Section 4

Thermodynamics

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Nomenclature and Units

Symbols are omitted that are correlation- or application-specific.

Symbol	Definition	SI units	U.S. customary units
A	Helmholtz energy	J	Btu
$\hat{a}_i$	Activity of species i in solution	Dimensionless	Dimensionless
B	2d virial coefficient, density expansion	cm^3/mol	cm^3/mol
C	3d virial coefficient, density expansion	cm^6/mol^2	cm^6/mol^2
D	4th virial coefficient, density expansion	cm^9/mol^3	cm^9/mol^3
B'	2d virial coefficient, pressure expansion	kPa^{-1}	kPa^{-1}
C'	3d virial coefficient, pressure expansion	kPa^{-2}	kPa^{-2}
D'	4th virial coefficient, pressure expansion	kPa^{-3}	kPa^{-3}
B_{ij}	Interaction 2d virial coefficient	cm^3/mol	cm^3/mol
C_{ijk}	Interaction 3d virial coefficient	cm^6/mol^2	cm^6/mol^2
C_P	Heat capacity at constant pressure	J/(mol·K)	Btu/(lb mol·R)
C_V	Heat capacity at constant volume	J/(mol·K)	Btu/(lb mol·R)
E_K	Kinetic energy	J	Btu
E_P	Gravitational potential energy	J	Btu
f_i	Fugacity of pure species i	kPa	psi
$\hat{f}_i$	Fugacity of species i in solution	kPa	psi
G	Molar or unit-mass Gibbs energy	J/mol or J/kg	Btu/lb mol or Btu/lbm
g	Acceleration of gravity	m/s^2	ft/s^2
g	$\equiv G^E/RT$		
H	Molar or unit-mass enthalpy	J/mol or J/kg	Btu/lb mol or Btu/lbm
K_i	Equilibrium K-value, y_i/x_i	Dimensionless	Dimensionless
K_j	Equilibrium constant for chemical reaction j	Dimensionless	Dimensionless
k_i	Henry's constant	kPa	psi
M	Molar or unit-mass value of any extensive thermodynamic property of a solution		
M_i	Molar or unit-mass value of any extensive property of pure species i		
$\overline{M}_i$	Partial molar property of species i in solution		
ΔM	Property change of mixing		
ΔM_j°	Standard property change of reaction j		
m	Mass	kg	lbm
$\dot{m}$	Mass flow rate	kg/s	lbm/s
n	Number of moles		
n_i	Number of moles of species i		
P	Absolute pressure	kPa	psi
P_c	Critical pressure	kPa	psi
P_i^{sat}	Saturation or vapor pressure of species i	kPa	psi
p_i	Partial pressure of species i in gas mixture ($\equiv y_iP$)	kPa	psi
Q	Heat	J	Btu
$\dot{Q}$	Rate of heat transfer	J/s	Btu/s
R	Universal gas constant	J/(mol·K)	Btu/(lb mol·R)
S	Molar or unit-mass entropy	J/(mol·K) or J/(kg·K)	Btu/(lb mol·R) or Btu/(lb·R)
T	Absolute temperature	K	R
T_c	Critical temperature,	K	R
U	Molar or unit-mass internal energy	J/mol or J/kg	Btu/lb mol or Btu/lbm
u	Velocity	m/s	ft/s
V	Molar or unit-mass volume	m^3/mol or m^3/kg	ft^3/lb mol or ft^3/lbm
W	Work	J	Btu
W_s	Shaft work for flow process	J	Btu
$\dot{W}_s$	Shaft power for flow process	J/s	Btu/s
x_i	Mole fraction in general or liquid-phase mole fraction of species i in solution	Dimensionless	Dimensionless
y_i	Vapor-phase mole fraction of species i in solution	Dimensionless	Dimensionless
Z	Compressibility factor	Dimensionless	Dimensionless
z	Elevation above a datum level	m	ft

Superscripts

E	Denotes excess thermodynamic property
id	Denotes value for an ideal solution
ig	Denotes value for an ideal gas
l	Denotes liquid phase
lv	Denotes phase transition from liquid to vapor
R	Denotes residual thermodynamic property
t	Denotes a total value of a thermodynamic property
v	Denotes vapor phase
∞	Denotes a value at infinite dilution

Subscripts

C	Denotes a value for a colder heat reservoir
c	Denotes a value for the critical state
H	Denotes a value for a hotter heat reservoir
r	Denotes a reduced value
rev	Denotes a reversible process

Greek letters

α,β	As superscripts, identify phases		
β_i	Volume expansivity, species i	K^{-1}	R^{-1}
ε_j	Reaction coordinate for reaction j	mol	lb mol
$\Gamma_i(T)$	Defined by Eq. (4-72)	J/mol	Btu/lb mol
γ	Heat-capacity ratio, C_P/C_V	Dimensionless	Dimensionless
γ_i	Activity coefficient of species i in solution	Dimensionless	Dimensionless
μ_i	Chemical potential of species i	J/mol	Btu/lb mol
$\nu_{i,j}$	Stoichiometric number of species i in reaction j	Dimensionless	Dimensionless
ρ	Molar density	$mols/m^3$	lb $moles/ft^3$
σ	As a subscript, denotes a heat reservoir		
Φ_i	Defined by Eq. (4-283)	Dimensionless	Dimensionless
ϕ_i	Fugacity coefficient of pure species i	Dimensionless	Dimensionless
$\hat{\phi}_i$	Fugacity coefficient of species i in solution	Dimensionless	Dimensionless
ω	Acentric factor	Dimensionless	Dimensionless

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INTRODUCTION

Thermodynamics is the branch of science that embodies the principles of energy transformation in macroscopic systems. The general restrictions which experience has shown to apply to all such transformations are known as the *laws of thermodynamics.* These laws are primitive; they cannot be derived from anything more basic.

The first law of thermodynamics states that energy is conserved; that, although it can be altered in form and transferred from one place to another, the total quantity remains constant. Thus, the first law of thermodynamics depends on the concept of energy; but, conversely, energy is an *essential* thermodynamic function because it allows the first law to be formulated. This coupling is characteristic of the primitive concepts of thermodynamics.

The words *system* and *surroundings* are similarly coupled. A *system* is taken to be any object, any quantity of matter, any region, and so on, selected for study and set apart (mentally) from everything else, which is called the *surroundings.* The imaginary envelope which encloses the system and separates it from its surroundings is called the *boundary* of the system.

Attributed to this boundary are special properties which may serve either (1) to *isolate* the system from its surroundings, or (2) to provide for *interaction* in specific ways between system and surroundings. An isolated system exchanges neither matter nor energy with its surroundings. If a system is not isolated, its boundaries may permit exchange of matter or energy or both with its surroundings. If the exchange of matter is allowed, the system is said to be *open;* if only energy and not matter may be exchanged, the system is *closed* (but not isolated), and its mass is constant.

When a system is isolated, it cannot be affected by its surroundings. Nevertheless, changes may occur within the system that are detectable with such measuring instruments as thermometers, pressure gauges, and so on. However, such changes cannot continue indefinitely, and the system must eventually reach a final static condition of *internal equilibrium.*

For a closed system which interacts with its surroundings, a final static condition may likewise be reached such that the system is not only internally at equilibrium but also in *external equilibrium* with its surroundings.

The concept of equilibrium is central in thermodynamics, for associated with the condition of internal equilibrium is the concept of *state.* A system has an identifiable, reproducible state when all its *properties,* such as temperature T, pressure P, and molar volume V, are fixed. The concepts of *state* and *property* are again coupled. One can equally well say that the properties of a system are fixed by its state. Although the properties T, P, and V may be detected with measuring instruments, the existence of the *primitive* thermodynamic properties (see Postulates 1 and 3 following) is recognized much more indirectly. The number of properties for which values must be specified in order to fix the state of a system depends on the nature of the system and is ultimately determined from experience.

When a system is displaced from an equilibrium state, it undergoes a *process,* a change of state, which continues until its properties attain new equilibrium values. During such a process the system may be caused to interact with its surroundings so as to interchange energy in the forms of heat and work and so to produce in the system changes considered desirable for one reason or another. A process that proceeds so that the system is never displaced more than differentially from an equilibrium state is said to be *reversible,* because such a process can be reversed at any point by an infinitesimal change in external conditions, causing it to retrace the initial path in the opposite direction.

Thermodynamics finds its origin in experience and experiment, from which are formulated a few postulates that form the foundation of the subject. The first two deal with energy:

POSTULATE 1

There exists a form of energy, known as **internal energy,** *which for systems at internal equilibrium is an intrinsic property of the system, functionally related to its characteristic coordinates.*

POSTULATE 2 (FIRST LAW OF THERMODYNAMICS)

The **total** *energy of any system and its surroundings is conserved.*

Internal energy is quite distinct from such external forms as the kinetic and potential energies of macroscopic bodies. Although a macroscopic property characterized by the macroscopic coordinates T and P, internal energy finds its origin in the kinetic and potential energies of molecules and submolecular particles. In applications of the first law of thermodynamics, all forms of energy must be considered, including the internal energy. It is therefore clear that Postulate 2 depends on Postulate 1. For an isolated system, the first law requires that its energy be constant. For a closed (but not isolated) system, the first law requires that energy changes of the system be exactly compensated by energy changes in the surroundings. Energy is exchanged between such a system and its surroundings in two forms: heat and work.

Heat is energy crossing the system boundary under the influence of a temperature difference or gradient. A quantity of heat Q represents an amount of energy in transit between a system and its surroundings, and is not a property of the system. The convention with respect to sign makes numerical values of Q positive when heat is added to the system and negative when heat leaves the system.

Work is again energy in transit between a system and its surroundings, but resulting from the displacement of an external force acting on the system. Like heat, a quantity of work W represents an amount of energy, and is not a property of the system. The sign convention, analogous to that for heat, makes numerical values of W positive when work is done on the system by the surroundings and negative when work is done on the surroundings by the system.

When applied to closed (constant-mass) systems for which the only form of energy that changes is the internal energy, the first law of thermodynamics is expressed mathematically as

$$dU^t = dQ + dW \tag{4-1}$$

where U^t is the total internal energy of the system. Note that dQ and dW, differential *quantities* representing energy exchanges between the system and its surroundings, serve to account for the energy change of the surroundings. On the other hand, dU^t is directly the differential *change* in internal energy of the system. Integration of Eq. (4-1) gives for a finite process

$$\Delta U^t = Q + W \tag{4-2}$$

where ΔU^t is the finite change given by the difference between the final and initial values of U^t. The heat Q and work W are finite quantities of heat and work; they are not properties of the system nor functions of the thermodynamic coordinates that characterize the system.

POSTULATE 3

There exists a property called **entropy,** *which for systems at internal equilibrium is an intrinsic property of the system, functionally related to the measurable coordinates which characterize the system. For* **reversible** *processes, changes in this property may be calculated by the equation:*

$$dS^t = dQ_{\text{rev}}/T \tag{4-3}$$

where S^t is the total entropy of the system and T is the absolute temperature of the system.

POSTULATE 4 (SECOND LAW OF THERMODYNAMICS)

The entropy change of any system and its surroundings, **considered together,** *resulting from any real process is positive, approaching zero when the process approaches reversibility.*

In the same way that the first law of thermodynamics cannot be formulated without the prior recognition of internal energy as a property, so also the second law can have no complete and quantitative expression without a prior assertion of the existence of entropy as a property.

The second law requires that the entropy of an isolated system either increase or, in the limit, where the system has reached an equilibrium state, remain constant. For a closed (but not isolated) system it requires that any entropy decrease in either the system or its surroundings be more than compensated by an entropy increase in the other part or that in the limit, where the process is reversible, the total entropy of the system plus its surroundings be constant.

The fundamental thermodynamic properties that arise in connection with the first and second laws of thermodynamics are internal energy and entropy. These properties, together with the two laws for which they are essential, apply to all types of systems. However, different types of systems are characterized by different sets of measurable coordinates or variables. The type of system most commonly encountered in chemical technology is one for which the primary characteristic variables are temperature T, pressure P, molar volume V, and composition, not all of which are necessarily independent. Such systems are usually made up of fluids (liquid or gas) and are called *PVT* systems.

For closed systems of this kind, the work of a *reversible* process may always be calculated from

$$dW_{\text{rev}} = -P\,dV^t \tag{4-4}$$

where P is the absolute pressure and V^t is the total volume of the system. This equation follows directly from the definition of mechanical work.

POSTULATE 5

The macroscopic properties of homogeneous PVT systems at internal equilibrium can be expressed as functions of temperature, pressure, and composition only.

This postulate imposes an idealization, and is the basis for all subsequent property relations for *PVT* systems. The *PVT* system serves as a satisfactory model in an enormous number of practical applications. In accepting this model one assumes that the effects of fields (e.g., electric, magnetic, or gravitational) are negligible and that surface and viscous-shear effects are unimportant.

Temperature, pressure, and composition are thermodynamic coordinates representing conditions imposed upon or exhibited by the system, and the functional dependence of the thermodynamic properties on these conditions is determined by experiment. This is quite direct for molar or specific volume V, which can be measured, and leads immediately to the conclusion that there exists an *equation of state* relating molar volume to temperature, pressure, and composition for any particular homogeneous *PVT* system. The equation of state is a primary tool in applications of thermodynamics.

Postulate 5 affirms that the other molar or specific thermodynamic properties of *PVT* systems, such as internal energy U and entropy S, are also functions of temperature, pressure, and composition. These molar or unit-mass properties, represented by the plain symbols V, U, and S, are independent of system size and are called *intensive.* Temperature, pressure, and the composition variables, such as mole fraction, are also intensive. Total-system properties (V^t, U^t, S^t) do depend on system size, and are *extensive.* For a system containing n moles of fluid, $M^t = nM$, where M is a molar property.

Applications of the thermodynamic postulates necessarily involve the abstract quantities internal energy and entropy. The solution of any problem in applied thermodynamics is therefore found through these quantities.

VARIABLES, DEFINITIONS, AND RELATIONSHIPS

Consider a single-phase closed system in which there are no chemical reactions. Under these restrictions the composition is fixed. If such a system undergoes a differential, reversible process, then by Eq. (4-1)

$$dU^t = dQ_{\text{rev}} + dW_{\text{rev}}$$

Substitution for dQ_{rev} and dW_{rev} by Eqs. (4-3) and (4-4) gives

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

Although derived for a *reversible* process, this equation relates properties only and is valid for *any* change between equilibrium states in a closed system. It may equally well be written

$$d(nU) = T\,d(nS) - P\,d(nV) \tag{4-5}$$

where n is the number of moles of fluid in the system and is constant for the special case of a closed, nonreacting system. Note that

$$n \equiv n_1 + n_2 + n_3 + \cdots = \sum_i n_i$$

where i is an index identifying the chemical species present. When U, S, and V represent *specific* (unit-mass) properties, n is replaced by m.

Equation (4-5) shows that for the single-phase, nonreacting, closed system specified,

$$nU = u(nS,\, nV)$$

Then $$d(nU) = \left[\frac{\partial(nU)}{\partial(nS)}\right]_{nV,n} d(nS) + \left[\frac{\partial(nU)}{\partial(nV)}\right]_{nS,n} d(nV)$$

where the subscript n indicates that all mole numbers n_i (and hence n) are held constant. Comparison with Eq. (4-5) shows that

$$\left[\frac{\partial(nU)}{\partial(nS)}\right]_{nV,n} = T \tag{4-6}$$

$$\left[\frac{\partial(nU)}{\partial(nV)}\right]_{nS,n} = -P \tag{4-7}$$

Consider now an *open* system consisting of a single phase and assume that

$$nU = \mathcal{U}(nS, nV, n_1, n_2, n_3, \ldots)$$

Then

$$d(nU) = \left[\frac{\partial(nU)}{\partial(nS)}\right]_{nV,n} d(nS) + \left[\frac{\partial(nU)}{\partial(nV)}\right]_{nS,n} d(nV) + \sum_i \left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_j} dn_i$$

where the summation is over all species present in the system and subscript n_j indicates that all mole numbers are held constant except the ith. Let

$$\mu_i \equiv \left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_j}$$

Together with Eqs. (4-6) and (4-7), this definition allows elimination of all the partial differential coefficients from the preceding equation:

$$d(nU) = T\,d(nS) - P\,d(nV) + \sum_i \mu_i\,dn_i \tag{4-8}$$

Equation (4-8) is the **fundamental property relation** for single-phase *PVT* systems, from which all other equations connecting properties of such systems are derived. The quantity μ_i is called the *chemical potential* of species i, and it plays a vital role in the thermodynamics of phase and chemical equilibria.

Additional property relations follow directly from Eq. (4-8). Since $n_i = x_i n$, where x_i is the mole fraction of species i, this equation may be rewritten:

$$d(nU) - T\,d(nS) + P\,d(nV) - \sum_i \mu_i\,d(x_i n) = 0$$

Upon expansion of the differentials and collection of like terms, this becomes

$$\left[dU - T\,dS + P\,dV - \sum_i \mu_i\,dx_i\right] n + \left[U - TS + PV - \sum_i x_i\mu_i\right] dn = 0$$

Since n and dn are independent and arbitrary, the terms in brackets must separately be zero. Then

$$dU = T\,dS - P\,dV + \sum_i \mu_i\,dx_i \tag{4-9}$$

$$U = TS - PV + \sum_i x_i\mu_i \tag{4-10}$$

Equations (4-8) and (4-9) are similar, but there is an important difference. Equation (4-8) applies to a system of n moles where n may vary; whereas Eq. (4-9) applies to a system in which n is unity and invariant. Thus Eq. (4-9) is subject to the constraint that $\sum_i x_i = 1$ or that $\sum_i dx_i = 0$. In this equation the x_i are not independent variables, whereas the n_i in Eq. (4-8) are.

Equation (4-10) dictates the possible combinations of terms that may be defined as additional primary functions. Those in common use are:

Enthalpy	$H \equiv U + PV$	(4-11)
Helmholtz energy	$A \equiv U - TS$	(4-12)
Gibbs energy	$G \equiv U + PV - TS = H - TS$	(4-13)

Additional thermodynamic properties are related to these and arise by arbitrary definition. Multiplication of Eq. (4-11) by n and differentiation yields the general expression:

$$d(nH) = d(nU) + P\,d(nV) + nV\,dP$$

Substitution for $d(nU)$ by Eq. (4-8) reduces this result to:

$$d(nH) = T\,d(nS) + nV\,dP + \sum_i \mu_i\,dn_i \tag{4-14}$$

The total differentials of nA and nG are obtained similarly:

$$d(nA) = -nS\,dT - P\,d(nV) + \sum_i \mu_i\,dn_i \tag{4-15}$$

$$d(nG) = -nS\,dT + nV\,dP + \sum_i \mu_i\,dn_i \tag{4-16}$$

Equations (4-8) and (4-14) through (4-16) are equivalent forms of the fundamental property relation. Each expresses a property nU, nH, and so on, as a function of a particular set of independent variables; these are the *canonical variables* for the property. The choice of which equation to use in a particular application is dictated by convenience. However, the Gibbs energy G is special, because of its unique functional relation to T, P, and the n_i, which are the variables of primary interest in chemical processing. A similar set of equations is developed from Eq. (4-9). This set also follows from the preceding set when $n = 1$ and $n_i = x_i$. The two sets are related exactly as Eq. (4-8) is related to Eq. (4-9). The equations written for $n = 1$ are, of course, less general. Furthermore, the interdependence of the x_i precludes those mathematical operations which depend on independence of these variables.

CONSTANT-COMPOSITION SYSTEMS

For 1 mole of a homogeneous fluid of constant composition Eqs. (4-8) and (4-14) through (4-16) simplify to:

$$dU = T\,dS - P\,dV \tag{4-17}$$

$$dH = T\,dS + V\,dP \tag{4-18}$$

$$dA = -S\,dT - P\,dV \tag{4-19}$$

$$dG = -S\,dT + V\,dP \tag{4-20}$$

Implicit in these are the following:

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \tag{4-21}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T \tag{4-22}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \tag{4-23}$$

$$-S = \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P \tag{4-24}$$

In addition, the common Maxwell equations result from application of the reciprocity relation for exact differentials:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{4-25}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{4-26}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{4-27}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \tag{4-28}$$

In all these equations the partial derivatives are taken with composition held constant.

Enthalpy and Entropy as Functions of T and P At constant composition the molar thermodynamic properties are functions of temperature and pressure (Postulate 5). Thus

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{4-29}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{4-30}$$

The obvious next step is to eliminate the partial-differential coefficients in favor of measurable quantities.

The *heat capacity at constant pressure* is defined for this purpose:

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P \tag{4-31}$$

It is a property of the material and a function of temperature, pressure, and composition.

Equation (4-18) may first be divided by dT and restricted to constant pressure, and then be divided by dP and restricted to constant temperature, yielding the two equations:

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

In view of Eq. (4-31), the first of these becomes

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \tag{4-32}$$

and in view of Eq. (4-28), the second becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{4-33}$$

Combination of Eqs. (4-29), (4-31), and (4-33) gives

$$dH = C_P\,dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \tag{4-34}$$

and in combination Eqs. (4-30), (4-32), and (4-28) yield

$$dS = \frac{C_P}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP \tag{4-35}$$

Equations (4-34) and (4-35) are general expressions for the enthalpy and entropy of homogeneous fluids *at constant composition* as functions of T and P. The coefficients of dT and dP are expressed in terms of measurable quantities.

Internal Energy and Entropy as Functions of *T* and *V* Because V is related to T and P through an equation of state, V rather than P can serve as an independent variable. In this case the internal energy and entropy are the properties of choice; whence

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{4-36}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{4-37}$$

The procedure now is analogous to that of the preceding section.

Define the *heat capacity at constant volume* by

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \tag{4-38}$$

It is a property of the material and a function of temperature, pressure, and composition.

Two relations follow immediately from Eq. (4-17):

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

As a result of Eq. (4-38) the first of these becomes

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{4-39}$$

and as a result of Eq. (4-27), the second becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{4-40}$$

Combination of Eqs. (4-36), (4-38), and (4-40) gives

$$dU = C_V\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV \tag{4-41}$$

and Eqs. (4-37), (4-39), and (4-27) together yield

$$dS = \frac{C_V}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_V dV \tag{4-42}$$

Equations (4-41) and (4-42) are general expressions for the internal energy and entropy of homogeneous fluids *at constant composition* as functions of temperature and molar volume. The coefficients of dT and dV are expressed in terms of measurable quantities.

Heat-Capacity Relations In Eqs. (4-34) and (4-41) both dH and dU are exact differentials, and application of the reciprocity relation leads to

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{4-43}$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \tag{4-44}$$

Thus, the pressure or volume dependence of the heat capacities may be determined from PVT data. The temperature dependence of the heat capacities is, however, determined empirically and is often given by equations such as

$$C_P = \alpha + \beta T + \gamma T^2$$

Equations (4-35) and (4-42) both provide expressions for dS, which must be equal for the same change of state. Equating them and solving for dT gives

$$dT = \frac{T}{C_P - C_V}\left(\frac{\partial V}{\partial T}\right)_P dP + \frac{T}{C_P - C_V}\left(\frac{\partial P}{\partial T}\right)_V dV$$

However, at constant composition $T = T(P,V)$, and

$$dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV$$

Equating coefficients of either dP or dV in these two expressions for dT gives

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V \tag{4-45}$$

Thus the *difference* between the two heat capacities may be determined from PVT data.

Division of Eq. (4-32) by Eq. (4-39) yields the *ratio* of these heat capacities:

$$\frac{C_P}{C_V} = \frac{(\partial S/\partial T)_P}{(\partial S/\partial T)_V} = \frac{(\partial S/\partial V)_P(\partial V/\partial T)_P}{(\partial S/\partial P)_V(\partial P/\partial T)_V}$$

Replacement of each of the four partial derivatives through the appropriate Maxwell relation gives finally

$$\gamma \equiv \frac{C_P}{C_V} = \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial V}\right)_S \tag{4-46}$$

where γ is the symbol conventionally used to represent the heat-capacity ratio.

The Ideal Gas The simplest equation of state is the ideal gas equation:

$$PV = RT$$

where R is a universal constant, values of which are given in Table 1-9. The following partial derivatives are obtained from the ideal gas equation:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} = \frac{P}{T} \qquad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} = \frac{V}{T} \qquad \left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}$$

The general equations for constant-composition fluids derived in the preceding subsections reduce to very simple forms when the relations for an ideal gas are substituted into them:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T = 0$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{R}{P} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{V}$$

$$dU = C_V\,dT$$

$$dH = C_P\, dT$$

$$dS = \left(\frac{C_V}{T}\right) dT + \left(\frac{R}{V}\right) dV$$

$$dS = \left(\frac{C_P}{T}\right) dT - \left(\frac{R}{P}\right) dP$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial C_P}{\partial P}\right)_T = 0$$

$$C_P - C_V = R \qquad \gamma \equiv \frac{C_P}{C_V} = -\left(\frac{\partial \ln P}{\partial \ln V}\right)_S$$

These equations clearly show that for an ideal gas U, H, C_P, and C_V are functions of temperature only and are independent of P and V. The entropy of an ideal gas, however, is a function of both T and P or of both T and V.

SYSTEMS OF VARIABLE COMPOSITION

The composition of a system may vary because the system is open or because of chemical reactions even in a closed system. The equations developed here apply regardless of the cause of composition changes.

Partial Molar Properties Consider a homogeneous fluid solution comprised of any number of chemical species. For such a PVT system let the symbol M represent the molar (or unit-mass) value of any extensive thermodynamic property of the solution, where M may stand in turn for U, H, S, and so on. A total-system property is then nM, where $n = \sum_i n_i$ and i is the index identifying chemical species. One might expect the solution property M to be related solely to the properties M_i of the pure chemical species which comprise the solution. However, no such generally valid relation is known, and the connection must be established experimentally for every specific system.

Although the chemical species which make up a solution do not in fact have separate properties of their own, a solution property may be arbitrarily apportioned among the individual species. Once an apportioning recipe is adopted, then the assigned property values are quite logically treated as though they were indeed properties of the species in solution, and reasoning on this basis leads to valid conclusions.

For a homogeneous PVT system, Postulate 5 requires that

$$nM = \mathcal{M}(T, P, n_1, n_2, n_3, \ldots)$$

The total differential of nM is therefore

$$d(nM) = \left[\frac{\partial(nM)}{\partial T}\right]_{P,n} dT + \left[\frac{\partial(nM)}{\partial P}\right]_{T,n} dP + \sum_i \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j} dn_i$$

where subscript n indicates that all mole numbers n_i are held constant, and subscript n_j signifies that all mole numbers are held constant except the ith. This equation may also be written

$$d(nM) = n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \sum_i \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j} dn_i$$

where subscript x indicates that all mole fractions are held constant. The derivatives in the summation are called *partial molar properties* $\overline{M}_i$; by definition,

$$\overline{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j} \tag{4-47}$$

The basis for calculation of partial properties from solution properties is provided by this equation. Moreover, the preceding equation becomes

$$d(nM) = n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \sum_i \overline{M}_i\, dn_i \tag{4-48}$$

Important equations follow from this result through the relations:

$$d(nM) = n\, dM + M\, dn$$
$$dn_i = d(x_i n) = x_i\, dn + n\, dx_i$$

Combining these expressions with Eq. (4-48) and collecting like terms gives

$$\left[dM - \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \sum_i \overline{M}_i\, dx_i\right] n + \left[M - \sum_i \overline{M}_i\, x_i\right] dn = 0$$

Since n and dn are independent and arbitrary, the terms in brackets must separately be zero; whence

$$dM = \left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \sum_i \overline{M}_i\, dx_i \tag{4-49}$$

and

$$M = \sum_i x_i \overline{M}_i \tag{4-50}$$

Equation (4-49) is merely a special case of Eq. (4-48); however, Eq. (4-50) is a vital new relation. Known as the *summability equation*, it provides for the calculation of solution properties from partial properties. Thus, a solution property apportioned according to the recipe of Eq. (4-47) may be recovered simply by adding the properties attributed to the individual species, each weighted by its mole fraction in solution. The equations for partial molar properties are also valid for partial specific properties, in which case m replaces n and the x_i are mass fractions. Equation (4-47) applied to the definitions of Eqs. (4-11) through (4-13) yields the partial-property relations:

$$\overline{H}_i = \overline{U}_i + P\overline{V}_i$$
$$\overline{A}_i = \overline{U}_i - T\overline{S}_i$$
$$\overline{G}_i = \overline{H}_i - T\overline{S}_i$$

Pertinent examples on partial molar properties are presented in Smith, Van Ness, and Abbott (*Introduction to Chemical Engineering Thermodynamics*, 5th ed., Sec. 10.3, McGraw-Hill, New York, 1996).

Gibbs/Duhem Equation Differentiation of Eq. (4-50) yields

$$dM = \sum_i x_i\, d\overline{M}_i + \sum_i \overline{M}_i\, dx_i$$

Since this equation and Eq. (4-49) are both valid in general, their right-hand sides can be equated, yielding

$$\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \sum_i x_i\, d\overline{M}_i = 0 \tag{4-51}$$

This general result, the Gibbs/Duhem equation, imposes a constraint on how the partial molar properties of any phase may vary with temperature, pressure, and composition. For the special case where T and P are constant:

$$\sum_i x_i\, d\overline{M}_i = 0 \qquad \text{(constant } T, P) \tag{4-52}$$

Symbol M may represent the molar value of any extensive thermodynamic property; for example, V, U, H, S, or G. When $M \equiv H$, the derivatives $(\partial H/\partial T)_P$ and $(\partial H/\partial P)_T$ are given by Eqs. (4-31) and (4-33). Equations (4-49), (4-50), and (4-51) then become

$$dH = C_P\, dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,x}\right] dP + \sum_i \overline{H}_i\, dx_i \tag{4-53}$$

$$H = \sum_i x_i \overline{H}_i \tag{4-54}$$

$$C_P\, dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,x}\right] dP - \sum_i x_i\, d\overline{H}_i = 0 \tag{4-55}$$

Similar equations are readily derived when M takes on other identities.

Equation (4-47), which defines a partial molar property, provides a general means by which partial property values may be determined. However, for a *binary* solution an alternative method is useful. Equation (4-50) for a binary solution is

$$M = x_1\, \overline{M}_1 + x_2\, \overline{M}_2 \tag{4-56}$$

Moreover, the Gibbs/Duhem equation for a solution at given T and P, Eq. (4-52), becomes

$$x_1\, d\overline{M}_1 + x_2\, d\overline{M}_2 = 0 \tag{4-57}$$

These two equations can be combined to give

$$\overline{M}_1 = M + x_2 \frac{dM}{dx_1} \tag{4-58a}$$

$$\overline{M}_2 = M - x_1 \frac{dM}{dx_1} \tag{4-58b}$$

Thus for a binary solution, the partial properties are given directly as functions of composition for given T and P. For multicomponent solutions such calculations are complex, and direct use of Eq. (4-47) is appropriate.

Partial Molar Gibbs Energy Implicit in Eq. (4-16) is the relation

$$\mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_j}$$

In view of Eq. (4-47), the chemical potential and the partial molar Gibbs energy are therefore identical:

$$\mu_i = \overline{G}_i \tag{4-59}$$

The reciprocity relation for an exact differential applied to Eq. (4-16) produces not only the Maxwell relation, Eq. (4-28), but also two other useful equations:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \left[\frac{\partial(nV)}{\partial n_i}\right]_{T,P,n_j} = \overline{V}_i \tag{4-60}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} = -\left[\frac{\partial(nS)}{\partial n_i}\right]_{T,P,n_j} = -\overline{S}_i \tag{4-61}$$

In a solution of constant composition, $\mu_i = \mu(T,P)$; whence

$$d\mu_i \equiv d\overline{G}_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} dP$$

or

$$d\overline{G}_i = -\overline{S}_i\, dT + \overline{V}_i\, dP \tag{4-62}$$

Comparison with Eq. (4-20) provides an example of the parallelism that exists between the equations for a constant-composition solution and those for the corresponding partial properties. This parallelism exists whenever the solution properties in the parent equation are related linearly (in the algebraic sense). Thus, in view of Eqs. (4-17), (4-18), and (4-19):

$$d\overline{U}_i = T\, d\overline{S}_i - P\, d\overline{V}_i \tag{4-63}$$

$$d\overline{H}_i = T\, d\overline{S}_i + \overline{V}_i\, dP \tag{4-64}$$

$$d\overline{A}_i = -\overline{S}_i\, dT - P\, d\overline{V}_i \tag{4-65}$$

Note that these equations hold only for species in a constant-composition solution.

The following equation is a mathematical identity:

$$d\left(\frac{nG}{RT}\right) \equiv \frac{1}{RT}\, d(nG) - \frac{nG}{RT^2}\, dT$$

Substitution for $d(nG)$ by Eq. (4-16) and for G by $H - TS$ (Eq. [4-13]) gives, after algebraic reduction,

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT}\, dP - \frac{nH}{RT^2}\, dT + \sum_i \frac{\mu_i}{RT}\, dn_i \tag{4-66}$$

Equation (4-66) is a useful alternative to the fundamental property relation given by Eq. (4-16). All terms in this equation have the units of moles; moreover, the enthalpy rather than the entropy appears on the right-hand side.

The Ideal Gas State and the Compressibility Factor The simplest equation of state for a PVT system is the ideal gas equation:

$$PV^{ig} = RT$$

where V^{ig} is the ideal-gas–state molar volume. Similarly, H^{ig}, S^{ig}, and G^{ig} are ideal gas–state values; that is, the molar enthalpy, entropy, and Gibbs energy values that a PVT system would have were the ideal gas equation the correct equation of state. These quantities provide reference values to which actual values may be compared. For example, the compressibility factor Z compares the true molar volume to the ideal gas molar volume as a ratio:

$$Z = \frac{V}{V^{ig}} = \frac{V}{RT/P} = \frac{PV}{RT}$$

Generalized correlations for the compressibility factor are treated in Sec. 2.

Residual Properties These quantities compare true and ideal gas properties through differences:

$$M^R \equiv M - M^{ig} \tag{4-67}$$

where M is the molar value of an extensive thermodynamic property of a fluid in its actual state and M^{ig} is the corresponding value for the ideal gas state of the fluid at the same T, P, and composition. Residual properties depend on interactions *between* molecules and not on characteristics of individual molecules. Since the ideal gas state presumes the absence of molecular interactions, residual properties reflect deviations from ideality. Most commonly used of the residual properties are:

Residual volume	$V^R \equiv V - V^{ig}$
Residual enthalpy	$H^R \equiv H - H^{ig}$
Residual entropy	$S^R \equiv S - S^{ig}$
Residual Gibbs energy	$G^R \equiv G - G^{ig}$

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IDEAL GAS MIXTURES

An ideal gas is a model gas comprising imaginary molecules of zero volume that do not interact. Each chemical species in an ideal gas mixture therefore has its own private properties, uninfluenced by the presence of other species. The *partial pressure* of species i in a gas mixture is defined as

$$p_i = x_i P \qquad (i = 1, 2, \ldots, N)$$

where x_i is the mole fraction of species i. The sum of the partial pressures clearly equals the total pressure. *Gibbs' theorem* for a mixture of ideal gases may be stated as follows:

> The partial molar property, other than the volume, of a constituent species in an ideal gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture.

This is expressed mathematically for generic partial property $\overline{M}_i^{ig}$ by the equation

$$\overline{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i) \quad (M \neq V) \tag{4-68}$$

For those properties of an ideal gas that are independent of P, for example, U, H, and C_P, this becomes simply

$$\overline{M}_i^{ig} = M_i^{ig}$$

where M_i^{ig} is evaluated at the *mixture T and P*. Thus, for the enthalpy,

$$\overline{H}_i^{ig} = H_i^{ig} \tag{4-69}$$

The entropy of an ideal gas *does* depend on pressure:

$$dS_i^{ig} = -R\, d \ln P \qquad (\text{constant } T)$$

Integration from p_i to P gives

$$S_i^{ig}(T, P) - S_i^{ig}(T, p_i) = -R \ln \frac{P}{p_i} = -R \ln \frac{P}{x_i P} = R \ln x_i$$

Whence

$$S_i^{ig}(T, p_i) = S_i^{ig}(T, P) - R \ln x_i$$

Substituting this result into Eq. (4-68) written for the entropy gives

$$\bar{S}_i^{ig} = S_i^{ig} - R \ln x_i \tag{4-70}$$

where S_i^{ig} is evaluated at the mixture T and P.

For the Gibbs energy of an ideal gas mixture, $G^{ig} = H^{ig} - TS^{ig}$; the parallel relation for partial properties is

$$\bar{G}_i^{ig} = \bar{H}_i^{ig} - T\bar{S}_i^{ig}$$

In combination with Eqs. (4-69) and (4-70), this becomes

$$\bar{G}_i^{ig} = \bar{H}_i^{ig} - TS_i^{ig} + RT \ln x_i$$

or

$$\mu_i^{ig} \equiv \bar{G}_i^{ig} = G_i^{ig} + RT \ln x_i \tag{4-71}$$

Elimination of G_i^{ig} from this equation is accomplished by Eq. (4-20), written for pure species i as:

$$dG_i^{ig} = V_i^{ig}\, dP = \frac{RT}{P}\, dP = RT\, d \ln P \qquad \text{(constant } T\text{)}$$

Integration gives

$$G_i^{ig} = \Gamma_i(T) + RT \ln P \tag{4-72}$$

where $\Gamma_i(T)$, the integration constant for a given temperature, is a function of temperature only. Equation (4-71) now becomes

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln x_i P \tag{4-73}$$

FUGACITY AND FUGACITY COEFFICIENT

The chemical potential μ_i plays a vital role in both phase and chemical-reaction equilibria. However, the chemical potential exhibits certain unfortunate characteristics which discourage its use in the solution of practical problems. The Gibbs energy, and hence μ_i, is defined in relation to the internal energy and entropy, both primitive quantities for which absolute values are unknown. Moreover, μ_i approaches negative infinity when either P or x_i approaches zero. While these characteristics do not preclude the use of chemical potentials, the application of equilibrium criteria is facilitated by introduction of the *fugacity*, a quantity that takes the place of μ_i but which does not exhibit its less desirable characteristics.

The origin of the fugacity concept resides in Eq. (4-72), an equation valid only for pure species i in the ideal gas state. For a *real* fluid, an analogous equation is written:

$$G_i \equiv \Gamma_i(T) + RT \ln f_i \tag{4-74}$$

in which a new property f_i replaces the pressure P. This equation serves as a partial definition of the *fugacity* f_i.

Subtraction of Eq. (4-72) from Eq. (4-74), both written for the same temperature and pressure, gives

$$G_i - G_i^{ig} = RT \ln \frac{f_i}{P}$$

According to the definition of Eq. (4-67), $G_i - G_i^{ig}$ is the residual Gibbs energy, G_i^R. The dimensionless ratio f_i/P is another new property called the *fugacity coefficient* ϕ_i. Thus,

$$G_i^R = RT \ln \phi_i \tag{4-75}$$

where

$$\phi_i \equiv \frac{f_i}{P} \tag{4-76}$$

The definition of fugacity is completed by setting the ideal-gas–state fugacity of pure species i equal to its pressure:

$$f_i^{ig} = P$$

Thus, for the special case of an ideal gas, $G_i^R = 0$, $\phi_i = 1$, and Eq. (4-72) is recovered from Eq. (4-74).

The definition of the fugacity of a species in solution is parallel to the definition of the pure-species fugacity. An equation analogous to the ideal gas expression, Eq. (4-73), is written for species i in a fluid mixture:

$$\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i \tag{4-77}$$

where the partial pressure $x_i P$ is replaced by $\hat{f}_i$, the fugacity of species i in solution. Since it is not a partial molar property, it is identified by a circumflex rather than an overbar.

Subtracting Eq. (4-73) from Eq. (4-77), both written for the same temperature, pressure, and composition, yields

$$\mu_i - \mu_i^{ig} = RT \ln \frac{\hat{f}_i}{x_i P}$$

Analogous to the defining equation for the residual Gibbs energy of a mixture, $G^R \equiv G - G^{ig}$, is the definition of a partial molar residual Gibbs energy:

$$\bar{G}_i^R \equiv \bar{G}_i - \bar{G}_i^{ig} = \mu_i - \mu_i^{ig}$$

Therefore

$$\bar{G}_i^R = RT \ln \hat{\phi}_i \tag{4-78}$$

where by definition

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{x_i P} \tag{4-79}$$

The dimensionless ratio $\hat{\phi}_i$ is called the *fugacity coefficient of species i in solution.*

Eq. (4-78) is the analog of Eq. (4-75), which relates ϕ_i to G_i^R. For an ideal gas, $\bar{G}_i^R$ is necessarily 0; therefore $\hat{\phi}_i^{ig} = 1$, and

$$\hat{f}_i^{ig} = x_i P$$

Thus, the fugacity of species i in an ideal gas mixture is equal to its partial pressure.

Pertinent examples are given in Smith, Van Ness, and Abbott (*Introduction to Chemical Engineering Thermodynamics*, 5th ed., Secs. 10.5–10.7, McGraw-Hill, New York, 1996).

FUNDAMENTAL RESIDUAL-PROPERTY RELATION

In view of Eq. (4-59), the fundamental property relation given by Eq. (4-66) may be written

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT}\, dP - \frac{nH}{RT^2}\, dT + \sum_i \frac{\bar{G}_i}{RT}\, dn_i \tag{4-80}$$

This equation is general, and may be written for the special case of an ideal gas:

$$d\left(\frac{nG^{ig}}{RT}\right) = \frac{nV^{ig}}{RT}\, dP - \frac{nH^{ig}}{RT^2}\, dT + \sum_i \frac{\bar{G}_i^{ig}}{RT}\, dn_i$$

Subtraction of this equation from Eq. (4-80) gives

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}\, dP - \frac{nH^R}{RT^2}\, dT + \sum_i \frac{\bar{G}_i^R}{RT}\, dn_i \tag{4-81}$$

where the definitions $G^R \equiv G - G^{ig}$ and $\bar{G}_i^R \equiv \bar{G}_i - \bar{G}_i^{ig}$ have been imposed. Equation (4-81) is the *fundamental residual-property relation.* An alternative form follows by introduction of the fugacity coefficient as given by Eq. (4-78):

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}\, dP - \frac{nH^R}{RT^2}\, dT + \sum_i \ln \hat{\phi}_i\, dn_i \tag{4-82}$$

These equations are of such generality that for practical application they are used only in restricted forms. Division of Eq. (4-82) by dP and restriction to constant T and composition leads to:

$$\frac{V^R}{RT} = \left[\frac{\partial(G^R/RT)}{\partial P}\right]_{T,x} \tag{4-83}$$

Similarly, division by dT and restriction to constant P and composition gives

$$\frac{H^R}{RT} = -T\left[\frac{\partial(G^R/RT)}{\partial T}\right]_{P,x} \tag{4-84}$$

Also implicit in Eq. (4-82) is the relation

$$\ln \hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{T,P,n_j} \tag{4-85}$$

This equation demonstrates that $\ln \hat{\phi}_i$ is a partial property with respect to G^R/RT. The partial-property analogs of Eqs. (4-83) and (4-84) are therefore:

$$\left(\frac{\partial \ln \hat{\phi}_i}{\partial P}\right)_{T,x} = \frac{\bar{V}_i^R}{RT} \tag{4-86}$$

$$\left(\frac{\partial \ln \hat{\phi}_i}{\partial T}\right)_{P,x} = -\frac{\bar{H}_i^R}{RT^2} \tag{4-87}$$

The partial-property relationship of $\ln \hat{\phi}_i$ to G^R/RT also means that the summability relation applies; thus

$$\frac{G^R}{RT} = \sum_i x_i \ln \hat{\phi}_i \tag{4-88}$$

THE IDEAL SOLUTION

The ideal gas is a useful model of the behavior of gases and serves as a standard to which real gas behavior can be compared. This is formalized by the introduction of residual properties. Another useful model is the *ideal solution,* which serves as a standard to which real solution behavior can be compared. This is formalized by introduction of *excess properties.*

The partial molar Gibbs energy of species i in an ideal gas mixture is given by Eq. (4-71). This equation takes on new meaning when G_i^{ig}, the Gibbs energy of pure species i in the ideal gas state, is replaced by G_i, the Gibbs energy of pure species i as it actually exists at the mixture T and P and in the same physical state (*real* gas, liquid, or solid) as the mixture. It then becomes applicable to species in real solutions; indeed, to liquids and solids as well as to gases. The ideal solution is therefore *defined* as one for which

$$\bar{G}_i^{id} \equiv G_i + RT \ln x_i \tag{4-89}$$

where superscript *id* denotes an ideal-solution property.

This equation is the basis for development of expressions for all other thermodynamic properties of an ideal solution. Equations (4-60) and (4-61), applied to an ideal solution with μ_i replaced by $\bar{G}_i$, can be written

$$\bar{V}_i^{id} = \left(\frac{\partial \bar{G}_i^{id}}{\partial P}\right)_{T,x} \qquad \text{and} \qquad \bar{S}_i^{id} = -\left(\frac{\partial \bar{G}_i^{id}}{\partial T}\right)_{P,x}$$

Appropriate differentiation of Eq. (4-89) in combination with these relations and Eqs. (4-23) and (4-24) yields

$$\bar{V}_i^{id} = V_i \tag{4-90}$$

$$\bar{S}_i^{id} = S_i - R \ln x_i \tag{4-91}$$

Since $\bar{H}_i^{id} = \bar{G}_i^{id} + T\bar{S}_i^{id}$, substitutions by Eqs. (4-89) and (4-91) yield

$$\bar{H}_i^{id} = H_i \tag{4-92}$$

The summability relation, Eq. (4-50), written for the special case of an ideal solution, may be applied to Eqs. (4-89) through (4-92):

$$G^{id} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i \tag{4-93}$$

$$V^{id} = \sum_i x_i V_i \tag{4-94}$$

$$S^{id} = \sum_i x_i S_i - R \sum_i x_i \ln x_i \tag{4-95}$$

$$H^{id} = \sum_i x_i H_i \tag{4-96}$$

A simple equation for the fugacity of a species in an ideal solution follows from Eq. (4-89). Written for the special case of species i in an ideal solution, Eq. (4-77) becomes

$$\mu_i^{id} \equiv \bar{G}_i^{id} = \Gamma_i(T) + RT \ln \hat{f}_i^{id}$$

When this equation and Eq. (4-74) are combined with Eq. (4-89), $\Gamma_i(T)$ is eliminated, and the resulting expression reduces to

$$\hat{f}_i^{id} = x_i f_i \tag{4-97}$$

This equation, known as the *Lewis/Randall rule,* applies to each species in an ideal solution at all conditions of T, P, and composition. It shows that the fugacity of each species in an ideal solution is proportional to its mole fraction; the proportionality constant is the fugacity of *pure* species i in the same physical state as the solution and at the same T and P. Division of both sides of Eq. (4-97) by x_iP and substitution of $\hat{\phi}_i^{id}$ for $\hat{f}_i^{id}/x_iP$ (Eq. [4-79]) and of ϕ_i for f_i/P (Eq. [4-76]) gives an alternative form:

$$\hat{\phi}_i^{id} = \phi_i \tag{4-98}$$

Thus, the fugacity coefficient of species i in an ideal solution is equal to the fugacity coefficient of *pure* species i in the same physical state as the solution and at the same T and P.

Ideal solution behavior is often approximated by solutions comprised of molecules not too different in size and of the same chemical nature. Thus, a mixture of isomers conforms very closely to ideal solution behavior. So do mixtures of adjacent members of a homologous series.

FUNDAMENTAL EXCESS-PROPERTY RELATION

The residual Gibbs energy and the fugacity coefficient are useful where experimental *PVT* data can be adequately correlated by equations of state. Indeed, if convenient treatment of all fluids by means of equations of state were possible, the thermodynamic-property relations already presented would suffice. However, *liquid* solutions are often more easily dealt with through properties that measure their deviations from ideal solution behavior, not from ideal gas behavior. Thus, the mathematical formalism of *excess* properties is analogous to that of the residual properties.

If M represents the molar (or unit-mass) value of any extensive thermodynamic property (e.g., V, U, H, S, G, and so on), then an excess property M^E is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure, and composition. Thus,

$$M^E \equiv M - M^{id} \tag{4-99}$$

This definition is analogous to the definition of a residual property as given by Eq. (4-67). However, excess properties have no meaning for pure species, whereas residual properties exist for pure species as well as for mixtures. In addition, analogous to Eq. (4-99) is the partial-property relation,

$$\bar{M}_i^E = \bar{M}_i - \bar{M}_i^{id} \tag{4-100}$$

where $\bar{M}_i^E$ is a partial excess property. The fundamental excess-property relation is derived in exactly the same way as the fundamental residual-property relation and leads to analogous results. Equation (4-80), written for the special case of an ideal solution, is subtracted from Eq. (4-80) itself, yielding:

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}\,dP - \frac{nH^E}{RT^2}\,dT + \sum_i \frac{\bar{G}_i^E}{RT}\,dn_i \tag{4-101}$$

This is the *fundamental excess-property relation,* analogous to Eq. (4-81), the fundamental residual-property relation.

The excess Gibbs energy is of particular interest. Equation (4-77) may be written:

$$\bar{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

In accord with Eq. (4-97) for an ideal solution, this becomes

$$\bar{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i$$

By difference

$$\bar{G}_i - \bar{G}_i^{id} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

The left-hand side is the partial excess Gibbs energy $\bar{G}_i^E$; the dimensionless ratio $\hat{f}_i/x_if_i$ appearing on the right is called the *activity coefficient of species i in solution,* and is given the symbol γ_i. Thus, *by definition,*

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} \tag{4-102}$$

and

$$\bar{G}_i^E = RT \ln \gamma_i \tag{4-103}$$

Comparison with Eq. (4-78) shows that Eq. (4-103) relates γ_i to $\bar{G}_i^E$ exactly as Eq. (4-78) relates $\hat{\phi}_i$ to $\bar{G}_i^R$. For an ideal solution, $\bar{G}_i^E = 0$, and therefore $\gamma_i = 1$.

An alternative form of Eq. (4-101) follows by introduction of the activity coefficient through Eq. (4-103):

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}\,dP - \frac{nH^E}{RT^2}\,dT + \sum_i \ln \gamma_i\, dn_i \qquad (4\text{-}104)$$

SUMMARY OF FUNDAMENTAL PROPERTY RELATIONS

For convenience, the three other fundamental property relations, Eqs. (4-16), (4-80), and (4-82), expressing the Gibbs energy and related properties as functions of T, P, and the n_i, are collected here:

$$d(nG) = nV\,dP - nS\,dT + \sum_i \mu_i\, dn_i \qquad (4\text{-}16)$$

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT}\,dP - \frac{nH}{RT^2}\,dT + \sum_i \frac{\bar{G}_i}{RT}\,dn_i \qquad (4\text{-}80)$$

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}\,dP - \frac{nH^R}{RT^2}\,dT + \sum_i \ln \hat{\phi}_i\, dn_i \qquad (4\text{-}82)$$

These equations and Eq. (4-104) may also be written for the special case of 1 mole of solution by setting $n = 1$ and $n_i = x_i$. The x_i are then subject to the constraint that $\sum_i x_i = 1$.

If written for 1 mole of a *constant-composition* solution, they become:

$$dG = V\,dP - S\,dT \qquad (4\text{-}105)$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}\,dP - \frac{H}{RT^2}\,dT \qquad (4\text{-}106)$$

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}\,dP - \frac{H^R}{RT^2}\,dT \qquad (4\text{-}107)$$

$$d\left(\frac{G^E}{RT}\right) = \frac{V^E}{RT}\,dP - \frac{H^E}{RT^2}\,dT \qquad (4\text{-}108)$$

These equations are, of course, valid as a special case for a pure species; in this event they are written with subscript i affixed to the appropriate symbols.

The partial-property analogs of these equations are:

$$d\bar{G}_i = d\mu_i = \bar{V}_i\,dP - \bar{S}_i\,dT \qquad (4\text{-}109)$$

$$d\left(\frac{\bar{G}_i}{RT}\right) = d\left(\frac{\mu_i}{RT}\right) = \frac{\bar{V}_i}{RT}\,dP - \frac{\bar{H}_i}{RT^2}\,dT \qquad (4\text{-}110)$$

$$d\left(\frac{\bar{G}_i^R}{RT}\right) = d\ln\hat{\phi}_i = \frac{\bar{V}_i^R}{RT}\,dP - \frac{\bar{H}_i^R}{RT^2}\,dT \qquad (4\text{-}111)$$

$$d\left(\frac{\bar{G}_i^E}{RT}\right) = d\ln\gamma_i = \frac{\bar{V}_i^E}{RT}\,dP - \frac{\bar{H}_i^E}{RT^2}\,dT \qquad (4\text{-}112)$$

Finally, a Gibbs/Duhem equation is associated with each fundamental property relation:

$$V\,dP - S\,dT = \sum_i x_i\,d\mu_i \qquad (4\text{-}113)$$

$$\frac{V}{RT}dP - \frac{H}{RT^2}\,dT = \sum_i x_i d\left(\frac{\bar{G}_i}{RT}\right) \qquad (4\text{-}114)$$

$$\frac{V^R}{RT}dP - \frac{H^R}{RT^2}\,dT = \sum_i x_i d\ln\hat{\phi}_i \qquad (4\text{-}115)$$

$$\frac{V^E}{RT}dP - \frac{H^E}{RT^2}\,dT = \sum_i x_i d\ln\gamma_i \qquad (4\text{-}116)$$

This depository of equations stores an enormous amount of information. The equations themselves are so general that their direct application is seldom appropriate. However, by inspection one can write a vast array of relations valid for particular applications. For example, Eqs. (4-83) and (4-84) come directly from Eq. (4-107); Eqs. (4-86) and (4-87), from (4-111). Similarly, from Eq. (4-108),

$$\frac{V^E}{RT} = \left[\frac{\partial(G^E/RT)}{\partial P}\right]_{T,x} \qquad (4\text{-}117)$$

$$\frac{H^E}{RT} = -T\left[\frac{\partial(G^E/RT)}{\partial T}\right]_{P,x} \qquad (4\text{-}118)$$

and from Eq. (4-104)

$$\ln\gamma_i = \left[\frac{\partial(nG^E/RT)}{\partial n_i}\right]_{T,P,n_j} \qquad (4\text{-}119)$$

The last relation demonstrates that $\ln \gamma_i$ is a partial property with respect to G^E/RT. The partial-property analogs of Eqs. (4-117) and (4-118) follow from Eq. (4-112):

$$\left(\frac{\partial \ln\gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{V}_i^E}{RT} \qquad (4\text{-}120)$$

$$\left(\frac{\partial \ln\gamma_i}{\partial T}\right)_{P,x} = -\frac{\bar{H}_i^E}{RT^2} \qquad (4\text{-}121)$$

Finally, an especially useful form of the Gibbs/Duhem equation follows from Eq. (4-116):

$$\sum_i x_i\,d\ln\gamma_i = 0 \qquad \text{(constant } T,P) \qquad (4\text{-}122)$$

Since $\ln \gamma_i$ is a partial property with respect to G^E/RT, the following form of the summability equation is valid:

$$\frac{G^E}{RT} = \sum_i x_i \ln\gamma_i \qquad (4\text{-}123)$$

The analogy between equations derived from the fundamental residual- and excess-property relations is apparent. Whereas the fundamental *residual*-property relation derives its usefulness from its direct relation to equations of state, the *excess*-property formulation is useful because V^E, H^E, and γ_i are all experimentally accessible. Activity coefficients are found from vapor/liquid equilibrium data, and V^E and H^E values come from mixing experiments.

PROPERTY CHANGES OF MIXING

If M represents a molar thermodynamic property of a homogeneous fluid solution, then by definition,

$$\Delta M \equiv M - \sum_i x_i M_i \qquad (4\text{-}124)$$

where ΔM is the property change of mixing, and M_i is the molar property of pure species i at the T and P of the solution and in the same physical state (gas or liquid). The summability relation, Eq. (4-50), may be combined with Eq. (4-124) to give

$$\Delta M = \sum_i x_i\,\overline{\Delta M_i} \qquad (4\text{-}125)$$

where by definition

$$\overline{\Delta M_i} \equiv \bar{M}_i - M_i \qquad (4\text{-}126)$$

All three quantities are for the same T, P, and physical state. Eq. (4-126) defines a partial molar property change of mixing, and Eq. (4-125) is the summability relation for these properties.

Each of Eqs. (4-93) through (4-96) is an expression for an ideal solution property, and each may be combined with the defining equation for an excess property (Eq. [4-99]), yielding

$$G^E = G - \sum_i x_i G_i - RT\sum_i x_i \ln x_i \qquad (4\text{-}127)$$

$$V^E = V - \sum_i x_i V_i \qquad (4\text{-}128)$$

$$S^E = S - \sum_i x_i S_i + R\sum_i x_i \ln x_i \qquad (4\text{-}129)$$

$$H^E = H - \sum_i x_i H_i \qquad (4\text{-}130)$$

In view of Eq. (4-124), these may be written

$$G^E = \Delta G - RT\sum_i x_i \ln x_i \qquad (4\text{-}131)$$

$$V^E = \Delta V \tag{4-132}$$

$$S^E = \Delta S + R \sum_i x_i \ln x_i \tag{4-133}$$

$$H^E = \Delta H \tag{4-134}$$

where ΔG, ΔV, ΔS, and ΔH are the Gibbs energy change of mixing, the volume change of mixing, the entropy change of mixing, and the enthalpy change of mixing. For an ideal solution, each excess property is zero, and for this special case

$$\Delta G^{id} = RT \sum_i x_i \ln x_i \tag{4-135}$$

$$\Delta V^{id} = 0 \tag{4-136}$$

$$\Delta S^{id} = -R \sum_i x_i \ln x_i \tag{4-137}$$

$$\Delta H^{id} = 0 \tag{4-138}$$

Property changes of mixing and excess properties are easily calculated one from the other. The most commonly encountered property changes of mixing are the volume change of mixing ΔV and the enthalpy change of mixing ΔH, commonly called the *heat of mixing*. These properties are directly measurable and are identical to the corresponding excess properties.

Pertinent examples are given in Smith, Van Ness, and Abbott (*Introduction to Chemical Engineering Thermodynamics*, 5th ed., Sec. 11.4, McGraw-Hill, New York, 1996).

BEHAVIOR OF BINARY LIQUID SOLUTIONS

Property changes of mixing and excess properties find greatest application in the description of liquid mixtures at low reduced temperatures, that is, at temperatures well below the critical temperature of each constituent species. The properties of interest to the chemical engineer are V^E ($\equiv \Delta V$), H^E ($\equiv \Delta H$), S^E, ΔS, G^E, and ΔG. The activity coefficient is also of special importance because of its application in phase-equilibrium calculations.

The behavior of binary liquid solutions is clearly displayed by plots of M^E, ΔM, and $\ln \gamma_i$ vs. x_1 at constant T and P. The volume change of mixing (or excess volume) is the most easily measured of these quantities and is normally small. However, as illustrated by Fig. 4-1, it is subject to individualistic behavior, being sensitive to the effects of molecular size and shape and to differences in the nature and magnitude of intermolecular forces.

The heat of mixing (excess enthalpy) and the excess Gibbs energy are also experimentally accessible, the heat of mixing by direct measurement and G^E (or $\ln \gamma_i$) indirectly as a product of the reduction of vapor/liquid equilibrium data. Knowledge of H^E and G^E allows calculation of S^E by Eq. (4-13) written for excess properties,

$$S^E = \frac{H^E - G^E}{T} \tag{4-139}$$

with ΔS then given by Eq. (4-133).

Figure 4-2 displays plots of ΔH, ΔS, and ΔG as functions of composition for 6 binary solutions at 50°C. The corresponding excess properties are shown in Fig. 4-3; the activity coefficients, derived from Eq. (4-119), appear in Fig. 4-4. The properties shown here are insensitive to pressure, and for practical purposes represent solution properties at 50°C (122°F) and low pressure ($P \approx 1$ bar [14.5 psi]).

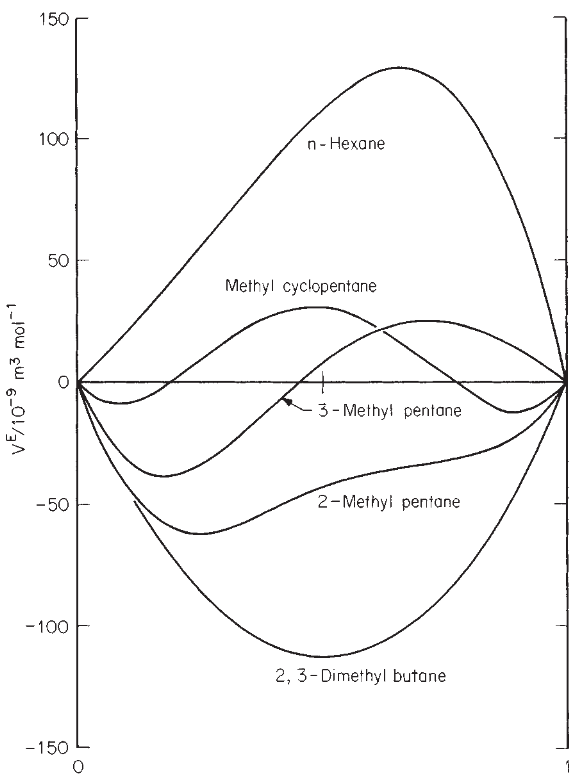

FIG. 4-1 Excess volumes at 25°C for liquid mixtures of cyclohexane(1) with some other C_6 hydrocarbons.

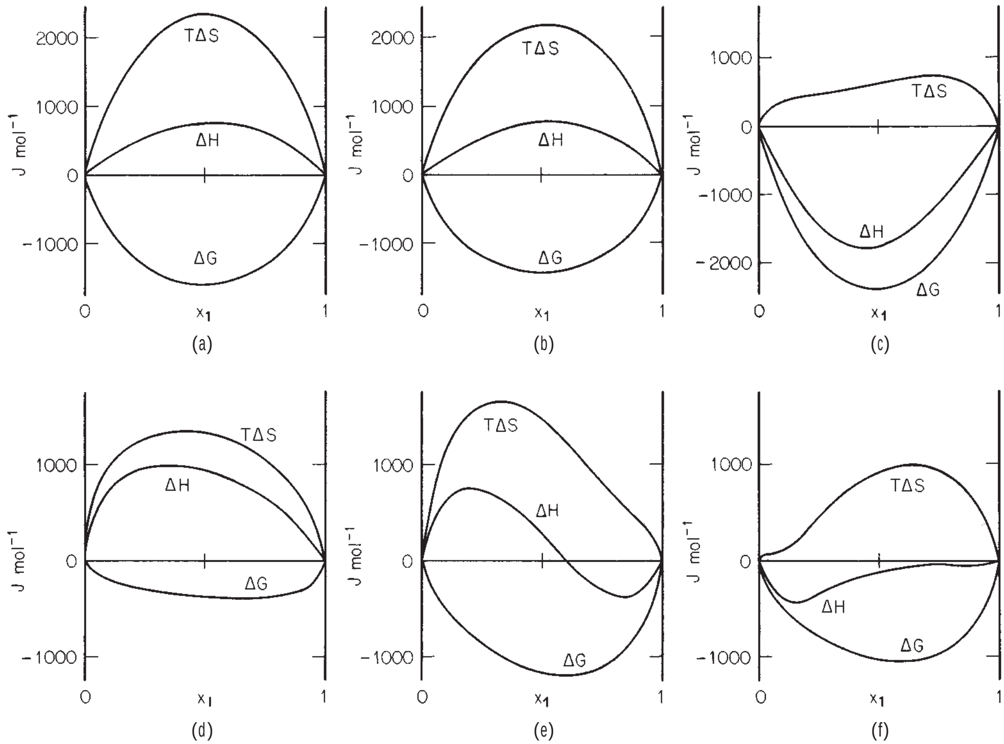

FIG. 4-2 Property changes of mixing at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2).

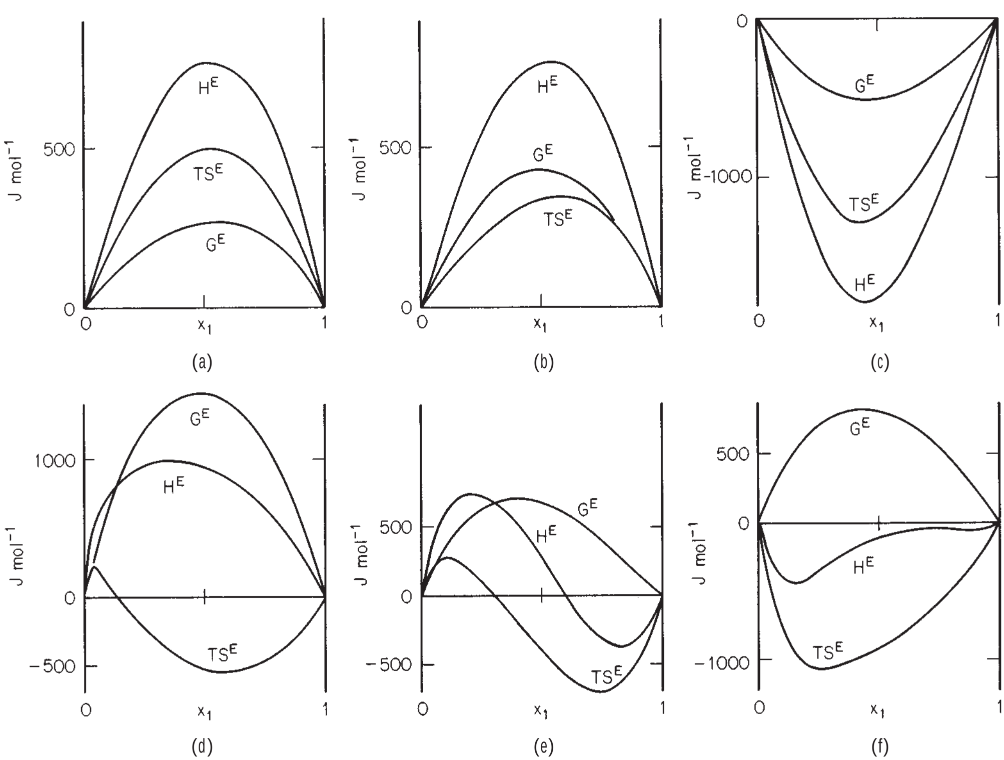

FIG. 4-3 Excess properties at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2).

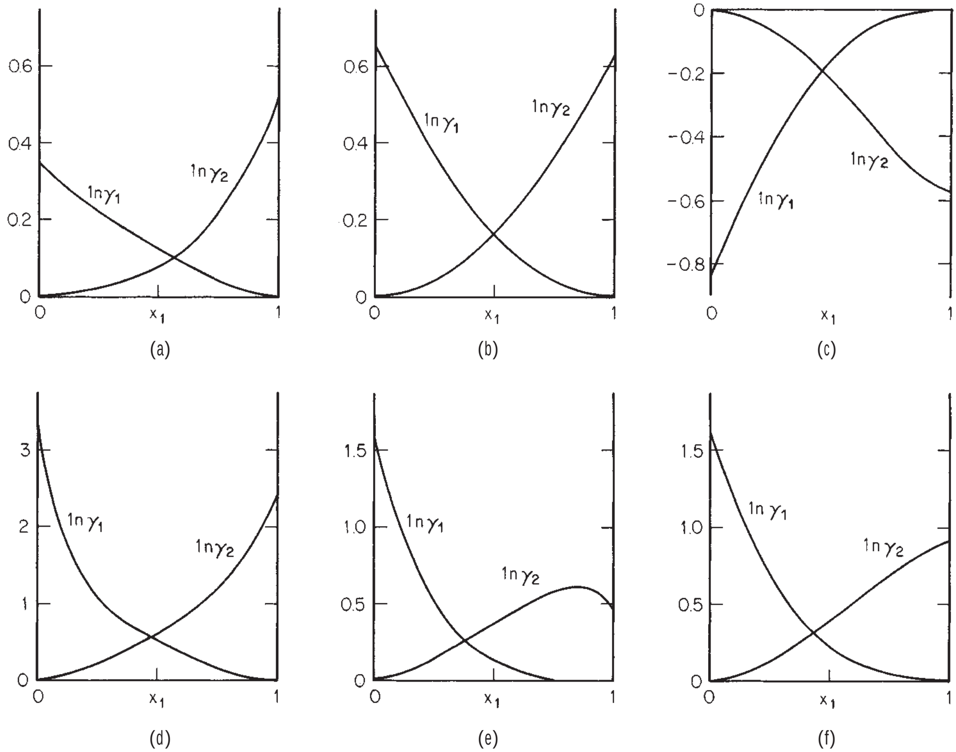

FIG. 4-4 Activity coefficients at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2).

EVALUATION OF PROPERTIES

RESIDUAL-PROPERTY FORMULATIONS

The most satisfactory calculational procedure for thermodynamic properties of gases and vapors requires *PVT* data and ideal gas heat capacities. The primary equations are based on the concept of the ideal gas state and the definitions of residual enthalpy and residual entropy:

$$H = H^{ig} + H^R \qquad \text{and} \qquad S = S^{ig} + S^R$$

The enthalpy and entropy are simple sums of the ideal gas and residual properties, which are evaluated separately.

For the ideal gas state at constant composition,

$$dH^{ig} = C_P^{ig}\, dT$$

$$dS^{ig} = C_P^{ig} \frac{dT}{T} - R \frac{dP}{P}$$

Integration from an initial ideal gas *reference state* at conditions T_0 and P_0 to the ideal gas state at T and P gives:

$$H^{ig} = H_0^{ig} + \int_{T_0}^{T} C_P^{ig}\, dT$$

$$S^{ig} = S_0^{ig} + \int_{T_0}^{T} C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0}$$

Substitution into the equations for H and S yields

$$H = H_0^{ig} + \int_{T_0}^{T} C_P^{ig}\, dT + H^R \tag{4-140}$$

$$S = S_0^{ig} + \int_{T_0}^{T} C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0} + S^R \tag{4-141}$$

The reference state at T_0 and P_0 is arbitrarily selected, and the values assigned to H_0^{ig} and S_0^{ig} are also arbitrary. In practice, only *changes* in H and S are of interest, and the reference-state values ultimately cancel in their calculation.

The ideal-gas–state heat capacity C_P^{ig} is a function of T but not of P. For a mixture, the heat capacity is simply the molar average $\sum_i x_i C_P^{ig}$. Empirical equations giving the temperature dependence of C_P^{ig} are available for many pure gases, often taking the form

$$C_P^{ig} = A + BT + CT^2 + DT^{-2} \tag{4-142}$$

where A, B, C, and D are constants characteristic of the particular gas, and either C or D is 0. Evaluation of the integrals $\int C_P^{ig}\, dT$ and $\int (C_P^{ig}/T) dT$ is accomplished by substitution for C_P^{ig}, followed by formal integration. For temperature limits of T_0 and T the results are conveniently expressed as follows:

$$\int_{T_0}^{T} C_P^{ig}\, dT = AT_0(\tau - 1) + \frac{B}{2} T_0^2(\tau^2 - 1) + \frac{C}{3} T_0^3(\tau^3 - 1) + \frac{D}{T_0}\left(\frac{\tau - 1}{\tau}\right) \tag{4-143}$$

and
$$\int_{T_0}^{T} \frac{C_P^{ig}}{T}\, dT = A \ln \tau + \left[BT_0 + \left(CT_0^2 + \frac{D}{\tau^2 T_0^2}\right)\left(\frac{\tau + 1}{2}\right)\right](\tau - 1) \tag{4-144}$$

where
$$\tau \equiv \frac{T}{T_0}$$

Equations (4-140) and (4-141) may sometimes be advantageously expressed in alternative form through use of mean heat capacities:

$$H = H_0^{ig} + \langle C_P^{ig} \rangle_H (T - T_0) + H^R \tag{4-145}$$

$$S = S_0^{ig} + \langle C_P^{ig} \rangle_S \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} + S^R \tag{4-146}$$

where $\langle C_P^{ig} \rangle_H$ and $\langle C_P^{ig} \rangle_S$ are mean heat capacities specific respectively to enthalpy and entropy calculations. They are given by the following equations:

$$\langle C_P^{ig} \rangle_H = A + \frac{B}{2} T_0 (\tau + 1) + \frac{C}{3} T_0^2 (\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2} \tag{4-147}$$

$$\langle C_P^{ig} \rangle_S = A + \left[BT_0 + \left(CT_0^2 + \frac{D}{\tau^2 T_0^2} \right) \left(\frac{\tau + 1}{2} \right) \right] \left(\frac{\tau - 1}{\ln \tau} \right) \tag{4-148}$$

LIQUID/VAPOR PHASE TRANSITION

When a differential amount of a pure liquid in equilibrium with its vapor in a piston-and-cylinder arrangement evaporates at constant temperature T and vapor pressure P_i^{sat}, Eq. (4-16) applied to the process reduces to $d(n_i G_i) = 0$, whence

$$n_i \, dG_i + G_i \, dn_i = 0$$

Since the system is closed, $dn_i = 0$ and, therefore, $dG_i = 0$; this requires the molar (or specific) Gibbs energy of the vapor to be identical with that of the liquid:

$$G_i^l = G_i^v \tag{4-149}$$

where G_i^l and G_i^v are the molar Gibbs energies of the individual phases.

If the temperature of a two-phase system is changed and if the two phases continue to coexist in equilibrium, then the vapor pressure must also change in accord with its temperature dependence. Since Eq. (4-149) holds throughout this change,

$$dG_i^l = dG_i^v$$

Substituting the expressions for dG_i^l and dG_i^v given by Eq. (4-16) yields

$$V_i^l \, dP_i^{sat} - S_i^l \, dT = V_i^v \, dP_i^{sat} - S_i^v \, dT$$

which upon rearrangement becomes

$$\frac{dP_i^{sat}}{dT} = \frac{S_i^v - S_i^l}{V_i^v - V_i^l} = \frac{\Delta S_i^{lv}}{\Delta V_i^{lv}}$$

The entropy change ΔS_i^{lv} and the volume change ΔV_i^{lv} are the changes which occur when a unit amount of a pure chemical species is transferred from phase l to phase v at constant temperature and pressure. Integration of Eq. (4-18) for this change yields the latent heat of phase transition:

$$\Delta H_i^{lv} = T \Delta S_i^{lv}$$

Thus, $\Delta S_i^{lv} = \Delta H_i^{lv}/T$, and substitution in the preceding equation gives

$$\frac{dP_i^{sat}}{dT} = \frac{\Delta H_i^{lv}}{T \Delta V_i^{lv}} \tag{4-150}$$

Known as the *Clapeyron equation,* this is an exact thermodynamic relation, providing a vital connection between the properties of the liquid and vapor phases. Its use presupposes knowledge of a suitable vapor pressure vs. temperature relation. Empirical in nature, such relations are approximated by the equation

$$\ln P^{sat} = A - \frac{B}{T} \tag{4-151}$$

where A and B are constants for a given species. This equation gives a rough approximation of the vapor-pressure relation for its entire temperature range. Moreover, it is an excellent basis for interpolation between values that are reasonably spaced.

The *Antoine equation,* which is more satisfactory for general use, has the form

$$\ln P^{sat} = A - \frac{B}{T + C} \tag{4-152}$$

A principal advantage of this equation is that values of the constants A, B, and C are readily available for a large number of species.

The accurate representation of vapor-pressure data over a wide temperature range requires an equation of greater complexity. The *Wagner equation,* one of the best, expresses the reduced vapor pressure as a function of reduced temperature:

$$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1 - \tau} \tag{4-153}$$

where here $\qquad \tau \equiv 1 - T_r$

and A, B, C, and D are constants. Values of the constants either for this equation or the Antoine equation are given for many species by Reid, Prausnitz, and Poling (*The Properties of Gases and Liquids,* 4th ed., App. A, McGraw-Hill, New York, 1987).

LIQUID-PHASE PROPERTIES

Given saturated-liquid enthalpies and entropies, the calculation of these properties for pure compressed liquids is accomplished by integration at constant temperature of Eqs. (4-34) and (4-35):

$$H_i = H_i^{sat} + \int_{P_i^{sat}}^{P} V_i(1 - \beta_i T) dP \tag{4-154}$$

$$S_i = S_i^{sat} - \int_{P_i^{sat}}^{P} \beta_i V_i \, dP \tag{4-155}$$

where the *volume expansivity* of species i at temperature T is

$$\beta_i \equiv \frac{1}{V_i} \left(\frac{\partial V_i}{\partial T} \right)_P \tag{4-156}$$

Since β_i and V_i are weak functions of pressure for liquids, they are usually assumed constant at the values for the saturated liquid at temperature T.

PROPERTIES FROM *PVT* CORRELATIONS

The empirical representation of the PVT surface for pure materials is treated later in this section. We first present general equations for evaluation of reduced properties from such representations.

Equation (4-83), applied to a pure material, may be written

$$d\left(\frac{G^R}{RT} \right) = \frac{V^R}{RT} dP \qquad \text{(constant } T\text{)}$$

Integration from zero pressure to arbitrary pressure P gives

$$\frac{G^R}{RT} = \int_0^P \frac{V^R}{RT} dP \qquad \text{(constant } T\text{)}$$

where at the lower limit G^R/RT is set equal to zero on the basis that the zero-pressure state is an ideal gas state. The residual volume is related directly to the compressibility factor:

$$V^R \equiv V - V^{ig} = \frac{ZRT}{P} - \frac{RT}{P} = (Z - 1)\frac{RT}{P}$$

whence

$$\frac{V^R}{RT} = \frac{Z - 1}{P} \tag{4-157}$$

Therefore

$$\frac{G^R}{RT} = \int_0^P (Z - 1) \frac{dP}{P} \qquad \text{(constant } T\text{)} \tag{4-158}$$

Differentiation of Eq. (4-158) with respect to temperature in accord with Eq. (4-84), gives

$$\frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} \qquad \text{(constant } T\text{)} \tag{4-159}$$

Equation (4-13) written for residual properties becomes

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} \tag{4-160}$$

In view of Eq. (4-75), Eqs. (4-158) and (4-160) may be expressed alternatively as

$$\ln \phi = \int_0^P (Z-1)\frac{dP}{P} \qquad \text{(constant } T\text{)} \tag{4-161}$$

and

$$\frac{S^R}{R} = \frac{H^R}{RT} - \ln \phi \tag{4-162}$$

Values of Z and of $(\partial Z/\partial T)_P$ come from experimental *PVT* data, and the integrals in Eqs. (4-158), (4-159), and (4-161) may be evaluated by numerical or graphical methods. Alternatively, the integrals are expressed analytically when Z is given by an equation of state. Residual properties are therefore evaluated from *PVT* data or from an appropriate equation of state.

Pitzer's Corresponding-States Correlation A three-parameter corresponding-states correlation of the type developed by Pitzer, K.S. (*Thermodynamics,* 3d ed., App. 3, McGraw-Hill, New York, 1995) is described in Sec. 2. It has as its basis an equation for the compressibility factor:

$$Z = Z^0 + \omega Z^1 \tag{4-163}$$

where Z^0 and Z^1 are each functions of reduced temperature T_r and reduced pressure P_r. The acentric factor ω is defined by Eq. (2-23). The T_r and P_r dependencies of functions Z^0 and Z^1 are shown by Figs. 2-1 and 2-2. Generalized correlations are developed here for the residual enthalpy, residual entropy, and the fugacity coefficient.

Equations (4-161) and (4-159) are put into generalized form by substitution of the relationships

$$P = P_c P_r \qquad T = T_c T_r$$
$$dP = P_c\, dP_r \qquad dT = T_c\, dT_r$$

The resulting equations are:

$$\ln \phi = \int_0^{P_r} (Z-1)\frac{dP_r}{P_r} \tag{4-164}$$

and

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \tag{4-165}$$

The terms on the right-hand sides of these equations depend only on the upper limit P_r of the integrals and on the reduced temperature at which they are evaluated. Thus, values of ln ϕ and H^R/RT_c may be determined once and for all at any reduced temperature and pressure from generalized compressibility factor data.

Substitution for Z in Eq. (4-164) by Eq. (4-163) yields

$$\ln \phi = \int_0^{P_r} (Z^0-1)\frac{dP_r}{P_r} + \omega \int_0^{P_r} Z^1 \frac{dP_r}{P_r}$$

This equation may be written in alternative form as

$$\ln \phi = \ln \phi^0 + \omega \ln \phi^1 \tag{4-166}$$

where

$$\ln \phi^0 \equiv \int_0^{P_r} (Z^0-1)\frac{dP_r}{P_r}$$

$$\ln \phi^1 \equiv \int_0^{P_r} Z^1 \frac{dP_r}{P_r}$$

Since Eq. (4-166) may also be written

$$\phi = (\phi^0)(\phi^1)^\omega \tag{4-167}$$

correlations may be presented for ϕ^0 and ϕ^1 as well as for their logarithms.

Differentiation of Eq. (4-163) yields

$$\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} + \omega \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r}$$

Substitution for $(\partial Z/\partial T_r)P_r$ in Eq. (4-165) gives:

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \omega T_r^2 \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}$$

Again, in alternative form,

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \tag{4-168}$$

where

$$\frac{(H^R)^0}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{(H^R)^1}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}$$

The residual entropy is given by Eq. (4-162), here written

$$\frac{S^R}{R} = \frac{1}{T_r}\left(\frac{H^R}{RT_c}\right) - \ln \phi \tag{4-169}$$

Pitzer's original correlations for Z and the derived quantities were determined graphically and presented in tabular form. Since then, analytical refinements to the tables have been developed, with extended range and accuracy. The most popular Pitzer-type correlation is that of Lee and Kesler (*AIChE J.,* **21,** pp. 510–527 [1975]). These tables cover both the liquid and gas phases, and span the ranges $0.3 \le T_r \le 4.0$ and $0.01 \le P_r \le 10.0$. Shown by Figs. 4-5 and 4-6 are isobars of $-(H^R)^0/RT_c$ and $-(H^R)^1/RT_c$ with T_r as independent variable drawn from these tables. Figures 4-7 and 4-8 are the corresponding plots for $-\ln \phi^0$ and $-\ln \phi^1$. Figures 4-9 and 4-10 are isotherms of ϕ^0 and ϕ^1 with P_r as independent variable.

Although the Pitzer correlations are based on data for pure materials, they may also be used for the calculation of mixture properties. A set of recipes is required relating the parameters T_c, P_c, and ω for a mixture to the pure-species values and to composition. One such set is given by Eqs. (2-80) through (2-82) in Sec. 2, which define *pseudoparameters,* so called because the defined values of T_c, P_c, and ω have no physical significance for the mixture.

Alternative Property Formulations Direct application of Eqs. (4-159) and (4-161) can be made only to equations of state that are solvable for volume, that is, that are *volume explicit.* Most equations of state are in fact *pressure explicit,* and alternative equations are required.

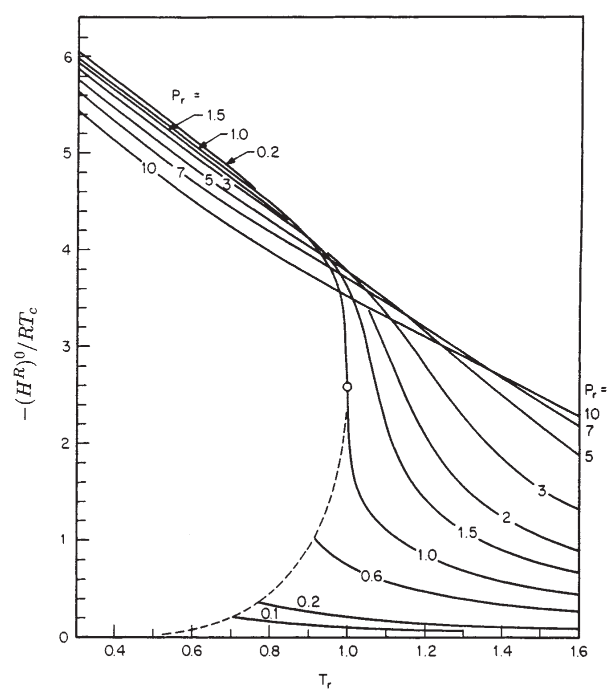

FIG. 4-5 Correlation of $-(H^R)^0/RT_c$, drawn from the tables of Lee and Kesler (*AIChE J.,* **21,** pp. 510–527 [1975]).

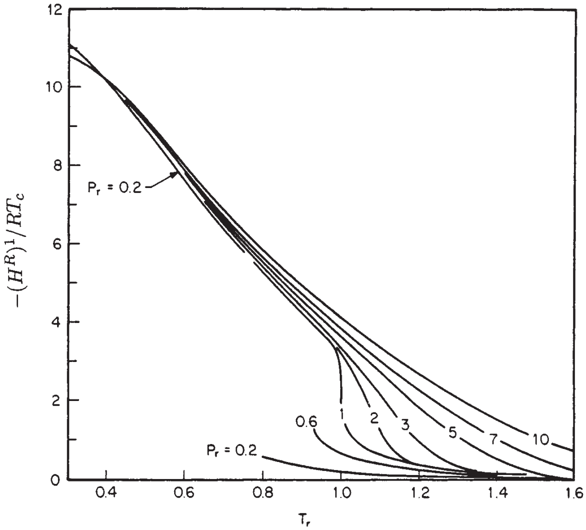

FIG. 4-6 Correlation of $-(H^R)^1/RT_c$, drawn from the tables of Lee and Kesler (*AIChE J.*, **21,** pp. 510–527 [1975]).

Equation (4-158) is converted through application of the general relation $PV = ZRT$. Differentiation at constant T gives

$$P\,dV + V\,dP = RT\,dZ \qquad (\text{constant } T)$$

which is readily transformed to

$$\frac{dP}{P} = \frac{dZ}{Z} - \frac{dV}{V} \qquad (\text{constant } T)$$

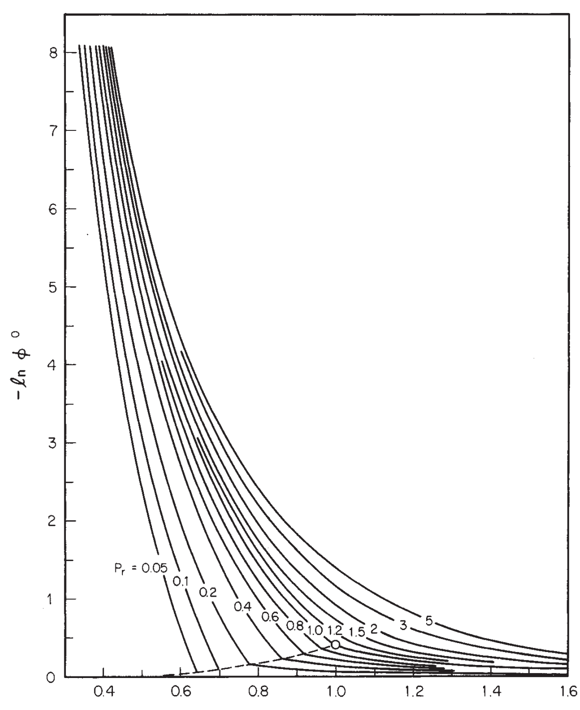

FIG. 4-7 Correlation of [$-\ln \phi^0$] vs. T_r, drawn from the tables of Lee and Kesler (*AIChE J.*, **21,** pp. 510–527 [1975]).

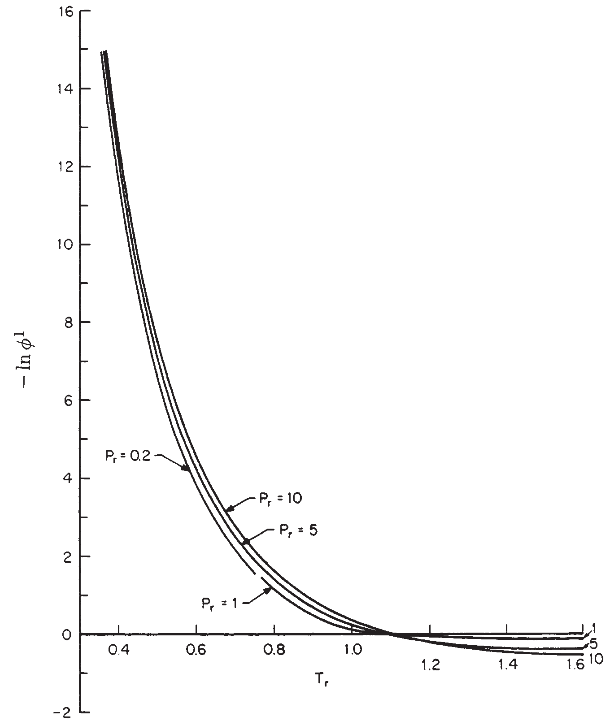

FIG. 4-8 Correlation of [$-\ln \phi^1$] vs. T_r, drawn from the tables of Lee and Kesler (*AIChE J.*, **21,** pp. 510–527 [1975]).

Substitution into Eq. (4-158) leads to

$$\frac{G^R}{RT} = Z - 1 - \ln Z - \int_\infty^V (Z - 1)\,\frac{dV}{V} \tag{4-170}$$

The molar volume may be eliminated in favor of the molar density, $\rho = V^{-1}$, to give

$$\frac{G^R}{RT} = Z - 1 - \ln Z + \int_0^\rho (Z - 1)\,\frac{d\rho}{\rho} \tag{4-171}$$

For a pure material, Eq. (4-75) shows that $G^R/RT = \ln \phi$, in which case Eqs. (4-170) and (4-171) directly yield values of $\ln \phi$:

$$\ln \phi = Z - 1 - \ln Z - \int_\infty^V (Z - 1)\,\frac{dV}{V} \tag{4-172}$$

$$\ln \phi = Z - 1 - \ln Z + \int_0^\rho (Z - 1)\,\frac{d\rho}{\rho} \tag{4-173}$$

where subscript i is omitted for simplicity.

The corresponding equations for H^R are most readily found from Eq. (4-107) applied to a pure material. In view of Eqs. (4-75) and (4-157), this equation may be written

$$d \ln \phi = (Z - 1)\,\frac{dP}{P} - \frac{H^R}{RT^2}\,dT$$

Division by dT and restriction to constant V gives, upon rearrangement,

$$\frac{H^R}{RT^2} = \frac{Z - 1}{P}\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial \ln \phi}{\partial T}\right)_V$$

Differentiation of $P = ZRT/V$ provides the first derivative on the right and differentiation of Eq. (4-172) provides the second. Substitution then leads to

$$\frac{H^R}{RT} = Z - 1 + T\int_\infty^V \left(\frac{\partial Z}{\partial T}\right)_V \frac{dV}{V} \tag{4-174}$$

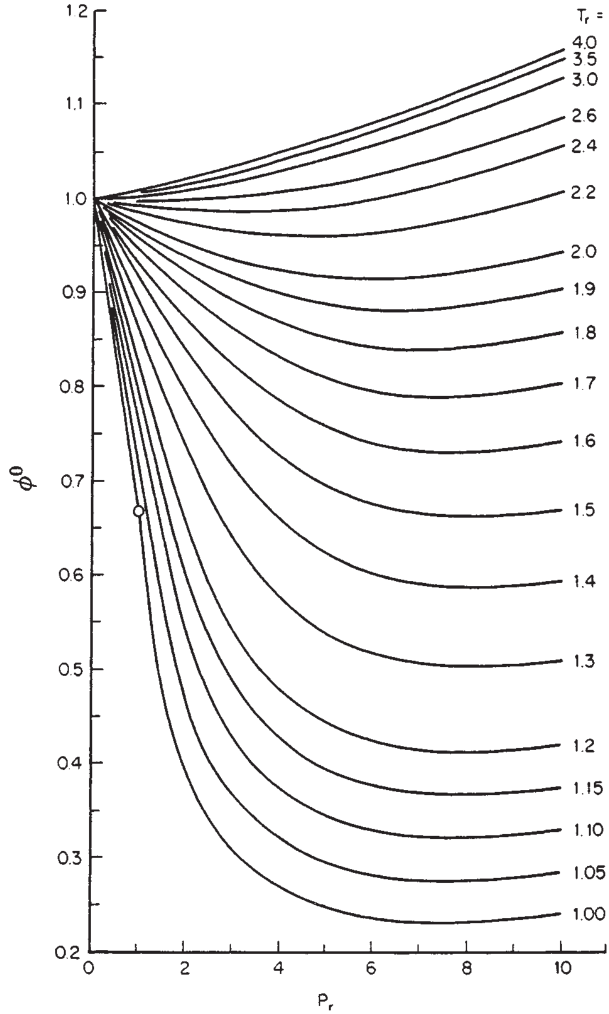

FIG. 4-9 Correlation of ϕ^0 vs. P_r, drawn from the tables of Lee and Kesler (*AIChE J.*, **21,** pp. 510–527 [1975]).

Alternatively,
$$\frac{H^R}{RT} = Z - 1 - T\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{4-175}$$

As before, the residual entropy is found by Eq. (4-162).

In applications to equilibrium calculations, the fugacity coefficients of species in a mixture $\hat{\phi}_i$ are required. Given an expression for G^R/RT as determined from Eq. (4-158) for a constant-composition mixture, the corresponding recipe for $\ln \hat{\phi}_i$ is found through the partial-property relation

$$\ln \hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{T,P,n_j} \tag{4-85}$$

There are two ways to proceed: operate on the *result* of the integration of Eq. (4-158) in accord with Eq. (4-85) or apply Eq. (4-85) *directly* to Eq. (4-158), obtaining

$$\ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1)\frac{dP}{P} \tag{4-176}$$

where $\bar{Z}_i$ is the partial compressibility factor, defined as

$$\bar{Z}_i \equiv \left[\frac{\partial(nZ)}{\partial n_i}\right]_{T,P,n_j} \tag{4-177}$$

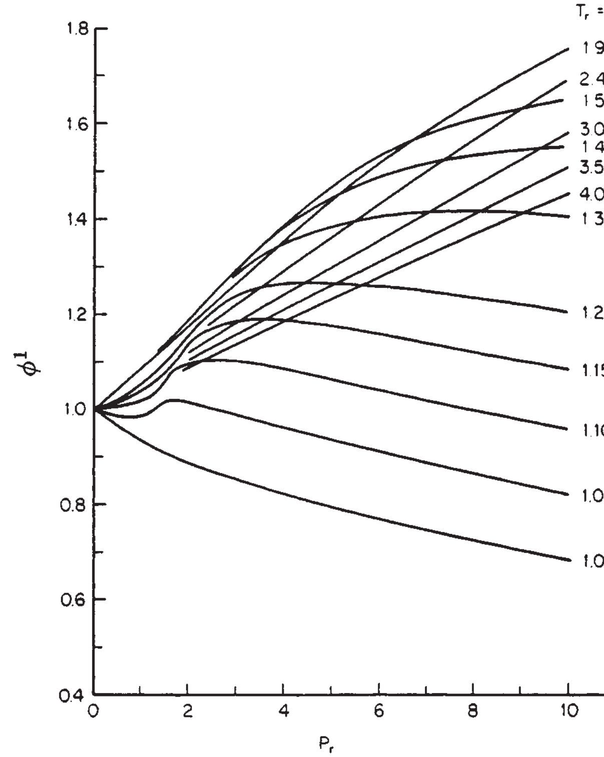

FIG. 4-10 Correlation of ϕ^1 vs. P_r, drawn from the tables of Lee and Kesler (*AIChE J.*, **21,** pp. 510–527 [1975]).

Direct application of these results is possible only to equations of state explicit in volume. For pressure-explicit equations of state, alternative recipes are required. The basis is Eq. (4-82), which in view of Eq. (4-157) may be written

$$d\left(\frac{nG^R}{RT}\right) = \frac{n(Z-1)}{P}\,dP - \frac{nH^R}{RT^2}\,dT + \sum_i \ln \hat{\phi}_i\, dn_i$$

Division by dn_i and restriction to constant T, nV, and n_j $(j \neq i)$ leads to

$$\ln \hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{T,nV,n_j} - \frac{n(Z-1)}{P}\left(\frac{\partial P}{\partial n_i}\right)_{T,nV,n_j}$$

But $P = (nZ)RT/nV$, and therefore

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,nV,n_j} = \frac{P}{nZ}\left[\frac{\partial(nZ)}{\partial n_i}\right]_{T,nV,n_j}$$

Combination of the last two equations gives

$$\ln \hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{T,nV,n_j} - \left(\frac{Z-1}{Z}\right)\left[\frac{\partial(nZ)}{\partial n_i}\right]_{T,nV,n_j} \tag{4-178}$$

Alternatively,

$$\ln \hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{T,\rho/n,n_j} - \left(\frac{Z-1}{Z}\right)\left[\frac{\partial(nZ)}{\partial n_i}\right]_{T,\rho/n,n_j} \tag{4-179}$$

These equations may either be applied to the results of integrations of Eqs. (4-170) and (4-171) or *directly* to Eqs. (4-170) and (4-171) as written for a mixture. In the latter case the following analogs of Eq. (4-176) are obtained:

$$\ln \hat{\phi}_i = -\int_\infty^V \left\{\left[\frac{\partial(nZ)}{\partial n_i}\right]_{T,nV,n_j} - 1\right\}\frac{dV}{V} - \ln Z \tag{4-180}$$

$$\ln \hat{\phi}_i = -\int_0^\rho \left\{\left[\frac{\partial(nZ)}{\partial n_i}\right]_{T,\rho/n,n_j} - 1\right\}\frac{d\rho}{\rho} - \ln Z \tag{4-181}$$

Virial Equations of State The virial equation in *density* is an infinite-series representation of the compressibility factor Z in powers of molar density ρ (or reciprocal molar volume V^{-1}) about the real-gas state at zero density (zero pressure):

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots \tag{4-182}$$

The density-series virial coefficients $B, C, D, \ldots$, depend on temperature and composition only. The composition dependencies are given by the exact recipes

$$B = \sum_i \sum_j y_i y_j B_{ij} \tag{4-183}$$

$$C = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk} \tag{4-184}$$

and so on

where y_i, y_j, and y_k are mole fractions for a gas mixture, with indices i, j, and k identifying species.

The coefficient B_{ij} characterizes a bimolecular interaction between molecules i and j, and therefore $B_{ij} = B_{ji}$. Two kinds of second virial coefficient arise: B_{ii} and B_{jj}, wherein the subscripts are the same ($i = j$); and B_{ij}, wherein they are different ($i \neq j$). The first is a virial coefficient for a pure species; the second is a mixture property, called a *cross coefficient.* Similarly for the third virial coefficients: C_{iii}, C_{jjj}, and C_{kkk} are for the pure species; and $C_{iij} = C_{iji} = C_{jii}$, and so on, are cross coefficients.

Although the virial equation itself is easily rationalized on empirical grounds, the "mixing rules" of Eqs. (4-183) and (4-184) follow rigorously from the methods of statistical mechanics. The temperature derivatives of B and C are given exactly by

$$\frac{dB}{dT} = \sum_i \sum_j y_i y_j \frac{dB_{ij}}{dT} \tag{4-185}$$

$$\frac{dC}{dT} = \sum_i \sum_j \sum_k y_i y_j y_k \frac{dC_{ijk}}{dT} \tag{4-186}$$

An alternative form of the virial equation expresses Z as an expansion in powers of pressure about the real-gas state at zero pressure (zero density):

$$Z = 1 + B'P + C'P^2 + D'P^3 + \cdots \tag{4-187}$$

Equation (4-187) is the virial equation in *pressure,* and $B', C', D', \ldots$, are the pressure-series virial coefficients. Like the density-series coefficients, they depend on temperature and composition only. Moreover, the two sets of coefficients are related:

$$B' = \frac{B}{RT} \tag{4-188}$$

$$C' = \frac{C - B^2}{(RT)^2} \tag{4-189}$$

and so on

Application of an *infinite* series to practical calculations is, of course, impossible, and *truncations* of the virial equations are in fact employed. The degree of truncation is conditioned not only by the temperature and pressure but also by the availability of correlations or data for the virial coefficients. Values can usually be found for B (see Sec. 2), and often for C (see, e.g., De Santis and Grande, *AIChE J.*, **25,** pp. 931–938 [1979]), but rarely for higher-order coefficients. Application of the virial equations is therefore usually restricted to two- or three-term truncations. For pressures up to several bars, the two-term expansion in pressure, with B' given by Eq. (4-188), is usually preferred:

$$Z = 1 + \frac{BP}{RT} \tag{4-190}$$

For supercritical temperatures, it is satisfactory to ever-higher pressures as the temperature increases. For pressures above the range where Eq. (4-190) is useful, but below the critical pressure, the virial expansion in density truncated to three terms is usually suitable:

$$Z = 1 + B\rho + C\rho^2 \tag{4-191}$$

Equations for derived properties may be developed from each of these expressions. Consider first Eq. (4-190), which is explicit in volume. Equations (4-159), (4-161), and (4-176) are therefore applicable. Direct substitution for Z in Eq. (4-161) gives

$$\ln \phi = \frac{BP}{RT} \tag{4-192}$$

Differentiation of Eq. (4-190) yields

$$\left(\frac{\partial Z}{\partial T}\right)_P = \left(\frac{dB}{dT} - \frac{B}{T}\right)\frac{P}{RT}$$

Whence, by Eq. (4-159)

$$\frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right) \tag{4-193}$$

and by Eq. (4-162),

$$\frac{S^R}{R} = -\frac{P}{R}\frac{dB}{dT} \tag{4-194}$$

Multiplication of Eq. (4-190) by n gives

$$nZ = n + (nB)\frac{P}{RT}$$

Differentiation in accord with Eq. (4-177) yields

$$\bar{Z}_i = 1 + \left[\frac{\partial (nB)}{\partial n_i}\right]_{T,n_j}\frac{P}{RT}$$

Whence, by Eq. (4-176),

$$\ln \hat{\phi}_i = \left[\frac{\partial (nB)}{\partial n_i}\right]_{T,n_j}\frac{P}{RT}$$

Equation (4-183) can be written

$$nB = \frac{1}{n}\sum_k \sum_l n_k n_l B_{kl}$$

from which, by differentiation,

$$\left[\frac{\partial (nB)}{\partial n_i}\right]_{T,n_j} = 2\sum_k y_k B_{ki} - B \tag{4-195}$$

Whence

$$\ln \hat{\phi}_i = \left(2\sum_k y_k B_{ki} - B\right)\frac{P}{RT} \tag{4-196}$$

Equation (4-191) is explicit in pressure, and Eqs. (4-173), (4-175), and (4-181) are therefore applicable. Direct substitution of Eq. (4-191) into Eq. (4-173) yields

$$\ln \phi = 2B\rho + \frac{3}{2}C\rho^2 - \ln Z \tag{4-197}$$

Moreover,

$$\left(\frac{\partial Z}{\partial T}\right)_\rho = \frac{dB}{dT}\rho + \frac{dC}{dT}\rho^2$$

whence

$$\frac{H^R}{RT} = \left(B - T\frac{dB}{dT}\right)\rho + \left(C - \frac{T}{2}\frac{dC}{dT}\right)\rho^2 \tag{4-198}$$

The residual entropy is given by Eq. (4-162).

Application of Eq. (4-181) provides an expression for $\ln \hat{\phi}_i$. First, from Eq. (4-191),

$$\left[\frac{\partial (nZ)}{\partial n_i}\right]_{T,\rho/n,n_j} = 1 + \left\{B + \left[\frac{\partial (nB)}{\partial n_i}\right]_{T,n_j}\right\}\rho + \left\{2C + \left[\frac{\partial (nC)}{\partial n_i}\right]_{T,n_j}\right\}\rho^2$$

Substitution into Eq. (4-181) gives, on integration,

$$\ln \hat{\phi}_i = \left\{B + \left[\frac{\partial (nB)}{\partial n_i}\right]_{T,n_j}\right\}\rho + \frac{1}{2}\left\{2C + \left[\frac{\partial (nC)}{\partial n_i}\right]_{T,n_j}\right\}\rho^2 - \ln Z$$

The mole-number derivative of nB is given by Eq. (4-195); the corresponding derivative of nC, similarly found from Eq. (4-184), is

$$\left[\frac{\partial (nC)}{\partial n_i}\right]_{T,n_j} = 3\sum_k \sum_l y_k y_l C_{kli} - 2C \tag{4-199}$$

Finally,

$$\ln \hat{\phi}_i = 2\rho \sum_k y_k B_{ki} + \frac{3}{2}\rho^2 \sum_k \sum_l y_k y_l C_{kli} - \ln Z \qquad (4\text{-}200)$$

In a process calculation, T and P, rather than T and ρ (or T and V), are usually the favored independent variables. Application of Eqs. (4-197), (4-198), and (4-200) therefore requires prior solution of Eq. (4-191) for Z or ρ. Since $Z = P/\rho RT$, Eq. (4-191) may be written in two equivalent forms:

$$Z^3 - Z^2 - \left(\frac{BP}{RT}\right)Z - \frac{CP^2}{(RT)^2} = 0 \qquad (4\text{-}201)$$

or

$$\rho^3 + \left(\frac{B}{C}\right)\rho^2 + \left(\frac{1}{C}\right)\rho - \frac{P}{CRT} = 0 \qquad (4\text{-}202)$$

In the event that three real roots obtain for these equations, only the largest Z (smallest ρ) appropriate for the vapor phase has physical significance, because the virial equations are suitable only for vapors and gases.

Generalized Correlation for the Second Virial Coefficient Perhaps the most useful of all Pitzer-type correlations is the one for the second virial coeffieient. The basic equation (see Eq. [2-68]) is

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 \qquad (4\text{-}203)$$

where for a pure material B^0 and B^1 are functions of reduced temperature only. Substitution for B by this expression in Eq. (4-190) yields

$$Z = 1 + (B^0 + \omega B^1)\frac{P_r}{T_r} \qquad (4\text{-}204)$$

By differentiation,

$$\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = P_r\left(\frac{dB^0/dT_r}{T_r} - \frac{B^0}{T_r^2}\right) + \omega P_r\left(\frac{dB^1/dT_r}{T_r} - \frac{B^1}{T_r^2}\right)$$

Substitution of these equations into Eqs. (4-164) and (4-165) and integration gives

$$\ln \phi = (B^0 + \omega B^1)\frac{P_r}{T_r} \qquad (4\text{-}205)$$

and

$$\frac{H^R}{RT_c} = P_r\left[B^0 - T_r\frac{dB^0}{dT_r} + \omega\left(B^1 - T_r\frac{dB^1}{dT_r}\right)\right] \qquad (4\text{-}206)$$

The residual entropy follows from Eq. (4-162):

$$\frac{S^R}{R} = -P_r\left(\frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}\right) \qquad (4\text{-}207)$$

In these equations, B^0 and B^1 and their derivatives are well represented by

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad (4\text{-}208)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad (4\text{-}209)$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \qquad (4\text{-}210)$$

$$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} \qquad (4\text{-}211)$$

Though limited to pressures where the two-term virial equation in pressure has approximate validity, this correlation is applicable to most chemical-processing conditions. As with all generalized correlations, it is least accurate for polar and associating molecules.

Although developed for pure materials, this correlation can be extended to gas or vapor mixtures. Basic to this extension is the mixing rule for second virial coefficients and its temperature derivative:

$$B = \sum_i \sum_j y_i y_j B_{ij} \qquad (4\text{-}183)$$

$$\frac{dB}{dT} = \sum_i \sum_j y_i y_j \frac{dB_{ij}}{dT} \qquad (4\text{-}185)$$

Values for the cross coefficients and their derivatives in these equations are provided by writing Eq. (4-203) in extended form:

$$B_{ij} = \frac{RT_{cij}}{P_{cij}}(B^0 + \omega_{ij}B^1) \qquad (4\text{-}212)$$

where B^0, B^1, dB^0/dT_r, and dB^1/dT_r are the same functions of T_r as given by Eqs. (4-208) through (4-211). Differentiation produces

$$\frac{dB_{ij}}{dT} = \frac{RT_{cij}}{P_{cij}}\left(\frac{dB^0}{dT} + \omega_{ij}\frac{dB^1}{dT}\right)$$

or

$$\frac{dB_{ij}}{dT} = \frac{R}{P_{cij}}\left(\frac{dB^0}{dT_{rij}} + \omega_{ij}\frac{dB^1}{dT_{rij}}\right) \qquad (4\text{-}213)$$

where $T_{rij} = T/T_{cij}$. The following are combining rules for calculation of ω_{ij}, T_{cij}, and P_{cij} as given by Prausnitz, Lichtenthaler, and de Azevedo (*Molecular Thermodynamics of Fluid-Phase Equilibria*, 2d ed., pp. 132 and 162, Prentice-Hall, Englewood Cliffs, N.J., 1986):

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \qquad (4\text{-}214)$$

$$T_{cij} = (T_{ci}T_{cj})^{1/2}(1 - k_{ij}) \qquad (4\text{-}215)$$

$$P_{cij} = \frac{Z_{cij}RT_{cij}}{V_{cij}} \qquad (4\text{-}216)$$

with

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \qquad (4\text{-}217)$$

$$V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3 \qquad (4\text{-}218)$$

In Eq. (4-215), k_{ij} is an empirical interaction parameter specific to an i-j molecular pair. When $i = j$ and for chemically similar species, $k_{ij} = 0$. Otherwise, it is a small (usually) positive number evaluated from minimal PVT data or in the absence of data set equal to zero.

When $i = j$, all equations reduce to the appropriate values for a pure species. When $i \neq j$, these equations define a set of interaction parameters having no physical significance. For a mixture, values of B_{ij} and dB_{ij}/dT from Eqs. (4-212) and (4-213) are substituted into Eqs. (4-183) and (4-185) to provide values of the mixture second virial coefficient B and its temperature derivative. Values of H^R and S^R for the mixture are then given by Eqs. (4-193) and (4-194), and values of $\ln \hat{\phi}_i$ for the component fugacity coefficients are given by Eq. (4-196).

Cubic Equations of State The simplest expressions that can (in principle) represent both the vapor- and liquid-phase volumetric behavior of pure fluids are equations cubic in molar volume. All such expressions are encompassed by the generic equation

$$P = \frac{RT}{V - b} - \frac{a(V - \eta)}{(V - b)(V^2 + \delta V + \varepsilon)} \qquad (4\text{-}219)$$

where parameters b, θ, δ, ε, and η can each depend on temperature and composition. Special cases are obtained by specification of values or expressions for the various parameters.

The modern development of cubic equations of state started in 1949 with publication of the Redlich/Kwong equation (Redlich and Kwong, *Chem. Rev.*, **44,** pp. 233–244 [1949]):

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \qquad (4\text{-}220)$$

where

$$a(T) = \frac{a}{T^{1/2}}$$

and a and b are functions of composition only. This equation, like other cubic equations of state, has three volume roots, of which two may be complex. Physically meaningful values of V are always real, positive, and greater than the constant b. When $T > T_c$, solution for V at any positive value of P yields only one real positive root. When $T = T_c$, this is also true, except at the critical pressure, where there are three roots, all equal to V_c. For $T < T_c$, only one real positive root exists at high pressures, but for a range of lower pressures there are three real positive roots. Here, the middle root is of no significance; the smallest root is a liquid or liquidlike volume, and the largest root is a vapor or vaporlike volume. The volumes of saturated liquid and saturated vapor are given by the smallest and largest roots when P is the saturation vapor pressure P^{sat}.

The application of cubic equations of state to mixtures requires expression of the equation-of-state parameters as functions of composition. No exact theory like that for the virial coefficients prescribes this composition dependence, and empirical *mixing rules* provide approximate relationships. The mixing rules that have found general favor for the Redlich/Kwong equation are:

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{4-221}$$

with $a_{ij} = a_{ji}$, and

$$b = \sum_i y_i b_i \tag{4-222}$$

The a_{ij} are of two types: *pure-species parameters* (like subscripts) and *interaction parameters* (unlike subscripts). The b_i are parameters for the pure species.

Parameter evaluation may be accomplished with the equations

$$a_{ij} = \frac{0.42748 R^2 T_{cij}^{2.5}}{P_{cij}} \tag{4-223}$$

$$b_i = \frac{0.08664 R T_{ci}}{P_{ci}} \tag{4-224}$$

where Eqs. (4-215) through (4-218) provide for the calculation of the T_{cij} and P_{cij}.

Multiplication of the Redlich/Kwong equation (Eq. [4-220]) by V/RT leads to its expression in alternative form:

$$Z = \frac{1}{1-h} - \frac{a}{bRT^{1.5}}\left(\frac{h}{1+h}\right) \tag{4-225}$$

Whence

$$Z - 1 = \frac{h}{1-h} - \frac{a}{bRT^{1.5}}\left(\frac{h}{1+h}\right) \tag{4-226}$$

where

$$h = \frac{bP}{ZRT} \tag{4-227}$$

Equations (4-170) and (4-174) in combination with Eq. (4-226) give

$$\frac{G^R}{RT} = Z - 1 - \ln(1-h)Z - \left(\frac{a}{bRT^{1.5}}\right)\ln(1+h) \tag{4-228}$$

and

$$\frac{H^R}{RT} = Z - 1 - \left(\frac{3a}{2bRT^{1.5}}\right)\ln(1+h) \tag{4-229}$$

Once a and b are determined by Eqs. (4-221) through (4-224), then for given T and P values of Z, G^R/RT, and H^R/RT are found by Eqs. (4-225), (4-228), and (4-229) and S^R/R by Eq. (4-160). The procedure requires initial solution of Eqs. (4-225) and (4-227) for Z and h.

The original Redlich/Kwong equation is rarely satisfactory for vapor/liquid equilibrium calculations, and equations have been developed specific to this purpose. The two most popular are the Soave/Redlich/Kwong (SRK) equation, a modification of the Redlich/Kwong equation (Soave, *Chem. Eng. Sci.*, **27,** pp. 1197–1203 [1972]), and the Peng/Robinson (PR) equation (Peng and Robinson, *Ind. Eng. Chem. Fundam.*, **15,** pp. 59–64 [1976]). Both equations are designed specifically to yield reasonable vapor pressures for pure fluids. Thus, there is no assurance that molar volumes calculated by these equations are more accurate than values given by the original Redlich/Kwong equation. Written for pure species i the SRK and PR equations are special cases of the following:

$$P = \frac{RT}{V_i - b_i} - \frac{a_i(T)}{(V_i + \varepsilon b_i)(V_i + \sigma b_i)} \tag{4-230}$$

where

$$a_i(T) = \frac{\Omega_a \alpha(T_{ri};\,\omega_i) R^2 T_{ci}^2}{P_{ci}}$$

$$b_i = \frac{\Omega_b R T_{ci}}{P_{ci}}$$

and ε σ, Ω_a, and Ω_b are equation-specific constants. For the Soave/Redlich/Kwong equation:

$$\alpha(T_{ri};\,\omega_i) = [1 + (0.480 + 1.574\omega_i - 0.176\omega_i^2)\,(1 - T_{ri}^{1/2})]^2$$

For the Peng/Robinson equation:

$$\alpha(T_{ri};\,\omega_i) = [1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2)\,(1 - T_{ri}^{1/2})]^2$$

Written for a mixture, Eq. (4-230) becomes

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)} \tag{4-231}$$

where a and b are mixture values, related to the a_i and b_i by *mixing rules.* Equation (4-170) applied to Eq. (4-231) leads to

$$\ln\hat{\phi}_i = \frac{\bar{b}_i}{b}(Z-1) - \ln\frac{(V-b)Z}{V} + \frac{a/bRT}{\varepsilon - \sigma}\left(1 + \frac{\bar{a}_i}{a} - \frac{\bar{b}_i}{b}\right)\ln\frac{V+\sigma b}{V+\varepsilon b} \tag{4-232}$$

where a_i and b_i are *partial parameters* for species i, defined by

$$a_i = \left[\frac{\partial(na)}{\partial n_i}\right]_{T,n_j} \tag{4-233}$$

and

$$b_i = \left[\frac{\partial(nb)}{\partial n_i}\right]_{T,n_j} \tag{4-234}$$

These are general equations that do not depend on the particular *mixing rules* adopted for the composition dependence of a and b. The mixing rules given by Eqs. (4-221) and (4-222) can certainly be employed with these equations. However, for purposes of vapor/liquid equilibrium calculations, a special pair of mixing rules is far more appropriate, and will be introduced when these calculations are treated. Solution of Eq. (4-232) for fugacity coefficient $\hat{\phi}_i$ at given T and P requires prior solution of Eq. (4-231) for V, from which is found $Z = PV/RT$.

Benedict/Webb/Rubin Equation of State The BWR equation of state with Z as the dependent variable is written

$$Z = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right)\rho + \left(b - \frac{a}{RT}\right)\rho^2 + \frac{a\alpha}{RT}\rho^5 + \frac{c}{RT^3}\rho^2(1+\gamma\rho^2)\exp(-\gamma\rho^2) \tag{4-235}$$

All eight parameters depend on composition; moreover, parameters C_0, b, and γ are for some applications treated as functions of T. By Eq. (4-171), the residual Gibbs energy is

$$\frac{G^R}{RT} = 2\left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right)\rho + \frac{3}{2}\left(b - \frac{a}{RT}\right)\rho^2 + \frac{6a\alpha}{5RT}\rho^5 + \frac{c}{2\gamma RT^3}\left[(2\gamma^2\rho^4 + \gamma\rho^2 - 2)\exp(-\gamma\rho^2) + 2\right] - \ln Z \tag{4-236}$$

With allowance for T dependence of C_0, b, and γ, Eq. (4-175) yields

$$\begin{aligned}\frac{H^R}{RT} = {} & \left(B_0 - \frac{2A_0}{RT} - \frac{4C_0}{RT^3} + \frac{1}{RT^2}\frac{dC_0}{dT}\right)\rho \\ & - \frac{1}{2}\left(T\frac{db}{dT} - 2b + \frac{3a}{RT}\right)\rho^2 + \frac{6a\alpha}{5RT}\rho^5 \\ & + \frac{c}{2\gamma RT^3}\left[(2\gamma^2\rho^4 - \gamma\rho^2 - 6)\exp(-\gamma\rho^2) + 6\right] \\ & - \frac{c}{2\gamma^2 RT^2}\frac{d\gamma}{dT}\left[(\gamma^2\rho^4 + 2\gamma\rho^2 + 2)\exp(-\gamma\rho^2) - 2\right]\end{aligned} \tag{4-237}$$

The residual entropy is given by Eq. (4-160).

Computation of $\ln\hat{\phi}_i$ is done via Eq. (4-181). The result is

$$\begin{aligned}\ln\hat{\phi}_i = {} & \left(B_0 + \bar{B}_{0_i} - \frac{A_0 + \bar{A}_{0_i}}{RT} - \frac{C_0 + \bar{C}_{0_i}}{RT^3}\right)\rho \\ & + \frac{1}{2}\left(2b + \bar{b}_i - \frac{2a + \bar{a}_i}{RT}\right)\rho^2 + \left(\frac{4a\alpha + a\bar{\alpha}_i + \alpha\bar{a}_i}{5RT}\right)\rho^5 \\ & + \frac{c}{2\gamma RT^3}\left\{\left[\left(1 + \frac{\bar{\gamma}_i}{\gamma}\right)\gamma^2\rho^4 + \left(\frac{2\,\bar{\gamma}_i}{\gamma} - \frac{\bar{c}_i}{c}\right)\rho^2\right.\right. \\ & \left.\left. - 2\left(1 + \frac{\bar{c}_i}{c} - \frac{\bar{\gamma}_i}{\gamma}\right)\right]\exp(-\gamma\rho^2) + 2\left(1 + \frac{\bar{c}_i}{c} - \frac{\bar{\gamma}_i}{\gamma}\right)\right\} - \ln Z\end{aligned} \tag{4-238}$$

Here the quantities with overbars are *partial parameters* for species i, defined for arbitrary parameter π by

$$\bar{\pi}_i \equiv \left[\frac{\partial(n\pi)}{\partial n_i}\right]_{T,n_j} \tag{4-239}$$

Application of these equations requires specific mixing rules. For example, if

$$\pi = \left(\sum_k y_k \pi_k^{1/r}\right)^r \tag{4-240}$$

where r is a small integer, the recipe for $\bar{\pi}_i$ is

$$\bar{\pi}_i = \pi\left[r\left(\frac{\pi_i}{\pi}\right)^{1/r} - (r-1)\right] \tag{4-241}$$

Specifically, if $r = 3$ for $\pi \equiv c$; then

$$\bar{c}_i = c\left[3\left(\frac{c_i}{c}\right)^{1/3} - 2\right]$$

where c_i is the parameter for pure i and c is the parameter for the mixture, given by

$$c = \left(\sum_k y_k c_k^{1/3}\right)^3$$

Equation-of-state examples are given in Smith, Van Ness, and Abbott (*Introduction to Chemical Engineering Thermodynamics*, 5th ed., Secs. 3.4–3.7 and 6.2–6.6, McGraw-Hill, New York, 1996).

EXPRESSIONS FOR THE EXCESS GIBBS ENERGY

In principle, equation-of-state procedures can be used for the calculation of liquid-phase as well as gas-phase properties, and much has been accomplished in the development of *PVT* equations of state suitable for both phases. However, a widely used alternative for the liquid phase is application of excess properties.

The excess property of primary importance for engineering calculations is the excess Gibbs energy G^E, because its canonical variables are T, P, and composition, the variables usually specified or sought in a design calculation. Knowing G^E as a function of T, P, and composition, one can in principle compute from it all other excess properties (see, for example, Eqs. [4-117] through [4-119]). As noted with respect to Fig. 4-1, the excess volume for liquid mixtures is usually small; the pressure dependence of G^E may then be safely ignored. Thus, the engineering efforts at describing G^E center on representing its composition and temperature dependence.

For binary systems *at constant T*, G^E is a function of just x_1, and the quantity most conveniently represented by an equation is G^E/x_1x_2RT. The simplest procedure is to express this quantity as a power series in x_1:

$$\frac{G^E}{x_1x_2RT} = a + bx_1 + cx_1^2 + \cdots \qquad (\text{constant } T)$$

An equivalent power series with certain advantages is known as the *Redlich/Kister expansion* (Redlich, Kister, and Turnquist, *Chem. Eng. Progr. Symp. Ser. No. 2,* **48,** pp. 49–61 [1952]):

$$\frac{G^E}{x_1x_2RT} = B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \cdots$$

In application, different truncations of this series are appropriate. For each particular expression representing G^E/x_1x_2RT, specific expressions for $\ln \gamma_1$ and $\ln \gamma_2$ result from application of Eq. (4-119). When all parameters are zero, $G^E/RT = 0$, and the solution is ideal. If $C = D = \cdots = 0$, then

$$\frac{G^E}{x_1x_2RT} = B$$

where B is a constant for a given temperature. The corresponding equations for $\ln \gamma_1$ and $\ln \gamma_2$ are

$$\ln \gamma_1 = Bx_2^2 \tag{4-242}$$

$$\ln \gamma_2 = Bx_1^2 \tag{4-243}$$

The symmetrical nature of these relations is evident. The infinite-dilution values of the activity coefficients are $\ln \gamma_1^\infty = \ln \gamma_2^\infty = B$.

If $D = \cdots = 0$, then

$$\frac{G^E}{x_1x_2RT} = B + C(x_1 - x_2) = B + C(2x_1 - 1)$$

and in this case G^E/x_1x_2RT is linear in x_1. The substitutions, $B + C = A_{21}$ and $B - C = A_{12}$ transform this expression into the *Margules equation:*

$$G^E/x_1x_2RT = A_{21}x_1 + A_{12}x_2 \tag{4-244}$$

Application of Eq. (4-119) yields

$$\ln \gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1] \tag{4-245}$$

$$\ln \gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2] \tag{4-246}$$

An alternative equation is obtained when the reciprocal quantity x_1x_2RT/G^E is expressed as a linear function of x_1:

$$\frac{x_1x_2}{G^E/RT} = B' + C'(x_1 - x_2) = B' + C'(2x_1 - 1)$$

This may also be written:

$$\frac{x_1x_2}{G^E/RT} = B'(x_1 + x_2) + C'(x_1 - x_2) = (B' + C')x_1 + (B' - C')x_2$$

The substitutions $B' + C' = 1/A'_{21}$ and $B' - C' = 1/A'_{12}$ produce

$$\frac{x_1x_2}{G^E/RT} = \frac{x_1}{A'_{21}} + \frac{x_2}{A'_{12}} = \frac{A'_{12}x_1 + A'_{21}x_2}{A'_{12}A'_{21}}$$

or

$$\frac{G^E}{x_1x_2RT} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2} \tag{4-247}$$

The activity coefficients implied by this equation are given by

$$\ln \gamma_1 = A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2} \tag{4-248}$$

$$\ln \gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2} \tag{4-249}$$

These are known as the *van Laar equations.* When $x_1 = 0$, $\ln \gamma_1^\infty = A'_{12}$; when $x_2 = 0$, $\ln \gamma_2^\infty = A'_{21}$.

The Redlich/Kister expansion, the Margules equations, and the van Laar equations are all special cases of a very general treatment based on rational functions, that is, on equations for G^E given by ratios of polynomials (Van Ness and Abbott, *Classical Thermodynamics of Nonelectrolyte Solutions: With Applications to Phase Equilibria*, Sec. 5-7, McGraw-Hill, New York, 1982). Although providing great flexibility in the fitting of VLE data for binary systems, they are without theoretical foundation, with no rational basis for their extension to multicomponent systems. Nor do they incorporate an explicit temperature dependence for the parameters.

Modern theoretical developments in the molecular thermodynamics of liquid-solution behavior are often based on the concept of *local compositon,* presumed to account for the short-range order and nonrandom molecular orientations that result from differences in molecular size and intermolecular forces. Introduced with the publication of a model of G^E behavior known as the *Wilson equation* (*J. Am. Chem. Soc.,* **86,** pp. 127–130 [1964]), it prompted the development of alternative local-composition models, most notably the NRTL (**N**on-**R**andom-**T**wo-**L**iquid) equation of Renon and Prausnitz (*AIChE J.,* **14,** pp. 135–144 [1968]) and the UNIQUAC (**UNI**versal **QUA**si-**C**hemical) equation of Abrams and Prausnitz (*AIChE J.,* **21,** pp. 116–128 [1975]). A further significant development, based on the UNIQUAC equation, is the UNIFAC method (**UNI**QUAC **F**unctional-group **A**ctivity **C**oefficients). Proposed by Fredenslund, Jones, and Prausnitz (*AIChE J.,* **21,** pp. 1086–1099 [1975]) and given detailed treatment by Fredenslund, Gmehling, and Rasmussen (*Vapor-Liquid Equilibrium Using UNIFAC*, Elsevier, Amsterdam, 1977), it provides for the calculation of activity coefficients from contributions of the various groups making up the molecules of a solution.

The Wilson equation, like the Margules and van Laar equations, contains just two parameters for a binary system (Λ_{12} and Λ_{21}), and is written:

$$\frac{G^E}{RT} = -x_1 \ln (x_1 + x_2\Lambda_{12}) - x_2 \ln (x_2 + x_1\Lambda_{21}) \qquad (4\text{-}250)$$

$$\ln \gamma_1 = -\ln (x_1 + x_2\Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} \right) \qquad (4\text{-}251)$$

$$\ln \gamma_2 = -\ln (x_2 + x_1\Lambda_{21}) - x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} \right) \qquad (4\text{-}252)$$

whence

$$\ln \gamma_1^\infty = -\ln \Lambda_{12} + 1 - \Lambda_{21}$$

$$\ln \gamma_2^\infty = -\ln \Lambda_{21} + 1 - \Lambda_{12}$$

Both Λ_{12} and Λ_{21} must be positive numbers.

The NRTL equation contains three parameters for a binary system and is written:

$$\frac{G^E}{x_1x_2RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}} \qquad (4\text{-}253)$$

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12}\tau_{12}}{(x_2 + x_1 G_{12})^2} \right] \qquad (4\text{-}254)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{G_{21}\tau_{21}}{(x_1 + x_2 G_{21})^2} \right] \qquad (4\text{-}255)$$

Here

$$G_{12} = \exp (-\alpha\tau_{12}) \qquad G_{21} = \exp (-\alpha\tau_{21})$$

and

$$\tau_{12} = \frac{b_{12}}{RT} \qquad \tau_{21} = \frac{b_{21}}{RT}$$

where α, b_{12}, and b_{21}, parameters specific to a particular pair of species, are independent of composition and temperature. The infinite-dilution values of the activity coefficients are given by the equations:

$$\ln \gamma_1^\infty = \tau_{21} + \tau_{12} \exp (-\alpha\tau_{12})$$

$$\ln \gamma_2^\infty = \tau_{12} + \tau_{21} \exp (-\alpha\tau_{21})$$

The local-composition models have limited flexibility in the fitting of data, but they are adequate for most engineering purposes. Moreover, they are implicitly generalizable to multicomponent systems without the introduction of any parameters beyond those required to describe the constituent binary systems. For example, the Wilson equation for multicomponent systems is written:

$$\frac{G^E}{RT} = -\sum_i x_i \ln \sum_j x_j \Lambda_{ij} \qquad (4\text{-}256)$$

and

$$\ln \gamma_i = 1 - \ln \sum_j x_j \Lambda_{ij} - \sum_k \frac{x_k\Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \qquad (4\text{-}257)$$

where $\Lambda_{ij} = 1$ for $i = j$, and so on. All indices in these equations refer to the same species, and all summations are over *all* species. For each ij pair there are two parameters, because $\Lambda_{ij} \neq \Lambda_{ji}$. For example, in a ternary system the three possible ij pairs are associated with the parameters Λ_{12}, Λ_{21}; Λ_{13}, Λ_{31}; and Λ_{23}, Λ_{32}.

The temperature dependence of the parameters is given by:

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \frac{-a_{ij}}{RT} \qquad (i \neq j) \qquad (4\text{-}258)$$

where V_j and V_i are the molar volumes at temperature T of pure liquids j and i, and a_{ij} is a constant independent of composition and temperature. Thus the Wilson equation, like all other local-composition models, has built into it an *approximate* temperature dependence for the parameters. Moreover, all parameters are found from data for binary (in contrast to multicomponent) systems. This makes parameter determination for the local-composition models a task of manageable proportions.

The UNIQUAC equation treats $g \equiv G^E/RT$ as comprised of two additive parts, a *combinatorial* term g^C, accounting for molecular size and shape differences, and a *residual* term g^R (not a residual property), accounting for molecular interactions:

$$g = g^C + g^R \qquad (4\text{-}259)$$

Function g^C contains pure-species parameters only, whereas function g^R incorporates two *binary* parameters for each pair of molecules. For a multicomponent system,

$$g^C = \sum_i x_i \ln \frac{\Phi_i}{x_i} + 5 \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \qquad (4\text{-}260)$$

$$g^R = -\sum_i q_i x_i \ln \left(\sum_j \theta_j \tau_{ji} \right) \qquad (4\text{-}261)$$

where

$$\Phi_i \equiv \frac{x_i r_i}{\sum_j x_j r_j} \qquad (4\text{-}262)$$

and

$$\theta_i \equiv \frac{x_i q_i}{\sum_j x_j q_j} \qquad (4\text{-}263)$$

Subscript i identifies species, and j is a dummy index; all summations are over all species. Note that $\tau_{ji} \neq \tau_{ij}$; however, when $i = j$, then $\tau_{ii} = \tau_{jj} = 1$. In these equations r_i (a relative molecular volume) and q_i (a relative molecular surface area) are pure-species parameters. The influence of temperature on g enters through the interaction parameters τ_{ji} of Eq. (4-261), which are temperature dependent:

$$\tau_{ji} = \exp \frac{-(u_{ji} - u_{ii})}{RT} \qquad (4\text{-}264)$$

Parameters for the UNIQUAC equation are therefore values of $(u_{ji} - u_{ii})$.

An expression for $\ln \gamma_i$ is found by application of Eq. (4-119) to the UNIQUAC equation for g (Eqs. [4-259] through [4-261]). The result is given by the following equations:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad (4\text{-}265)$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i} \right) \qquad (4\text{-}266)$$

$$\ln \gamma_i^R = q_i \left(1 - \ln s_i - \sum_j \theta_j \frac{\tau_{ij}}{s_j} \right) \qquad (4\text{-}267)$$

where in addition to Eqs. (4-263) and (4-264)

$$J_i = \frac{r_i}{\sum_j r_j x_j} \qquad (4\text{-}268)$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \qquad (4\text{-}269)$$

$$s_i = \sum_l \theta_l \tau_{li} \qquad (4\text{-}270)$$

Again subscript i identifies species, and j and l are dummy indicies. Values for the parameters r_i, q_i, and $(u_{ij} - u_{jj})$ are given by Gmehling, Onken, and Arlt (*Vapor-Liquid Equilibrium Data Collection*, Chemistry Data Series, vol. I, parts 1–8, DECHEMA, Frankfurt/Main, 1974–1990).

The Wilson parameters Λ_{ij}, NRTL parameters G_{ij}, and UNIQUAC parameters τ_{ij} all inherit a Boltzmann-type T dependence from the origins of the expressions for G^E, but it is only approximate. Computations of properties sensitive to this dependence (e.g., heats of mixing and liquid/liquid solubility) are in general only qualitatively correct.

EQUILIBRIUM

CRITERIA

The equations developed in preceding sections are for *PVT* systems in states of internal equilibrium. The criteria for internal thermal and mechanical equilibrium are well known, and need not be discussed in detail. They simply require uniformity of temperature and pressure throughout the system. The criteria for phase and chemical-reaction equilibria are less obvious.

Consider a closed *PVT* system, either homogeneous or heterogeneous, of uniform T and P, which is in thermal and mechanical equilibrium with its surroundings, but which is not initially at internal equilibrium with respect to mass transfer or with respect to chemical reaction. Changes occurring in the system are then irreversible, and must necessarily bring the system closer to an equilibrium state. The first and second laws written for the entire system are

$$dU^t = dQ + dW$$

$$dS^t \geq \frac{dQ}{T}$$

Combination gives

$$dU^t - dW - T\,dS^t \leq 0$$

Since mechanical equilibrium is assumed,

$$dW = -P\,dV^t$$

Whence
$$dU^t + P\,dV^t - T\,dS^t \leq 0$$

The inequality applies to all incremental changes toward the equilibrium state, whereas the equality holds at the equilibrium state where any change is reversible.

Various constraints may be put on this expression to produce alternative criteria for the directions of irreversible processes and for the condition of equilibrium. For example, it follows immediately that

$$dU^t_{S^t,V^t} \leq 0$$

Alternatively, other pairs of properties may be held constant. The most useful result comes from fixing T and P, in which case

$$d(U^t + PV^t - TS^t)_{T,P} \leq 0$$

or
$$dG^t_{T,P} \leq 0$$

This expression shows that all irreversible processes occurring at constant T and P proceed in a direction such that the total Gibbs energy of the system decreases. Thus the equilibrium state of a closed system is the state with the minimum total Gibbs energy attainable at the given T and P. At the equilibrium state, differential variations may occur in the system at constant T and P without producing a change in G^t. This is the meaning of the equilibrium criterion

$$dG^t_{T,P} = 0 \tag{4-271}$$

This equation may be applied to a closed, nonreactive, two-phase system. Each phase taken separately is an *open* system, capable of exchanging mass with the other, and Eq. (4-16) may be written for each phase:

$$d(nG)' = -(nS)'\,dT + (nV)'\,dP + \sum_i \mu_i'\,dn_i'$$

$$d(nG)'' = -(nS)''\,dT + (nV)''\,dP + \sum_i \mu_i''\,dn_i''$$

where the primes and double primes denote the two phases and the presumption is that T and P are uniform throughout the two phases. The change in the Gibbs energy of the two-phase system is the sum of these equations. When each total-system property is expressed by an equation of the form

$$nM = (nM)' + (nM)''$$

this sum is given by

$$d(nG) = (nV)\,dP - (nS)\,dT + \sum_i \mu_i'\,dn_i' + \sum_i \mu_i''\,dn_i''$$

If the two-phase system is at equilibrium, then application of Eq. (4-271) yields

$$dG^t_{T,P} \equiv d(nG)_{T,P} = \sum_i \mu_i'\,dn_i' + \sum_i \mu_i''\,dn_i'' = 0$$

Since the system is closed and without chemical reaction, material balances require that

$$dn_i'' = -dn_i'$$

Therefore
$$\sum_i (\mu_i' - \mu_i'')\,dn_i' = 0$$

Since the dn'_i are independent and arbitrary, it follows that

$$\mu_i' = \mu_i''$$

This is the criterion of two-phase equilibrium. It is readily generalized to multiple phases by successive application to pairs of phases. The general result is

$$\mu_i' = \mu_i'' = \mu_i''' = \cdots \tag{4-272}$$

Substitution for each μ_i by Eq. (4-77) produces the equivalent result

$$\hat{f}_i' = \hat{f}_i'' = \hat{f}_i''' = \cdots \tag{4-273}$$

These are the criteria of phase equilibrium applied in the solution of practical problems.

For the case of equilibrium with respect to chemical reaction within a single-phase closed system, combination of Eqs. (4-16) and (4-271) leads immediately to

$$\sum_i \mu_i\,dn_i = 0 \tag{4-274}$$

For a system in which both phase and chemical-reaction equilibrium prevail, the criteria of Eqs. (4-272) and (4-274) are superimposed.

THE PHASE RULE

The *intensive* state of a *PVT* system is established when its temperature and pressure and the compositions of all phases are fixed. However, for equilibrium states these variables are not all independent, and fixing a limited number of them automatically establishes the others. This number of independent variables is given by the phase rule, and is called the *number of degrees of freedom* of the system. It is the number of variables which may be arbitrarily specified and which must be so specified in order to fix the *intensive* state of a system at equilibrium. This number is the difference between the number of variables needed to characterize the system and the number of equations that may be written connecting these variables.

For a system containing N chemical species distributed at equilibrium among π phases, the phase-rule variables are temperature and pressure, presumed uniform throughout the system, and $N - 1$ mole fractions in each phase. The number of these variables is $2 + (N - 1)\pi$. The masses of the phases are not phase-rule variables, because they have nothing to do with the intensive state of the system.

The equations that may be written connecting the phase-rule variables are:

1. Equation (4-272) for each species, giving $(\pi - 1)N$ phase-equilibrium equations.
2. Equation (4-274) for each independent chemical reaction, giving r equations.

The total number of independent equations is therefore $(\pi - 1)N + r$. In their fundamental forms these equations relate chemical potentials, which are functions of temperature, pressure, and composition, the phase-rule variables. Since the degrees of freedom of the system F is the difference between the number of variables and the number of equations,

$$F = 2 + (N - 1)\pi - (\pi - 1)N - r$$

or
$$F = 2 - \pi + N - r \tag{4-275}$$

The number of independent chemical reactions r can be determined as follows:

1. Write *formation* reactions from the elements for each chemical compound present in the system.
2. Combine these reaction equations so as to eliminate from the set all elements not present as elements in the system. A systematic procedure is to select one equation and combine it with each of the other equations of the set so as to eliminate a particular element. This usually reduces the set by one equation for each element eliminated, though two or more elements may be simultaneously eliminated.

The resulting set of r equations is a complete set of independent reactions. More than one such set is often possible, but all sets number r and are equivalent.

Example 1: Application of the Phase Rule

a. For a system of two miscible nonreacting species in vapor/liquid equilibrium,

$$F = 2 - \pi + N - r = 2 - 2 + 2 - 0 = 2$$

The two degrees of freedom for this system may be satisfied by setting T and P, or T and y_1, or P and x_1, or x_1 and y_1, and so on, at fixed values. Thus, for equilibrium at a particular T and P, this state (if possible at all) exists only at one liquid and one vapor composition. Once the two degrees of freedom are used up, no further specification is possible that would restrict the phase-rule variables. For example, one cannot *in addition* require that the system form an azeotrope (assuming this possible), for this requires $x_1 = y_1$, an equation not taken into account in the derivation of the phase rule. Thus, the requirement that the system form an azeotrope imposes a special constraint and reduces the number of degrees of freedom to one.

b. For a gaseous system consisting of CO, CO_2, H_2, H_2O, and CH_4 in chemical-reaction equilibrium,

$$F = 2 - \pi + N - r = 2 - 1 + 5 - 2 = 4$$

The value of $r = 2$ is found from the formation reactions:

$$C + \text{a}\, O_2 \rightarrow CO$$
$$C + O_2 \rightarrow CO_2$$
$$H_2 + \text{a}\, O_2 \rightarrow H_2O$$
$$C + 2H_2 \rightarrow CH_4$$

Systematic elimination of C and O_2 from this set of chemical equations reduces the set to two. Three possible pairs of equations may result, depending on how the combination of equations is effected. Any *pair* of the following three equations represents a complete set of independent reactions, and all pairs are equivalent.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

The result, $F = 4$, means that one is free to specify, for example, T, P, and two mole fractions in an equilibrium mixture of these five chemical species, provided nothing else is arbitrarily set. Thus, it cannot simultaneously be required that the system be prepared from specified amounts of particular constituent species.

Since the phase rule treats only the intensive state of a system, it applies to both closed and open systems. **Duhem's theorem,** on the other hand, is a rule relating to closed systems only: *For any closed system formed initially from given masses of prescribed chemical species, the equilibrium state is* completely determined *by any two properties of the system, provided only that the two properties are independently variable at the equilibrium state.* The meaning of *completely determined* is that both the intensive and extensive states of the system are fixed; not only are T, P, and the phase compositions established, but so also are the masses of the phases.

VAPOR/LIQUID EQUILIBRIUM

Vapor/liquid equilibrium (VLE) relationships (as well as other interphase equilibrium relationships) are needed in the solution of many engineering problems. The required data can be found by experiment, but such measurements are seldom easy, even for binary systems, and they become rapidly more difficult as the number of constituent species increases. This is the incentive for application of thermodynamics to the calculation of phase-equilibrium relationships.

The general VLE problem involves a multicomponent system of N constituent species for which the independent variables are T, P, $N - 1$ liquid-phase mole fractions, and $N - 1$ vapor-phase mole fractions. (Note that $\sum_i x_i = 1$ and $\sum_i y_i = 1$, where x_i and y_i represent liquid and vapor mole fractions respectively.) Thus there are $2N$ independent variables, and application of the phase rule shows that exactly N of these variables must be fixed to establish the intensive state of the system. This means that once N variables have been specified, the remaining N variables can be determined by simultaneous solution of the N equilibrium relations:

$$\hat{f}_i^l = \hat{f}_i^v \qquad (i = 1, 2, \ldots, N) \tag{4-276}$$

where superscripts l and v denote the liquid and vapor phases, respectively.

In practice, either T or P *and* either the liquid-phase or vapor-phase composition are specified, thus fixing $1 + (N - 1) = N$ independent variables. The remaining N variables are then subject to calculation, provided that sufficient information is available to allow determination of all necessary thermodynamic properties.

Gamma/Phi Approach For many VLE systems of interest the pressure is low enough that a relatively simple equation of state, such as the two-term virial equation, is satisfactory for the vapor phase. Liquid-phase behavior, on the other hand, may be conveniently described by an equation for the excess Gibbs energy, from which activity coefficients are derived. The fugacity of species i in the liquid phase is then given by Eq. (4-102), written

$$\hat{f}_i^l = \gamma_i x_i f_i$$

while the vapor-phase fugacity is given by Eq. (4-79), written

$$\hat{f}_i^v = \hat{\phi}_i^v y_i P$$

Equation (4-276) is now expressed as

$$\gamma_i x_i f_i = \hat{\phi}_i y_i P \qquad (i = 1, 2, \ldots, N) \tag{4-277}$$

The identifying superscripts l and v are omitted here with the understanding that γ_i and f_i are liquid-phase properties, whereas $\hat{\phi}_i$ is a vapor-phase property. Applications of Eq. (4-277) represent what is known as the *gamma/phi* approach to VLE calculations.

Evaluation of $\hat{\phi}_i$ is usually by Eq. (4-196), based on the two-term virial equation of state, but other equations, such as Eq. (4-200), are also applicable. The activity coefficient γ_i is evaluated by Eq. (4-119), which relates $\ln \gamma_i$ to G^E/RT as a partial property. Thus, what is required for the liquid phase is a relation between G^E/RT and composition. Equations in common use for this purpose have already been described.

The fugacity f_i of pure compressed liquid i must be evaluated at the T and P of the equilibrium mixture. This is done in two steps. First, one calculates the fugacity coefficient of saturated vapor $\phi_i^v = \phi_i^{sat}$ by an integrated form of Eq. (4-161), written for pure species i and evaluated at temperature T and the corresponding vapor pressure $P = P_i^{sat}$. Equation (4-276) written for pure species i becomes

$$f_i^v = f_i^l = f_i^{sat} \tag{4-278}$$

where f_i^{sat} indicates the value both for saturated liquid and for saturated vapor. The corresponding fugacity coefficient is

$$\phi_i^{sat} = \frac{f_i^{sat}}{P_i^{sat}} \tag{4-279}$$

This fugacity coefficient applies equally to saturated vapor and to saturated liquid at given temperature T. Equation (4-278) can therefore equally well be written

$$\phi_i^v = \phi_i^l \tag{4-280}$$

The second step is the evaluation of the change in fugacity of the liquid with a change in pressure to a value above or below P_i^{sat}. For this isothermal change of state from saturated liquid at P_i^{sat} to liquid at pressure P, Eq. (4-105) is integrated to give

$$G_i - G_i^{sat} = \int_{P_i^{sat}}^{P} V_i\, dP$$

Equation (4-74) is then written twice: for G_i and for G_i^{sat}. Subtraction provides another expression for $G_i - G_i^{sat}$:

$$G_i - G_i^{\text{sat}} = RT \ln \frac{f_i}{f_i^{\text{sat}}}$$

Equating the two expressions for $G_i - G_i^{\text{sat}}$ yields

$$\ln \frac{f_i}{f_i^{\text{sat}}} = \frac{1}{RT} \int_{P_i^{\text{sat}}}^{P} V_i \, dP$$

Since V_i, the liquid-phase molar volume, is a very weak function of P at temperatures well below T_c, an excellent approximation is often obtained when evaluation of the integral is based on the assumption that V_i is constant at the value for saturated liquid, V_i^l:

$$\ln \frac{f_i}{f_i^{\text{sat}}} = \frac{V_i^l (P - P_i^{\text{sat}})}{RT}$$

Substituting $f_i^{\text{sat}} = \phi_i^{\text{sat}} P_i^{\text{sat}}$ (Eq. [4-279]), and solving for f_i gives

$$f_i = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \frac{V_i^l (P - P_i^{\text{sat}})}{RT} \tag{4-281}$$

The exponential is known as the *Poynting factor.*

Equation (4-277) may now be written

$$y_i P \Phi_i = x_i \gamma_i P_i^{\text{sat}} \qquad (i = 1, 2, \ldots, N) \tag{4-282}$$

where
$$\Phi_i = \left(\frac{\hat{\phi}_i}{\phi_i^{\text{sat}}} \right) \exp \frac{-V_i^l (P - P_i^{\text{sat}})}{RT} \tag{4-283}$$

If evaluation of ϕ_i^{sat} and $\hat{\phi}_i$ is by Eqs. (4-192) and (4-196), this reduces to

$$\Phi_i = \exp \left[\frac{P \bar{B}_i - P_i^{\text{sat}} B_{ii} - V_i^l (P - P_i^{\text{sat}})}{RT} \right] \tag{4-284}$$

where $\bar{B}_i$ is given by Eq. (4-195):

$$\bar{B}_i \equiv \left[\frac{\partial (nB)}{\partial n_i} \right]_{T, n_j} = 2 \sum_k y_k B_{ki} - B \tag{4-285}$$

with B evaluated by Eq. (4-183).

The N equations represented by Eq. (4-282) in conjunction with Eq. (4-284) may be used to solve for N unspecified phase-equilibrium variables. For a multicomponent system the calculation is formidable, but well suited to computer solution. The types of problems encountered for nonelectrolyte systems at low to moderate pressures (well below the critical pressure) are discussed by Smith, Van Ness, and Abbott (*Introduction to Chemical Engineering Thermodynamics,* 5th ed., McGraw-Hill, New York, 1996).

When Eq. (4-282) is applied to VLE for which the vapor phase is an ideal gas and the liquid phase is an ideal solution, it reduces to a very simple expression. For ideal gases, fugacity coefficients $\hat{\phi}_i$ and ϕ_i^{sat} are unity, and the right-hand side of Eq. (4-283) reduces to the Poynting factor. For the systems of interest here this factor is always very close to unity, and for practical purposes $\Phi_i = 1$. For ideal solutions, the activity coefficients γ_i are also unity. Equation (4-282) therefore reduces to

$$y_i P = x_i P_i^{\text{sat}} \qquad (i = 1, 2, \ldots, N)$$

an equation which expresses *Raoult's law.* It is the simplest possible equation for VLE, and as such fails to provide a realistic representation of real behavior for most systems. Nevertheless, it is useful as a standard of comparison.

When an appropriate correlating equation for G^E is not available, reliable estimates of activity coefficients may often be obtained from a group-contribution correlation. The Analytical Solution of Groups (ASOG) method (Kojima and Tochigi, *Prediction of Vapor-Liquid Equilibrium by the ASOG Method,* Elsevier, Amsterdam, 1979) and the UNIFAC method are both well developed. Additional references of interest include Hansen et al. (*Ind. Eng. Chem. Res.,* **30,** pp. 2352–2355 [1991]), Gmehling and Schiller (Ibid., **32,** pp. 178–193 [1993]); Larsen et al. (Ibid., **26,** pp. 2274–2286 [1987]); and Tochigi et al. (*J. Chem. Eng. Japan,* **23,** pp. 453–463 [1990]).

Data Reduction Correlations for G^E and the activity coefficients are based on VLE data taken at low to moderate pressures. The ASOG and UNIFAC group-contribution methods depend for validity on parameters evaluated from a large base of such data. The process of finding a suitable analytic relation for g ($\equiv G^E/RT$) as a function of its independent variables T and x_1, thus producing a correlation of VLE data, is known as *data reduction.* Although g is in principle also a function of P, the dependence is so weak as to be universally and properly neglected. Given here is a brief description of the treatment of data taken for *binary* systems under *isothermal* conditions. A more comprehensive development is given by Van Ness (*J. Chem. Thermodyn.,* **27,** pp. 113–134 [1995]; *Pure & Appl. Chem.,* **67,** pp. 859–872 [1995]).

Presumed in all that follows is the existence of an equation inherently capable of representing correct values of G^E for the liquid phase as a function of x_1:

$$g \equiv G^E/RT = \mathcal{G}(x_1; \alpha, \beta, \ldots) \tag{4-286}$$

where α, β, and so on, represent adjustable parameters.

The measured variables of binary VLE are x_1, y_1, T, and P. Experimental values of the activity coefficient of species i in the liquid are related to these variables by Eq. (4-282), written:

$$\gamma^*_i = \frac{y_i^* P^*}{x_i P_i^{\text{sat}}} \Phi_i \qquad (i = 1, 2) \tag{4-287}$$

where Φ_i is given by Eq. (4-283), and the asterisks denote experimental values. A simple summability relation analogous to Eq. (4-123) defines an experimental value of g^*:

$$g^* \equiv x_1 \ln \gamma_1^* + x_2 \ln \gamma_2^* \tag{4-288}$$

Moreover, Eq. (4-122), the Gibbs/Duhem equation, may be written for experimental values in a binary system as

$$x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} = 0 \tag{4-289}$$

Because experimental measurements are subject to systematic error, sets of values of $\ln \gamma_1^*$ and $\ln \gamma_2^*$ determined by experiment may not satisfy, that is, may not be *consistent* with, the Gibbs/Duhem equation. Thus, Eq. (4-289) applied to sets of experimental values becomes a test of the thermodynamic consistency of the data, rather than a valid general relationship.

Values of g given by the correlating equation, Eq. (4-286), are called *derived* values, and associated derived values of the activity coefficients are given by specialization of Eqs. (4-58):

$$\gamma_1 = \exp \left(g + x_2 \frac{dg}{dx_1} \right) \tag{4-290}$$

$$\gamma_2 = \exp \left(g - x_1 \frac{dg}{dx_1} \right) \tag{4-291}$$

These two equations may be combined to yield

$$\frac{dg}{dx_1} = \ln \frac{\gamma_1}{\gamma_2} \tag{4-292}$$

This equation applies to *derived* property values. The corresponding *experimental* values are given by differentiation of Eq. (4-288):

$$\frac{dg^*}{dx_1} = x_1 \frac{d \ln \gamma_1^*}{dx_1} + \ln \gamma_1^* + x_2 \frac{d \ln \gamma_2^*}{dx_1} - \ln \gamma_2^*$$

or
$$\frac{dg^*}{dx_1} = \ln \frac{\gamma_1^*}{\gamma_2^*} + x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} \tag{4-293}$$

Subtraction of Eq. (4-293) from Eq. (4-292) gives

$$\frac{dg}{dx_1} - \frac{dg^*}{dx_1} = \ln \frac{\gamma_1}{\gamma_2} - \ln \frac{\gamma_1^*}{\gamma_2^*} - \left(x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} \right)$$

The differences between like terms represent *residuals* between derived and experimental values. Defining these residuals as

$$\delta g \equiv g - g^* \qquad \text{and} \qquad \delta \ln \frac{\gamma_1}{\gamma_2} \equiv \ln \frac{\gamma_1}{\gamma_2} - \ln \frac{\gamma_1^*}{\gamma_2^*}$$

puts this equation into the form

$$\frac{d \delta g}{dx_1} = \delta \ln \frac{\gamma_1}{\gamma_2} - \left(x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} \right)$$

If a data set is reduced so as to make the δg residuals scatter about zero, then the derivative on the left is effectively zero, and the preceding equation becomes

$$\delta \ln \frac{\gamma_1}{\gamma_2} = x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} \tag{4-294}$$

The right-hand side of this equation is exactly the quantity that Eq. (4-289), the Gibbs/Duhem equation, requires to be zero for consistent data. The residual on the left is therefore a direct measure of deviations from the Gibbs/Duhem equation. The extent to which values of this residual fail to scatter about zero measures the departure of the data from consistency with respect to this equation.

The data-reduction procedure just described provides parameters in the correlating equation for g that make the δg residuals scatter about zero. This is usually accomplished by finding the parameters that minimize the sum of squares of the residuals. Once these parameters are found, they can be used for the calculation of derived values of both the pressure P and the vapor composition y_1. Equation (4-282) is solved for y_iP and written for species 1 and for species 2. Adding the two equations gives

$$P = \frac{x_1\gamma_1 P_1^{\text{sat}}}{\Phi_1} + \frac{x_2\gamma_2 P_2^{\text{sat}}}{\Phi_2} \tag{4-295}$$

whence by Eq. (4-282),

$$y_1 = \frac{x_1\gamma_1 P_1^{\text{sat}}}{\Phi_1 P} \tag{4-296}$$

These equations allow calculation of the *primary* residuals:

$$\delta P \equiv P - P^* \qquad \text{and} \qquad \delta y_1 \equiv y_1 - y_1^*$$

If the experimental values P^* and y_1^* are closely reproduced by the correlating equation for g, then these residuals, evaluated at the experimental values of x_1, scatter about zero. This is the result obtained when the data are thermodynamically consistent. When they are not, these residuals do not scatter about zero, and the correlation for g does not properly reproduce the experimental values P^* and y_1^*. Such a correlation is, in fact, unnecessarily divergent. An alternative is to process just the P-x_1 data; this is possible because the P-x_1-y_1 data set includes more information than necessary. Assuming that the correlating equation is appropriate to the data, one merely searches for values of the parameters α, β, and so on, that yield pressures by Eq. (4-295) that are as close as possible to the measured values. The usual procedure is to minimize the sum of squares of the residuals δP. Known as *Barker's method* (*Austral. J. Chem.*, **6,** pp. 207–210 [1953]), it provides the best possible fit of the experimental pressures. When the experimental data do not satisfy the Gibbs/Duhem equation, it cannot precisely represent the experimental y_1 values; however, it provides a better fit than does the procedure that minimizes the sum of the squares of the δg residuals.

Worth noting is the fact that Barker's method does not require experimental y_1^* values. Thus the correlating parameters α, β, and so on, can be evaluated from a P-x_1 data subset. Common practice now is, in fact, to measure just such data. They are, of course, not subject to a test for consistency by the Gibbs/Duhem equation. The world's store of VLE data has been compiled by Gmehling et al. (*Vapor-Liquid Equilibrium Data Collection,* Chemistry Data Series, vol. I, parts 1–8, DECHEMA, Frankfurt am Main, 1979–1990).

Solute/Solvent Systems The gamma/phi approach to VLE calculations presumes knowledge of the vapor pressure of each species at the temperature of interest. For certain binary systems species 1, designated the *solute,* is either unstable at the system temperature or is *supercritical* ($T > T_c$). Its vapor pressure cannot be measured, and its fugacity as a pure liquid at the system temperature f_1 cannot be calculated by Eq. (4-281).

Equations (4-282) and (4-283) are applicable to species 2, designated the *solvent,* but not to the solute, for which an alternative approach is required. Figure 4-11 shows a typical plot of the liquid-phase fugacity of the solute $\hat{f}_1$ vs. its mole fraction x_1 at constant temperature. Since the curve representing $\hat{f}_1$ does not extend all the way to $x_1 = 1$, the location of f_1, the liquid-phase fugacity of pure species 1, is not established. The tangent line at the origin, representing *Henry's law,* provides alternative information. The slope of the tangent line is *Henry's constant,* defined as

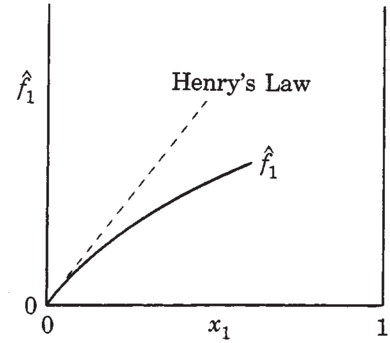

FIG. 4-11 Plot of solute fugacity $\hat{f}_1$ vs. solute mole fraction.

$$k_1 \equiv \lim_{x_1 \to 0} \frac{\hat{f}_1}{x_1} \tag{4-297}$$

This is the definition of k_1 for temperature T and for a pressure equal to the vapor pressure of the pure solvent P_2^{sat}.

The activity coefficient of the solute at infinite dilution is

$$\lim_{x_1 \to 0} \gamma_1 = \lim_{x_1 \to 0} \frac{\hat{f}_1}{x_1 f_1} = \frac{1}{f_1} \lim_{x_1 \to 0} \frac{\hat{f}_1}{x_1}$$

In view of Eq. (4-297), this becomes $\gamma_1^\infty = k_1/f_1$, or

$$f_1 = \frac{k_1}{\gamma_1^\infty} \tag{4-298}$$

where γ_1^∞ represents the infinite-dilution value of the activity coefficient of the solute. Since both k_1 and γ_1^∞ are evaluated at P_2^{sat}, this pressure also applies to f_1. However, the effect of P on a liquid-phase fugacity, given by a Poynting factor, is very small, and for practical purposes may usually be neglected. The activity coefficient of the solute, given by

$$\gamma_1 \equiv \frac{\hat{f}_1}{x_1 f_1} = \frac{y_1 P \hat{\phi}_1}{x_1 f_1}$$

then becomes

$$\gamma_1 = \frac{y_1 P \hat{\phi}_1 \gamma_1^\infty}{x_1 k_1}$$

For the solute, this equation takes the place of Eqs. (4-282) and (4-283). Solution for y_1 gives

$$y_1 = \frac{x_1(\gamma_1/\gamma_1^\infty)k_1}{\hat{\phi}_1 P} \tag{4-299}$$

For the solvent, species 2, the analog of Eq. (4-296) is

$$y_2 = \frac{x_2\gamma_2 P_2^{\text{sat}}}{\Phi_2 P} \tag{4-300}$$

Since $y_1 + y_2 = 1$,

$$P = \frac{x_1(\gamma_1/\gamma_1^\infty)k_1}{\hat{\phi}_1} + \frac{x_2\gamma_2 P_2^{\text{sat}}}{\Phi_2} \tag{4-301}$$

Note that the same correlation that provides for the evaluation of γ_1 also allows evaluation of γ_1^∞.

There remains the problem of finding Henry's constant from the available VLE data. For equilibrium

$$\hat{f}_1 \equiv \hat{f}_1^l = \hat{f}_1^v = y_1 P \hat{\phi}_1$$

Division by x_1 gives

$$\frac{\hat{f}_1}{x_1} = P\hat{\phi}_1 \frac{y_1}{x_1}$$

Henry's constant is defined as the limit as $x_1 \to 0$ of the ratio on the left; therefore

$$k_1 = P_2^{sat} \hat{\phi}_1^{\infty} \lim_{x_1 \to 0} \frac{y_1}{x_1}$$

The limiting value of y_1/x_1 can be found by plotting y_1/x_1 vs. x_1 and extrapolating to zero.

***K*-Values** A measure of how a given chemical species distributes itself between liquid and vapor phases is the equilibrium ratio:

$$K_i \equiv \frac{y_i}{x_i} \qquad (4\text{-}302)$$

Usually called simply a *K*-value, it adds nothing to thermodynamic knowledge of VLE. However, its use may make for computational convenience, allowing formal elimination of one set of mole fractions $\{y_i\}$ or $\{x_i\}$ in favor of the other. Moreover, it characterizes *lightness* of a constituent species. For a *light* species, tending to concentrate in the vapor phase, $K > 1$; for a *heavy* species, tending to concentrate in the liquid phase, $K < 1$.

Empirical correlations for *K*-values found in the older literature have little relation to thermodynamics. Their proper evaluation comes directly from Eq. (4-277):

$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i f_i}{\hat{\phi}_i P} \qquad (4\text{-}303)$$

When Raoult's law applies, this becomes $K_i = P_i^{sat}/P$. In general, *K*-values are functions of *T, P,* liquid composition, and vapor composition, making their direct and accurate correlation impossible. Those correlations that do exist are approximate and severely limited in application. The DePriester correlation, for example, gives *K*-values for light hydrocarbons (*Chem. Eng. Prog. Symp. Ser. No. 7,* **49,** pp. 1–43 [1953]).

Equation-of-State Approach Although the gamma/phi approach to VLE is in principle generally applicable to systems comprised of subcritical species, in practice it has found use primarily where pressures are no more than a few bars. Moreover, it is most satisfactory for correlation of constant-temperature data. A temperature dependence for the parameters in expressions for G^E is included only for the local-composition equations, and it is at best only approximate.

A generally applicable alternative to the gamma/phi approach results when both the liquid and vapor phases are described by the same equation of state. The defining equation for the fugacity coefficient, Eq. (4-79), may be applied to each phase:

$$\text{Liquid:} \qquad \hat{f}_i^l = \hat{\phi}_i^l x_i P$$

$$\text{Vapor:} \qquad \hat{f}_i^v = \hat{\phi}_i^v y_i P$$

Equation (4-276) now becomes

$$x_i \hat{\phi}_i^l = y_i \hat{\phi}_i^v \qquad (i = 1, 2, \ldots, N) \qquad (4\text{-}304)$$

This introduces the compositions x_i and y_i into the equilibrium equations, but neither is explicit, because the $\hat{\phi}_i$ are functions, not only of *T* and *P,* but of composition. Thus Eq. (4-304) represents *N* complex relationships connecting *T, P,* the x_i, and the y_i, suitable for computer solution. Given an appropriate equation of state, one or another of Eqs. (4-178) through (4-181) provides for expression of the $\hat{\phi}_i$ as functions of *T, P,* and composition.

Because of inadequacies in empirical mixing rules, such as those given by Eqs. (4-221) and (4-222), the equation-of-state approach was long limited to systems exhibiting modest and well-behaved deviations from ideal solution behavior in the liquid phase; for example, to systems containing hydrocarbons and cryogenic fluids. However, the introduction by Wong and Sandler (*AIChE J.,* **38,** pp. 671–680 [1992]) of a new class of mixing rules for cubic equations of state has greatly expanded their useful application to VLE.

The Soave/Redlich/Kwong (SRK) and the Peng/Robinson (PR) equations of state, both expressed by Eqs. (4-230) and (4-231), were developed specifically for VLE calculations. The fugacity coefficients implicit in these equations are given by Eq. (4-232). When combined with the theoretically based Wong/Sandler mixing rules for parameters *a* and *b* these equations provide the means for accurate correlation and prediction of VLE data.

The first of the Wong/Sandler mixing rules relates the difference in mixture quantities *b* and *a/RT* to the corresponding differences (identified by subscripts) for the pure species:

$$b - \frac{a}{RT} = \sum_p \sum_q x_p x_q E_{pq} \qquad (4\text{-}305)$$

where
$$E_{pq} \equiv \frac{1}{2}\left(b_p - \frac{a_p}{RT} + b_q - \frac{a_q}{RT}\right)(1 - k_{pq}) \qquad (4\text{-}306)$$

Binary interaction parameters k_{pq} are determined for each *pq* pair $(p \neq q)$ from experimental data. Note that $k_{pq} = k_{qp}$ and $k_{pp} = k_{qq} = 0$. Since the quantity on the left-hand side of Eq. (4-305) represents the second virial coefficient as predicted by Eq. (4-231), the basis for Eq. (4-305) lies in Eq. (4-183), which expresses the quadratic dependence of the mixture second virial coefficient on mole fraction.

The second Wong/Sandler mixing rule relates ratios of *a/RT* to *b:*

$$\frac{a}{bRT} = 1 - D \qquad (4\text{-}307)$$

where
$$D \equiv 1 + \frac{G^E}{cRT} - \sum_p x_p \frac{a_p}{b_p RT} \qquad (4\text{-}308)$$

The quantity G^E/RT is given by an appropriate correlation for the excess Gibbs energy of the liquid phase, and is evaluated at the mixture composition, regardless of whether the mixture is liquid or vapor. The constant *c* is specific to the equation of state. The theoretical basis for these equations can be found in the literature (Wong and Sandler, op. cit.; *Ind. Eng. Chem. Res.,* **31,** pp. 2033–2039 [1992]; Eubank, et al., *Ind. Eng. Chem. Res.,* **34,** pp. 314–323 [1995]).

Elimination of *a* from Eq. (4-305) by Eq. (4-307) provides an expression for *b:*

$$b = \frac{1}{D} \sum_p \sum_q x_p x_q E_{pq} \qquad (4\text{-}309)$$

Mixture parameter *a* then follows from Eq. (4-307):

$$a = bRT(1 - D) \qquad (4\text{-}310)$$

Equations (4-233) and (4-234) may now be applied for the evaluation of partial parameters $\bar{a}_i$ and $\bar{b}_i$:

$$\bar{b}_i = \frac{1}{D}\left[2\sum_j x_j E_{ij} - b\left(1 + \frac{\ln \gamma_i}{c} - \frac{a_i}{b_i RT}\right)\right] \qquad (4\text{-}311)$$

and
$$\bar{a}_i = bRT\left(\frac{a_i}{b_i RT} - \frac{\ln \gamma_i}{c}\right) + a\left(\frac{\bar{b}_i}{b} - 1\right) \qquad (4\text{-}312)$$

For pure species *i,* Eq. (4-232) reduces to

$$\ln \phi_i = Z_i - 1 - \ln \frac{(V_i - b_i)Z_i}{V_i} + \frac{a_i/b_i RT}{\varepsilon - \sigma} \ln \frac{V_i + \sigma b_i}{V_i + \varepsilon b_i} \qquad (4\text{-}313)$$

This equation may be applied separately to the liquid phase and to the vapor phase to yield the pure-species values ϕ_i^l and ϕ_i^v. For vapor/liquid equilibrium (Eq. [4-280]), these two quantities are equal. Given parameters a_i and b_i, the pressure *P* in Eq. (4-230) that makes these two values equal is P_i^{sat}, the equilibrium vapor pressure of pure species *i* as predicted by the equation of state.

The correlations for $\alpha(T_{ri}; \omega_i)$ that follow Eq. (4-230) are designed to provide values of a_i that yield pure-species vapor pressures which, on average, are in reasonable agreement with experiment. However, reliable correlations for P_i^{sat} as a function of temperature are available for many pure species. Thus when P_i^{sat} is known for a particular temperature, a_i should be evaluated so that the equation of state correctly predicts this known value. The procedure is to write Eq. (4-313) for each of the phases, combining the two equations in accord with Eq. (4-280), written

$$\ln \phi_i^l = \ln \phi_i^v$$

The resulting expression may be solved for a_i:

$$a_i = \frac{b_i RT(\varepsilon - \sigma)\left(\ln \dfrac{V_i^l - b_i}{V_i^v - b_i} + Z_i^v - Z_i^l\right)}{\ln \dfrac{(V_i^l + \sigma b_i)(V_i^v + \varepsilon b_i)}{(V_i^l + \varepsilon b_i)(V_i^v + \sigma b_i)}} \tag{4-314}$$

where $Z_i^v = P_i^{sat}V_i^v/RT$ and $Z_i^l = P_i^{sat}V_i^l/RT$. Values of V_i^v and V_i^l come from solution of Eq. (4-230) for each phase with $P = P_i^{sat}$ at temperature T. Since a value of a_i is *required* for these calculations, an iterative procedure is implemented with an initial value for a_i from the appropriate correlation for $\alpha(T_{ri}; \omega_i)$.

The binary interaction parameters k_{pq} are evaluated from liquid-phase G^E correlations for binary systems. The most satisfactory procedure is to apply at infinite dilution the relation between a liquid-phase activity coefficient and its underlying fugacity coefficients, $\gamma_i^\infty = \hat{\phi}_i^\infty/\phi_i$. Rearrangement of the logarithmic form yields

$$\ln \hat{\phi}_i^\infty = \ln \gamma_i^\infty + \ln \phi_i \tag{4-315}$$

where $\ln \gamma_i^\infty$ comes from the G^E correlation and $\ln \phi_i$ is given by Eq. (4-313) written for the liquid phase. Equation (4-315) supplies a value for $\ln \hat{\phi}_i^\infty$ which, when used with Eq. (4-232), ultimately (see following) leads to values for k_{pq}.

For a binary system comprised of species p and q, Eqs. (4-232), (4-312), and (4-315) may be written for species p at infinite dilution. The three resulting equations are then combined to yield

$$\frac{\bar{b}_p^\infty}{b_q} = \frac{\ln \gamma_p^\infty + \ln \phi_p - M_p}{Z_q - 1} \tag{4-316}$$

where

$$M_p \equiv -\ln \frac{(V_q - b_q)Z_q}{V_q} + \frac{1}{\varepsilon - \sigma}\left(\frac{a_p}{b_p RT} - \frac{\ln \gamma_p^\infty}{c}\right)\ln \frac{V_q + \sigma b_q}{V_q + \varepsilon b_q} \tag{4-317}$$

By Eq. (4-311) written for species p at infinite dilution in a pq binary,

$$\frac{\bar{b}_p^\infty}{b_q} = \frac{\dfrac{2E_{pq}}{b_q} - 1 - \dfrac{\ln \gamma_p^\infty}{c} + \dfrac{a_p}{b_p RT}}{1 - \dfrac{a_q}{b_q RT}} \tag{4-318}$$

Equations (4-316) and (4-318) are set equal, E_{pq} is eliminated by Eq. (4-306), and k_{pq} is replaced by k_p, its infinite-dilution value at $x_p \to 0$. Solution for k_p then yields

$$k_p = 1 - \frac{\left(b_q - \dfrac{a_q}{RT}\right)\left(\dfrac{\ln \gamma_p^\infty + \ln \phi_p - M_p}{Z_q - 1}\right) + b_q\left(1 + \dfrac{\ln \gamma_p^\infty}{c} - \dfrac{a_p}{b_p RT}\right)}{b_p - \dfrac{a_p}{RT} + b_q - \dfrac{a_q}{RT}} \tag{4-319}$$

where $\ln \phi_p$ comes from Eq. (4-313). All values in Eq. (4-319) are for the liquid phase at $P = P_q^{sat}$. The analogous equation for k_q, the infinite-dilution value of k_{pq} at $x_q \to 0$ is written

$$k_q = 1 - \frac{\left(b_p - \dfrac{a_p}{RT}\right)\left(\dfrac{\ln \gamma_q^\infty + \ln \phi_q - M_q}{Z_p - 1}\right) + b_p\left(1 + \dfrac{\ln \gamma_q^\infty}{c} - \dfrac{a_q}{b_q RT}\right)}{b_p - \dfrac{a_p}{RT} + b_q - \dfrac{a_q}{RT}} \tag{4-320}$$

where M_q is given by an equation analogous to Eq. (4-317) but with subscripts reversed. All values in Eq. (4-320) are for the liquid phase at $P = P_p^{sat}$.

One advantage of this procedure is that k_p and k_q are found directly from the pure-species parameters a_p, a_q, b_p, and b_q. In addition, the required values of $\ln \gamma_p^\infty$ and $\ln \gamma_q^\infty$ can be found from experimental data for the pq binary system, independent of the correlating expression used for G^E.

A second advantage is that the procedure, applied for infinite dilution of each species, yields two values of k_{pq} from which a composition-dependent function can be generated, a simple linear relation proving fully satisfactory:

$$k_{pq} = k_p x_q + k_q x_p \tag{4-321}$$

The two values k_p and k_q are usually not very different, and k_{pq} is not strongly composition dependent. Nevertheless, the quadratic dependence of $b - (a/RT)$ on composition indicated by Eq. (4-305) is not exactly preserved. Since this quantity is not a *true* second virial coefficient, only a value predicted by a cubic equation of state, a strict quadratic dependence is not required. Moreover, the composition-dependent k_{pq} leads to better results than does use of a constant value.

The equation-specific constants for the SRK and PR equations are given by the following table:

	SRK equation	PR equation
ε	0	−0.414214
σ	1	2.414214
Ω_a	0.42748	0.457235
Ω_b	0.08664	0.077796
c	0.69315	0.62323

Outlined below are the steps required for of a VLE calculation of vapor-phase composition and pressure, given the liquid-phase composition and temperature. A choice must be made of an equation of state. Only the Soave/Redlich/Kwong and Peng/Robinson equations, as represented by Eqs. (4-230) and (4-231), are considered here. These two equations usually give comparable results. A choice must also be made of a two-parameter correlating expression to represent the liquid-phase composition dependence of G^E for each pq binary. The Wilson, NRTL (with α fixed), and UNIQUAC equations are of general applicability; for binary systems, the Margules and van Laar equations may also be used. The equation selected depends on evidence of its suitability to the particular system treated. Reasonable estimates of the parameters in the equation must also be known at the temperature of interest. These parameters are directly related to infinite-dilution values of the activity coefficients for each pq binary.

Input information includes the known values of T and $\{x_i\}$, as well as the equation-of-state and G^E-expression parameters. Estimates are also needed of P and $\{y_i\}$, the quantities to be evaluated, and these require some preliminary calculations:

1. For the chosen equation of state (with appropriate values of ε, σ, and c), find values of b_i and preliminary values of a_i for each species from the information following Eq. (4-230).
2. If the vapor pressure P_i^{sat} for species i at temperature T is known, determine a new value for a_i by Eqs. (4-314) and (4-230).
3. Evaluate k_p and k_q by Eqs. (4-319) and (4-320) for each pq binary.
4. Although pressure P is to be determined, an estimate is required to permit any VLE calculations at all. A reasonable initial value is the sum of the pure-species vapor pressures, each weighted by its known liquid-phase mole fraction.
5. The vapor-phase composition is also to be determined, and it, too, is required to initiate calculations. Assuming both the liquid and vapor phases to be ideal solutions, Eqs. (4-98) and (4-304) combine to give

$$y_i = x_i \frac{\phi_i^l}{\phi_i^v}$$

Evaluation of the pure-species values ϕ_i^l and ϕ_i^v by Eq. (4-313) then provides values for y_i. Since these are not constrained to sum to unity, they should be normalized to yield an initial vapor-phase composition.

Given estimates for P and $\{y_i\}$ an iterative procedure can be initiated:

1. At the known *liquid-phase* composition, evaluate D by Eq. (4-308), b and a by Eqs. (4-309) and (4-310), and $\{\bar{b}_i\}$ and $\{\bar{a}_i\}$ by Eqs. (4-311) and (4-312).

2. Evaluate $\{\hat{\phi}_i^l\}$. The mixture volume V is determined from the equation of state, Eq. (4-231), applied to the liquid phase at the given composition, T, and P.

3. Repeat the two preceding items for the *vapor-phase* composition, thus evaluating $\{\hat{\phi}_i^v\}$.

4. Eq. (4-304) is now written

$$y_i = x_i \frac{\hat{\phi}_i^l}{\hat{\phi}_i^v}$$

The values of y_i so calculated are normalized by division by $\sum_i y_i$.

5. Recalculate the $\hat{\phi}_i^v$, and continue this iterative procedure until it converges to a fixed value for $\sum_i y_i$. This sum is appropriate to the pressure P for which the calculations have been made. Unless the sum is unity, the pressure is adjusted and the iteration process is repeated. Systematic adjustment of pressure P continues until $\sum_i y_i = 1$. The pressure and vapor compositions so found are the equilibrium values for the given temperature and liquid-phase composition as predicted by the equation of state.

A vast store of liquid-phase excess-property data for binary systems at temperatures near 30°C and somewhat higher is available in the literature. Effective use of these data to extend G^E correlations to higher temperatures is critical to the procedure considered here. The key relations are Eq. (4-118),

$$d\left(\frac{G^E}{RT}\right) = -\frac{H^E}{RT^2}\,dT \qquad \text{(constant } P, x)$$

and the excess-property analog of Eq. (4-31),

$$dH^E = C_P^E\,dT \qquad \text{(constant } P, x)$$

Integration of the first of these equations from T_0 to T gives

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)_{T_0} - \int_{T_0}^{T} \frac{H^E}{RT^2}\,dT \tag{4-322}$$

Similarly, the second equation may be integrated from T_1 to T:

$$H^E = H_1^E + \int_{T_1}^{T} C_P^E\,dT \tag{4-323}$$

In addition, we may write

$$dC_P^E = \left(\frac{\partial C_P^E}{\partial T}\right)_{P,x} dT$$

Integration from T_2 to T yields

$$C_P^E = C_{P_2}^E + \int_{T_2}^{T} \left(\frac{\partial C_P^E}{\partial T}\right)_{P,x} dT$$

Combining this equation with Eqs. (4-322) and (4-323) leads to

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)_{T_0} - \left(\frac{H^E}{RT}\right)_{T_1}\left(\frac{T}{T_0} - 1\right)\frac{T_1}{T} - \frac{C_{P_2}^E}{R}\left[\ln\frac{T}{T_0} - \left(\frac{T}{T_0} - 1\right)\frac{T_1}{T}\right] - I \tag{4-324}$$

where $$I \equiv \int_{T_0}^{T} \frac{1}{RT^2} \int_{T_1}^{T} \int_{T_2}^{T} \left(\frac{\partial C_P^E}{\partial T}\right)_{P,x} dT\,dT\,dT$$

This general equation makes use of excess Gibbs-energy data at temperature T_0, excess enthalpy (heat-of-mixing) data at T_1, and excess heat-capacity data at T_2. Evaluation of the integral I requires information with respect to the temperature dependence of C_P^E. Because of the relative paucity of excess heat-capacity data, the most reasonable assumption is that this quantity is constant, independent of T. In this event, the integral is zero, and the closer T_0 and T_1 are to T, the less the influence of this assumption. When no information is available with respect to C_P^E, and excess enthalpy data are available at only a single temperature, the excess heat capacity must be assumed zero. In this case only the first two terms on the right-hand side of Eq. (4-324) are retained, and it more rapidly becomes imprecise as T increases.

Our primary interest in Eq. (4-324) is its application to binary systems at infinite dilution of one of the constituent species. For this purpose, we divide Eq. (4-324) by the product x_1x_2. For C_P^E independent of T (and thus with $I = 0$), it then becomes

$$\frac{G^E}{x_1x_2RT} = \left(\frac{G^E}{x_1x_2RT}\right)_{T_0} - \left(\frac{H^E}{x_1x_2RT}\right)_{T_1}\left(\frac{T}{T_0} - 1\right)\frac{T_1}{T} - \frac{C_P^E}{x_1x_2R}\left[\ln\frac{T}{T_0} - \left(\frac{T}{T_0} - 1\right)\frac{T_1}{T}\right]$$

As shown by Smith, Van Ness and Abbott (*Introduction to Chemical Engineering Thermodynamics,* 5th ed., Chap. 11, McGraw-Hill, New York, 1996),

$$\left(\frac{G^E}{x_1x_2RT}\right)_{x_i=0} \equiv \ln \gamma_i^\infty$$

The preceding equation may therefore be written

$$\ln \gamma_i^\infty = (\ln \gamma_i^\infty)_{T_0} - \left(\frac{H^E}{x_1x_2RT}\right)_{T_1, x_i=0}\left(\frac{T}{T_0} - 1\right)\frac{T_1}{T} - \left(\frac{C_P^E}{x_1x_2R}\right)_{x_i=0}\left[\ln\frac{T}{T_0} - \left(\frac{T}{T_0} - 1\right)\frac{T_1}{T}\right] \tag{4-325}$$

The methanol(1)/acetone(2) system serves as a specific example in conjunction with the Peng/Robinson equation of state. At a base temperature T_0 of 323.15 K (50°C), both VLE data (Van Ness and Abbott, *Int. DATA Ser., Ser. A, Sel. Data Mixtures,* **1978,** p. 67 [1978]) and excess enthalpy data (Morris, et al., *J. Chem. Eng. Data,* **20,** pp. 403–405 [1975]) are available. From the former,

$$(\ln \gamma_1^\infty)_{T_0} = 0.6281 \qquad \text{and} \qquad (\ln \gamma_2^\infty)_{T_0} = 0.6557$$

and from the latter

$$\left(\frac{H^E}{x_1x_2RT}\right)_{T_0, x_1=0} = 1.3636 \qquad \text{and} \qquad \left(\frac{H^E}{x_1x_2RT}\right)_{T_0, x_2=0} = 1.0362$$

The Margules equations (Eqs. [4-244], [4-245], and [4-246]) are well suited to this system, and the parameters for this equation are given as

$$A_{12} = \ln \gamma_1^\infty \qquad \text{and} \qquad A_{21} = \ln \gamma_2^\infty$$

This information allows prediction of VLE at 323.15 K and at the higher temperatures, 372.8, 397.7, and 422.6 K, for which measured VLE values are given by Wilsak, et al. (*Fluid Phase Equilibria,* **28,** pp. 13–37 [1986]). Values of $\ln \gamma_i^\infty$ and hence of the Margules parameters at the higher temperatures are given by Eq. (4-325) with $C_P^E = 0$. The pure-species vapor pressures in all cases are the measured values reported with the data sets. Results of these calculations are displayed in Table 4-1, where the parentheses enclose values from the gamma/phi approach as reported in the papers cited.

The results at 323.15 K (581.67 R) show both the suitability of the Margules equation for correlation of data for this system and the capability of the equation-of-state method to reproduce the data. Results for the three higher temperatures indicate the quality of predictions based only on vapor-pressure data for the pure species and on mixture data at 323.15 K (581.67 R). Extrapolations based on the same data to still higher temperatures can be expected to become progressively less accurate. When Eq. (4-325) can no longer be expected to produce reasonable values, better results are obtained for higher temperatures by assuming that the parameters, A_{12}, A_{21}, k_1, and k_2, do not change further at still-higher temperatures. This is also the course to be followed for extrapolation to supercritical temperatures.

Only the Wilson, NRTL, and UNIQUAC equations are suited to the treatment of multicomponent systems. For such systems, the parameters are determined for pairs of species exactly as for binary systems.

Examples treating the calculation of *VLE* are given in Smith, Van Ness, and Abbott (*Introduction to Chemical Engineering Thermodynamics,* 5th ed., Chap. 12, McGraw-Hill, New York, 1996).

LIQUID/LIQUID AND VAPOR/LIQUID/LIQUID EQUILIBRIA

Equation (4-273) is the basis for both liquid/liquid equilibria (LLE) and vapor/liquid/liquid equilibria (VLLE). Thus, for LLE with superscripts α and β denoting the two phases, Eq. (4-273) is written

TABLE 4-1 VLE Results for Methanol(1)/Acetone(2)

T, K	$\ln \gamma_1^\infty$	$\ln \gamma_2^\infty$	k_1	k_2	RMS δP, kPa	RMS % δP	RMS δy_1
323.15	0.6281	0.6557	0.1395	0.0955	0.08	0.12	
	(0.6281)	(0.6557)			(0.06)		
372.8	0.4465	0.5177	0.1432	0.1056	0.85	0.22	0.004
	(0.4607)	(0.5271)			(0.83)		(0.006)
397.7	0.3725	0.4615	0.1454	0.1118	2.46	0.32	0.014
	(0.3764)	(0.4640)			(1.39)		(0.013)
422.6	0.3072	0.4119	0.1480	0.1192	7.51	0.55	0.009
	(0.3079)	(0.3966)			(2.38)		(0.006)

$$\hat{f}_i^\alpha = \hat{f}_i^\beta \qquad (i = 1, 2, \ldots, N) \tag{4-326}$$

Eliminating fugacities in favor of activity coefficients gives

$$x_i^\alpha \gamma_i^\alpha = x_i^\beta \gamma_i^\beta \qquad (i = 1, 2, \ldots, N) \tag{4-327}$$

For most LLE applications, the effect of pressure on the γ_i can be ignored, and thus Eq. (4-327) constitutes a set of N equations relating equilibrium compositions to each other and to temperature. For a given temperature, solution of these equations requires a single expression for the composition dependence of G^E suitable for both liquid phases. Not all expressions for G^E suffice, even in principle, because some cannot represent liquid/liquid phase splitting. The UNIQUAC equation is suitable, and therefore prediction is possible by the UNIFAC method. A special table of parameters for LLE calculations is given by Magnussen, et al. (*Ind. Eng. Chem. Process Des. Dev.*, **20,** pp. 331–339 [1981]).

A comprehensive treatment of LLE is given by Sorensen, et al. (*Fluid Phase Equilibria,* **2,** pp. 297–309 [1979]; **3,** pp. 47–82 [1979]; **4,** pp. 151–163 [1980]). Data for LLE are collected in a three-part set compiled by Sorensen and Arlt (*Liquid-Liquid Equilibrium Data Collection,* Chemistry Data Series, vol. V, parts 1–3, DECHEMA, Frankfurt am Main, 1979–1980).

For vapor/liquid/liquid equilibria, Eq. (4-273) gives

$$\hat{f}_i^\alpha = \hat{f}_i^\beta = \hat{f}_i^v \qquad (i = 1, 2, \ldots, N) \tag{4-328}$$

where α and β designate the two liquid phases. With activity coefficients applied to the liquid phases and fugacity coefficients to the vapor phase, the $2N$ equilibrium equations for subcritical VLLE are

$$\left.\begin{aligned} x_i^\alpha \gamma_i^\alpha f_i^\alpha &= y_i \hat{\phi}_i P \\ x_i^\beta \gamma_i^\beta f_i^\beta &= y_i \hat{\phi}_i P \end{aligned}\right\} \qquad (\text{all } i) \tag{4-329}$$

As for LLE, an expression for G^E capable of representing liquid/liquid phase splitting is required; as for VLE, a vapor-phase equation of state for computing the $\hat{\phi}_i$ is also needed.

CHEMICAL-REACTION STOICHIOMETRY

Consider a phase in which a chemical reaction occurs according to the equation

$$|\nu_1|A_1 + |\nu_2|A_2 + \cdots \rightarrow |\nu_3|A_3 + |\nu_4|A_4 + \cdots$$

where the $|\nu_i|$ are stoichiometric coefficients and the A_i stand for chemical formulas. The ν_i themselves are called *stoichiometric numbers,* and associated with them is a sign convention such that the value is positive for a product and negative for a reactant. More generally, for a system containing N chemical species, any or all of which can participate in r chemical reactions, the reactions can be represented by the equations:

$$0 = \sum_i \nu_{i,j} A_i \qquad (j = \text{I, II}, \ldots, r) \tag{4-330}$$

where
$$\text{sign } (\nu_{i,j}) = \begin{cases} - \text{ for a reactant species} \\ + \text{ for a product species} \end{cases}$$

If species i does not participate in reaction j, then $\nu_{i,j} = 0$.

The stoichiometric numbers provide relations among the changes in mole numbers of chemical species which occur as the result of chemical reaction. Thus, for reaction j:

$$\frac{\Delta n_{1,j}}{\nu_{1,j}} = \frac{\Delta n_{2,j}}{\nu_{2,j}} = \cdots = \frac{\Delta n_{N,j}}{\nu_{N,j}} \tag{4-331}$$

Since all of these terms are equal, they can be equated to the change in a single quantity ε_j, called the *reaction coordinate* for reaction j, thereby giving

$$\Delta n_{i,j} = \nu_{i,j} \Delta\varepsilon_j \qquad \begin{cases} i = 1, 2, \ldots, N \\ j = \text{I, II}, \ldots, r \end{cases} \tag{4-332}$$

Since the total change in mole number Δn_i is just the sum of the changes $\Delta n_{i,j}$ resulting from the various reactions,

$$\Delta n_i = \sum_j \Delta n_{i,j} = \sum_j \nu_{i,j} \Delta\varepsilon_j \qquad (i = 1, 2, \ldots, N) \tag{4-333}$$

If the initial number of moles of species i is n_{i^0} and if the convention is adopted that $\varepsilon_j = 0$ for each reaction in this initial state, then

$$n_i = n_{i_0} + \sum_j \nu_{i,j}\, \varepsilon_j \qquad (i = 1, 2, \ldots, N) \tag{4-334}$$

Equation (4-334) is the basic expression of material balance for a closed system in which r chemical reactions occur. It shows for a reacting system that at most r mole number–related quantities ε_j are capable of independent variation. Note the absence of implied restrictions with respect to chemical-reaction equilibria; the reaction-coordinate formalism is merely an accounting scheme, valid for tracking the progress of each reaction to any arbitrary level of conversion. The reaction coordinate has units of moles. A change in ε_j of 1 mole signifies a *mole of reaction,* meaning that reaction j has proceeded to such an extent that the change in mole number of each reactant and product is equal to its stoichiometric number.

CHEMICAL-REACTION EQUILIBRIA

The general criterion of chemical-reaction equilibria is given by Eq. (4-274). For a system in which just a single reaction occurs, Eq. (4-334) becomes

$$n_i = n_{i_0} + \nu_i \varepsilon$$

whence
$$dn_i = \nu_i\, d\varepsilon$$

Substitution for dn_i in Eq. (4-274) leads to

$$\sum_i \nu_i \mu_i = 0 \tag{4-335}$$

Generalization of this result to multiple reactions produces

$$\sum_i \nu_{i,j}\, \mu_i = 0 \qquad (j = \text{I, II}, \ldots, r) \tag{4-336}$$

Standard Property Changes of Reaction A *standard* property change for the reaction

$$aA + bB \rightarrow lL + mM$$

is defined as the property change that occurs when a moles of A and b moles of B in their *standard states at temperature* T react to form l moles of L and m moles of M in their *standard states also at temperature T.* A *standard state* of species i is its real or hypothetical state as a pure species *at temperature* T and at a standard-state pressure $P°$. The standard property change of reaction j is given the symbol $\Delta M_j°$, and its general mathematical definition is

$$\Delta M_j° \equiv \sum_i \nu_{i,j} M_i° \tag{4-337}$$

For species present as gases in the actual reactive system, the standard state is the pure *ideal gas* at pressure $P°$. For liquids and solids, it is usually the state of pure real liquid or solid at $P°$. The standard-state pressure $P°$ is fixed at 100 kPa. Note that the standard states may represent different physical states for different species; any or all of the species may be gases, liquids, or solids.

The most commonly used standard property changes of reaction are

$$\Delta G_j^\circ \equiv \sum_i \nu_{i,j} G_i^\circ = \sum_i \nu_{i,j} \mu_i^\circ \qquad (4\text{-}338)$$

$$\Delta H_j^\circ \equiv \sum_i \nu_{i,j} H_i^\circ \qquad (4\text{-}339)$$

$$\Delta C_{P_j}^\circ \equiv \sum_i \nu_{i,j} C_{P_i}^\circ \qquad (4\text{-}340)$$

The standard Gibbs-energy change of reaction ΔG_j° is used in the calculation of equilibrium compositions. The standard heat of reaction ΔH_j° is used in the calculation of the heat effects of chemical reaction, and the standard heat-capacity change of reaction is used for extrapolating ΔH_j° and ΔG_j° with T. Numerical values for ΔH_j° and ΔG_j° are computed from tabulated formation data, and $\Delta C_{P_j}^\circ$ is determined from empirical expressions for the T dependence of the $C_{P_i}^\circ$ (see, e.g., Eq. [4-142]).

Equilibrium Constants For practical application, Eq. (4-336) must be reformulated. The initial step is elimination of the μ_i in favor of fugacities. Equation (4-74) for species i in its standard state is subtracted from Eq. (4-77) for species i in the equilibrium mixture, giving

$$\mu_i = G_i^\circ + RT \ln \hat{a}_i \qquad (4\text{-}341)$$

where, by definition, $\hat{a}_i \equiv \hat{f}_i/f_i^\circ$ and is called an *activity*. Substitution of this equation into Eq. (4-341) yields, upon rearrangement,

$$\sum_i [\nu_{i,j}(G_i^\circ + RT \ln \hat{a}_i)] = 0$$

or

$$\sum_i (\nu_{i,j} G_i^\circ) + RT \sum_i \ln \hat{a}_i^{\nu_{i,j}} = 0$$

or

$$\ln \prod_i \hat{a}_i^{\nu_{i,j}} = \frac{-\sum_i (\nu_{i,j} G_i^\circ)}{RT}$$

The right-hand side of this equation is a function of temperature only for given reactions and given standard states. Convenience suggests setting it equal to $\ln K_j$; whence

$$\prod_i \hat{a}_i^{\nu_{i,j}} = K_j \qquad (\text{all } j) \qquad (4\text{-}342)$$

where

$$K_j \equiv \exp\left(\frac{-\Delta G_j^\circ}{RT}\right) \qquad (4\text{-}343)$$

Quantity K_j is the chemical-reaction equilibrium constant for reaction j, and ΔG_j° is the corresponding standard Gibbs-energy change of reaction (see Eq. [4-338]). Although called a "constant," K_j is a function of T, but only of T.

The activities in Eq. (4-342) provide the connection between the *equilibrium* states of interest and the *standard* states of the constituent species, for which data are presumed available. The standard states are always at the equilibrium temperature. Although the standard state need not be the same for all species, for a *particular* species it must be the state represented by both G_i° and the f_i° upon which the activity $\hat{a}_i$ is based.

The application of Eq. (4-342) requires explicit introduction of composition variables. For gas-phase reactions this is accomplished through the fugacity coefficient:

$$\hat{a}_i \equiv \hat{f}_i/f_i^\circ = y_i \hat{\phi}_i P/f_i^\circ$$

However, the standard state for gases is the ideal gas state at the standard-state pressure, for which $f_i^\circ = P°$. Therefore

$$\hat{a}_i = \frac{y_i \hat{\phi}_i P}{P°}$$

and Eq. (4-342) becomes

$$\prod_i (y_i \hat{\phi}_i)^{\nu_{i,j}} \left(\frac{P}{P°}\right)^{\nu_j} = K_j \qquad (\text{all } j) \qquad (4\text{-}344)$$

where $\nu_j \equiv \sum_i \nu_{i,j}$ and $P°$ is the standard-state pressure of 100 kPa, expressed in the same units used for P. The y_i may be eliminated in favor of equilibrium values of the reaction coordinates ε_j. Then, for fixed temperature Eqs. (4-344) relate the ε_j to P. In principle, specification of the pressure allows solution for the ε_j. However, the problem may be complicated by the dependence of the $\hat{\phi}_i$ on composition, that is, on the ε_j. If the equilibrium mixture is assumed an ideal solution, then each $\hat{\phi}_i$ becomes ϕ_i, the fugacity coefficient of pure species i at the mixture T and P. This quantity does not depend on composition and may be determined from experimental data, from a generalized correlation, or from an equation of state.

An important special case of Eq. (4-344) is obtained for gas-phase reactions when the phase can be assumed an ideal gas. In this event $\hat{\phi}_i = 1$, and

$$\prod_i (y_i)^{\nu_{i,j}} \left(\frac{P}{P°}\right)^{\nu_j} = K_j \qquad (\text{all } j) \qquad (4\text{-}345)$$

In the general case the evaluation of the $\hat{\phi}_i$ requires an iterative process. An initial step is to set the $\hat{\phi}_i$ equal to unity and to solve the problem by Eq. (4-345). This provides a set of y_i values, allowing evaluation of the $\hat{\phi}_i$ by, for example, Eq. (4-196), (4-200), or (4-231). Equation (4-344) can then be solved for a new set of y_i values, and the process continues to convergence.

For liquid-phase reactions, Eq. (4-342) is modified by introduction of the activity coefficient, $\gamma_i = \hat{f}_i/x_i f_i$, where x_i is the liquid-phase mole fraction. The activity is then

$$\hat{a}_i \equiv \frac{\hat{f}_i}{f_i^\circ} = \gamma_i x_i \frac{f_i}{f_i^\circ}$$

Both f_i and f_i° represent fugacity of pure liquid i at temperature T, but at pressures P and $P°$, respectively. Except in the critical region, pressure has little effect on the properties of liquids, and the ratio f_i/f_i° is often taken as unity. When this is not acceptable, this ratio is evaluated by the equation

$$\ln \frac{f_i}{f_i^\circ} = \frac{1}{RT} \int_{P°}^{P} V_i \, dP \simeq \frac{V_i(P - P°)}{RT}$$

When the ratio f_i/f_i° is taken as unity, $\hat{a}_i = \gamma_i x_i$, and Eq. (4-342) becomes

$$\prod_i (\gamma_i x_i)^{\nu_{i,j}} = K_j \qquad (\text{all } j) \qquad (4\text{-}346)$$

Here the difficulty is to determine the γ_i, which depend on the x_i. This problem has not been solved for the general case. Two courses are open: the first is experiment; the second, assumption of solution ideality. In the latter case, $\gamma_i = 1$, and Eq. (4-346) reduces to

$$\prod_i (x_i)^{\nu_{i,j}} = K_j \qquad (\text{all } j) \qquad (4\text{-}347)$$

the *law of mass action*. The significant feature of Eqs. (4-345) and (4-347), the simplest expressions for gas- and liquid-phase reaction equilibrium, is that the temperature-, pressure-, and composition-dependent terms are distinct and separate.

Example 2: Single-Reaction Equilibrium Consider the equilibrium state at 1,000 K and atmospheric pressure for the reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

Let the feed stream contain 3 mol CO, 1 mol H_2O, and 2 mol CO_2 for every mole of H_2 present. This initial constitution forms the *basis* for calculation, and for this single reaction, Eq. (4-334) becomes $n_i = n_{i_0} + \nu_i\varepsilon$. Whence

$$n_{CO} = 3 - \varepsilon$$
$$n_{H_2O} = 1 - \varepsilon$$
$$n_{CO_2} = 2 + \varepsilon$$
$$n_{H_2} = 1 + \varepsilon$$
$$\sum_i n_i = 7$$

Each mole fraction is therefore given by $y_i = n_i/7$.

At 1,000 K, $\Delta G° = -2680$ J per mole of reaction; whence by Eq. (4-343)

$$K = \exp \frac{2680}{(8.314)(1000)} = 1.38$$

For the given conditions, the assumption of ideal gases is appropriate; Eq. (4-345) written for a single reaction (subscript j omitted) with $\nu = 0$ becomes

$$\prod_i y_i^{\nu_i} = \frac{\left(\frac{2+\varepsilon}{7}\right)\left(\frac{1+\varepsilon}{7}\right)}{\left(\frac{3-\varepsilon}{7}\right)\left(\frac{1-\varepsilon}{7}\right)} = K = 1.38$$

or

$$\frac{(2+\varepsilon)(1+\varepsilon)}{(3-\varepsilon)(1-\varepsilon)} = 1.38$$

whence $\varepsilon = 0.258$

Thus, for the equilibrium mixture,

$n_{CO} = 2.74$ mol	$y_{CO} = 0.391$
$n_{H_2O} = 0.74$ mol	$y_{H_2O} = 0.106$
$n_{CO_2} = 2.26$ mol	$y_{CO_2} = 0.323$
$n_{H_2} = 1.26$ mol	$y_{H_2} = 0.180$
$\sum_i n_i = 7.00$ mol	$\sum_i y_i = 1.000$

The effect of temperature on the equilibrium constant follows from Eq. (4-106):

$$\frac{d(\Delta G_j°/RT)}{dT} = \frac{-\Delta H_j°}{RT^2} \tag{4-348}$$

The total derivative is appropriate here because property changes of reaction are functions of temperature only. In combination with Eq. (4-343) this gives

$$\frac{d \ln K_j}{dT} = \frac{\Delta H_j°}{RT^2} \tag{4-349}$$

For an endothermic reaction $\Delta H_j°$ is positive; for an exothermic reaction it is negative. The temperature dependence of $\Delta H_j°$ is given by

$$\frac{d\Delta H_j°}{dT} = \Delta C_{P_j}° \tag{4-350}$$

Integration of Eq. (4-350) from reference temperature T_0 (usually 298.15 K) to temperature T gives

$$\Delta H° = \Delta H_0° + R \int_{T_0}^{T} \frac{\Delta C_P°}{R}\, dT \tag{4-351}$$

where for simplicity subscript j has been suppressed. A convenient integrated form of Eq. (4-349) is

$$\ln K = \frac{-\Delta G°}{RT} = \frac{\Delta H_0° - \Delta G_0°}{RT} - \frac{\Delta H°}{RT} + \frac{1}{T}\int_{T_0}^{T} \frac{C_P°}{R}\, dT \tag{4-352}$$

where $\Delta H°/RT$ is given by Eq. (4-351).

In the more extensive compilations of data, values of $\Delta G°$ and $\Delta H°$ for formation reactions are given for a wide range of temperatures, rather than just at the reference temperature of 298.15 K. (See in particular *TRC Thermodynamic Tables—Hydrocarbons* and *TRC Thermodynamic Tables—Non-hydrocarbons,* serial publications of the Thermodynamics Research Center, Texas A & M University System, College Station, Tex.; "The NBS Tables of Chemical Thermodynamic Properties," *J. Physical and Chemical Reference Data,* **11,** supp. 2 [1982]. Where data are lacking, methods of estimation are available; these are reviewed by Reid, Prausnitz, and Poling, *The Properties of Gases and Liquids,* 4th ed., Chap. 6, McGraw-Hill, New York, 1987. For an estimation procedure based on molecular structure, see Constantinou and Gani, *Fluid Phase Equilibria,* **103,** pp. 11–22 [1995]. (See also Sec. 2.)

Complex Chemical-Reaction Equilibria When the composition of an equilibrium mixture is determined by a number of simultaneous reactions, calculations based on equilibrium constants become complex and tedious. A more direct procedure (and one suitable for general computer solution) is based on minimization of the total Gibbs energy G^t in accord with Eq. (4-271). The treatment here is limited to gas-phase reactions for which the problem is to find the equilibrium composition for given T and P and for a given initial feed.

1. Formulate the constraining material-balance equations, based on conservation of the total number of atoms of each *element* in a system comprised of w elements. Let subscript k identify a particular atom, and define A_k as the total number of atomic masses of the kth element in the feed. Further, let a_{ik} be the number of atoms of the kth element present in each molecule of chemical species i. The material balance for element k is then

$$\sum_i n_i a_{ik} = A_k \qquad (k = 1, 2, \ldots, w) \tag{4-353}$$

or

$$\sum_i n_i a_{ik} - A_k = 0 \qquad (k = 1, 2, \ldots, w)$$

2. Multiply each element balance by λ_k, a Lagrange multiplier:

$$\lambda_k \left(\sum_i n_i a_{ik} - A_k\right) = 0 \qquad (k = 1, 2, \ldots, w)$$

Summed over k, these equations give

$$\sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k\right) = 0$$

3. Form a function F by addition of this sum to G^t:

$$F = G^t + \sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k\right)$$

Function F is identical with G^t, because the summation term is zero. However, the partial derivatives of F and G^t with respect to n_i are different, because function F incorporates the constraints of the material balances.

4. The minimum value of both F and G^t is found when the partial derivatives of F with respect to n_i are set equal to zero:

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial G^t}{\partial n_i}\right)_{T,P,n_j} + \sum_k \lambda_k a_{ik} = 0$$

The first term on the right is the definition of the chemical potential; whence

$$\mu_i + \sum_k \lambda_k a_{ik} = 0 \qquad (i = 1, 2, \ldots, N) \tag{4-354}$$

However, the chemical potential is given by Eq. (4-341); for gas-phase reactions and standard states as the pure ideal gases at $P°$, this equation becomes

$$\mu_i = G_i° + RT \ln \frac{\hat{f}_i}{P°}$$

If $G_i°$ is arbitrarily set equal to zero for all *elements* in their standard states, then for compounds $G_i° = \Delta G_{f_i}°$, the standard Gibbs-energy change of formation for species i. In addition, the fugacity is eliminated in favor of the fugacity coefficient by Eq. (4-79), $\hat{f}_i = y_i \hat{\phi}_i P$. With these substitutions, the equation for μ_i becomes

$$\mu_i = \Delta G_{f_i}° + RT \ln \frac{y_i \hat{\phi}_i P}{P°}$$

Combination with Eq. (4-354) gives

$$\Delta G_{f_i}° + RT \ln \frac{y_i \hat{\phi}_i P}{P°} + \sum_k \lambda_k a_{ik} = 0 \qquad (i = 1, 2, \ldots, N) \tag{4-355}$$

If species i is an element, $\Delta G_{f_i}°$ is zero. There are N equilibrium equations (Eqs. [4-355]), one for each chemical species, and there are w material-balance equations (Eqs. [4-353]), one for each element—a total of $N + w$ equations. The unknowns in these equations are the n_i (note that $y_i = n_i/\sum_i n_i$), of which there are N, and the λ_k, of which there are w—a total of $N + w$ unknowns. Thus, the number of equations is sufficient for the determination of all unknowns.

Equation (4-355) is derived on the presumption that the $\hat{\phi}_i$ are known. If the phase is an ideal gas, then each $\hat{\phi}_i$ is unity. If the phase is an ideal solution, each $\hat{\phi}_i$ becomes ϕ_i, and can at least be estimated. For real gases, each $\hat{\phi}_i$ is a function of the y_i, the quantities being calculated. Thus an iterative procedure is indicated, initiated with each $\hat{\phi}_i$

set equal to unity. Solution of the equations then provides a preliminary set of y_i. For low pressures or high temperatures this result is usually adequate. Where it is not satisfactory, an equation of state with the preliminary y_i gives a new and more nearly correct set of $\hat{\phi}_i$ for use in Eq. (4-355). Then a new set of y_i is determined. The process is repeated to convergence. All calculations are well suited to computer solution.

In this procedure, the question of what chemical reactions are involved never enters directly into any of the equations. However, the choice of a set of species is entirely equivalent to the choice of a set of independent reactions among the species. In any event, a set of species or an equivalent set of independent reactions must always be assumed, and different assumptions produce different results.

Example 3: Minimization of Gibbs Energy Calculate the equilibrium compositions at 1,000 K and 1 bar of a gas-phase system containing the species CH_4, H_2O, CO, CO_2, and H_2. In the initial unreacted state there are present 2 mol of CH_4 and 3 mol of H_2O. Values of ΔG_f° at 1,000 K are

$$\Delta G^\circ_{f_{CH_4}} = 19{,}720 \text{ J/mol}$$
$$\Delta G^\circ_{f_{H_2O}} = -192{,}420 \text{ J/mol}$$
$$\Delta G^\circ_{f_{CO}} = -200{,}240 \text{ J/mol}$$
$$\Delta G^\circ_{f_{CO_2}} = -395{,}790 \text{ J/mol}$$

The required values of A_k are determined from the initial numbers of moles, and the values of a_{ik} come directly from the chemical formulas of the species. These are shown in the accompanying table.

	Element k		
	Carbon	Oxygen	Hydrogen
	A_k = no. of atomic masses of k in the system		
	$A_C = 2$	$A_O = 3$	$A_H = 14$
Species i	a_{ik} = no. of atoms of k per molecule of i		
CH_4	$a_{CH_4,C} = 1$	$a_{CH_4,O} = 0$	$a_{CH_4,H} = 4$
H_2O	$a_{H_2O,C} = 0$	$a_{H_2O,O} = 1$	$a_{H_2O,H} = 2$
CO	$a_{CO,C} = 1$	$a_{CO,O} = 1$	$a_{CO,H} = 0$
CO_2	$a_{CO_2,C} = 1$	$a_{CO_2,O} = 2$	$a_{CO_2,H} = 0$
H_2	$a_{H_2,C} = 0$	$a_{H_2,O} = 0$	$a_{H_2,H} = 2$

At 1 bar and 1,000 K the assumption of ideal gases is justified, and the $\hat{\phi}_i$ are all unity. Since $P = 1$ bar, Eq. (4-355) is written:

$$\frac{\Delta G^\circ_{f_i}}{RT} + \ln \frac{n_i}{\Sigma_i n_i} + \sum_k \frac{\lambda_k}{RT} a_{ik} = 0$$

The five equations for the five species then become:

$$CH_4: \quad \frac{19{,}720}{RT} + \ln \frac{n_{CH_4}}{\sum_i n_i} + \frac{\lambda_C}{RT} + \frac{4\lambda_H}{RT} = 0$$

$$H_2O: \quad \frac{-192{,}420}{RT} + \ln \frac{n_{H_2O}}{\sum_i n_i} + \frac{2\lambda_H}{RT} + \frac{\lambda_O}{RT} = 0$$

$$CO: \quad \frac{-200{,}240}{RT} + \ln \frac{n_{CO}}{\sum_i n_i} + \frac{\lambda_C}{RT} + \frac{\lambda_O}{RT} = 0$$

$$CO_2: \quad \frac{-395{,}790}{RT} + \ln \frac{n_{CO_2}}{\sum_i n_i} + \frac{\lambda_C}{RT} + \frac{2\lambda_O}{RT} = 0$$

$$H_2: \quad \ln \frac{n_{H_2}}{\sum_i n_i} + \frac{2\lambda_H}{RT} = 0$$

The three material-balance equations (Eq. [4-353]) are:

$$C: \quad n_{CH_4} + n_{CO} + n_{CO_2} = 2$$
$$H: \quad 4n_{CH_4} + 2n_{H_2O} + 2n_{H_2} = 14$$
$$O: \quad n_{H_2O} + n_{CO} + 2n_{CO_2} = 3$$

Simultaneous computer solution of these eight equations, with RT = 8,314 J/mol and

$$\sum_i n_i = n_{CH_4} + n_{H_2O} + n_{CO} + n_{CO_2} + n_{H_2}$$

produces the following results ($y_i = n_i/\sum_i n_i$):

$$y_{CH_4} = 0.0196 \qquad \frac{\lambda_C}{RT} = 0.7635$$
$$y_{H_2O} = 0.0980$$
$$y_{CO} = 0.1743 \qquad \frac{\lambda_O}{RT} = 25.068$$
$$y_{CO_2} = 0.0371$$
$$y_{H_2} = 0.6711 \qquad \frac{\lambda_H}{RT} = 0.1994$$
$$\sum_i y_i = 1.000$$

The values of λ_k/RT are of no significance, but are included to make the results complete.

THERMODYNAMIC ANALYSIS OF PROCESSES

Real irreversible processes can be subjected to thermodynamic analysis. The goal is to calculate the efficiency of energy use or production and to show how energy loss is apportioned among the steps of a process. The treatment here is limited to steady-state, steady-flow processes, because of their predominance in chemical technology.

CALCULATION OF IDEAL WORK

In any steady-state, steady-flow process *requiring* work, a minimum amount must be expended to bring about a specific change of state in the flowing fluid. In a process *producing* work, a maximum amount is attainable for a specific change of state in the flowing fluid. In either case, the limiting value obtains when the specific change of state is accomplished *completely reversibly.* The implications of this requirement are:

1. The process is internally reversible within the control volume.
2. Heat transfer external to the control volume is reversible.

The second item means that heat exchange between system and surroundings must occur at the temperature of the surroundings, presumed to constitute a heat reservoir at a constant and uniform temperature T_σ. This may require Carnot engines or heat pumps internal to the system that provide for the reversible transfer of heat from the temperature of the flowing fluid to that of the surroundings. Since Carnot engines and heat pumps are cyclic, they undergo no net change of state.

The entropy change of the surroundings, found by integration of Eq. (4-3), is $\Delta S_\sigma = Q_\sigma/T_\sigma$; whence

$$Q_\sigma = T_\sigma \Delta S_\sigma \tag{4-356}$$

Since heat transfer with respect to the surroundings and with respect to the system are equal but of opposite sign, $Q_\sigma = -Q$. Moreover, the second law requires for a reversible process that the entropy changes of system and surroundings be equal but of opposite sign: $\Delta S_\sigma = -\Delta S^t$. Equation (4-356) can therefore be written $Q = T_\sigma \Delta S^t$. In terms of rates this becomes

$$\dot{Q} = T_\sigma \Delta(S\dot{m})_{fs} \tag{4-357}$$

where $\dot{Q}$ = rate of heat transfer with respect to the system
$\dot{m}$ = mass rate of flow of fluid

In addition, Δ denotes the difference between exit and entrance streams, and fs indicates that the term applies to all flowing streams.

The energy balance for a steady-state steady-flow process resulting from the first law of thermodynamics is

$$\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{\mathrm{fs}}=\dot{Q}+\dot{W}_s \tag{4-358}$$

where H = specific enthalpy of flowing fluid
u = velocity of flowing fluid
z = elevation of flowing fluid above datum level
g = local acceleration of gravity
W_s = shaft work

Eliminating $\dot{Q}$ in Eq. (4-358) by Eq. (4-357) gives

$$\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{\mathrm{fs}}=T_\sigma\Delta(S\dot{m})_{\mathrm{fs}}+\dot{W}_s(\mathrm{rev})$$

where $\dot{W}_s(\mathrm{rev})$ indicates that the shaft work is for a completely reversible process. This work is called the *ideal work* $\dot{W}_{\mathrm{ideal}}$. Thus

$$\dot{W}_{\mathrm{ideal}}=\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{\mathrm{fs}}-T_\sigma\Delta(S\dot{m})_{\mathrm{fs}} \tag{4-359}$$

In most applications to chemical processes, the kinetic- and potential-energy terms are negligible compared with the others; in this event Eq. (4-359) is written

$$\dot{W}_{\mathrm{ideal}}=\Delta(H\dot{m})_{\mathrm{fs}}-T_\sigma\Delta(S\dot{m})_{\mathrm{fs}} \tag{4-360}$$

For the special case of a single stream flowing through the system, Eq. (4-360) becomes

$$\dot{W}_{\mathrm{ideal}}=\dot{m}(\Delta H-T_\sigma\Delta S) \tag{4-361}$$

Division by $\dot{m}$ puts this equation on a unit-mass basis

$$W_{\mathrm{ideal}}=\Delta H-T_\sigma\Delta S \tag{4-362}$$

A completely reversible processes is hypothetical, devised solely to find the ideal work associated with a given change of state. Its only connection with an actual process is that it brings about the same change of state as the actual process, allowing comparison of the actual work of a process with the work of the hypothetical reversible process.

Equations (4-359) through (4-362) give the work of a completely reversible process associated with given property changes in the flowing streams. When the same property changes occur in an actual process, the actual work $\dot{W}_s$ (or W_s) is given by an energy balance, and comparison can be made of the actual work with the ideal work. When $\dot{W}_{\mathrm{ideal}}$ (or W_{ideal}) is positive, it is the *minimum work required* to bring about a given change in the properties of the flowing streams, and is smaller than $\dot{W}_s$. In this case a thermodynamic efficiency η_t is defined as the ratio of the ideal work to the actual work:

$$\eta_t(\text{work required})=\frac{\dot{W}_{\mathrm{ideal}}}{\dot{W}_s} \tag{4-363}$$

When $\dot{W}_{\mathrm{ideal}}$ (or W_{ideal}) is negative, $|\dot{W}_{\mathrm{ideal}}|$ is the *maximum work obtainable* from a given change in the properties of the flowing streams, and is larger than $|\dot{W}_s|$. In this case, the thermodynamic efficiency is defined as the ratio of the actual work to the ideal work:

$$\eta_t(\text{work produced})=\frac{\dot{W}_s}{\dot{W}_{\mathrm{ideal}}} \tag{4-364}$$

LOST WORK

Work that is wasted as the result of irreversibilities in a process is called *lost work* $\dot{W}_{\mathrm{lost}}$, and is defined as the difference between the actual work of a process and the ideal work for the process. Thus, by definition,

$$W_{\mathrm{lost}}\equiv W_s-W_{\mathrm{ideal}} \tag{4-365}$$

In terms of rates this is written

$$\dot{W}_{\mathrm{lost}}\equiv\dot{W}_s-\dot{W}_{\mathrm{ideal}} \tag{4-366}$$

The actual work rate comes from Eq. (4-358)

$$\dot{W}_s=\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{\mathrm{fs}}-\dot{Q}$$

Subtracting the ideal work rate as given by Eq. (4-359) yields

$$\dot{W}_{\mathrm{lost}}=T_\sigma\Delta(S\dot{m})_{\mathrm{fs}}-\dot{Q} \tag{4-367}$$

For the special case of a single stream flowing through the control volume,

$$\dot{W}_{\mathrm{lost}}=\dot{m}T_\sigma\Delta S-\dot{Q} \tag{4-368}$$

Division of this equation by $\dot{m}$ gives

$$W_{\mathrm{lost}}=T_\sigma\Delta S-Q \tag{4-369}$$

where the basis is now a unit amount of fluid flowing through the control volume.

The total rate of entropy increase (in both system and surroundings) as a result of a process is

$$\dot{S}_{\mathrm{total}}=\Delta(S\dot{m})_{\mathrm{fs}}-\frac{\dot{Q}}{T_\sigma} \tag{4-370}$$

For a single stream, division by $\dot{m}$ provides an equation based on a unit amount of fluid flowing through the control volume:

$$S_{\mathrm{total}}=\Delta S-\frac{Q}{T_\sigma} \tag{4-371}$$

Multiplication of Eq. (4-370) by T_σ gives

$$T_\sigma\dot{S}_{\mathrm{total}}=T_\sigma\Delta(S\dot{m})_{\mathrm{fs}}-\dot{Q}$$

Since the right-hand sides of this equation and of Eq. (4-367) are identical, it follows that

$$\dot{W}_{\mathrm{lost}}=T_\sigma\dot{S}_{\mathrm{total}} \tag{4-372}$$

For flow of a single stream on the basis of a unit amount of fluid, this becomes

$$W_{\mathrm{lost}}=T_\sigma S_{\mathrm{total}} \tag{4-373}$$

Since the second law of thermodynamics requires that

$$\dot{S}_{\mathrm{total}}\geq 0 \qquad \text{and} \qquad S_{\mathrm{total}}\geq 0$$

it follows that

$$\dot{W}_{\mathrm{lost}}\geq 0 \qquad \text{and} \qquad W_{\mathrm{lost}}\geq 0$$

When a process is completely reversible, the equality holds, and the lost work is zero. For irreversible processes the inequality holds, and the lost work, that is, the energy that becomes unavailable for work, is positive. The engineering significance of this result is clear: The greater the irreversibility of a process, the greater the rate of entropy production and the greater the amount of energy that becomes unavailable for work. Thus, every irreversibility carries with it a price.

ANALYSIS OF STEADY-STATE, STEADY-FLOW PROCESSES

Many processes consist of a number of steps, and lost-work calculations are then made for each step separately. Writing Eq. (4-372) for each step of the process and summing gives

$$\sum\dot{W}_{\mathrm{lost}}=T_\sigma\sum\dot{S}_{\mathrm{total}}$$

Dividing Eq. (4-372) by this result yields

$$\frac{\dot{W}_{\mathrm{lost}}}{\sum\dot{W}_{\mathrm{lost}}}=\frac{\dot{S}_{\mathrm{total}}}{\sum\dot{S}_{\mathrm{total}}}$$

Thus, an analysis of the lost work, made by calculation of the fraction that each individual lost-work term represents of the total lost work, is the same as an analysis of the rate of entropy generation, made by expressing each individual entropy-generation term as a fraction of the sum of all entropy-generation terms.

An alternative to the lost-work or entropy-generation analysis is a work analysis. This is based on Eq. (4-366), written

$$\sum\dot{W}_{\mathrm{lost}}=\dot{W}_s-\dot{W}_{\mathrm{ideal}} \tag{4-374}$$

For a work-requiring process, all of these work quantities are positive and $\dot{W}_s>\dot{W}_{\mathrm{ideal}}$. The preceding equation is then expresed as

$$\dot{W}_s=\dot{W}_{\mathrm{ideal}}+\sum\dot{W}_{\mathrm{lost}} \tag{4-375}$$

A work analysis gives each of the individual work terms on the right as a fraction of $\dot{W}_s$.

TABLE 4-2 States and Values of Properties for the Process of Fig. 4-12*

Point	P, bar	T, K	Composition	State	H, J/mol	S, J/(mol · K)
1	55.22	300	Air	Superheated	12,046	82.98
2	1.01	295	Pure O_2	Superheated	13,460	118.48
3	1.01	295	91.48% N_2	Superheated	12,074	114.34
4	55.22	147.2	Air	Superheated	5,850	52.08
5	1.01	79.4	91.48% N_2	Saturated vapor	5,773	75.82
6	1.01	90	pure O_2	Saturated vapor	7,485	83.69
7	1.01	300	Air	Superheated	12,407	117.35

*Properties on the basis of Miller and Sullivan, U.S. Bur. Mines Tech. Pap. 424 (1928).

For a work-producing process, $\dot{W}_s$ and $\dot{W}_{\text{ideal}}$ are negative, and $|\dot{W}_{\text{ideal}}| > |\dot{W}_s|$. Equation (4-374) in this case is best written:

$$|\dot{W}_{\text{ideal}}| = |\dot{W}_s| + \sum \dot{W}_{\text{lost}} \tag{4-376}$$

A work analysis here expresses each of the individual work terms on the right as a fraction of $|\dot{W}_{\text{ideal}}|$. A work analysis cannot be carried out in the case where a process is so inefficient that $\dot{W}_{\text{ideal}}$ is negative, indicating that the process should produce work, but $\dot{W}_s$ is positive, indicating that the process in fact requires work. A lost-work or entropy-generation analysis is always possible.

Example 4: Lost-Work Analysis Make a work analysis of a simple Linde system for the separation of air into gaseous oxygen and nitrogen, as depicted in Fig. 4-12. Table 4-2 lists a set of operating conditions for the numbered points of the diagram. Heat leaks into the column of 147 J/mol of entering air and into the exchanger of 70 J/mol of entering air have been assumed. Take $T_\sigma = 300$ K.

The basis for analysis is 1 mol of entering air, assumed to contain 79 mol % N_2 and 21 mol % O_2. By a material balance on the nitrogen, $0.79 = 0.9148\,x$; whence

$$x = 0.8636 \text{ mol of nitrogen product}$$
$$1 - x = 0.1364 \text{ mol of oxygen product}$$

Calculation of Ideal Work If changes in kinetic and potential energies are neglected, Eq. (4-360) is applicable. From the tabulated data,

$$\Delta(H\dot{m})_{\text{fs}} = (13{,}460)(0.1364) + (12{,}074)(0.8636) - (12{,}407)(1) = -144 \text{ J}$$
$$\Delta(S\dot{m})_{\text{fs}} = (118.48)(0.1364) + (114.34)(0.8636) - (117.35)(1) = -2.4453 \text{ J/K}$$

Thus, by Eq. (4-360),

$$\dot{W}_{\text{ideal}} = -144 - (300)(-2.4453) = 589.6 \text{ J}$$

Calculation of Actual Work of Compression For simplicity, the work of compression is calculated by the equation for an ideal gas in a three-stage reciprocating machine with complete intercooling and with isentropic compression in each stage. The work so calculated is assumed to represent 80 percent of the actual work. The following equation may be found in any number of textbooks on thermodynamics:

$$\dot{W}_s = \frac{n\gamma RT_1}{(0.8)(\gamma-1)}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/n\gamma} - 1\right]$$

where n = number of stages, here taken as 3
γ = ratio of heat capacities, here taken as 1.4
T_1 = initial absolute temperature, 300 K
P_2/P_1 = overall pressure ratio, 54.5
R = universal gas constant, 8.314 J/(mol·K)

The efficiency factor of 0.8 is already included in the equation. Substitution of the remaining values gives

$$\dot{W}_s = \frac{(3)(1.4)(8.314)(300)}{(0.8)(0.4)}\left[(54.5)^{0.4/(3)(1.4)} - 1\right] = 15{,}171 \text{ J}$$

The heat transferred to the surroundings during compression as a result of intercooling and aftercooling to 300 K is found from the first law:

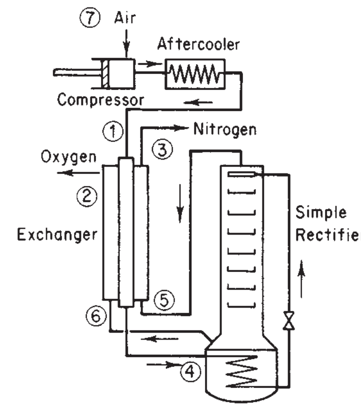

FIG. 4-12 Diagram of simple Linde system for air separation.

$$\dot{Q} = \dot{m}(\Delta H) - \dot{W}_s = (12{,}046 - 12{,}407) - 15{,}171 = -15{,}532 \text{ J}$$

Calculation of Lost Work Equation (4-367) may be applied to each of the major units of the process. For the compressor/cooler,

$$\dot{W}_{\text{lost}} = (300)[(82.98)(1) - (117.35)(1)] - (-15{,}532)$$
$$= 5{,}221.0 \text{ J}$$

For the exchanger,

$$\dot{W}_{\text{lost}} = (300)[(118.48)(0.1364) + (114.34)(0.8636) + (52.08)(1)$$
$$- (75.82)(0.8636) - (83.69)(0.1364) - (82.98)(1)] - 70$$
$$= 2{,}063.4 \text{ J}$$

Finally, for the rectifier,

$$\dot{W}_{\text{lost}} = (300)[(75.82)(0.8636) + (83.69)(0.1364) - (52.08)(1)] - 147$$
$$= 7{,}297.0 \text{ J}$$

Work Analysis Since the process requires work, Eq. (4-375) is appropriate for a work analysis. The various terms of this equation appear as entries in the following table, and are on the basis of 1 mol of entering air.

			% of $\dot{W}_s$
$\dot{W}_{\text{ideal}}$		589.6 J	3.9
$\dot{W}_{\text{lost}}$:	Compressor/cooler	5,221.0 J	34.4
$\dot{W}_{\text{lost}}$:	Exchanger	2,063.4 J	13.6
$\dot{W}_{\text{lost}}$:	Rectifier	7,297.0 J	48.1
$\dot{W}_s$		15,171.0 J	100.0

The thermodynamic efficiency of this process as given by Eq. (4-363) is only 3.9 percent. Significant inefficiencies reside with each of the primary units of the process.