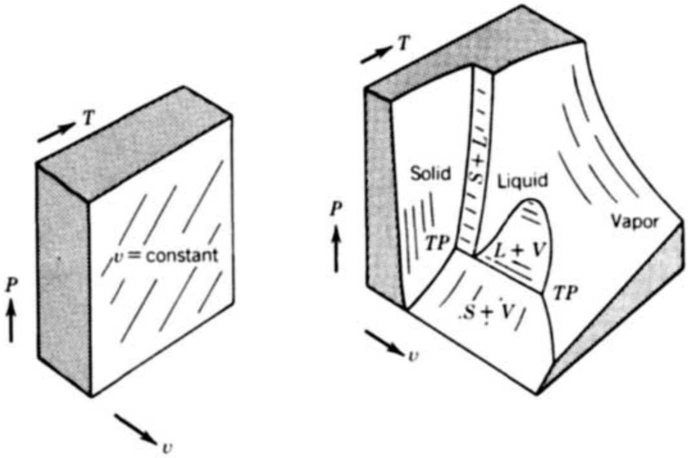
$$c_P - c_v = \frac{Tv\beta^2}{K}$$
$$\mu = \frac{1}{c_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]$$

The general equations relating the derived properties (u, h, s) to measurable quantities are

$$du = c_v\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv$$
$$dh = c_P\,dT + \left[-T\left(\frac{\partial v}{\partial T}\right)_P + v\right]dP$$
$$ds = \frac{c_v}{T}\,dT + \left(\frac{\partial v}{\partial T}\right)_v dv \quad \text{or} \quad ds = \frac{c_P}{T}\,dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

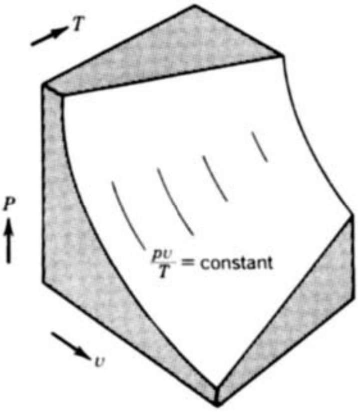
These relations also suggest the following identities:

$$\left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right) = c_v \qquad \left(\frac{\partial h}{\partial T}\right)_P = T\left(\frac{\partial s}{\partial T}\right)_P = c_P$$



Incompressible substance

Pure substance



Ideal gas

Fig. 41.3 The (P, v, T) surface for a pure substance that contracts upon freezing, showing regions of ideal gas and incompressible fluid behavior. (In this figure, S = solid, V = vapor, L = liquid, TP = triple point.)

41.6 IDEAL GASES

The relationships between thermodynamic properties and the analysis associated with applying the laws of thermodynamics are simplified considerably in cases where the pure substance exhibits ideal gas behavior. As shown in Fig. 41.3, this behavior sets in at sufficiently high temperatures and low pressures; in this limit, the (P, v, T) surface is fitted closely by the simple expression

$$\frac{Pv}{T} = R \quad \text{(constant)}$$

where R is the ideal gas constant of the substance of interest (Table 41.1). The formulas for internal energy, enthalpy, and entropy, which concluded the preceding section, assume the following form in the ideal-gas limit:

Table 41.1 Values of Ideal-Gas Constant and Specific Heat at Constant Volume for Gases Encountered in Mechanical Engineering[1]

Ideal Gas	R $\left(\frac{\text{J}}{\text{kg}\cdot\text{K}}\right)$	c_v $\left(\frac{\text{J}}{\text{kg}\cdot\text{K}}\right)$
Air	286.8	715.9
Argon, Ar	208.1	316.5
Butane, $C_4 H_{10}$	143.2	1595.2
Carbon dioxide, CO_2	188.8	661.5
Carbon monoxide, CO	296.8	745.3
Ethane, C_2H_6	276.3	1511.4
Ethylene, C_2H_4	296.4	1423.5
Helium, He_2	2076.7	3152.7
Hydrogen, H	4123.6	10216.0
Methane, CH_4	518.3	1687.3
Neon, Ne	412.0	618.4
Nitrogen, N_2	296.8	741.1
Octane, C_8H_{18}	72.85	1641.2
Oxygen, O_2	259.6	657.3
Propane, C_3H_8	188.4	1515.6
Steam, H_2O	461.4	1402.6

$$du = c_v \, dT; \qquad c_v = c_v(T)$$
$$dh = c_P \, dT; \qquad c_P = c_P(T) = c_v + R$$
$$ds = \frac{c_v}{T} dT + \frac{R}{v} dv \quad \text{or} \quad ds = \frac{c_P}{T} dT - \frac{R}{P} dP \quad \text{or} \quad ds = \frac{c_v}{P} dP + \frac{c_P}{v} dv$$

If the coefficients c_v and c_P are constant in the temperature domain of interest, then the *changes* in specific internal energy, enthalpy, and entropy relative to a reference state $(\ )_0$ are given by the formulas

$$u - u_0 = c_v (T - T_0)$$
$$h - h_0 = c_P (T - T_0) \quad (\text{where } h_0 = u_0 + RT_0)$$
$$s - s_0 = c_v \ln \frac{T}{T_0} + R \ln \frac{v}{v_0}$$
$$s - s_0 = c_P \ln \frac{T}{T_0} - R \ln \frac{P}{P_0}$$
$$s - s_0 = c_v \ln \frac{P}{P_0} + c_P \ln \frac{v}{v_0}$$

The ideal-gas model rests on two empirical constants, c_v and c_P, or c_v and R, or c_P and R. The ideal-gas limit is also characterized by

$$\mu = 0, \qquad \beta = \frac{1}{T}, \qquad K = \frac{1}{P}, \qquad c_T = 0$$

The extent to which a thermodynamic system destroys available work is intimately tied to the system's entropy generation, that is, to the system's departure from the theoretical limit of reversible operation. Idealized processes that can be modeled as reversible occupy a central role in engineering thermodynamics, because they can serve as standard in assessing the goodness of real processes. Two benchmark reversible processes executed by closed ideal-gas systems are particularly simple and useful. A *quasi-static adiabatic process* 1 → 2 executed by a closed ideal-gas system has the following characteristics:

- Energy interactions

$$\int_1^2 \delta Q = 0$$

$$\int_1^2 \delta W = \frac{P_2 V_2}{\gamma - 1}\left[\left(\frac{V_2}{V_1}\right)^{\gamma-1} - 1\right]$$

  where $\gamma = c_P / c_v$
- Path

$$PV^\gamma = P_1 V_1^\gamma = P_2 V_2^\gamma \quad \text{(constant)}$$

- Entropy change

$$S_1 - S_1 = 0$$

  hence the name *isoentropic* or *isentropic* for this process
- Entropy generation

$$S_{\text{gen}_{1\to2}} = S_2 - S_1 - \int_1^2 \frac{\delta Q}{T} = 0 \quad \text{(reversible)}$$

A *quasi-static isothermal process* 1 → 2 executed by a closed ideal-gas system in communication with a single temperature reservoir T is characterized by

- Energy interactions

$$\int_1^2 \delta Q = \int_1^2 \delta W = m\,RT \ln \frac{V_2}{V_1}$$

- Path

$$T = T_1 = T_2 \text{ (constant) or } PV = P_1 V_1 = P_2 V_2 \text{ (constant)}$$

- Entropy change

$$S_2 - S_1 = m\,R \ln \frac{V_2}{V_1}$$

- Entropy generation

$$S_{\text{gen}_{1\to2}} = S_2 - S_1 - \int_1^2 \frac{\delta Q}{T} = 0 \quad \text{(reversible)}$$

Mixtures of ideal gases also behave as ideal gases in the high-temperature, low-pressure limit. If a certain mixture of mass m contains ideal gases mixed in mass proportions m_i, and if the ideal-gas constants of each component are (c_{v_i}, c_{P_i}, R_i), then the equivalent ideal gas constants of the mixture are

$$c_v = \frac{1}{m} \sum_i m_i\, c_{v_i}$$

$$c_P = \frac{1}{m} \sum_i m_i\, c_{P_i}$$

$$R = \frac{1}{m} \sum_i m_i\, R_i$$

where $m = \Sigma_i\, m_i$.

One mole is the amount of substance of a system that contains as many elementary entities (e.g., molecules) as there are in 12 g of carbon 12; the number of such entities is Avogadro's constant, $N_0 \cong 6.022 \times 10^{23}$. The mole is not a mass unit, since the mass of 1 mole is not the same for all substances. The *molar mass* M of a given molecular species is the mass of 1 mole of that species, so that the total mass m is equal to M times the number of moles n,

$$m = nM$$

Thus, the ideal-gas equation of state can be written as

$$PV = nMRT$$

where the product MR is the *universal gas constant*

$$\overline{R} = MR = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

The equivalent molar mass of a mixture of ideal gases with individual molar masses M_i is

$$M = \frac{1}{n} \Sigma\, n_i\, M_i$$

where $n = \Sigma n_i$. The molar mass of air, as a mixture of nitrogen, oxygen, and traces of other gases, is 28.966 g/mol (or 28.966 kg/kmol). A more useful model of the air gas mixture relies on only nitrogen and oxygen as constituents, in the proportion 3.76 moles of nitrogen to every mole of oxygen; this simple model is used frequently in the field of combustion.

41.7 INCOMPRESSIBLE SUBSTANCES

At the opposite end of the spectrum, that is, at sufficiently high pressures and low temperatures in Fig. 41.3, solids and liquids behave so that their density or specific volume is practically constant. In this limit the (P, v, T) surface is adequately represented by the equation

$$v = \overline{v} \quad \text{(constant)}$$

The formulas for calculating changes in internal energy, enthalpy, and entropy become (see the end of the section on relations among thermodynamic properties)

$$\begin{aligned} du &= c\, dT \\ dh &= c\, dT + \overline{v}\, dP \\ ds &= \frac{c}{T}\, dT \end{aligned}$$

where c is the sole specific heat of the incompressible substance,

$$c = c_v = c_P$$

The specific heat c is a function of temperature only. In a sufficiently narrow temperature range where c can be regarded as constant, the finite changes in internal energy, enthalpy, and entropy relative to a reference state denoted by $(\ )_0$ are

$$\begin{aligned} u - u_0 &= c\,(T - T_0) \\ h - h_0 &= c\,(T - T_0) + \overline{v}(P - P_0) \quad (\text{where } h_0 = u_0 + P_0\overline{v}) \\ s - s_0 &= c \ln \frac{T}{T_0} \end{aligned}$$

The incompressible substance model rests on two empirical constants, c and $\overline{v}$.

41.8 TWO-PHASE STATES

As shown in Fig. 41.3, the domains in which the pure substance behaves either as an ideal gas or as an incompressible substance are bounded by regions where the substance exists as a mixture of two phases, liquid and vapor, solid and liquid, or solid and vapor. The two-phase regions themselves intersect along the *triple point* line labeled *TP–TP* on the middle sketch of Fig. 41.3. In engineering cycle calculations, more useful are the projections of the (P, v, T) surface on the P–v plane or, through the relations reviewed earlier, on the T–s plane. The terminology associated with two-phase equilibrium states is easier to understand by focusing on the P–v diagram of Fig. 41.4*a* and by

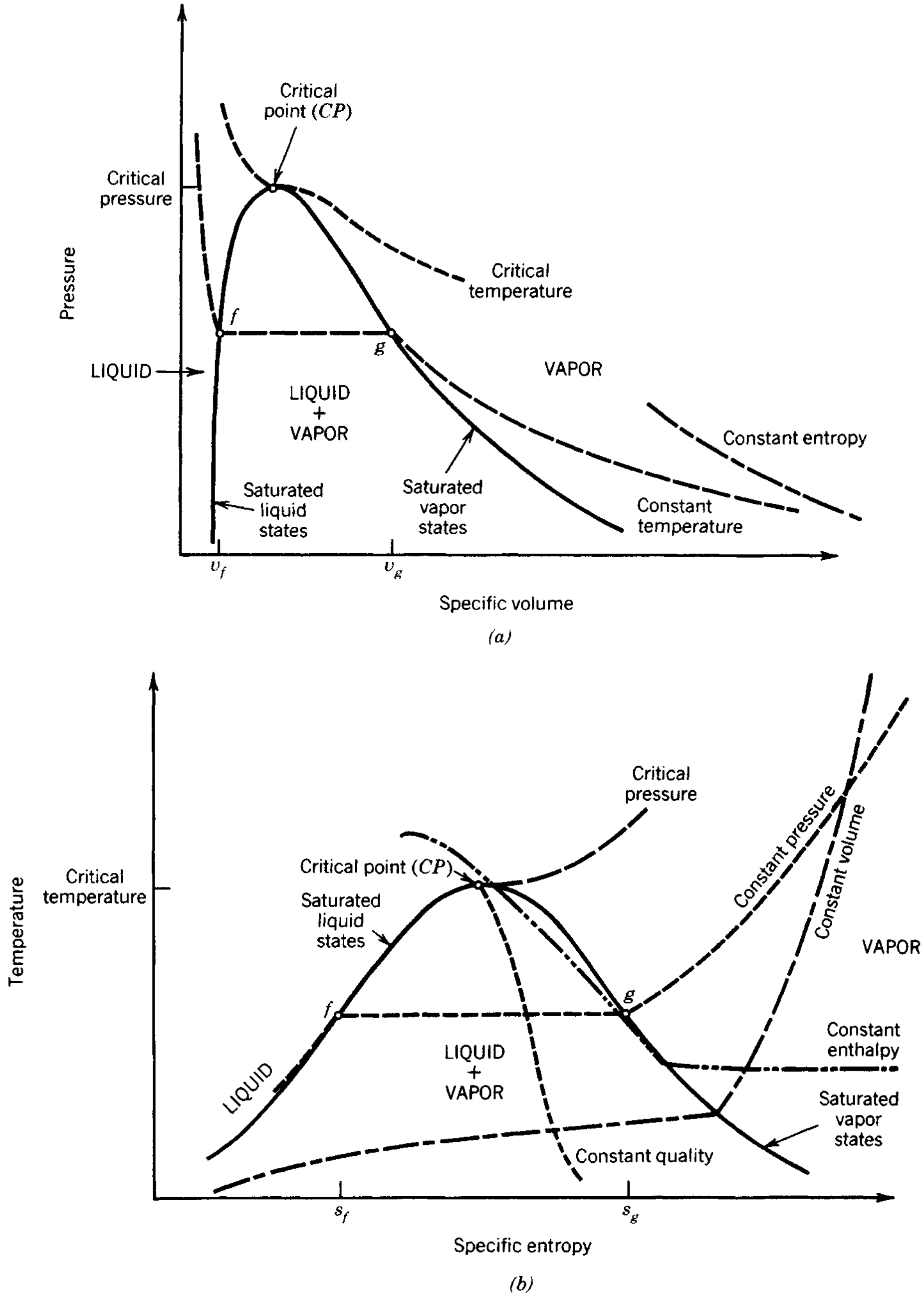


Fig. 41.4 The locus of two-phase (liquid and vapor) states, projected on (*a*) the *P*–*v* plane, and (*b*) the *T*–*s* plane.

imagining the isothermal compression of a unit mass of substance (a closed system). As the specific volume v decreases, the substance ceases to be a pure vapor at state g, where the first droplets of liquid are formed. State g is a *saturated vapor state.* It is observed that isothermal compression beyond g proceeds at constant pressure up to state f, where the last bubble (immersed in liquid) is suppressed. State f is a *saturated liquid state.* Isothermal compression beyond f is accompanied by a steep rise in pressure, depending on the compressibility of the liquid phase. The *critical state* is the intersection of the locus of saturated vapor states with the locus of saturated liquid states (Fig. 41.4*a*). The temperature and pressure corresponding to the critical state are the *critical temperature* and *critical pressure.* Table 41.2 contains a compilation of critical-state properties of some of the more common substances.

Figure 41.4*b* shows the projection of the liquid and vapor domain on the T–s plane. On the same drawing is shown the relative positioning (the relative slopes) of the traces of various constant-property cuts through the three-dimensional surface on which all the equilibrium states are positioned. In the two-phase region, the temperature is a unique function of pressure. This one-to-one relationship is indicated also by the *Clapeyron* relation

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_g - h_f}{T(v_g - v_f)} = \frac{s_g - s_f}{v_g - v_f}$$

where the subscript sat is a reminder that the relation holds for saturated states (such as g and f) and for mixtures of two saturated phases. Subscripts g and f indicate properties corresponding to the saturated vapor and liquid states found at temperature T_{sat} (and pressure P_{sat}). Built into the last equation is the identity

$$h_g - h_f = T(s_g - s_f)$$

Table 41.2 Critical-State Properties[1]

Fluid	Critical Temperature [K (°C)]	Critical Pressure [MPa (atm)]	Critical Specific Volume (cm^3/g)
Air	133.2 (−140)	3.77 (37.2)	2.9
Alcohol (methyl)	513.2 (240)	7.98 (78.7)	3.7
Alcohol (ethyl)	516.5 (243.3)	6.39 (63.1)	3.6
Ammonia	405.4 (132.2)	11.3 (111.6)	4.25
Argon	150.9 (−122.2)	4.86 (48)	1.88
Butane	425.9 (152.8)	3.65 (36)	4.4
Carbon dioxide	304.3 (31.1)	7.4 (73)	2.2
Carbon monoxide	134.3 (−138.9)	3.54 (35)	3.2
Carbon tetrachloride	555.9 (282.8)	4.56 (45)	1.81
Chlorine	417 (143.9)	7.72 (76.14)	1.75
Ethane	305.4 (32.2)	4.94 (48.8)	4.75
Ethylene	282.6 (9.4)	5.85 (57.7)	4.6
Helium	5.2 (−268)	0.228 (2.25)	14.4
Hexane	508.2 (235)	2.99 (29.5)	4.25
Hydrogen	33.2 (−240)	1.30 (12.79)	32.3
Methane	190.9 (−82.2)	4.64 (45.8)	6.2
Methyl chloride	416.5 (143.3)	6.67 (65.8)	2.7
Neon	44.2 (−288.9)	2.7 (26.6)	2.1
Nitric oxide	179.2 (−93.9)	6.58 (65)	1.94
Nitrogen	125.9 (−147.2)	3.39 (33.5)	3.25
Octane	569.3 (296.1)	2.5 (24.63)	4.25
Oxygen	154.3 (−118.9)	5.03 (49.7)	2.3
Propane	368.7 (95.6)	4.36 (43)	4.4
Sulfur dioxide	430.4 (157.2)	7.87 (77.7)	1.94
Water	647 (373.9)	22.1 (218.2)	3.1

which is equivalent to the statement that the Gibbs free energy is the same for the saturated states and their mixtures found at the same temperature, $g_g = g_f$.

The properties of a two-phase mixture depend on the proportion in which saturated vapor, m_g, and saturated liquid, m_f, enter the mixture. The composition of the mixture is described by the property *quality*

$$x = \frac{m_g}{m_f + m_g}$$

whose value varies between 0 at state f and 1 at state g. Other properties of the mixture can be calculated in terms of the properties of the saturated states found at the same temperature.

$$u = u_f + xu_{fg} \qquad s = s_f + xs_{fg}$$
$$h = h_f + xh_{fg} \qquad v = v_f + xv_{fg}$$

with the notation $(\,)_{fg} = (\,)_g - (\,)_f$.

Similar relations can be used to calculate the properties of two-phase states other than liquid and vapor, namely, solid and vapor or solid and liquid. For example, the enthalpy of a solid and liquid mixture is given by $h = h_s + xh_{sf}$, where subscript s stands for the *saturated solid state* found at the same temperature as for the two-phase state, and where h_{sf} is the latent heat of melting or solidification.

In general, the states situated immediately outside the two-phase dome sketched in Figs. 41.3 and 41.4 do not follow very well the limiting models discussed already (ideal gas, incompressible substance). Since the properties of closely neighboring states are usually not available in tabular form, the following approximate calculation proves useful. For a *moderately compressed liquid state*, which is indicated by the subscript $(\,)_*$, that is, for a state situated close to the left of the dome in Fig. 41.4, the properties may be calculated as slight deviations from those of the saturated liquid state found at the same temperature as the compressed liquid state of interest,

$$h_* \cong (h_f)_{T^*} + (v_f)_{T^*}[P_* - (P_f)_{T^*}]$$
$$s \cong (s_f)_{T^*}$$

For a *slightly superheated vapor state*, that is, a state situated close to the right of the dome in Fig. 41.4, the properties may be estimated in terms of those of the saturated vapor state found at the same temperature,

$$h_+ \cong (h_g)_{T+}$$
$$s_+ \cong (s_g)_{T+} + \left(\frac{P_g v_g}{T_g}\right)_{T+} \ln \frac{(P_g)_{T+}}{P_+}$$

In these expressions, subscript $(\,)_+$ indicates the properties of the slightly superheated vapor state.

41.9 ANALYSIS OF ENGINEERING SYSTEM COMPONENTS

This section contains a summary of the equations obtained by applying the first and second laws of thermodynamics to the components encountered in most engineering systems, such as power cycles and refrigeration cycles. It is assumed that each component operates in *steady flow*.

- *Valve* (throttle) or adiabatic duct with friction (Fig. 41.5*a*):

First law $\quad h_1 = h_2$

Second law $\quad \dot{S}_{\text{gen}} = \dot{m}(s_2 - s_1) > 0$

- *Expander* or *turbine* with negligible heat transfer to the ambient (Fig. 41.5*b*):

First law $\quad \dot{W}_T = \dot{m}(h_1 - h_2)$

Second law $\quad \dot{S}_{\text{gen}} = \dot{m}(s_2 - s_1) \geq 0$

Efficiency $\quad \eta_T = \dfrac{h_1 - h_2}{h_1 - h_{2,\text{rev}}} \leq 1$

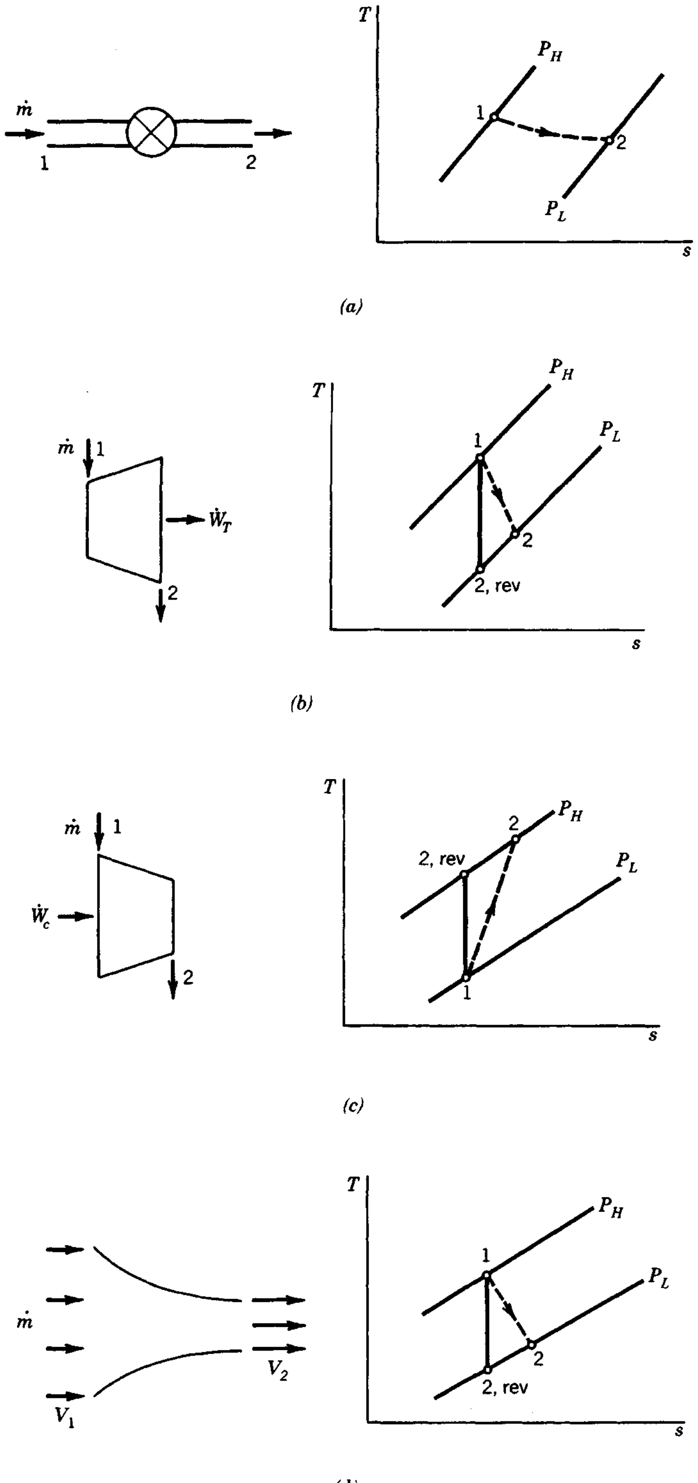
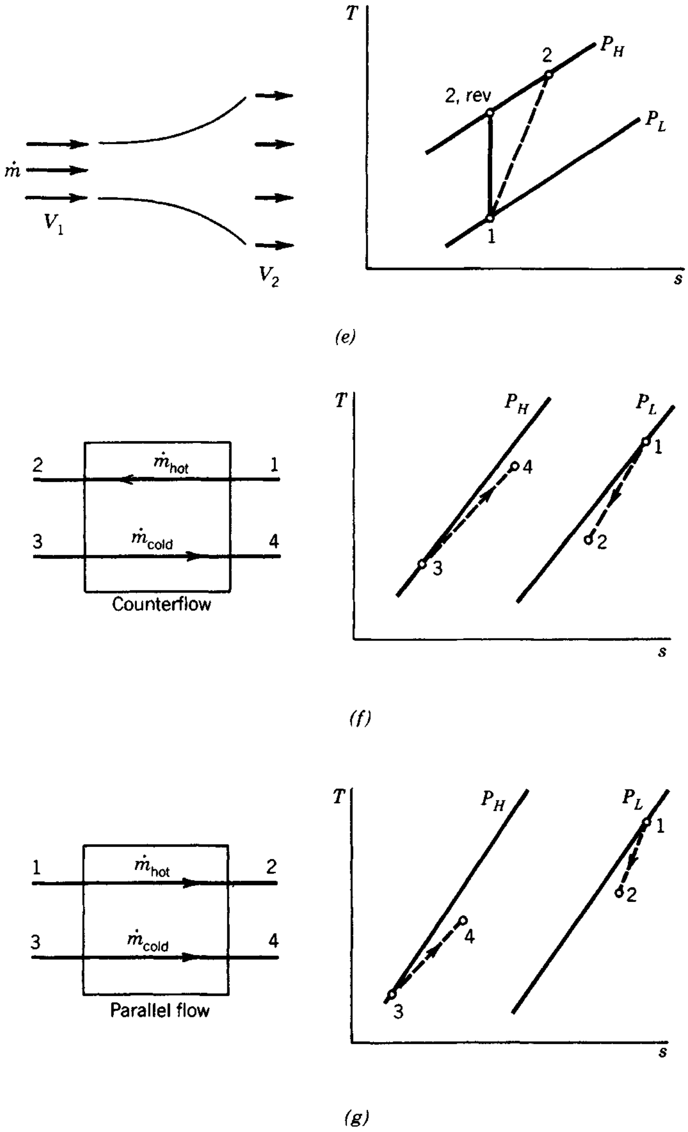


Fig. 41.5 Engineering system components, and their inlet and outlet states on the *T*–*s* plane, (P_H = high pressure; P_L = low pressure.)



(e)

(f)

(g)

Fig. 41.5 (Continued)

- *Compressor* or *pump* with negligible heat transfer to the ambient (Fig. 41.5*c*):

$$\text{First law} \qquad \dot{W}_C = \dot{m}(h_2 - h_1)$$

$$\text{Second law} \qquad \dot{S}_{\text{gen}} = \dot{m}(s_2 - s_1) \geq 0$$

$$\text{Efficiency} \qquad \eta_c = \frac{h_{2,\text{rev}} - h_1}{h_2 - h_1} \leq 1$$

- *Nozzle* with negligible heat transfer to the ambient (Fig. 41.5*d*):

$$\text{First law} \qquad \frac{1}{2}(V_2^2 - V_1^2) = h_1 - h_2$$

$$\text{Second law} \qquad \dot{S}_{\text{gen}} = \dot{m}(s_2 - s_1) \geq 0$$

$$\text{Efficiency} \qquad \eta_N = \frac{V_2^2 - V_1^2}{V_{2,\text{rev}}^2 - V_1^2} \leq 1$$

- *Diffuser* with negligible heat transfer to the ambient (Fig. 41.5*e*):

$$\text{First law} \qquad h_2 - h_1 = \frac{1}{2}(V_1^2 - V_2^2)$$

$$\text{Second law} \qquad \dot{S}_{\text{gen}} = \dot{m}(s_2 - s_1) \geq 0$$

$$\text{Efficiency} \qquad \eta_D = \frac{h_{2,\text{rev}} - h_1}{h_2 - h_1} \leq 1$$

- *Heat exchangers* with negligible heat transfer to the ambient (Figs. 41.5*f* and 41.5*g*)

$$\text{First law} \qquad \dot{m}_{\text{hot}}(h_1 - h_2) = \dot{m}_{\text{cold}}(h_4 - h_3)$$

$$\text{Second law} \qquad \dot{S}_{\text{gen}} = \dot{m}_{\text{hot}}(s_2 - s_1) + \dot{m}_{\text{cold}}(s_4 - s_3) \geq 0$$

Figures 41.5*f* and 41.5*g*, show that a pressure drop always occurs in the direction of flow, in any heat exchanger flow passage.

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