This page intentionally left blank
INTRODUCTION

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

VARIABLES, DEFINITIONS, AND RELATIONSHIPS

<table>
<thead>
<tr>
<th>Constant-Composition Systems</th>
<th>The Ideal Gas Model</th>
<th>Residual Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PROPERTY CALCULATIONS FOR GASES AND VAPORS

<table>
<thead>
<tr>
<th>Evaluation of Enthalpy and Entropy in the Ideal Gas State</th>
<th>Residual Enthalpy and Entropy from PVT Correlations</th>
<th>Virial Equations of State</th>
<th>Cubic Equations of State</th>
<th>Pitzer's Generalized Correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

OTHER PROPERTY FORMULATIONS

<table>
<thead>
<tr>
<th>Liquid Phase</th>
<th>Liquid/Vapor Phase Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

THERMODYNAMICS OF FLOW PROCESSES

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PHASE EQUILIBRIUM

<table>
<thead>
<tr>
<th>Criterial Equations</th>
<th>Phase Rule</th>
<th>Example 2: Application of the Phase Rule</th>
<th>Duhamel's Theorem</th>
<th>Example 3: Dew and Bubble Point Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SYSTEMS OF VARIABLE COMPOSITION

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

OTHER PROPERTY FORMULATIONS

<table>
<thead>
<tr>
<th>Liquid Phase</th>
<th>Liquid/Vapor Phase Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

THERMODYNAMICS OF FLOW PROCESSES

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PHASE EQUILIBRIUM

<table>
<thead>
<tr>
<th>Criterial Equations</th>
<th>Phase Rule</th>
<th>Example 2: Application of the Phase Rule</th>
<th>Duhamel's Theorem</th>
<th>Example 3: Dew and Bubble Point Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td>SI units</td>
<td>U.S. Customary System units</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>----------</td>
<td>---------------------------</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Molar (or unit-mass)</td>
<td>J/mol [J/kg]</td>
<td>Btu/lbm mol</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Cross-sectional area in flow</td>
<td>m²</td>
<td>ft²</td>
<td></td>
</tr>
<tr>
<td>Bₗ</td>
<td>Partial parameter, cubic equation of state</td>
<td>cm³/mol</td>
<td>cm³/mol</td>
<td></td>
</tr>
<tr>
<td>B₂ₗ</td>
<td>Reduced second virial coefficient</td>
<td>cm³/mol</td>
<td>cm³/mol</td>
<td></td>
</tr>
<tr>
<td>B₃ₗ</td>
<td>3rd virial coefficient, density expansion</td>
<td>cm³/mol³</td>
<td>cm³/mol³</td>
<td></td>
</tr>
<tr>
<td>B₄ₗ</td>
<td>4th virial coefficient, density expansion</td>
<td>cm³/mol⁴</td>
<td>cm³/mol⁴</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3rd virial coefficient, density expansion</td>
<td>cm³/mol³</td>
<td>cm³/mol³</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>Reduced third virial coefficient</td>
<td>cm³/mol³</td>
<td>cm³/mol³</td>
<td></td>
</tr>
<tr>
<td>C₂₈</td>
<td>Interaction 2nd virial coefficient</td>
<td>cm³/mol</td>
<td>cm³/mol</td>
<td></td>
</tr>
<tr>
<td>C₁₈</td>
<td>Interaction 3rd virial coefficient</td>
<td>cm³/mol³</td>
<td>cm³/mol³</td>
<td></td>
</tr>
<tr>
<td>Cₚ</td>
<td>Heat capacity at constant pressure</td>
<td>J/(mol·K)</td>
<td>Btu/(lb·mol·R)</td>
<td></td>
</tr>
<tr>
<td>Cᵥ</td>
<td>Heat capacity at constant volume</td>
<td>J/(mol·K)</td>
<td>Btu/(lb·mol·R)</td>
<td></td>
</tr>
<tr>
<td>fᵢ</td>
<td>Fugacity of pure species i</td>
<td>kPa</td>
<td>psi</td>
<td></td>
</tr>
<tr>
<td>fₛᵢ</td>
<td>Fugacity of species i in solution</td>
<td>kPa</td>
<td>psi</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Molar (or unit-mass) Gibbs energy</td>
<td>J/mol [J/kg]</td>
<td>Btu/(lb·mol)</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>Acceleration of gravity</td>
<td>m/s²</td>
<td>ft/s²</td>
<td></td>
</tr>
<tr>
<td>ḡ</td>
<td>Reduced acceleration of gravity</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Molar (or unit-mass) enthalpy</td>
<td>J/mol [J/kg]</td>
<td>Btu/(lb·mol)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>Equilibrium K value, yᵢ/xᵢ</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>Kᵢ</td>
<td>Equilibrium constant for chemical reaction j</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>kᵢ</td>
<td>Henry's constant for solute species i</td>
<td>kPa</td>
<td>psi</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Molar or unit-mass solution property (A, G, H, S, U, V)</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>Mᵢ</td>
<td>Molar or unit-mass pure-species property</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>Mᵢᵢ</td>
<td>Partial property of species i in solution</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>Mᵢᵢᵢ</td>
<td>Residual thermodynamic property</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>Mᵢᵢᵢᵢ</td>
<td>Excess thermodynamic property</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>ΔMᵢ</td>
<td>Partial molar excess thermodynamic property</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>ΔMᵢ ᵗ</td>
<td>Property change of mixing</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
<td>kg</td>
<td>lbm</td>
<td></td>
</tr>
<tr>
<td>mᵢ</td>
<td>Mass flow rate</td>
<td>kg/s</td>
<td>lbm/s</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>Number of moles</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>nᵢ</td>
<td>Number of moles</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>Absolute pressure</td>
<td>kPa</td>
<td>psi</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>SI units</th>
<th>U.S. Customary System units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pᵢ</td>
<td>Saturation or vapor pressure of species i</td>
<td>kPa</td>
<td>psi</td>
</tr>
<tr>
<td>Q</td>
<td>Heat</td>
<td>J</td>
<td>Btu</td>
</tr>
<tr>
<td>q</td>
<td>Volumetric flow rate</td>
<td>m³/s</td>
<td>ft³/s</td>
</tr>
<tr>
<td>Q</td>
<td>Rate of heat transfer</td>
<td>J/s</td>
<td>Btu/s</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>J/(mol·K)</td>
<td>Btu/(lb·mol·R)</td>
</tr>
<tr>
<td>S</td>
<td>Molar (or unit-mass) entropy</td>
<td>J/(mol·K)</td>
<td>Btu/(lb·mol·R)</td>
</tr>
<tr>
<td>Sᵢ</td>
<td>Rate of entropy generation, Eq. (4-151)</td>
<td>J/(K·s)</td>
<td>Btu/(R·s)</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature</td>
<td>K</td>
<td>R</td>
</tr>
<tr>
<td>Tᵢ</td>
<td>Critical temperature</td>
<td>K</td>
<td>R</td>
</tr>
<tr>
<td>U</td>
<td>Molar (or unit-mass) internal energy</td>
<td>J/mol [J/kg]</td>
<td>Btu/(lb·mol)</td>
</tr>
<tr>
<td>W</td>
<td>Work</td>
<td>J</td>
<td>Btu</td>
</tr>
<tr>
<td>Wᵢ</td>
<td>Shaft work for flow process</td>
<td>J</td>
<td>Btu</td>
</tr>
<tr>
<td>Wᵢᵢ</td>
<td>Shaft power for flow process</td>
<td>J/s</td>
<td>Btu/s</td>
</tr>
<tr>
<td>xᵢ</td>
<td>Mole fraction in general</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>xᵢᵢ</td>
<td>Mole fraction of species i in liquid phase</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>yᵢ</td>
<td>Mole fraction of species i in vapor phase</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>z</td>
<td>Compressibility factor</td>
<td>Dimensionless</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>zᵢ</td>
<td>Elevation above a datum level</td>
<td>m</td>
<td>ft</td>
</tr>
</tbody>
</table>

**Superscripts**
- E Denotes excess thermodynamic property
-  id Denotes value for an ideal solution
-  ñ Denotes value for an ideal gas
-  l Denotes liquid phase
-  lc Denotes phase transition, liquid to vapor
-  R Denotes residual thermodynamic property
- t Denotes total value of property
-  u Denotes vapor phase
-  oo Denotes value at infinite dilution

**Subscripts**
- c Denotes value for the critical state
-  co Denotes the control volume
-  fs Denotes flowing streams
-  n Denotes the normal boiling point
-  r Denotes a reduced value
-  rev Denotes a reversible process

**Greek Letters**
- α, β As superscripts, identify phases
- β Volume expansivity | Dimensionless | Dimensionless |
- εᵢ Reaction coordinate for reaction j | mol | lb·mol |
- Γᵢ(T) Defined by Eq. (4-196) | J/mol | Btu/(lb·mol) |
- γ Heat capacity ratio Cᵢ/Cᵥ | Dimensionless | Dimensionless |
- γᵢ Activity coefficient of species i in solution | Dimensionless | Dimensionless |
- κ Isobaric compressibility | kPa⁻¹ | psi⁻¹ |
- μᵢ Chemical potential of species i | J/mol | Btu/(lb·mol) |
- νᵢ,j Stoichiometric number of species i in reaction j | Dimensionless | Dimensionless |
- ρ Molar density | mol/m³ | lb·mol/lft³ |
- σ As subscript, denotes a heat reservoir | Dimensionless | Dimensionless |
- Φᵢ Defined by Eq. (4-304) | Dimensionless | Dimensionless |
- φᵢ Fugacity coefficient of pure species i | Dimensionless | Dimensionless |
- φᵢᵢ Fugacity coefficient of species i in solution | Dimensionless | Dimensionless |
- ω Acentric factor | Dimensionless | Dimensionless |
Thermodynamics is the branch of science that lends substance to the principles of energy transformation in macroscopic systems. The general restrictions shown by experience 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 can be an object, a quantity of matter, or a region of space, selected for study and set apart (mentally) from everything else, which is called the surroundings. An envelope, imagined to enclose the system and to separate it from its surroundings, is called the boundary of the system.

Attributed to this boundary are special properties which may serve either to isolate the system from its surroundings or to provide for interaction in specific ways between the 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 measuring instruments such as thermometers and pressure gauges. 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.

**INTRODUCTION**

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 the measurable coordinates that characterize the system.

**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 it is 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. For such systems energy is exchanged between 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 in which only internal-energy changes occur, the first law of thermodynamics is expressed mathematically as

$$dU = dQ + dW$$

where $U$ 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, $dU$ is directly the differential change in internal energy of the system. Integration of Eq. (4-1) gives for a finite process

$$\Delta U = Q + W$$

where $\Delta U$ is the finite change given by the difference between the final and initial values of $U$. The heat $Q$ and work $W$ are finite quantities of heat and work; they are not properties of the system or 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 that characterize the system. For reversible processes, changes in this property may be calculated by the equation

\[ dS = \frac{dQ_{rev}}{T} \]  

where \( S \) 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.

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)

\[ dU = dQ_{rev} + dW_{rev} \]

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

\[ dU = TdS - PdV \]

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 is equally well written as

\[ d(nU) = Td(nS) - Pd(nV) \]  

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

\[ n = n_1 + n_2 + n_3 + \cdots = \sum n_i \]

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 a single-phase, nonreacting, closed system, \( nU = u(nS, nV) \).

Then

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

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

\[ \left[ \frac{\partial(nU)}{\partial(nS)} \right]_{V,n} = T \quad \text{and} \quad \left[ \frac{\partial(nU)}{\partial(nV)} \right]_{S,n} = -P \]

For an open single-phase system, we assume that \( nU = U(nS, nV, n_1, n_2, n_3, \ldots) \). In consequence,

\[ d(nU) = \left[ \frac{\partial(nU)}{\partial(nS)} \right]_{V,n} d(nS) + \left[ \frac{\partial(nU)}{\partial(nV)} \right]_{S,n} d(nV) + \sum \left[ \frac{\partial(nU)}{\partial(n_i)} \right]_{S,S,V,n} dn_i \]

where the summation is over all species present in the system and subscript \( n_i \) indicates that all mole numbers are held constant except the \( i \)th. Define

\[ \mu_i = \left[ \frac{\partial(nU)}{\partial(n_i)} \right]_{S,S,V,n} \]

The expressions for \( T \) and \(-P\) of the preceding paragraph and the definition of \( \mu \) allow replacement of the partial differential coefficients in the preceding equation by \( T \), \(-P\), and \( \mu \). The result is Eq. (4-6) of Table 4-1, where important equations of this section are collected.

Equation (4-6) is the fundamental property relation for single-phase PVT systems, from which all other equations connecting properties of
### 4-6 THERMODYNAMICS

#### TABLE 4-1 Mathematical Structure of Thermodynamic Property Relations

<table>
<thead>
<tr>
<th>Primary thermodynamic functions</th>
<th>Fundamental property relations</th>
<th>For homogeneous systems of constant composition</th>
<th>Maxwell equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U = TS - PV + \sum_i x_i \mu_i$</td>
<td>$d(nU) = Td(nS) - Pd(nV) + \sum_i \mu_i d(nx_i)$</td>
<td>$dU = TdS - PdV$</td>
<td>$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$</td>
</tr>
<tr>
<td>$H = U + PV$</td>
<td>$d(nH) = Td(nS) + nVdP + \sum_i \mu_i d(nx_i)$</td>
<td>$dH = TdS + VdP$</td>
<td>$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$</td>
</tr>
<tr>
<td>$A = U - TS$</td>
<td>$d(nA) = -SdT - PdV + \sum_i \mu_i d(nx_i)$</td>
<td>$dA = -SdT - PdV$</td>
<td>$\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial S}{\partial V}\right)_P$</td>
</tr>
<tr>
<td>$G = H - TS$</td>
<td>$d(nG) = -nSdT + nVdP + \sum_i \mu_i d(nx_i)$</td>
<td>$dG = -SdT + VdP$</td>
<td>$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{-\partial S}{\partial P}\right)_V$</td>
</tr>
</tbody>
</table>

$U = $ Internal energy; $H = $ enthalpy; $A = $ Helmholtz energy; $G = $ Gibbs energy.

Such systems are derived. The quantity $\mu_i$ 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. (4-6). Because $n_i = x_i \mu_i$, where $x_i$ is the mole fraction of species $i$, this equation may be rewritten as

$$d(nU) = Td(nS) + Pd(nV) + \sum_i \mu_i d(nx_i) = 0$$

Expansion of the differentials and collection of like terms yield

$$\left[dU - TdS + PdV - \sum_i \mu_i d(x_i)\right]n + [U - TS + PV - \sum_i \mu_i]dn = 0$$

Because $n$ and $dn$ are independent and arbitrary, the terms in brackets must separately be zero. This provides two useful equations:

$$dU = TdS - PdV + \sum_i \mu_i d(nx_i)$$

The first is similar to Eq. (4-6). However, Eq. (4-6) applies to a system of $n$ mol where $n$ may vary. Here, however, $n$ is unity and invariant. It is therefore subject to the constraints $\sum_i x_i = 1$ and $\sum_i dx_i = 0$. Mole fractions are not independent of one another, whereas the mole numbers in Eq. (4-6) are.

The second of the preceding equations dictates the possible combinations of terms that may be defined as additional primitive functions. Those in common use are shown in Table 4-1 as Eqs. (4-7) through (4-10). Additional thermodynamic properties are related to these and arise by arbitrary definition.

Multiplication of Eq. (4-8) of Table 4-1 by $n$ and differentiation yield the general expression

$$d(nH) = d(nU) + PdnV + nVdP$$

Substitution for $d(nU)$ by Eq. (4-6) reduces this result to Eq. (4-11). The total differentials of $nA$ and $nG$ are obtained similarly and are expressed by Eqs. (4-12) and (4-13). These equations and Eq. (4-6) are equivalent forms of the fundamental property relation, and appear under that heading in Table 4-1. Each expresses a total property—$d(nU)$, $nH$, $nA$, and $nG$—as a function of a particular set of independent variables, called 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 relation to the canonical variables $T$, $P$, and $[n_0]$, the variables of primary interest in chemical processing. Another set of equations results from the substitutions $n = 1$ and $n_i = x_i$. The resulting equations are of course less general than their parents. Moreover, because the mole fractions are not independent, mathematical operations requiring their independence are invalid.

### CONSTANT-COMPOSITION SYSTEMS

For 1 mol of a homogeneous fluid of constant composition, Eqs. (4-6) and (4-11) through (4-13) simplify to Eqs. (4-14) through (4-17) of Table 4-1. Because these equations are exact differential expressions, application of the reciprocity relation for such expressions produces the common Maxwell relations as described in the subsection “Multivariable Calculus Applied to Thermodynamics” in Sec. 3. These are Eqs. (4-18) through (4-21) of Table 4-1, in which the partial derivatives are taken with composition held constant.

$U$, $H$, and $S$ as Functions of $T$ and $P$ or $T$ and $V$ at constant composition, molar thermodynamic properties can be considered functions of $T$ and $P$ (postulate 5). Alternatively, because $V$ is related to $T$ and $P$ through an equation of state, $V$ can serve rather than $P$ as the second independent variable. The useful equations for the total differentials of $U$, $H$, and $S$ that result are given in Table 4-1 by Eqs. (4-22) through (4-25). The obvious next step is substitution for the partial differential coefficients in favor of measurable quantities. This purpose is served by definition of two heat capacities, one at constant pressure and the other at constant volume:

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

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$
Equation (4-15) of Table 4-1 may be divided by \(dT\) and restricted to constant \(P\), yielding \(\partial H/\partial T\)_\(r\) as given by the first equality of Eq. (4-28). Division of Eq. (4-15) by \(dP\) and restriction to constant \(T\) yield \(\partial H/\partial P\)_\(r\) as given by the first equality of Eq. (4-29). Equation (4-28) is completed by Eq. (4-26), and Eq. (4-29) is completed by Eq. (4-21). Similarly, equations for \(\partial U/\partial T\)_\(r\) and \(\partial U/\partial V\)_\(r\) derive from Eq. (4-14), and these with Eqs. (4-27) and (4-20) yield Eqs. (4-30) and (4-31) of Table 4-1.

Equations (4-22), (4-26), and (4-29) combine to yield Eq. (4-32); Eqs. (4-23), (4-28), and (4-21) to yield Eq. (4-33); Eqs. (4-24), (4-27), and (4-31) to yield Eq. (4-34); and Eqs. (4-25), (4-30), and (4-20) to yield Eq. (4-35).

Equations (4-32) and (4-33) are general expressions for the enthalpy and entropy of homogeneous fluids at constant composition as functions of \(T\) and \(P\). Equations (4-34) and (4-35) 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 \(dT\), \(dP\), and \(dV\) are all composed of measurable quantities.

### The Ideal Gas Model

An ideal gas is a model gas comprising imaginary molecules of zero volume that do not interact. Its \(PVT\) behavior is represented by the simplest of equations of state \(P_{\text{ig}}V_{\text{ig}} = RT\), where \(R\) is a universal constant, values of which are given in Table 1-9. The following partial derivatives, all taken at constant composition, are obtained from this equation:

\[
\begin{align*}
\left(\frac{\partial P}{\partial V}\right)_T = \frac{R}{V} & \quad \left(\frac{\partial P}{\partial T}\right)_V = -\frac{P}{V} \\
\left(\frac{\partial V}{\partial P}\right)_T = \frac{P}{\partial T} & \quad \left(\frac{\partial V}{\partial V}\right)_T = 0
\end{align*}
\]

The first two of these relations when substituted appropriately into Eqs. (4-29) and (4-31) of Table 4-1 lead to very simple expressions for ideal gases:

\[
\begin{align*}
\left(\frac{\partial V}{\partial V}\right)_T &= \left(\frac{\partial H}{\partial P}\right)_T = 0 & \left(\frac{\partial S}{\partial P}\right)_T &= -\frac{R}{P}
\end{align*}
\]

Moreover, Eqs. (4-32) through (4-35) become

\[
\begin{align*}
dH &= C_p^0 dT & dS &= C_v^0 dT - \frac{R}{P} dP \\
dU &= C_v^0 dT & dS &= C_v^0 dT + \frac{R}{V} dV
\end{align*}
\]

In these equations \(V_{\text{ig}}, U_{\text{ig}}, H_{\text{ig}}, C_v^0,\) and \(C_p^0\) are ideal gas state values—the values that a \(PVT\) system would have were the ideal gas equation the true equation of state. They apply equally to pure species and to constant-composition mixtures, and they show that \(U_{\text{ig}}, C_v^0,\) and \(C_p^0\) are functions of temperature only, independent of \(P\) and \(V\). The entropy, however, is a function of both \(T\) and \(P\) or of both \(T\) and \(V\). Regardless of composition, the ideal gas volume is given by \(V_{\text{ig}} = RT/P\), and it provides the basis for comparison with true molar volumes through the compressibility factor \(Z\). By definition,

\[
Z = \frac{V}{V_{\text{ig}}} = \frac{V}{RT/P} = \frac{PV}{RT} \quad \text{(4-36)}
\]

The ideal gas state properties of mixtures are directly related to the ideal gas state properties of the constituent pure species. For those properties that are independent of \(P\)—\(U_{\text{ig}}, H_{\text{ig}}, C_v^0,\) and \(C_p^0\)—the mixture property is the sum of the properties of the pure constituent species, each weighted by its mole fraction:

\[
M^c = \sum_{i} y_i M_i^c \quad \text{(4-37)}
\]

where \(M^c\) can represent any of the properties listed. For the entropy, which is a function of both \(T\) and \(P\), an additional term is required to account for the difference in partial pressure of a species between its pure state and its state in a mixture:

\[
S^c = \sum_{i} y_i S_i^c - R \sum_{i} y_i \ln y_i \quad \text{(4-38)}
\]

For the Gibbs energy, \(G^c = H^c - TS^c\), whence by Eqs. (4-37) and (4-38):

\[
G^c = \sum_{i} y_i G_i^c + RT \sum_{i} y_i \ln y_i \quad \text{(4-39)}
\]

The ideal gas model may serve as a reasonable approximation to reality under conditions indicated by Fig. 4-1.

### Residual Properties

The differences between true and ideal gas state properties are defined as residual properties \(M^r\):

\[
M^r = M - M^c \quad \text{(4-40)}
\]

where \(M\) is the molar value of an extensive thermodynamic property of a fluid in its actual state and \(M^c\) is its corresponding ideal gas state value at the same \(T\), \(P\), and composition. Residual properties depend on interactions between molecules and not on characteristics of individual molecules. Because the ideal gas state presumes the absence of molecular interactions, residual properties reflect deviations from ideality. The most commonly used residual properties are as follows:

Residual volume \(V^r = V - V^c\)  
Residual enthalpy \(H^r = H - H^c\)  
Residual entropy \(S^r = S - S^c\)  
Residual Gibbs energy \(G^r = G - G^c\)

Useful relations connecting these residual properties derive from Eq. (4-17), an alternative form of which follows from the mathematical identity:

\[
d\left(\frac{G}{RT}\right) = \frac{1}{RT} dG - \frac{G}{RT^2} dT
\]
Substitution for \( dG \) by Eq. (4-17) and for \( G \) by Eq. (4-10) gives, after algebraic reduction,
\[
\frac{d\left(\frac{G}{RT}\right)}{RT} = \frac{V}{RT} \, dP - \frac{H}{RT^2} \, dT \quad (4-41)
\]
This equation may be written for the special case of an ideal gas and subtracted from Eq. (4-41) itself, yielding
\[
\frac{d\left(\frac{G^I}{RT}\right)}{RT} = \frac{V^I}{RT} \, dP - \frac{H^I}{RT^2} \, dT
\quad (4-42)
\]
As a consequence,
\[
\frac{V^I}{RT} = \left[ \frac{\partial (G^I/RT)}{\partial P} \right]_T
\quad (4-43)
\]
and
\[
\frac{H^I}{RT} = -T \left[ \frac{\partial (G^I/RT)}{\partial T} \right]_P
\quad (4-44)
\]
Equation (4-43) provides a direct link to PVT correlations through the compressibility factor \( Z \) as given by Eq. (4-36). Thus, with \( V = ZRT/P \),
\[
V^I = V - V^c = \frac{ZRT}{P} - \frac{RT}{P} \quad (Z - 1)
\]
This equation in combination with a rearrangement of Eq. (4-43) yields
\[
\frac{d\left(\frac{G^I}{RT}\right)}{RT} = \frac{V^I}{RT} \, dP = (Z - 1) \frac{dP}{P} \quad \text{constant} \ T
\]
Integration from \( P = 0 \) to arbitrary pressure \( P \) gives
\[
\frac{G^I}{RT} = \frac{V^I}{P} (Z - 1) \frac{dP}{P} \quad \text{constant} \ T
\quad (4-45)
\]

THE PROPERTY CALCULATIONS FOR GASES AND VAPORS

The most satisfactory calculation procedure for the thermodynamic properties of gases and vapors is based on ideal gas state heat capacities and residual properties. Of primary interest are the enthalpy and entropy; these are given by rearrangement of the residual property definitions:
\[
H = H^s + H^R \quad \text{and} \quad S = S^s + S^R
\]
These are simple sums of the ideal gas and residual properties, evaluated separately.

EVALUATION OF ENTHALPY AND ENTROPY IN THE IDEAL GAS STATE

For the ideal gas state at constant composition:
\[
dH^s = C^s_\text{ig} dT \quad \text{and} \quad dS^s = C^s_\text{ig} \frac{dT}{T} - R d\ln \frac{P}{P_0}
\]
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
\[
H^s = H^s_0 + \int_{T_0}^T C^s_\text{ig} \, dT \\
S^s = S^s_0 + \int_{T_0}^T C^s_\text{ig} \frac{dT}{T} - R \ln \frac{P}{P_0}
\]
Substitution into the equations for \( H \) and \( S \) yields
\[
H = H^s + \int_{T_0}^T C^s_\text{ig} \, dT + H^R \\
S = S^s + \int_{T_0}^T C^s_\text{ig} \frac{dT}{T} - R \ln \frac{P}{P_0} + S^R
\quad (4-51)
\]
The reference state at \( T_0 \) and \( P_0 \) is arbitrarily selected, and the values assigned to \( H^s_0 \) and \( S^s_0 \) are also arbitrary. In practice, only changes in \( H \) and \( S \) are of interest, and fixed reference state values ultimately cancel in their calculation.

The ideal gas state heat capacity \( C^s_\text{ig} \) is a function of \( T \) but not of \( P \). For a mixture the heat capacity is simply the molar average \( \sum y_i C^s_\text{ig} \). Empirical equations relating \( C^s_\text{ig} \) to \( T \) are available for many pure gases; a common form is
\[
\frac{C^s_\text{ig}}{R} = A + BT + CT^2 + DT^3
\quad (4-52)
\]
where \( A, B, C, \) and \( D \) are constants characteristic of the particular gas, and either \( C \) or \( D \) is zero. The ratio \( C^s_\text{ig}/R \) is dimensionless; thus the units of \( C^s_\text{ig} \) are those of \( R \). Data for ideal gas state heat capacities are given for many substances in Table 2-155. Evaluation of the integrals \( \int C^s_\text{ig} \, dT \) and \( \int (C^s_\text{ig}/T) \, dT \) is accomplished by substitution for \( C^s_\text{ig} \), followed by integration. For temperature limits of \( T_0 \) and \( T \) and with \( \tau = T/T_0 \), the equations that follow from Eq. (4-52) are
\[
\int_{T_0}^T C^s_\text{ig} \, dT = AT_0(\tau - 1) + B \frac{\tau^2(\tau^2 - 1)}{2} + C \frac{\tau^2(\tau^3 - 1)}{3} + D \frac{\tau(\tau - 1)}{T_0}
\quad (4-53)
\]
\[
\int_{T_0}^T \frac{C^s_\text{ig}}{T} \, dT = A \ln \tau + \left[ BT_0 + \left( \frac{C T_0^2 + D \tau}{2} \right) \left( \frac{\tau - 1}{\tau} \right) \right] (\tau - 1)
\quad (4-54)
Equations (4-50) and (4-51) may sometimes be advantageously expressed in alternative form through use of mean heat capacities:

$$H = H^0 + (C_V^0)_{th}(T - T_r) + H^a$$
(4-55)

$$S = S^0 + (C_P^0)_{th} \ln \frac{T}{T_r} - R \ln \frac{P}{P_r} + S^a$$
(4-56)

where \((C_V^0)_{th}\) and \((C_P^0)_{th}\) are mean heat capacities specific, respectively, for enthalpy and entropy calculations. They are given by the following equations:

$$\frac{(C_V^0)_{th}}{R} = A + \frac{B}{2} T_r (\tau + 1) + \frac{C}{3} T_r^2 (\tau^2 + \tau + 1) + \frac{D}{\tau T_r^2}$$
(4-57)

$$\frac{(C_P^0)_{th}}{R} = A + B T_r + \left( C T_r^2 + \frac{D}{\tau T_r^2} \right) \frac{\tau + 1}{\tau} - \frac{1}{\tau}$$
(4-58)

**Residual Enthalpy and Entropy from PVT Correlations**

The residual properties of gases and vapors depend on their PVT behavior. This is often expressed through correlations for the compressibility factor \(Z\), defined by Eq. (4-36). Analytical expressions for \(Z\) as functions of \(T\) and \(P\) or \(T\) and \(V\) are known as equations of state. They may also be reformulated to give \(Z\) as a function of \(T\) and \(V\) or \(P\) as a function of \(T\) and \(P\).

**Virial Equations of State**

The virial equation in density is an infinite series expansion of the compressibility factor \(Z\) in powers of molar density \(\rho\) (or reciprocal molar volume \(V^{-1}\)) about the real gas state at zero density (zero pressure):

$$Z = 1 + B P + C P^2 + D P^3 + \cdots$$
(4-59)

The density series virial coefficients \(B, C, D, \ldots\) depend on temperature and composition only. In practice, truncation is to two or three terms. The composition dependencies of \(B\) and \(C\) are given by the exact mixing rules

$$B = \sum_{i} \sum_{j} y_i y_j B_{ij}$$
(4-60)

$$C = \sum_{i} \sum_{j} \sum_{k} y_i y_j y_k C_{ijk}$$
(4-61)

where \(y_i\), \(y_j\), and \(y_k\) are mole fractions for a gas mixture and \(i, j, \) and \(k\) identify species.

The coefficient \(B_{ij}\) characterizes a binomial interaction between molecules \(i\) and \(j\), and therefore \(B_{ij} = B_{ji}\). Two kinds of second virial coefficient arise: \(B_{ij}\) and \(B_{ik}\); wherein the subscripts are the same (\(i = j\)), and \(B_{ik}\) 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: \(C_{ijk}\) and \(C_{ikj}\) are for the pure species, and \(C_{ijk} = C_{ikj} = C_{jik}\) are cross coefficients.

Although the virial equation itself is easily rationalized on empirical grounds, the mixing rules of Eqs. (4-60) and (4-61) follow rigorously from the methods of statistical mechanics. The temperature derivatives of \(B\) and \(C\) are given exactly by

$$\frac{dB}{dT} = \sum_{i} \sum_{j} y_i y_j \frac{dB_{ij}}{dT}$$
(4-62)

$$\frac{dC}{dT} = \sum_{i} \sum_{j} \sum_{k} y_i y_j y_k \frac{dC_{ijk}}{dT}$$
(4-63)

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):

$$Z = 1 + B P + C P^2 + D P^3 + \cdots$$
(4-64)

Equation (4-64) is the virial equation in pressure, and \(B^*, C^*, D^*\) are the pressure series virial coefficients. Again, truncation is to two or three terms, with \(B^*\) and \(C^*\) depending on temperature and composition only. Moreover, the two sets of coefficients are related:

$$B^* = B / T$$
(4-65)

$$C^* = (C + B^*^2) / (RT)^2$$
(4-66)

Values can often be found for \(B\), but not so often for \(C\). Generalized correlations for both \(B\) and \(C\) are given by Meng, Duan, and Li [Fluid Phase Equilibria 226: 109–120 (2004)].

For pressures up to several bars, the two-term expansion in pressure, with \(B^*\) given by Eq. (4-65), is usually preferred:

$$Z = 1 + B^* P + 1 + B P / RT$$
(4-67)

For supercritical temperatures, it is satisfactory to ever higher pressures as the temperature increases. For pressures above the range where Eq. (4-67) is useful, but below the critical pressure, the virial expansion in density truncated to three terms is usually suitable:

$$Z = 1 + B P + C P^2$$
(4-68)

Equations for residual enthalpy and entropy may be developed from each of these expressions. Consider first Eq. (4-67), which is explicit in volume. Equations (4-45) and (4-46) are therefore applicable. Direct substitution for \(Z\) in Eq. (4-45) gives

$$\frac{G^0}{RT} = \frac{B P}{RT}$$
(4-69)

Differentiation of Eq. (4-67) yields

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

By Eq. (4-46),

$$\frac{H^0}{RT} = \frac{P}{T} \left( \frac{dB}{dT} - \frac{B}{T} \right)$$
(4-70)

and by Eq. (4-47),

$$\frac{S^0}{R} = - \frac{P}{R} \frac{dB}{dT}$$
(4-71)

An extensive set of three-parameter corresponding-states correlations has been developed by Pitzer and coworkers [Pitzer, Thermodynamics, 3d ed., App. 3, McGraw-Hill, New York (1995)]. Particularly useful is the one for the second virial coefficient. The basic equation is

$$\frac{B P_C}{RT_r} = B^* + \omega B^1$$
(4-72)

with the acentric factor defined by Eq. (2-17). For pure chemical species \(B^*\) and \(B^1\) are functions of reduced temperature only. Substitution for \(B\) in Eq. (4-67) by this expression gives

$$Z = 1 + (B^* + \omega B^1) P_r / T_r$$
(4-73)

By differentiation,

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

Upon substitution of these equations into Eqs. (4-48) and (4-49), integration yields

$$\frac{G^0}{RT} = (B^* + \omega B^1) P_r / T_r$$
(4-74)

$$\frac{H^0}{RT_r} = P_r \left( B^0 - T_r \frac{dB^0}{dT_r} + \omega (B^1 - T_r \frac{dB^1}{dT_r}) \right)$$
(4-75)

The residual entropy follows from Eq. (4-47):

$$\frac{S^0}{R} = - P_r \left( \frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right)$$
(4-76)
In these equations, \( B^0 \) and \( B^1 \) and their derivatives are well represented by Abbott's correlations [Smith and Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 3d ed., p. 87, McGraw-Hill, New York (1975)]:

\[
B^0 = 0.083 - \frac{0.422}{T_{i6}} \tag{4-77}
\]

\[
B^1 = 0.139 - \frac{0.172}{T_{i6}} \tag{4-78}
\]

\[
\frac{dB^0}{dT} = \frac{0.675}{T_{i6}^2} \tag{4-79}
\]

\[
\frac{dB^1}{dT} = \frac{0.722}{T_{i6}^2} \tag{4-80}
\]

Although limited to pressures where the two-term virial equation in pressure has approximate validity, these correlations are applicable for most chemical processing conditions. As with all generalized correlations, they are least accurate for polar and associating molecules.

Although developed for pure materials, these correlations can be extended to gas or vapor mixtures. Basic to this extension are the mixing rules for the second virial coefficient and its temperature derivative as given by Eqs. (4-60) and (4-62). Values for the cross coefficients \( B_{ij} \), with \( i \neq j \), and their derivatives are provided by Eq. (4-72) written in extended form:

\[
B_{ij} = \frac{RT_{ij}}{P_{ij}} (B^0 + \omega_i B^1) \tag{4-81}
\]

where \( B^0, B^1, dB^0/dT, \) and \( dB^1/dT \) are the same functions of \( T \), as given by Eqs. (4-77) through (4-80). Differentiation produces

\[
\frac{dB^0}{dT} = \frac{R T_{ij}}{P_{ij}} \left( \frac{dB^0}{dT} + \omega_i \frac{dB^1}{dT} \right) \tag{4-82}
\]

where \( T_{ij} = T_{i} T_{j}/V_{ij} \). The following combining rules for \( \omega_i, T_{ij}, \) and \( P_{ij} \) are 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)]:

\[
\omega_i = \frac{\omega_i + \omega_j}{2} \tag{4-83}
\]

\[
T_{ij} = (T_i T_j)^{1/2}(1 - k_{ij}) \tag{4-84}
\]

\[
P_{ij} = \frac{Z_{ij} R T_{ij}}{V_{ij}} \tag{4-85}
\]

with

\[
Z_{ij} = \frac{Z_i + Z_j}{2} \tag{4-86}
\]

and

\[
V_{ij} = \left( \frac{V_{i}^{1/3} + V_{j}^{1/3}}{2} \right)^3 \tag{4-87}
\]

In Eq. (4-84), \( k_{ij} \) is an empirical interaction parameter specific to an \( i \neq j \) 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, absence 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 without physical significance. For a mixture, values of \( B_{ij} \) and \( dB_{ij}/dT \) from Eqs. (4-81) and (4-82) are substituted into Eqs. (4-60) and (4-62) to provide values of the mixture second virial coefficient \( B \) and its temperature derivative. Values of \( H^0 \) and \( S^0 \) are then given by Eqs. (4-70) and (4-71).


Because Eq. (4-68) is explicit in \( P \), it is incompatible with Eqs. (4-45) and (4-46), and they must be transformed to make \( V \) (or molar density \( \rho \)) the variable of integration. The resulting equations are given by Smith, Van Ness, and Abbott [Introduction to Chemical Engineering Thermodynamics, 7th ed., pp. 216–217, McGraw-Hill, New York (2005)]:

\[
\frac{C^0}{RT} = Z - 1 - \ln Z + \left. \frac{\rho}{\rho_{ij}} \right|_{Z = 1} \frac{d\rho}{d\rho} \tag{4-88}
\]

\[
\frac{H^0}{RT} = Z - 1 - T_{ij}^0 \left( \frac{\partial Z}{\partial T} \right)_{\rho} \frac{d\rho}{d\rho} \tag{4-89}
\]

By differentiation of Eq. (4-68),

\[
\left( \frac{\partial Z}{\partial T} \right)_{\rho} = \frac{dB}{dT} \rho + \frac{dC}{dT} \rho^2 \tag{4-90}
\]

Substituting in Eqs. (4-88) and (4-89) for \( Z \) by Eq. (4-68) and in Eq. (4-89) for the derivative yields, upon integration and reduction,

\[
\frac{C^0}{RT} = 2B_{ij} + \frac{3}{2} \rho C_{ij} - \ln Z \tag{4-91}
\]

The residual entropy is given by Eq. (4-47).

In a process calculation, \( T \) and \( P \), rather than \( T \) and \( \rho \) (or \( T \) and \( V \)), are usually the favored independent variables. Applications of Eqs. (4-90) and (4-91) therefore require prior solution of Eq. (4-68) for \( Z \) or \( \rho \). With \( Z = P/\rho RT \), Eq. (4-68) may be written in two equivalent forms:

\[
Z^3 - Z^2 - \frac{BP}{RT} Z - \frac{CP^2}{(RT)^2} = 0 \tag{4-92}
\]

\[
\rho^3 + \frac{B}{C} \rho^2 + \frac{1}{C} \rho - \frac{P}{CRT} = 0 \tag{4-93}
\]

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

Data for third virial coefficients are often lacking, but generalized correlations are available. Equation (4-68) may be rewritten in reduced form as

\[
Z = 1 + \frac{BP}{RT} + \frac{C}{TZ} \left( \frac{P}{TZ} \right)^2 \tag{4-94}
\]

where \( \hat{B} \) is the reduced second virial coefficient given by Eq. (4-72). Thus by definition,

\[
\hat{B} = \frac{BP}{RT} = B^0 + \omega_i B^1 \tag{4-95}
\]

The reduced third virial coefficient \( \hat{C} \) is defined as

\[
\hat{C} = \frac{CP^2}{(RT)^2} \tag{4-96}
\]

A Fitzer-type correlation for \( \hat{C} \) is then written as

\[
\hat{C} = C^0 + \omega_i C^1 \tag{4-97}
\]
Correlations for $C^0$ and $C^1$ with reduced temperature are

$$C^0 = 0.01407 + \frac{0.02432}{T_r} - \frac{0.00313}{T_r^{0.5}} \quad (4-98)$$

$$C^1 = -0.02676 + \frac{0.05539}{T_r^{0.5}} - \frac{0.00242}{T_r} \quad (4-99)$$

The first is given by, and the second is inspired by, Orbey and Vera [AIChE J. 29:107–113 (1983)].

Equation (4-94) is cubic in $Z$; with $T$ and $P$, specified, solution for $Z$ is by iteration. An initial guess of $Z = 1$ on the right side usually leads to rapid convergence.

Another class of equations, known as extended virial equations, was introduced by Benedict, Webb, and Rubin [J. Chem. Phys. 8:334–345 (1940); 10:747–758 (1942)]. This equation contains eight parameters, all functions of composition. It and its modifications, despite their complexity, find application in the petroleum and natural gas industries for light hydrocarbons and a few other commonly encountered gases [see Lee and Kesler, AIChE J., 21:510–527 (1975)].

**Cubic Equations of State**

The modern development of cubic equations of state started in 1949 with publication of the Redlich-Kwong (RK) equation [Chem. Rev., 44:233–244 (1949)], and many others have since been proposed. An extensive review is given by Valderrama [Ind. Eng. Chem. Res. 42:1603–1618 (2003)]. Of the equations published more recently, the two most popular are the Soave-Redlich-Kwong (SRK) equation, a modification of the RK equation [Chem. Eng. Sci. 27:1197–1203 (1972)] and the Peng-Robinson (PR) equation [Ind. Eng. Chem. Fundam. 15:59–64 (1976)]. All are encompassed by a generic cubic equation of state, written as

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V + b)(V + \sigma b)} \quad (4-100)$$

For a specific form of this equation, $\sigma$ and $\varepsilon$ are pure numbers, the same for all substances, whereas parameters $a(T)$ and $b$ are substance-dependent. Suitable estimates of the parameters in cubic equations of state are usually found from values for the critical constants $T_c$ and $P_c$.

The procedure is discussed by Smith, Van Ness, and Abbott [Introduction to Chemical Engineering Thermodynamics, 7th ed., pp. 93–94, McGraw-Hill, New York (2005)], and for Eq. (4-100) the appropriate equations are given as

$$a(T) = \Psi \frac{\alpha(T)RT^2}{P_r} \quad (4-101)$$

$$b = \Omega \frac{RT}{P_r} \quad (4-102)$$

Function $\alpha(T)$ is an empirical expression, specific to a particular form of the equation of state. In these equations $\Psi$ and $\Omega$ are pure numbers, independent of substance and determined for a particular equation of state from the values assigned to $\varepsilon$ and $\sigma$.

As an example cubic in $V$, Eq. (4-100) has three volume roots, of which two may be complex. Physically meaningful values of $V$ are always real, positive, and greater than parameter $b$. 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 three roots exist, all equal to $V_c$. For $T < T_c$, only one real positive (liquidlike) root exists at high pressures, but for a range of lower pressures there are three. 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.

Equation (4-100) may be rearranged to facilitate its solution either for a vapor or vaporlike volume or for a liquid or liquidlike volume.

**Vapor:**

$$V = \frac{RT}{P} + b - \frac{a(T)}{P} \frac{V - b}{(V + b)(V + \sigma b)} \quad (4-103a)$$

**Liquid:**

$$V = b + (V + b)(V + \sigma b) \left[ \frac{RT - bP - VP}{a(T)} \right] \quad (4-103b)$$

Solution for $V$ is most convenient with the solve routine of a software package. An initial estimate for $V$ in Eq. (4-103a) is the ideal gas value $RT/P$; for Eq. (4-103b) it is $V = b$. In either case, iteration is initiated by substituting the estimate on the right side. The resulting value of $V$ on the left is returned to the right side, and the process continues until the change in $V$ is suitably small.

Equations for $Z$ equivalent to Eqs. (4-103) are obtained by substituting $V = ZRT/P$.

**Vapor:**

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \quad (4-104a)$$

**Liquid:**

$$Z = \beta + (Z + \epsilon b)(Z + \sigma b) \frac{1 + \beta - Z}{\epsilon\beta} \quad (4-104b)$$

where by definition

$$\beta = \frac{bP}{RT} \quad (4-105)$$

and

$$q = \frac{a(T)}{bRT} \quad (4-106)$$

These dimensionless quantities provide simplification, and when combined with Eqs. (4-101) and (4-102), they yield

$$\beta = \Omega \frac{P_r}{T_r} \quad (4-107)$$

$$q = \frac{\Psi a(T)}{\Omega T_r} \quad (4-108)$$

In Eq. (4-104a) the initial estimate is $Z = 1$; in Eq. (4-104b) it is $Z = \beta$. Iteration follows the same pattern as for Eqs. (4-103). The final value of $Z$ yields the volume root through $V = ZRT/P$.

Equations of state, such as the Redlich-Kwong (RK) equation, which expresses $Z$ as a function of $T$, and $P$, only yield two-parameter corresponding-states correlations. The SRK equation and the PR equation, in which the acentric factor $\omega$ enters through function $\alpha(T; \omega)$ as an additional parameter, yield three-parameter corresponding-states correlations. The numerical assignments for parameters $\varepsilon$, $\sigma$, $\omega$, and $\Psi$ are given in Table 4-2. Expressions are also given for $\alpha(T; \omega)$ for the SRK and PR equations.

As shown by Smith, Van Ness, and Abbott [Introduction to Chemical Engineering Thermodynamics, 7th ed., pp. 218–219, McGraw-Hill, New York (2005), Eqs. (4-104) in conjunction with Eqs. (4-88), (4-89), and (4-47) lead to

$$\frac{C^0}{RT} = \frac{Z - 1 - \ln(Z - \beta) - qI}{\ln Z} \quad (4-109)$$

$$\frac{H^0}{RT} = Z - 1 \left[ \frac{d}{d \ln T_r} \frac{\ln \alpha(T)}{\ln Z - 1} \right] qI \quad (4-110)$$

### Table 4-2 Parameter Assignments for Cubic Equations of State

For use with Eqs. (4-104) through (4-106)

<table>
<thead>
<tr>
<th>Equ. of state</th>
<th>$\alpha(T)$</th>
<th>$\sigma$</th>
<th>$\epsilon$</th>
<th>$\Omega$</th>
<th>$\Psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RK (1949)</td>
<td>$T_r^{-0.2}$</td>
<td>1</td>
<td>0</td>
<td>0.08664</td>
<td>0.42746</td>
</tr>
<tr>
<td>SRK (1972)</td>
<td>$\alpha_{SRK}(T; \omega)$</td>
<td>1</td>
<td>0</td>
<td>0.08664</td>
<td>0.42746</td>
</tr>
<tr>
<td>PR (1976)</td>
<td>$\alpha_{PR}(T; \omega)$</td>
<td>1 + $\sqrt{2}$</td>
<td>1 - $\sqrt{2}$</td>
<td>0.07780</td>
<td>0.45724</td>
</tr>
</tbody>
</table>

\[
\frac{S^R}{R} = \ln \left( Z - \beta \right) + \frac{d \ln \alpha \left( T_e \right)}{d \ln T_e} qI \quad (4-111)
\]

where
\[
I = \frac{1}{\sigma - \epsilon} \ln \left( \frac{Z + \sigma \beta}{Z + \epsilon \beta} \right) \quad (4-112)
\]

Preliminary to application of these equations Z is found by solution of either Eq. (4-104c) or (4-104b). Cubic equations of state may be applied to mixtures through expressions that give the parameters as functions of composition. No established theory prescribes the form of this dependence, and empirical mixing rules are often used to relate mixture parameters to pure-species parameters. The simplest realistic expressions are a linear mixing rule for parameter \(b\) and a quadratic mixing rule for parameter \(a\)
\[
b = \sum_j x_j b_j \quad (4-113)
\]
\[
a = \sum_j x_j a_{ij} \quad (4-114)
\]
with \(a_{ij} = a_{ij}\). The \(a_{ij}\) are of two types: pure-species parameters (like subscripts) and interaction parameters (unlike subscripts). Parameter \(b_j\) is for pure species \(i\). The interaction parameter \(a_{ij}\) is often evaluated from pure-species parameters by a geometric mean combining rule
\[
a_{ij} = (a_{ij})^{1/2} \quad (4-115)
\]

These traditional equations yield mixture parameters solely from parameters for the pure constituent species. They are most likely to be satisfactory for mixtures comprised of simple and chemically similar molecules.

**Pitzer’s Generalized Correlations** In addition to the corresponding-states correlation for the second virial coefficient, Pitzer and coworkers [Thermodynamics, 3d ed., App. 3, McGraw-Hill, New York (1995)] developed a full set of generalized correlations. They have as their basis an equation for the compressibility factor, as given by Eq. (2-63):
\[
Z = Z^0 + \omega Z^1 \quad (2-63)
\]

where \(Z^0\) and \(Z^1\) are each functions of reduced temperature \(T_r\) and reduced pressure \(P_r\). Acentric factor \(\omega\) is defined by Eq. (2-17). Correlations for \(Z\) appear in Sec. 2.

Generalized correlations are developed here for the residual enthalpy and residual entropy from Eqs. (4-48) and (4-49). Substitution for \(Z\) by Eq. (2-63) puts Eq. (4-48) into generalized form:
\[
\frac{G^R}{RT_e} = \left[ \frac{r}{\rho} \left( Z^0 - 1 \right) - \frac{dP_r}{P_r} \right] + \omega \left[ \frac{r}{\rho} Z^1 \frac{dP_r}{P_r} \right] \quad (4-116)
\]

Differentiation of Eq. (2-63) yields
\[
\left( \frac{\partial Z}{\partial T_e} \right)_P = \left( \frac{\partial Z^0}{\partial T_e} \right)_P + \omega \left( \frac{\partial Z^1}{\partial T_e} \right)_P \quad (4-117)
\]

Substitution for \(\partial Z/\partial T_e\) in Eq. (4-49) gives
\[
\frac{H^R}{RT_e} = -T_r^2 \left[ \frac{r}{\rho} \left( \frac{\partial Z^0}{\partial T_e} \right)_P + \omega \left( \frac{\partial Z^1}{\partial T_e} \right)_P \right] \frac{dP_r}{P_r} \quad (4-117a)
\]

By Eq. (4-47),
\[
\frac{S^R}{R} = \frac{1}{T_r} \frac{\frac{H^R}{RT_r}}{G^R} \frac{G^R}{RT_r} \quad (4-116a)
\]

Combination of Eqs. (4-116) and (4-117) leads to
\[
\frac{S^R}{R} = -T_r^2 \left[ \frac{r}{\rho} \left( \frac{\partial Z^0}{\partial T_e} \right)_P + Z^0 - 1 \right] \frac{dP_r}{P_r} - \omega T_r^2 \left[ \frac{r}{\rho} \left( \frac{\partial Z^1}{\partial T_e} \right)_P + Z^1 \right] \frac{dP_r}{P_r} \quad (4-117b)
\]

If the first terms on the right sides of Eq. (4-117) and of this equation (including the minus signs) are represented by \(\left( H^R \right)/RT_e\) and \(\left( S^R \right)/R\) and if the second terms, excluding \(\omega\) but including the minus signs, are represented by \(\left( H^R \right)/RT_e\) and \(\left( S^R \right)/R\) then

\[
\frac{H^R}{RT_e} = \frac{\left( H^R \right)}{RT_e} + \omega \frac{\left( S^R \right)}{RT_e} \quad (4-118)
\]
\[
\frac{S^R}{R} = \frac{\left( S^R \right)}{R} + \omega \frac{\left( S^R \right)}{R} \quad (4-119)
\]

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 Kessler [AIChE J. 21: 510–527 (1975); see also Smith, Van Ness, and Abbott, Introduction to Chemical Engineering Thermodynamics, 5th, 6th, and 7th eds., App. E, McGraw-Hill, New York (1996, 2001, 2005)]. These tables cover both the liquid and gas phases and span the ranges \(0.3 \leq T_r \leq 4.0\) and \(0.01 \leq P_r \leq 10.0\). They list values of \(Z^0, Z^1, \left( H^R \right)/RT_e, \left( S^R \right)/R, \) and \(\omega \left( S^R \right)/R\).

Lee and Kessler also included a Pitzer-type correlation for vapor pressures:
\[
\ln P^a(T_e) = \ln P^b(T_e) + \omega \ln P^c(T_e) \quad (4-120)
\]

where
\[
\ln P^b(T_e) = 5.92714 - \frac{6.09648}{T_e} - 1.28862 \ln T_e + 0.169347 T_e^6 \quad (4-121)
\]

and
\[
\ln P^c(T_e) = 15.2518 - \frac{15.6875}{T_e} - 13.4721 \ln T_e + 0.43577 T_e^6 \quad (4-122)
\]

The value of \(\omega\) to be used with Eq. (4-120) is found from the correlation by requiring that it reproduce the normal boiling point; that is, \(\omega\) for a particular substance is determined from
\[
\omega = \frac{\ln P^a(T_e) - \ln P^b(T_e)}{\ln P^c(T_e)} \quad (4-123)
\]

where \(T_e\) is the reduced normal boiling point and \(P^{a\text{crit}}\) is the reduced vapor pressure corresponding to 1 standard atmosphere (1.01325 bar).

Although the tables representing 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 \(T_e, P_e,\) and \(\omega\) to a mixture to the pure-species values and to composition. One such set is given by Eqs. (2-80) through (2-82) in the Seventh Edition of Perry’s Chemical Engineers’ Handbook (1987). These equations define pseudoparameters, so called because the defined values of \(T_{e\text{mix}}, P_{e\text{mix}},\) and \(\omega\) have no physical significance for the mixture.

The Lee-Kessler correlations provide reliable data for nonpolar and slightly polar gases; errors of less than 3 percent are likely. Larger errors can be expected in applications to highly polar and associating gases.

The quantum gases (e.g., hydrogen, helium, and neon) do not conform to the same corresponding-states behavior as do normal fluids. Prausnitz, Lichtenthaler, and de Azevedo [Molecular Thermodynamics of Fluid-Phase Equilibria, 3d ed., pp. 172–173, Prentice-Hall PTR, Upper Saddle River, N.J. (1999)] propose the use of temperature-dependent effective critical parameters. For hydrogen, the quantum gas most commonly found in chemical processing, the recommended equations are
\[
\frac{T}{K} = \frac{43.6}{1 + 21.8/2.016 T} \quad (\text{for } H_2) \quad (4-124)
\]
\[
\frac{P}{\text{bar}} = \frac{20.5}{1 + 44.2/2.016 T} \quad (\text{for } H_2) \quad (4-125)
\]
\[
\frac{V}{\text{cm}^3\text{mol}^{-1}} = \frac{51.5}{1 + 9.91/2.016 T} \quad (\text{for } H_2) \quad (4-126)
\]

where \(T\) is absolute temperature in kelvins. Use of these effective critical parameters for hydrogen requires the further specification that \(\omega = 0.\)
OTHER PROPERTY FORMULATIONS

LIQUID PHASE

Although residual properties have formal reality for liquids as well as for gases, their advantageous use as small corrections to ideal gas state properties is lost. Calculation of property changes for the liquid state are usually based on alternative forms of Eqs. (4-32) through (4-35), shown in Table 4-1. Useful here are the definitions of two-liquid-phase properties—the volume expansivity $\beta$ and the isothermal compressibility $\kappa$:

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

For $V = f(T, P)$, $dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$

This equation in combination with Eqs. (4-127) and (4-128) becomes:

$$\frac{dV}{V} = \beta dT - \kappa dP$$

If $V$ is constant,

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}$$

Because liquid-phase isotherms of $P$ versus $V$ are very steep and closely spaced, both $\beta$ and $\kappa$ are small. Moreover (outside the critical region), they are weak functions of $T$ and $P$ and are often assumed constant at average values. Integration of Eq. (4-129) then gives:

$$\ln \frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

Substitution for the partial derivatives in Eqs. (4-32) through (4-35) by Eqs. (4-127) and (4-130) yields:

$$dH = C_v dT + (1 - \beta T)V dP$$

$$dS = C_v \frac{dT}{T} - \beta V dP$$

$$dU = C_v dT + \left( \frac{\beta}{\kappa} - T \right) dV$$

$$dS = \frac{C_v}{T} dT + \frac{\beta}{\kappa} dV$$

Integration of these equations is most common from the saturated-liquid state to the state of compressed liquid at constant $T$. For example, Eqs. (4-32) and (4-34) in integral form become:

$$H = H^s + \int_{T_1}^{T_2} (1 - \beta T)V dP$$

$$S = S^s - \int_{T_1}^{T_2} \beta V dP$$

Again, $\beta$ and $V$ are weak functions of pressure for liquids, and are often assumed constant at the values for the saturated liquid at temperature $T$. An alternative treatment of $V$ comes from Eq. (4-131), which for this application can be written:

$$V = V^s \exp[-\kappa(P - P^a)]$$

LIQUID/VAPOR PHASE TRANSITION

The isothermal vaporization of a pure liquid results in a phase change from saturated liquid to saturated vapor at vapor pressure $P^a$. The treatment of this transition is facilitated by definition of property changes of vaporization $\Delta M^v$:

$$\Delta M^v = M^v - M^f$$

where $M^v$ and $M^f$ are molar properties for states of saturated liquid and saturated vapor. Some experimental values of the enthalpy change of vaporization $\Delta H^v$, usually called the latent heat of vaporization, are listed in Table 2-150.

The enthalpy change and entropy change of vaporization are directly related:

$$\Delta H^v = T \Delta S^v$$

This equation follows from Eq. (4-15), because vaporization at the vapor pressure $P^a$ occurs at constant $T$.

As shown by Smith, Van Ness, and Abbott [Introduction to Chemical Engineering Thermodynamics, 7th ed., p. 221, McGraw-Hill, New York (2005)] the heat of vaporization is directly related to the slope of the vapor-pressure curve:

$$\Delta H^v = T \Delta T^v \frac{dP^a}{dT}$$

Known as the Clapeyron equation, this exact thermodynamic relation provides the connection between the properties of the liquid and vapor phases.

In application an empirical vapor pressure versus temperature relation is required. The simplest such equation is:

$$\ln P^a = A - \frac{B}{T}$$

where $A$ and $B$ are constants for a given chemical species. This equation approximates $P^a$ over its entire temperature range from triple point to critical point. It is also a sound basis for interpolation between reasonably spaced values of $T$. More satisfactory for general use is the Antoine equation:

$$\ln P^a = A - \frac{B}{T + C}$$

The Wagner equation is useful for accurate representation of vapor pressure data over a wide temperature range. It expresses the reduced vapor pressure as a function of reduced temperature:

$$\ln P^a = \frac{A + B \tau + C \tau^2 + D \tau^3}{1 - \tau}$$

where

$$\tau = 1 - T$$


Latent heats of vaporization are functions of temperature, and experimental values at a particular temperature are often not available. Recourse is then made to approximate methods. Trouton’s rule of 1884 provides a simple check on whether values calculated by other methods are reasonable:

$$\frac{\Delta H^v}{R T_c} \approx 10$$

Here, $T_c$ is the absolute temperature of the normal boiling point, and $\Delta H^v$ is the latent heat at this temperature. The units of $\Delta H^v/R T_c$ are dimensionless.

A much more accurate equation is that of Riedel [Chem. Ing. Tech. 26: 679–683 (1954)]:

$$\frac{\Delta H^v}{R T_c} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_c}$$
where \( P_c \) is the critical pressure in bars and \( T_c \) is the reduced temperature at \( T_c \). This equation provides reasonable approximations; errors rarely exceed 5 percent.

Estimation of the latent heat of vaporization of a pure liquid at any temperature from the known value at a single temperature may be based on an experimental value or on a value estimated by Eq. (4-144).

Watson’s equation [Ind. Eng. Chem. 35: 398–406 (1943)] has found wide acceptance:

\[
\Delta H_f^0 = \frac{(1 - T_c) \varphi_m}{1 - T_c} \quad (4-145)
\]

This equation is simple and fairly accurate.

## THERMODYNAMICS OF FLOW PROCESSES

The thermodynamics of flow encompasses mass, energy, and entropy balances for open systems, i.e., for systems whose boundaries allow the inflow and outflow of fluids. The common measures of flow are as follows:

- **Mass flow rate** \( \dot{m} \) molar flow rate \( \dot{n} \) volumetric flow rate \( q \) velocity \( u \)

Also \( \dot{m} = \dot{M} u \) and \( q = u A \)

where \( M \) is molar mass. **Mass flow rate** is related to velocity by \( \dot{m} = u A \) (4-146)

The operator \( \Delta \) signifies the difference between exit and entrance flows, and the subscript fs indicates that the term encompasses all flowing streams. When the mass flow rate \( \dot{m} \) is given by Eq. (4-146),

\[
\frac{dm_{fs}}{dt} + \Delta(m)_{fs} = 0 \quad (4-147)
\]

This form of the mass balance equation is often called the continuity equation. For the special case of steady-state flow, the control volume contains a constant mass of fluid, and the first term of Eq. (4-148) is zero.

**General Energy Balance** Because energy, like mass, is conserved, the time rate of change of energy within the control volume equals the net rate of flow of energy into the control volume. The flow is positive when directed into the control volume and negative when directed out. The mass balance is expressed mathematically by

\[
\frac{dm_{fs}}{dt} + \Delta(Mu)_{fs} = 0 \quad (4-148)
\]

This equivalent equation of energy balance is

\[
\Delta(S)_{fs} + \frac{d(mS)_{cv}}{dt} + \frac{dS_{sur}}{dt} = S_c \geq 0 \quad (4-151)
\]

where \( S_c \) is the entropy generation term. In accord with the second law, it must be positive, with zero as a limiting value. This equation is the general rate form of the entropy balance, applicable at any instant. The three terms on the left are the net rate of gain in entropy of the flowing streams, the time rate of change of the entropy of the fluid contained within the control volume, and the time rate of change of the entropy of the surroundings.

The entropy change of the surroundings results from heat transfer between system and surroundings. Let \( \dot{Q} \) represent the heat-transfer rate at a particular location on the control surface associated with a surroundings temperature \( T_{sj} \). In accord with Eq. (4-3), the rate of entropy change in the surroundings as a result of this transfer is \( -\dot{Q}/T_{sj} \). The minus sign converts \( \dot{Q} \), defined with respect to the system, to a heat rate with respect to the surroundings. The third term in Eq. (4-151) is therefore the sum of all such quantities, and Eq. (4-151) can be written

\[
\Delta(S)_{fs} + \frac{d(mS)_{cv}}{dt} = \sum_{j} \dot{Q}_j / T_{s,j} = S_c \geq 0 \quad (4-152)
\]

For any process, the two kinds of irreversibility are (1) those internal to the control volume and (2) those resulting from heat transfer across finite temperature differences that may exist between the
The continuity equation given by Eq. (4-148) here becomes

\[ \frac{dm}{dt} + \Delta (\dot{m})_h = 0 \]  

(4-147)

System and surroundings. In the limiting case where \( \dot{S}_c = 0 \), the process is completely reversible, implying that

• The process is internally reversible within the control volume.
• Heat transfer between the control volume and its surroundings is reversible.

Summary of Equations of Balance for Open Systems Only the most general equations of mass, energy, and entropy balance appear in the preceding sections. In each case important applications require less general versions. The most common restricted case is for steady flow processes, wherein the mass and thermodynamic properties of the fluid within the control volume are not time-dependent. A further simplification results when there is but one entrance and one exit to the control volume. In this event, \( \dot{m} \) is the same for both streams, and the equations may be divided through by this rate to put them on the basis of a unit amount of fluid flowing through the control volume. Summarized in Table 4-3 are the basic equations of balance and their important restricted forms.

Applications to Flow Processes

Duct Flow of Compressible Fluids Thermodynamics provides equations interrelating pressure changes, velocity, duct cross-sectional area, enthalpy, entropy, and specific volume within a flowing stream. Considered here is the adiabatic, steady-state, one-dimensional flow of a compressible fluid in the absence of shaft work and changes in potential energy. The appropriate energy balance is Eq. (4-155). With \( Q, W_c \), and \( \Delta z \) all set equal to zero,

\[ \Delta H + \frac{\Delta u^2}{2} = 0 \]

In differential form,

\[ dh = -u \frac{du}{A} \]  

(4-158)

The continuity equation given by Eq. (4-148) here becomes \( d(\rho u A) = d(\rho u A) \), whence

\[ dV - \frac{du}{u} = \frac{dA}{A} = 0 \]  

(4-159)

Smith, Abbott, and Van Ness [Introduction to Chemical Engineering Thermodynamics, 7th ed., pp. 255–258, McGraw-Hill, New York (2005)] show that these basic equations in combination with Eq. (4-15) and other property relations yield two very general equations

\[ V(1 - M^2) \frac{dP}{dx} + T \left[ \frac{1 + \frac{\beta u^2}{C_p}}{1 - M^2} \right] \frac{dS}{dx} + \frac{u^2}{A} \frac{dA}{dx} = 0 \]  

(4-160)

\[ v \frac{du}{dx} - T \left[ \frac{\beta u^2}{C_p} + M^2 \right] \frac{dS}{dx} + \frac{1}{1 - M^2} \frac{u^2}{A} \frac{dA}{dx} = 0 \]  

(4-161)

Mach number \( M \) is the ratio of the speed of fluid in the duct to the speed of sound in the fluid. The derivatives in these equations are rates of change with length as the fluid passes through a duct. Equations (4-160) relates the pressure derivative, and Eq. (4-161), the velocity derivative, to the entropy and area derivatives. According to the second law, the irreversibilities of fluid friction in adiabatic flow cause an entropy increase in the fluid in the direction of flow. In the limit as the flow approaches reversibility, this increase approaches zero. In general, then, \( ds/dx \geq 0 \).

Pipe Flow For a pipe of constant cross-sectional area, \( dA/dx = 0 \), and Eqs. (4-160) and (4-161) reduce to

\[ \frac{dP}{dx} = -T \left[ \frac{1 + \frac{\beta u^2}{C_p}}{1 - M^2} \right] \frac{ds}{dx} + \frac{u}{A} \frac{dA}{dx} = -u \frac{1}{A} \frac{1}{1 - M^2} \frac{dA}{dx} \]

When flow is subsonic, \( M^2 < 1 \), all terms on the right in these equations are then positive, and \( dp/dx < 0 \) and \( dudx > 0 \). Pressure therefore decreases and velocity increases in the direction of flow. The velocity increase is, however, limited, because these inequalities would reverse if the velocity were to become supersonic. This is not possible in a pipe of constant cross-sectional area, and the maximum fluid velocity obtainable is the speed of sound, reached at the exit of the pipe. Here, \( ds/dx \) reaches its limiting value of zero. For a discharge pressure low enough, the flow becomes sonic and lengthening the pipe does not alter this result; the mass rate of flow decreases so that the sonic velocity is still obtained at the outlet of the lengthened pipe.

According to the equations for supersonic pipe flow, pressure increases and velocity decreases in the direction of flow. However, this flow regime is unstable, and a supersonic stream entering a pipe of constant cross section undergoes a compression shock, the result of which is an abrupt and finite increase in pressure and decrease in velocity to a subsonic value.

Nozzles Nozzle flow is quite different from pipe flow. In a properly designed nozzle, its cross-sectional area changes with length in such a way as to make the flow nearly frictionless. The limit is reversible flow, for which the rate of entropy increase is zero. In this event \( ds/dx = 0 \), and Eqs. (4-160) and (4-161) become

\[ \frac{dP}{dx} = u^2 \frac{1}{V(1 - M^2)} \frac{dA}{dx} \]

\[ v \frac{du}{dx} = \beta u^2 \frac{C_p}{1 - M^2} \frac{dA}{dx} \]

The characteristics of flow depend on whether the flow is subsonic \( (M < 1) \) or supersonic \( (M > 1) \). The possibilities are summarized in Table 4-4. Thus, for subsonic flow in a converging nozzle, the velocity increases and the pressure decreases as the cross-sectional area

<table>
<thead>
<tr>
<th>Table 4-3 Equations of Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>General equations of balance</td>
</tr>
<tr>
<td>( \frac{dm}{dt} + \Delta (\dot{m})_h = 0 )</td>
</tr>
<tr>
<td>( d(mu)_{tc} + \Delta \left( H + \frac{1}{2} u^2 + zg \right)_h = Q + W )</td>
</tr>
<tr>
<td>( d(mS)_{tc} + \sum \frac{Q}{T} = S_c \geq 0 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4-4 Nozzle Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsonic: ( M &lt; 1 )</td>
</tr>
<tr>
<td>( \frac{dA}{dx} )</td>
</tr>
<tr>
<td>( \frac{dP}{dx} )</td>
</tr>
<tr>
<td>( \frac{dx}{dx} )</td>
</tr>
<tr>
<td>( \frac{dx}{dx} )</td>
</tr>
</tbody>
</table>
Integration, with nozzle entrance and exit conditions denoted by 1 and 2, yields
\[ u_d u = -V dP \]
where the final term is obtained upon elimination of \( V \) by \( PV^\gamma = \text{const} \), an equation valid for ideal gases with constant heat capacities. Here, \( \gamma = C_p/C_v \).

**Throttling Process** Fluid flowing through a restriction, such as an orifice, without appreciable change in kinetic or potential energy undergoes a finite pressure drop. This **throttling process** produces no shaft work, and in the absence of heat transfer, Eq. (4-155) reduces to \( \Delta H = 0 \) or \( H_2 = H_1 \). The process therefore occurs at constant enthalpy.

The temperature of an ideal gas is not changed by a throttling process, because its enthalpy depends on temperature only. For most real gases at moderate conditions of \( T \) and \( P \), a reduction in pressure at constant enthalpy results in a decrease in temperature, although the effect is usually small. Throttling of a wet vapor to a sufficiently low pressure causes the liquid to evaporate and the vapor to become superheated. This results in a considerable temperature drop because of the evaporation of liquid.

If a saturated liquid is throttled to a lower pressure, some of the liquid vaporizes or **flashes**, producing a mixture of saturated liquid and saturated vapor at the lower pressure. Again, the temperature drop results from evaporation of liquid.

**Turbines (Expanders)** High-velocity streams from nozzles impinging on blades attached to a rotating shaft form a turbine (or expander) through which vapor or gas flows in a steady-state expansion process which converts internal energy of a high-pressure stream into shaft work. The motive force may be provided by steam (turbine) or by a high-pressure gas (expander).

In any properly designed turbine, heat transfer and changes in potential and kinetic energy are negligible. Equation (4-155) therefore reduces to
\[ W_s = \Delta H = H_2 - H_1 \]  
(4-163)
The rate form of this equation is
\[ W_s = n \dot{H} = n \dot{H}_2 \]  
(4-164)
When inlet conditions \( T_1 \) and \( P_1 \) and discharge pressure \( P_2 \) are known, the value of \( H_1 \) is fixed. In Eq. (4-163) both \( H_2 \) and \( W_s \) are unknown, and the energy balance alone does not allow their calculation. However, if the fluid expands **reversibly and adiabatically**, i.e., isentropically, in the turbine, then \( S_2 = S_1 \). This second equation establishes the final state of the fluid and allows calculation of \( H_2 \). Equation (4-164) then gives the isentropic work:
\[ W_s(\text{isentropic}) = (\Delta H)_s \]  
(4-165)
The absolute value \( |W_s(\text{isentropic})| \) is the maximum work that can be produced by an adiabatic turbine with given inlet conditions and given discharge pressure. Because the actual expansion process is irreversible, **turbine efficiency** is defined as
\[ \eta = \frac{W_s}{W(\text{isentropic})} \]
where \( W_s \) is the actual shaft work.

The HS diagram of Fig. 4-2 compares the path of an actual expansion in a turbine with that of an isentropic expansion for the same intake conditions and the same discharge pressure. The isentropic path is the dashed vertical line from point 1 at intake pressure \( P_1 \) to point 2 at \( P_2 \). The irreversible path (solid line) starts at point 1 and terminates at point 2 on the isobar for \( P_2 \). The process is adiabatic, and irreversibilities cause the path to be directed toward increasing entropy. The greater the irreversibility, the farther point 2 lies to the right on the \( P_2 \) isobar, and the lower the value of \( \eta \).

**Compression Processes** Compressors, pumps, fans, blowers, and vacuum pumps are all devices designed to bring about pressure increase. Their energy requirements for steady-state operation are of interest here. Compression of gases may be accomplished in rotating equipment (high-volume flow) or for high pressures in cylinders with reciprocating pistons. The energy equations are the same; indeed, based on the same assumptions, they are the same as for turbines or expanders. Thus, Eqs. (4-159) through (4-161) apply to adiabatic compression.

The isentropic work of compression, as given by Eq. (4-165), is the minimum shaft work required for compression of a gas from a given initial state to a given discharge pressure. A compressor efficiency is defined as
\[ \eta = \frac{W_s(\text{isentropic})}{W} \]
where \( W_s \) is the isentropic work of compression.

In view of Eqs. (4-163) and (4-165), this becomes
\[ \eta = \frac{(\Delta H)_s}{\Delta H} \]  
(4-167)
Compressor efficiencies are usually in the range of 0.7 to 0.8.

The compression process is shown on an HS diagram in Fig. 4-3. The vertical dashed line rising from point 1 to point 2 represents the reversible adiabatic (isentropic) compression process from \( P_1 \) to \( P_2 \).
The actual irreversible compression process follows the solid line from point 1 upward and to the right in the direction of increasing entropy, terminating at point 2. The more irreversible the process, the farther this point lies to the right on the $P_2$ isobar, and the lower the efficiency $\eta$ of the process.

Liquids are moved by pumps, usually by rotating equipment. The same equations apply to adiabatic pumps as to adiabatic compressors. Thus, Eqs. (4-163) through (4-165) and Eq. (4-167) are valid. However, application of Eq. (4-163) requires values of the enthalpy of compressed (subcooled) liquids, and these are seldom available. The fundamental property relation, Eq. (4-15), provides an alternative. For an isentropic process,

$$dH = V \, dP \quad \text{(constant } S)$$

Combining this with Eq. (4-165) yields

$$W_{i}^{(\text{isentropic})} = \int_{P_1}^{P_2} V \, dP$$

The usual assumption for liquids (at conditions well removed from the critical point) is that $V$ is independent of $P$. Integration then gives

$$W_{i}^{(\text{isentropic})} = (\Delta H)_S = V(P_2 - P_1) \quad (4-168)$$

Also useful are Eqs. (4-132) and (4-133). Because temperature changes in the pumped fluid are very small and because the properties of liquids are insensitive to pressure (again at conditions not close to the critical point), these equations are usually integrated on the assumption that $C_p$, $V$, and $\beta$ are constant, usually at initial values. Thus, to a good approximation,

$$\Delta H = C_p \Delta T + V(1 - \beta T) \Delta P \quad (4-169)$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} - \beta V \Delta P \quad (4-170)$$

**Example 1: LNG Vaporization and Compression**

A port facility for unloading liquefied natural gas (LNG) is under consideration. The LNG arrives by ship, stored as saturated liquid at 115 K and 1.325 bar, and is unloaded at the rate of 450 kg s$^{-1}$. It is proposed to vaporize the LNG with heat discarded from a heat engine operating between 300 K, the temperature of atmospheric air, and 115 K, the temperature of the vaporizing LNG. The saturated-vapor LNG so produced is compressed adiabatically to 20 bar, using the work produced by the heat engine to supply part of the compression work. Estimate the work to be supplied from an external source.

For estimation purposes we need not be concerned with the design of the heat engine, but assume that a suitable engine can be built to deliver 30 percent of the work of a Carnot engine operating between the temperatures of 300 and 115 K. The equations that apply to Carnot engines can be found in any thermodynamics text.

By the first law:

$$|W| = |Q_d| - |Q_a|$$

By the second law:

$$|Q_d| = T_a \frac{|Q_c|}{T_c}$$

In combination:

$$|W| = |Q_d| \left(\frac{T_a}{T_c} - 1\right)$$

Here, $|W|$ is the work produced by the Carnot engine; $|Q_d|$ is the heat transferred at the cold temperature, i.e., to vaporize the LNG; $T_a$ and $T_c$ are the hot and cold temperatures of the heat reservoirs between which the heat engine operates, or 300 and 115 K, respectively. LNG is essentially pure methane, and enthalpy values from Table 2-281 of the Seventh Edition of Perry’s Chemical Engineers’ Handbook provide its heat of vaporization:

$$\Delta H = H_l - H_v = 802.5 - 297.7 = 504.8 \text{ kJ kg}^{-1}$$

For a flow rate of 450 kg s$^{-1}$,

$$|Q_d| = (450)(504.8) = 227,160 \text{ kJ s}^{-1}$$

The equation for work gives

$$|W| = \frac{227,160}{300} \left(\frac{300}{115} - 1\right) = 3.654 \times 10^3 \text{ kJ s}^{-1} = 3.654 \times 10^2 \text{ kW}$$

This is the reversible work of a Carnot engine. The assumption is that the actual power produced is 30 percent of this, or 1.096 × 10$^3$ kW.

The enthalpy and entropy of saturated vapor at 115 K and 1.325 bar are given in Table 2-281 of the Seventh Edition of Perry’s as

$$H = 802.5 \text{ kJ kg}^{-1} \quad \text{and} \quad S = 9.436 \text{ kJ kg}^{-1} \text{ K}^{-1}$$

Isentropic compression of saturated vapor at 1.325 to 20 bar produces superheated vapor with an entropy of 9.436 kJ kg$^{-1}$ K$^{-1}$. Interpolation in Table 2-282 at 20 bar yields an enthalpy of $H = 3026.2$ kJ kg$^{-1}$ at 234.65 K. The enthalpy change of isentropic compression is then

$$\Delta H_i = 1026.2 - 802.5 = 223.7 \text{ kJ kg}^{-1}$$

For a compressor efficiency of 75 percent, the actual enthalpy change of compression is

$$\Delta H = \frac{\Delta H_i}{\eta} = \frac{223.7}{0.75} = 298.3 \text{ kJ kg}^{-1}$$

The actual enthalpy of superheated LNG at 20 bar is then

$$H = 802.5 + 298.3 = 1100.8 \text{ kJ kg}^{-1}$$

Interpolation in Table 2-282 of the Seventh Edition of Perry’s indicates an actual temperature of 265.9 K for the compressed LNG, which is quite suitable for its entry into the distribution system.

The work of compression is

$$|W| = m \Delta H = (450 \text{ kg s}^{-1})(298.3 \text{ kJ kg}^{-1}) = 1.342 \times 10^5 \text{ kJ s}^{-1} = 1.342 \times 10^4 \text{ kW}$$

The estimated power which must be supplied from an external source is

$$|W| = 1.342 \times 10^5 - 1.096 \times 10^5 = 24,600 \text{ kW}$$

**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**

For a homogeneous $PVT$ system comprised of any number of chemical species, let symbol $M$ represent the molar (or unit-mass) value of an extensive thermodynamic property, say, $U$, $H$, $S$, $A$, or $G$. A total-system property is then $nM$, where $n = \Sigma n_i$ 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 have their own individual properties, a solution property may be arbitrarily
apportioned among the individual species. Once an apportioning recipe is adopted, the assigned property values are quite logically treated as though they were indeed properties of the individual species in solution, and reasoning on this basis leads to valid conclusions.

For a homogeneous PVT system, postulate 5 requires that
\[ nM = \dot{M}(T, P, n_1, n_2, n_3, \ldots) \]
The total differential of \( nM \) is therefore
\[ d(nM) = \left[ \frac{\partial(nM)}{\partial T} \right]_{P,x} dT + \left[ \frac{\partial(nM)}{\partial P} \right]_{T,x} dP + \sum_i \left[ \frac{\partial(nM)}{\partial n_i} \right]_{T,P,x} dn_i \]
where subscript \( n \) indicates that all mole numbers \( n \) are held constant, and subscript \( x \) signifies that all mole numbers are held constant except the \( i \)th. This equation may also be written
\[ d(nM) = n \left[ \frac{\partial M}{\partial T} \right]_{P,x} dT + n \left[ \frac{\partial M}{\partial P} \right]_{T,x} dP + \sum_i \left[ \frac{\partial (nM)}{\partial n_i} \right]_{T,P,x} dn_i \]
where subscript \( x \) indicates that all mole fractions are held constant. These two equations combine to yield
\[ \sum_i x_i \frac{dM_i}{dT} + \sum_i \frac{dT}{dM} x_i = 0 \]

This general result, the Gibbs-Duhem equation, imposes a constraint on how the partial 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 \frac{dM_i}{dT} = 0 \quad \text{(constant \( T, P \))} \]

Symbol \( M \) may represent the molar value of any extensive thermodynamic property, say, \( V, U, H, S, \) or \( G \). When \( M = H \), the derivatives \( (\partial H/\partial T)_P \) and \( (\partial H/\partial P)_T \) are given by Eqs. (4-28) and (4-29), and Eqs. (4-173), (4-174), and (4-175) specialize to
\[ dH = C_T dT + \left[ V - T \frac{\partial V}{\partial T} \right]_P dP + \sum_i \dot{H}_i dx_i \]
\[ H = \sum_i x_i \dot{H}_i \]
\[ C_T dT + \left[ V - T \frac{\partial V}{\partial T} \right]_P dP - \sum_i x_i d\dot{H}_i = 0 \]

Similar equations are readily derived when \( M \) takes on other identities. Equation (4-171), 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 (4-174) for a binary solution is
\[ M = x_1 \bar{M}_1 + x_2 \bar{M}_2 \]

Moreover, the Gibbs-Duhem equation for a solution at given \( T \) and \( P \), Eq. (4-176), becomes
\[ x_1 \frac{dM_1}{dT} + x_2 \frac{dM_2}{dT} = 0 \]

These two equations combine to yield
\[ \bar{M}_1 = M - x_1 \frac{dM}{dx_1} \]
\[ \bar{M}_2 = M - x_1 \frac{dM}{dx_1} \]

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. (4-171) is appropriate.

Partial Molar Equation-of-State Parameters The parameters in equations of state as applied to mixtures are related to composition by mixing rules. For the second virial coefficient
\[ B = \sum_i y_i B_i \]

The partial molar second virial coefficient is by definition
\[ \bar{B}_i = \left[ \frac{\partial (nB)}{\partial n_i} \right]_{T,P} \]

Because \( B \) is independent of \( P \), this is in accord with Eq. (4-171). These two equations lead through derivation to useful expressions for \( B_i \) as shown in detail by Van Ness and Abbott Classical Thermodynamics of Nonelectrolyte Solutions: With Applications to Phase
**SOLUTION THERMODYNAMICS**

**Ideal Gas Mixture Model** The ideal gas mixture model is useful because it is molecularly based, is analytically simple, is realistic in the limit of zero pressure, and provides a conceptual basis upon which to build the structure of solution thermodynamics. Smith, Van Ness, and Abbott ([Introduction to Chemical Engineering Thermodynamics](#), 7th ed., pp. 391–394, McGraw-Hill, New York (2005)] develop the following property relations for the ideal gas model.

\[
\overline{V_i}^c = V_i^c = \frac{RT}{P}
\]  (4-192)

Because the enthalpy is independent of pressure,

\[
\overline{H_i}^c = H_i^c
\]  (4-193)

where \( S_i^c \) is evaluated at the mixture \( T \) and \( P \). The entropy of an ideal gas does depend on pressure, and here

\[
\overline{S_i}^c = S_i^c - R \ln y_i
\]  (4-194)

where \( S_i^c \) is evaluated at the mixture \( T \) and \( P \).

From the definition of the Gibbs energy, \( G_i^c = H_i^c - TS_i^c \). In combination with Eqs. (4-193) and (4-194), this becomes

\[
G_i^c = H_i^c - TS_i^c + RT \ln y_i
\]  (4-195)

Elimination of \( G_i^c \) from this equation is accomplished through Eq. (4-17), written for pure species \( i \) as an ideal gas:

\[
dG_i^c = V_i^c dP = \frac{RT}{P} dP = RT d \ln P \quad \text{(constant } T)\]

Integration gives

\[
G_i^c = \Gamma_i(T) + RT \ln P
\]  (4-196)

where integration constant \( \Gamma_i(T) \) is a function of temperature only. Equation (4-195) now becomes

\[
\mu_i^c = \overline{G_i}^c = \Gamma_i(T) + RT \ln (y_i P)
\]  (4-197)

By Eq. (4-172)

\[
G^d = \sum_i y_i \Gamma_i(T) + RT \sum_i \ln (y_i P)
\]  (4-198)

A dimensional ambiguity is apparent with Eqs. (4-196) through (4-198) in that \( P \) has units, whereas \( \ln P \) must be dimensionless. In practice this is of no consequence, because only differences in Gibbs energy appear, along with ratios of the quantities with units of pressure in the arguments of the logarithms. Consistency in the units of pressure is, of course, required.

**Fugacity and Fugacity Coefficient** The chemical potential \( \mu \) plays a vital role in both phase and chemical reaction equilibria. However, the chemical potential exhibits certain unfortunate characteristics that discourage its use in the solution of practical problems. The Gibbs energy, and hence \( \mu \), is defined in relation to the internal energy and entropy, both primitive quantities for which absolute values are unknown. Moreover, \( \mu \) approaches negative infinity when either \( P \) or \( y \) 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 \( \mu \) but that does not exhibit its less desirable characteristics.

The origin of the fugacity concept resides in Eq. (4-196), an equation valid only for pure species \( i \) in the ideal gas state. For a real fluid, an analogous equation is written as

\[
G_i = \Gamma_i(T) + RT \ln f_i
\]  (4-199)

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. (4-196) from Eq. (4-199), both written for the same temperature and pressure, gives

\[
G_i - G_i^c = RT \ln \frac{f_i}{P}
\]
The definition of fugacity is completed by setting the ideal gas state fugacity of pure species $i$ equal to its pressure, $f^i=P$. Thus for the special case of an ideal gas, $G^i = 0$, $\phi = 1$, and Eq. (4-196) is recovered from Eq. (4-199).

The definition of the fugacity of a species in solution is parallel to the definition of the pure-species fugacity. An equation analogous to Eq. (4-209), the fugacity of species $i$ in an ideal gas mixture is given by Eq. (4-195), written as

$$
\mu^i = G^i + RT \ln y_i
$$

This equation takes on new meaning when $G^i(T, P)$ is replaced by $G_i(T, P)$, the Gibbs energy of pure species $i$ in its real physical state of gas, liquid, or solid at the mixture $T$ and $P$. The ideal solution is therefore defined as one for which

$$
\mu^i = G^i = G_i(T, P) + RT \ln y_i
$$

where superscript $id$ denotes an ideal solution property and $x_i$ represents the mole fraction because application is usually to liquids.

This equation is the basis for development of expressions for all other thermodynamic properties of an ideal solution. Equations (4-185) and (4-186), applied to an ideal solution with $\mu$ replaced by $G_i$, are written as

$$
\ln y_i = \ln \phi + \frac{\ln \phi^i}{\ln \phi}
$$

where $\phi = \phi^i$ if $\phi^i = 1$ and $f^i = y_iP$. Thus the fugacity of species $i$ in an ideal gas mixture is equal to its partial pressure.

Subtracting Eq. (4-197) from Eq. (4-202), both written for the same temperature, pressure, and composition, yields

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

where the partial pressure $y_iP$ is replaced by $f^i$, the fugacity of species $i$ in solution. Because it is not a partial property, it is identified by a circumflex rather than an overbar.

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

Equation (4-203) is the analog of Eq. (4-200), which relates $\phi$ to $G^i$. For an ideal gas, $G^i$ is necessarily zero; therefore $\hat{\phi}_i = 1$ and $f^i = y_iP$. Thus the fugacity of species $i$ in an ideal gas mixture is equal to its partial pressure.

Equation (4-203) with Eq. (4-45) gives

$$
\ln \phi = \frac{G^i}{RT} = \int_{y_iP}^{f^i} \left( Z - 1 \right) \frac{dP}{P}
$$

Subscript $i$ is omitted, with the understanding that $\phi$ here is for a pure species. Clearly, all correlations for $G^i/RT$ are also correlations for $\ln \phi$.

Combining Eq. (4-200) and (4-45) with Eqs. (4-48) and (4-73) yields

$$
\ln \phi = \int_{y_iP}^{f^i} \left( Z - 1 \right) \frac{dP}{P} = (B^i + \omega B^i) \frac{P_f}{T_f}
$$

This equation, used in conjunction with Eqs. (4-77) and (4-78), provides a useful generalized correlation for the fugacity coefficients of pure species.

A more comprehensive generalized correlation results from Eqs. (4-200) and (4-116):

$$
\ln \phi = \int_{y_iP}^{f^i} \left( Z - 1 \right) \frac{dP}{P} + \omega \int_{y_iP}^{f^i} Z^i \frac{dP}{P_f}
$$

An alternative form is

$$
\ln \phi = \ln \phi^0 + \omega \ln \phi^i
$$

where

$$
\ln \phi^0 = \int_{y_iP}^{f^i} \left( Z - 1 \right) \frac{dP}{P} \quad \text{and} \quad \ln \phi^i = \int_{y_iP}^{f^i} Z^i \frac{dP}{P}
$$

By Eq. (4-207),

$$
\phi = (\phi^0)(\phi^i)^\omega
$$

Correlations may therefore be presented for $\phi^0$ and $\phi^i$, as was done by Lee and Kesler [AIChE J. 21: 510–527 (1975)].
Thus the fugacity coefficient of species $i$ in an ideal solution equals 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.

**Excess Properties** 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 $T$, $P$, and composition. Thus,

$$M^E = M - M^d$$  \hspace{1cm} (4-219)

where $M$ represents the molar (or unit-mass) value of any extensive thermodynamic property (say, $V$, $U$, $H$, $S$, $G$). This definition is analogous to the definition of a residual property as given by Eq. (4-40).

However, excess properties have no meaning for pure species, whereas residual properties exist for pure species as well as for mixtures. Partial molar excess properties $M_i^E$ are defined analogously:

$$M_i^E = M_i - M_i^d$$  \hspace{1cm} (4-220)

Of particular interest is the partial molar excess Gibbs energy. Equation (4-202) may be written as

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

In accord with Eq. (4-217) for an ideal solution, this becomes

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

By difference

$$\bar{G}_i - \bar{G}_i^d = RT \ln \frac{f_i}{x_i}$$

The left side is the partial excess Gibbs energy $\bar{G}_i^E$; the dimensionless ratio $f_i/x_i$, on the right is the activity coefficient of species $i$ in solution, given the symbol $\gamma$, and by definition,

$$\gamma_i = \frac{f_i}{x_i}$$  \hspace{1cm} (4-221)

Thus,

$$\bar{G}_i^E = RT \ln \gamma_i$$  \hspace{1cm} (4-222)

Comparison with Eq. (4-203) shows that Eq. (4-222) relates $\gamma_i$ to $\bar{G}_i^E$ exactly as Eq. (4-203) relates $\gamma_i$ to $G_i^E$. For an ideal solution, $G_i^E = 0$, and therefore $\gamma_i = 1$.

**Property Changes of Mixing** A property change of mixing is defined by

$$\Delta M = M - \sum_i x_i M_i$$  \hspace{1cm} (4-223)

where $M$ represents a molar thermodynamic property of a homogeneous solution 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. Applications are usually to liquids.

Each of Eqs. (4-213) through (4-216) is an expression for an ideal solution property, and each may be combined with the defining equation for an excess property [Eq. (4-219)], yielding the equations of the first column of Table 4-5. In view of Eq. (4-223) these may be written as shown in the second column of Table 4-5, where $\Delta G$, $\Delta V$, $\Delta S$, and $\Delta H$ 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 the equations reduce to those shown in the third column of Table 4-5.

Property changes of mixing and excess properties are easily calculated one from the other. The most common property changes of mixing are the volume change of mixing $\Delta V$ and the enthalpy change of mixing $\Delta H$, commonly called the heat of mixing. These properties are identical to the corresponding excess properties. Moreover, they are directly measurable, providing an experimental entry into the network of equations of solution thermodynamics.

**FUNDAMENTAL PROPERTY RELATIONS BASED ON THE GIBBS ENERGY**

Of the four fundamental property relations shown in the second column of Table 4-1, only Eq. (4-13) has as its special or canonical variables $T$, $P$, and $[n_i]$. It is therefore the basis for extension to several useful supplementary thermodynamic properties. Indeed an alternative form has been developed as Eq. (4-191). These equations are the first two entries in the upper left quadrant of Table 4-6, which is now to be filled out with important derived relationships.

**Fundamental Residual-Property Relation** Equation (4-191) is general and may be written for the special case of an ideal gas

$$d\left(\frac{n G^c}{RT}\right) = \frac{n V^c}{RT} dP - \frac{n H^c}{RT} dT + \sum_i \frac{G_i^c}{RT} d[n_i]$$  \hspace{1cm} (4-236)

Subtraction of this equation from Eq. (4-191) gives

$$d\left(\frac{n G^a}{RT}\right) = \frac{n V^a}{RT} dP - \frac{n H^a}{RT} dT + \sum_i \frac{G_i^a}{RT} d[n_i]$$  \hspace{1cm} (4-237)

Limited forms of this equation are particularly useful. Division by $dP$ and restriction to constant $T$ and composition lead to

$$\frac{V^a}{RT} = \left[\frac{\partial (n G^a/RT)}{\partial P}\right]_T$$  \hspace{1cm} (4-238)

Similarly, the result of division by $dT$ and restriction to constant $P$ and composition is

$$\frac{H^a}{RT} = T \left[\frac{\partial (n G^a/RT)}{\partial T}\right]_P$$  \hspace{1cm} (4-239)

Also implicit in Eq. (4-237) is the relation

$$\ln \phi_i = \left[\frac{\partial (n G^a/RT)}{\partial n_i}\right]_T$$  \hspace{1cm} (4-240)

This equation demonstrates that $\ln \phi_i$ is a partial property with respect to $G^a/RT$. The summability relation therefore applies, and

$$\frac{G^a}{RT} = \sum_i x_i \ln \phi_i$$  \hspace{1cm} (4-241)

---

**TABLE 4-5  Relations Connecting Property Changes of Mixing and Excess Properties**

<table>
<thead>
<tr>
<th>$M^E$ in relation to $M$</th>
<th>$M^E$ in relation to $\Delta M$</th>
<th>Expressions for $\Delta M^E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G^E = G - \sum_i x_i \bar{G}_i - RT \sum_i x_i \ln x_i$</td>
<td>$G^E = \Delta G - RT \sum_i x_i \ln x_i$</td>
<td>$\Delta G^E = RT \sum_i x_i \ln x_i$</td>
</tr>
<tr>
<td>$V^E = V - \sum_i x_i V_i$</td>
<td>$V^E = \Delta V$</td>
<td>$\Delta V^E = 0$</td>
</tr>
<tr>
<td>$S^E = S - \sum_i x_i S_i + R \sum_i x_i \ln x_i$</td>
<td>$S^E = \Delta S + R \sum_i x_i \ln x_i$</td>
<td>$\Delta S^E = - R \sum_i x_i \ln x_i$</td>
</tr>
<tr>
<td>$H^E = H - \sum_i x_i H_i$</td>
<td>$H^E = \Delta H$</td>
<td>$\Delta H^E = 0$</td>
</tr>
</tbody>
</table>
Application of Eq. (4-240) to an expression giving \( G^i \) as a function of composition yields an equation for \( \ln \phi_i \). In the simplest case of a gas mixture for which the virial equation [Eq. (4-67)] is appropriate, Eq. (4-69) provides the relation

\[
\frac{nG^i}{RT} = \frac{P}{RT} (nB)
\]

Differentiation in accord with Eqs. (4-240) and (4-181) yields

\[
\ln \phi_i = \frac{P}{RT} \frac{\partial B_i}{\partial \gamma}
\]

where \( B_i \) is given by Eq. (4-182). For a binary system these equations reduce to

\[
\ln \phi_1 = \frac{P}{RT} (B_{11} + y\hat{\delta}_{12})
\]

\[
\ln \phi_2 = \frac{P}{RT} (B_{22} + y\hat{\delta}_{12})
\]

where

\[
\hat{\delta}_{12} = 2B_{12} - B_{11} - B_{22}
\]

For the special case of pure species \( i \), these equations reduce to

\[
\ln \phi_i = \frac{P}{RT} B_i
\]

For the generic cubic equation of state [Eqs. (4-104)], \( G^i/RT \) is given by Eq. (4-109), which in view of Eq. (4-208) for a pure species becomes

\[
\ln \phi_i = Z_i - 1 - \ln(Z_i - \beta) - q_i I
\]


\[
\ln \hat{\phi}_i = \frac{T}{b} (Z - 1) - \ln(Z - \beta) - \bar{q} I
\]

Symbols without subscripts represent mixture properties, and \( I \) is given by Eq. (4-112).

**Fundamental Excess-Property Relation**

Equations for excess properties are developed in much the same way as those for residual properties. For the special case of an ideal solution, Eq. (4-191) becomes

\[
d \left( \frac{nG^i}{RT} \right) = \frac{nV}{RT} dP - \frac{nH}{RT} dT + \sum_i \frac{\partial G^i}{\partial P} \frac{\partial n_i}{\partial P}
\]

Subtraction of this equation from Eq. (4-191) yields

\[
d \left( \frac{nG^i}{RT} \right) = \frac{nV^e}{RT} dP - \frac{nH^e}{RT^2} dT + \sum_i \frac{\partial G^i}{\partial P} \frac{\partial n_i}{\partial P} - \frac{\partial G^i}{\partial T} \frac{\partial n_i}{\partial T}
\]

where the definitions \( G^e = G - G^i \) and \( G^i = G_i - G^i \) have been imposed. Equation (4-247) is the fundamental excess-property relation. An alternative form follows by introduction of the activity coefficient as given by Eq. (4-222). This result is listed as Eq. (4-248) in the upper left quadrant of Table 4-6.

The following equations are in complete analogy to those for residual properties.

\[
\frac{V}{RT} = \frac{\partial (G^e/RT)}{\partial P}
\]

\[
\frac{H^e}{RT} = -T \frac{\partial (G^e/RT)}{\partial T}
\]

\[
\ln \gamma_i = \frac{\partial (nG^e/RT)}{\partial P}
\]

This last equation demonstrates that \( \ln \gamma_i \) is a partial property with respect to \( G^e/RT \), implying also the validity of the summability relation

\[
\frac{G^e}{RT} = \sum_i \frac{n_i}{P} \ln \gamma_i
\]

The equations of the upper left quadrant of Table 4-6 reduce to those of the upper right quadrant for \( n = 1 \) and \( d n_i = 0 \). Each equation in the upper left quadrant has a partial-property analog, as shown in the lower left quadrant. Each equation of the upper left quadrant is a special case of Eq. (4-172) and therefore has associated with it a Gibbs-Duhem equation of the form of Eq. (4-173). These are shown in the lower right quadrant. The equations of Table 4-6 store an enormous amount of information, but they 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, one sees immediately from Eqs. (4-258) and (4-259) that

\[
\frac{\partial \ln \phi_i}{\partial P} = \frac{V_i^p}{RT} \quad (4-264)
\]

\[
\frac{\partial \ln \phi_i}{\partial T} = -\frac{H_i^p}{RT^2} \quad (4-265)
\]

\[
\frac{\partial \ln \gamma_i}{\partial P} = \frac{V_i^p}{RT} \quad (4-266)
\]

\[
\frac{\partial \ln \gamma_i}{\partial T} = -\frac{H_i^p}{RT} \quad (4-267)
\]

**MODELS FOR THE EXCESS GIBBS ENERGY**

Excess properties find application in the treatment of liquid solutions. 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 design calculations. Knowing \(G^E\) as a function of \(T, P,\) and composition, one can in principle compute from it all other excess properties.

The excess volume for liquid mixtures is usually small, and in accord with Eq. (4-249) the pressure dependence of \(G^E\) is usually ignored. Thus, engineering efforts to model \(G^E\) center on representing its composition and temperature dependence. For binary systems at constant \(T, G^E\) becomes a function of just \(x_i,\) and the quantity most conveniently represented by an equation is \(G^E/x_i^3RT.\) The simplest procedure is to express this quantity as a power series in \(x_i:

\[
\frac{G^E}{x_i^3RT} = a + bx_i + cx_i^2 + \cdots \quad \text{(constant } T)\]


\[
\frac{G^E}{x_i^3RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots
\]

In application, different truncations of this expansion are appropriate, and for each truncation specific expressions for \(\ln \gamma_i\) and \(\ln \gamma_i^E\) result from application of Eq. (4-251). When all parameters are zero, \(G^E/RT = 0,\) and the solution is ideal. If \(B = C = \cdots = 0,\) then

\[
\frac{G^E}{x_i^3RT} = A
\]

where \(A\) is a constant for a given temperature. The corresponding equations for \(\ln \gamma_i\) and \(\ln \gamma_i^E\) are

\[
\ln \gamma_i = A x_i^2 \quad (4-268a)
\]

\[
\ln \gamma_i^E = A x_i^2 \quad (4-268b)
\]

The symmetric nature of these relations is evident. The infinite dilution values of the activity coefficients are \(\ln \gamma_i^E = \ln \gamma_i^E = A.\)

If \(C = \cdots = 0,\) then

\[
\frac{G^E}{x_i^3RT} = A + B(x_1 - x_2) = A + B(2x_1 - 1)
\]

and in this case \(G^E/x_i^3RT\) is linear in \(x_i.\) The substitutions \(A + B = A_{12}\) and \(A - B = A_{12}\) transform this expression to the Margules equation:

\[
\frac{G^E}{x_i^3RT} = A_{12}x_i + A_{12}x_2 \quad (4-269)
\]

Application of Eq. (4-251) yields

\[
\ln \gamma_i = x_i^2 \left[ A_{12} + 2(A_{22} - A_{12})x_1 \right] \quad (4-270a)
\]

\[
\ln \gamma_i^E = x_i^2 \left[ A_{22} + 2(A_{22} - A_{12})x_2 \right] \quad (4-270b)
\]

When \(x_1 = 0, \ln \gamma_i^E = A_{12};\) when \(x_2 = 0, \ln \gamma_i^E = A_{22}.\)

An alternative equation is obtained when the reciprocal quantity \(x_i^3RT/G^E\) is expressed as a linear function of \(x_i.\)

\[
\frac{x_i^3RT}{G^E} = A' + B'(x_1 - x_2) = A' + B'(2x_1 - 1)
\]

This may also be written as

\[
\frac{x_i^3RT}{G^E} = A'(x_1 + x_2) + B'(x_1 - x_2) = (A' + B')x_1 + (A' - B')x_2
\]

The substitutions \(A' + B' = 1/A_{12}\) and \(A' - B' = 1/A_{22}\) ultimately produce

\[
\frac{G^E}{x_i^3RT} = \frac{A_{12}A_{22}}{A_{12}x_1 + A_{22}x_2} \quad (4-271)
\]

The activity coefficients implied by this equation are given by

\[
\ln \gamma_i = A_{12}' \left( 1 + \frac{A_{12}^2}{A_{12}'x_1} \right)^{-2} \quad (4-272a)
\]

\[
\ln \gamma_i^E = A_{12}' \left( 1 + \frac{A_{12}^2}{A_{12}'x_2} \right)^{-2} \quad (4-272b)
\]

These are the van Laar equations. When \(x_1 = 0, \ln \gamma_i^E = A_{12}^+;\) when \(x_2 = 0, \ln \gamma_i^E = A_{22}^+.\)

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, i.e., 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 basis in theory for their extension to multicomponent systems. Nor do they incorporate an explicit temperature dependence for the parameters.


The Wilson equation, like the Margules and van Laar equations, contains just two parameters for a binary system \((A_{12} and A_{31}),\) and is written as

\[
\frac{G^E}{RT} = -x_1 \ln (x_1 + x_2A_{12}) - x_2 \ln (x_2 + x_1A_{21}) \quad (4-273)
\]

\[
\ln \gamma_i = -\ln (x_1 + x_2A_{12}) + x_2 \left( \frac{A_{12}}{x_1 + x_2A_{12}} - \frac{A_{21}}{x_2 + x_1A_{21}} \right) \quad (4-274a)
\]

\[
\ln \gamma_i^E = -\ln (x_2 + x_1A_{21}) - x_1 \left( \frac{A_{12}}{x_1 + x_2A_{12}} - \frac{A_{21}}{x_2 + x_1A_{21}} \right) \quad (4-274b)
\]

At infinite dilution,

\[
\ln \gamma_i^E = -\ln A_{12} + 1 - A_{31} \quad \ln \gamma_i^E = -\ln A_{21} + 1 - A_{32}
\]

Both \(A_{12}\) and \(A_{21}\) must be positive numbers.
The NRTL equation contains three parameters for a binary system and is written as

$$\frac{G^G}{x_1x_2RT} = \frac{G_{12}\tau_{12}}{x_1 + x_2G_{12}} + \frac{G_{21}\tau_{21}}{x_2 + x_1G_{21}}$$

(4-275)

$$\ln \gamma_1 = x_1^{\tau_1} \left[ \tau_1 \left( \frac{G_{12}}{x_1 + x_2G_{12}} \right)^{\alpha_{12}} + \frac{G_{21}\tau_{21}}{x_2 + x_1G_{21}} \right]$$

(4-276a)

$$\ln \gamma_2 = x_2^{\tau_2} \left[ \tau_2 \left( \frac{G_{12}}{x_2 + x_1G_{12}} \right)^{\alpha_{12}} + \frac{G_{21}\tau_{21}}{x_1 + x_2G_{21}} \right]$$

(4-276b)

Here

$$G_{12} = \exp(-\alpha_{12}) \quad G_{21} = \exp(-\alpha_{21})$$

and

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

where $\alpha$, $b_{12}$, 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

$$\ln \gamma_1^\infty = \tau_1 + \tau_1 \exp(-\alpha_{12}) \quad \ln \gamma_2^\infty = \tau_2 + \tau_2 \exp(-\alpha_{21})$$

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 as

$$\frac{G^G}{RT} = -\sum_i x_i \ln \left( \sum_j x_j \Lambda_{ij} \right)$$

(4-277)

and

$$\ln \gamma = 1 - \ln \left( \sum_j x_j \Lambda_{ij} \right) - \sum_i x_i \Lambda_{ii}$$

(4-278)

where $\Lambda_{ii} = 1$ for $i = j$, etc. 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 $\Lambda_{12}$, $\Lambda_{23}$, $\Lambda_{31}$; $\Lambda_{13}$, $\Lambda_{31}$; and $\Lambda_{32}$.

The temperature dependence of the parameters is given by

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \left( -\frac{a_{ij}}{RT} \right) \quad i \neq j$$

(4-279)

where $V_i$ and $V_j$ are the molar volumes of pure liquids $j$ and $i$ and $a_{ij}$ is a constant independent of composition and temperature. Molar volumes $V_i$ and $V_j$ themselves weak functions of temperature, form ratios that in practice may be taken as independent of $T$, and are usually evaluated at or near 25°C.

The Wilson parameters $\Lambda_{ij}$ and NRTL parameters $G_{ij}$ inherit a Boltzmann-type $T$ dependence from the origins of the expressions for $G^G$, 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. However, all parameters are found from data for binary (in contrast to multicomponent) systems, and this makes parameter determination for the local composition models a task of manageable proportions.

The UNIQUAC equation treats $g = G^G/RT$ as made up 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:

$$g = g^C + g^R$$

(4-280)

**FIG. 4-4** Property changes of mixing at 50°C for six 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).

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,

\[
g^C = \sum_i x_i \ln \frac{\Phi_i}{x_i} + 5 \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \quad (4-281)
\]

\[
g^R = -\sum_i q_i x_i \ln \left( \sum_j \theta_{ij} \right) \quad (4-282)
\]

where

\[
\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (4-283)
\]

and

\[
\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (4-284)
\]

Subscript \( i \) identifies species, and \( j \) is a dummy index; all summations are over all species. Note that \( \tau_{ij} \neq \tau_{ji} \); 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 \( \tau_{ij} \) of Eq. (4-282), which are temperature-dependent:

\[
\tau_{ij} = \exp \left( \frac{- (u_i - u_0)}{RT} \right) \quad (4-285)
\]

Parameters for the UNIQUAC equation are therefore values of \( u_i - u_0 \).

An expression for \( \ln \gamma \) is found by application of Eq. (4-251) to the UNIQUAC equation for \( g \) [Eqs. (4-280) through (4-282)]. The result is given by the following equations:

\[
\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (4-286)
\]

\[
\ln \gamma_i^C = 1 - J_i + \ln J_i - 5 q_i \left( 1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i} \right) \quad (4-287)
\]

\[
\ln \gamma_i^R = q_i \left( 1 - \ln s_i - \sum_j \theta_{ij} \right) \quad (4-288)
\]

where in addition to Eqs. (4-284) and (4-285),

\[
J_i = \frac{r_i}{\sum_j r_j x_j} \quad (4-289)
\]

\[
L_i = \frac{q_i}{\sum_j q_j x_j} \quad (4-290)
\]

\[
s_i = \sum_j \theta_{ij} \tau_{ij} \quad (4-291)
\]

Again subscript \( i \) identifies species, and \( j \) and \( l \) are dummy indices. Values for the parameters of the commonly used models for the excess Gibbs energy are given by Gmehling, Onken, and Arlt [Vapor-Liquid Equilibrium Data Collection, Chemistry Data Series, vol. 1, parts 1–8, DECHEMA, Frankfurt/Main (1974–1990)].

**FIG. 4-5** Excess properties at 50°C for six 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). [Smith, Van Ness, and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th ed., p. 420, McGraw-Hill, New York (2005).]
**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, i.e., at temperatures well below the critical temperature of each constituent species. The properties of interest to the chemical engineer are properties well below the critical temperature of each constituent species.

The first and second laws written for the entire system are reversible and necessarily bring the system closer to an equilibrium state. The criteria for phase and chemical reaction equilibria are less obvious.

**Mixing and Excess Properties**

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

$$dU = dQ + dW \quad dS \geq \frac{dQ}{T}$$

$G^E$ allows calculation of $S^E$ by Eq. (4-10), written for excess properties as

$$S^E = \frac{H^E - G^E}{T} \quad (4-292)$$

with $S^E$ then given by Eq. (4-230).

Figure 4-4 displays plots of $dH^E$, $dS$, and $dG$ as functions of composition for six binary solutions at 50°C. The corresponding excess properties are shown in Fig. 4-5; the activity coefficients, derived from Eq. (4-251), appear in Fig. 4-6. The properties shown here are insensitive to pressure and for practical purposes represent solution properties at 50°C and low pressure ($P = 1$ bar).

<table>
<thead>
<tr>
<th>EQUILIBRIUM</th>
</tr>
</thead>
</table>
| The equations developed in preceding sections are for PVT systems in states of internal equilibrium. The criteria for internal thermal and mechanical equilibrium simply require uniformity of temperature and pressure throughout the system. The criteria for phase and chemical reaction equilibria are less obvious.

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

$$dU = dQ + dW \quad dS \geq \frac{dQ}{T}$$

Combination gives $$dU - dW -TdS \leq 0$$

Because mechanical equilibrium is assumed, $dW = -PdV$, whence

$$dU + PdV - TdS \leq 0$$

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

Constraints put on this expression produce alternative criteria for the directions of irreversible processes and for the condition of equilibrium. For example, $dU_{\gamma,\gamma'} \leq 0$. Particularly important is fixing $T$ and $P$; this produces

$$d(U' + PV' - TS')_{T, P} \leq 0 \quad \text{or} \quad dG_{T,P} \leq 0$$

<table>
<thead>
<tr>
<th>CRITERIA</th>
</tr>
</thead>
</table>
| The volume change of mixing ($V^E = \Delta V$), the heat of mixing ($H^E = \Delta H$), and the excess Gibbs energy $G^E$ are experimentally accessible, $\Delta V$ and $\Delta H$ by direct measurement and $G^E$ (or $\ln \gamma$ ) indirectly by reduction of vapor/liquid equilibrium data. Knowledge of $H^E$ and $G^E$ allows calculation of $S^E$ by Eq. (4-10), written for excess properties as

$$S^E = \frac{H^E - G^E}{T} \quad (4-292)$$

with $S^E$ then given by Eq. (4-230).

Figure 4-4 displays plots of $dH^E$, $dS$, and $dG$ as functions of composition for six binary solutions at 50°C. The corresponding excess properties are shown in Fig. 4-5; the activity coefficients, derived from Eq. (4-251), appear in Fig. 4-6. The properties shown here are insensitive to pressure and for practical purposes represent solution properties at 50°C and low pressure ($P = 1$ bar).
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 $G$. This is the meaning of the equilibrium criterion

$$dG_{\text{TF}} = 0 \quad (4-293)$$

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; Eq. (4-13) is written for each phase:

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

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

where the primes and double primes denote the two phases; 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

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

If the two-phase system is at equilibrium, then application of Eq. (4-293) yields

$$dG_{\text{TF}} = d(nG)_{\text{TF}} = \sum \mu_i' dn_i' + \sum \mu_i'' dn_i'' = 0$$

The system is closed and without chemical reaction; material balances therefore require that $dn_i'' = -dn_i'$, reducing the preceding equation to

$$\sum (\mu_i' - \mu_i'')dn_i = 0$$

Because 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

$$\mu_i = \mu_i' = \mu_i'' = \cdots \quad (4-294)$$

Substitution for each $\mu_i$ by Eq. (4-202) produces the equivalent result:

$$f_i' = f_i'' = f_i''' = \cdots \quad (4-295)$$

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. (4-13) and (4-293) leads immediately to

$$\sum \mu_i dn_i = 0 \quad (4-296)$$

For a system in which both phase and chemical reaction equilibrium prevail, the criteria of Eqs. (4-295) and (4-296) are superimposed.

**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 not all these variables are independent, and fixing a limited number of them automatically establishes the others. This number of independent variables is given by the phase rule, and it is called the number of degrees of freedom of the system. It is the number of variables that may be arbitrarily specified and that 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 $\pi$ phases, the phase rule variables are $T$ and $P$, 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 equilibrium equations that may be written express chemical potentials or fugacities as functions of $T$, $P$, and the phase compositions, the phase rule variables:

1. Equation (4-295) for each species, giving $(\pi - 1)N$ phase equilibrium equations
2. Equation (4-296) for each independent chemical reaction, giving $r$ equations

The total number of independent equations is therefore $(\pi - 1)N + r$. Because 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

$$F = 2 + \pi + N - r \quad (4-297)$$

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, although 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 such sets number $r$ and all are equivalent.

**Example 2: Application of the Phase Rule**

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

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

The 2 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 $y_1$, etc., 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 2 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 azo trope (assuming this is 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 azo trope imposes a special constraint, making $F = 1$.

b. For a gaseous system consisting of CO, CO$_2$, H$_2$, H$_2$O, and CH$_4$ in chemical reaction equilibrium,

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

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

$$C + \frac{1}{2}O_2 \rightarrow CO \quad C + O_2 \rightarrow CO_2$$
$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad C + 2H_2 \rightarrow CH_4$$

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$_2$O $\rightarrow$ CO + 3H$_2$
- CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$
- CH$_4$ + 2H$_2$O $\rightarrow$ 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.

**Duhem’s Theorem** Because 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
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 \( P_{\text{sat}} \). For this isothermal change of state from saturated liquid at \( P_{\text{sat}} \) to liquid at pressure \( P \), Eq. (4-17) is integrated to give

\[
G_i - G_i^{\text{sat}} = \int_{P_{\text{sat}}}^{P} V_i dP
\]

Equation (4-199) is then written twice: for \( G_i \) and for \( G_i^{\text{sat}} \). Subtraction provides another expression for \( G_i - G_i^{\text{sat}} \):

\[
G_i - G_i^{\text{sat}} = RT \ln \frac{f_i}{f_i^{\text{sat}}}
\]

Equating the two expressions for \( G_i - G_i^{\text{sat}} \) yields

\[
\ln \frac{f_i}{f_i^{\text{sat}}} = \frac{1}{RT} \int_{P_{\text{sat}}}^{P} V_i dP
\]

Because \( V_i \), the liquid-phase molar volume, is a very weak function of \( P \) at temperatures well below \( T \), an excellent approximation is usually obtained when evaluation of the integral is based on the assumption that \( V_i \) is constant at the value for saturated liquid \( V_i^{\text{sat}} \):

\[
\ln \frac{f_i}{f_i^{\text{sat}}} = \frac{V_i(P - P_{\text{sat}})}{RT}
\]

Substituting \( f_i^{\text{sat}} = \phi_i^{\text{sat}} P_i^{\text{sat}} \) and solving for \( f_i \), give

\[
f_i = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \frac{V_i(P - P_{\text{sat}})}{RT}
\]

The exponential is known as the Poynting factor. Equation (4-299) may now be written as

\[
y_i P \Phi_i = x_i \gamma_i P_i^{\text{sat}} \quad i = 1, 2, \ldots, N
\]

where

\[
\Phi_i = \frac{\phi_i^{\text{sat}}}{\phi_i} \exp \frac{-V_i(P - P_{\text{sat}})}{RT}
\]

If evaluation of \( \Phi_i \) is by Eqs. (4-244) and (4-243), this reduces to

\[
\Phi_i = \exp \frac{P B_i - P_i^{\text{sat}} B_i - V_i(P - P_{\text{sat}})}{RT}
\]

where \( B_i \) is given by Eq. (4-182).

The \( N \) equations represented by Eq. (4-303) in conjunction with Eq. (4-305) may be solved for \( N \) unknown phase equilibrium variables. For a multicomponent system the calculation is formidable, but well suited to computer solution.

When Eq. (4-303) 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 \( \phi_i^{\text{sat}} \) and \( \phi_i \) are unity, and the right side of Eq. (4-304) 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 \( \gamma_i \) are also unity, and Eq. (4-303) reduces to

\[
y_i P = x_i \gamma_i P_i^{\text{sat}} \quad i = 1, 2, \ldots, N
\]

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.

**Modified Raoult’s Law** Of the qualifications that lead to Raoult’s law, the one least often reasonable is the supposition of solution ideality for the liquid phase. Real solution behavior is reflected by values of activity coefficients that differ from unity. When \( \gamma_i \) of Eq. (4-303) is retained in the equilibrium equation, the result is the modified Raoult’s law:

\[
y_i P = x_i \gamma_i P_i^{\text{sat}} \quad i = 1, 2, \ldots, N
\]
This equation is often adequate when applied to systems at low to moderate pressures and is therefore widely used. Bubble point and dew point calculations are only a bit more complex than the same calculations with Raoult’s law.

Activity coefficients are functions of temperature and liquid-phase composition and are correlated through equations for the excess Gibb’s energy. When an appropriate correlating equation for $G^e$ is not available, suitable estimates of activity coefficients may often be obtained from a group contribution correlation. This is the “solution of groups” approach, wherein activity coefficients are found as sums of contributions from the structural groups that make up the molecules of a solution. The most widely applied such correlations are based on the UNIFAC equation, and they have their origin in the UNIFAC method ([UNIFAC Functional-group Activity Coefficients], proposed by Fredenslund, Jones, and Prausnitz [AIChE J. 21: 1086–1099 (1975)], and given detailed treatment by Fredenslund, Gmehling, and Rasmussen [Vapor-Liquid Equilibrium Using UNIFAC, Elsevier, Amsterdam (1977)].


The range of applicability of the original UNIFAC model has been greatly extended and its reliability enhanced. Its most recent revision and extension is treat by Wittig, Lohmann, and Gmehling [Ind. Eng. Chem. Res. 42: 183–188 (2003)], wherein are cited earlier pertinent papers. Because it is based on temperature-independent parameters, its application is largely restricted to 0 to 150°C.

Two modified versions of the UNIFAC model, based on temperature-dependent parameters, have come into use. Not only do they provide a wide temperature range of applicability, but also they allow correlation of various kinds of property data, including phase equilibria, infinite dilution activity coefficients, and excess properties. The most recent revision and extension of the modified UNIFAC (Dortmund) model is provided by Gmehling et al. [Ind. Eng. Chem. Res. 41: 1675–1688 (2002)]. An extended UNIFAC model called KT-UNIFAC is described in detail by K. M. and Gmehling et al. [Ind. Eng. Chem. Res. 41: 3260–3273 (2002)]. Both papers contain extensive literature citations.

The UNIFAC model has also been combined with the predictive Soave-Redlich-Kwong (PSRK) equation of state. The procedure is most completely described (with background literature citations) by Horstmann et al. [Fluid Phase Equilibria 227: 157–164 (2005)].

Because $\sum y_i = 1$, Eq. (4-307) may be summed over all species to yield

$$ P = \sum x_i \gamma_i P_i^{sat} $$

Alternatively, Eq. (4-307) may be solved for $x_i$, in which case summing over all species yields

$$ P = \frac{1}{\sum y_i \gamma_i P_i^{sat}} $$

### Example 3: Dew and Bubble Point Calculations

As indicated by Example 2n, a binary system in vapor/liquid equilibrium has 2 degrees of freedom. Thus of the four phase rule variables $T$, $P$, $x_1$, and $y_1$, two must be fixed to allow calculation of the other two, regardless of the formulation of the equilibrium equations. Modified Raoult’s law [Eq. (4-307)] may therefore be applied to the calculation of any pair of phase rule variables, given the other two.

The necessary vapor pressures and activity coefficients are supplied by data correlations. For the system acetone/hexane, vapor pressures are given by Eq. (4-142), the Antoine equation:

$$ \ln P_i^{sat}/\text{atm} = A_i - \frac{B_i}{T/K + C_i} \quad i = 1, 2 $$

### with parameters

<table>
<thead>
<tr>
<th></th>
<th>$A_i$</th>
<th>$B_i$</th>
<th>$C_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.3145</td>
<td>2776.22</td>
<td>-45.090</td>
</tr>
<tr>
<td>2</td>
<td>13.8193</td>
<td>2696.04</td>
<td>-48.533</td>
</tr>
</tbody>
</table>

Activity coefficients are given by Eq. (4-274), the Wilson equation:

$$ \ln \gamma_i = -x_i (x_i + x_i A_{12}) + x_i \Lambda $$

$$ \ln \gamma_i = -x_i (x_i + x_i A_{12}) - x_i \Lambda $$

where

$$ \lambda = x_i + x_i A_{12} - x_i + x_i A_{21} $$

By Eq. (4-279)

$$ \Lambda = \frac{V_i}{V_1} \exp \left[ -\frac{a_{ij}}{RT} \right] $$

with parameters [Gmehling et al., Vapor-Liquid Data Collection, Chemistry Data Series, vol. 1, part 3, DECEMA, Frankfurt/Main (1983)]

<table>
<thead>
<tr>
<th></th>
<th>$a_{12}$ cal mol$^{-1}$</th>
<th>$a_{21}$ cal mol$^{-1}$</th>
<th>$V_1$ cm$^3$ mol$^{-1}$</th>
<th>$V_2$ cm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>985.05</td>
<td>453.57</td>
<td>74.05</td>
<td>131.61</td>
</tr>
</tbody>
</table>

When $T$ and $x_1$ are given, the calculation is direct, with final values for vapor pressures and activity coefficients given immediately by Eqs. (A), (B), and (C). In all other cases either $T$ or $x_1$ or both are initially unknown, and calculations require trial or iteration.

#### a. BULB T calculation:

Find $y_1$ and $P$, given $x_1$ and $T$. Calculation here is direct. For $y_1 = 0.4$ and $T = 325.15$ K (52°C), Eqs. (A), (B), and (C) yield the values listed in the table on the following page. Equations (4-308) and (4-307) then become

$$ P = x_1 \gamma_1 P_i^{sat} + x_1 \gamma_1 P_i^{sat} = \left( 0.40 \right) \left( 0.8053 \right) \left( 87.616 \right) + \left( 0.60 \right) \left( 1.2869 \right) \left( 58.105 \right) $$

$$ y_1 = x_1 \gamma_1 P_i^{sat} = \left( 0.40 \right) \left( 0.8053 \right) \left( 87.616 \right) = 0.5851 $$

#### b. DEW P calculation:

Find $x_1$ and $P$, given $y_1$ and $T$. With $x_1$ an unknown, the activity coefficients cannot be immediately calculated. However, an iteration scheme based on Eqs. (4-309) and (4-307) is readily devised, and is part of any solve routine of a software package. Starting values result from setting each $\gamma = 1$. For $y_1 = 0.4$ and $P = 325.15$ kPa (52°C), results are listed in the accompanying table.

#### c. BULB T calculation:

Find $y_1$ and $T$, given $x_1$ and $P$. With $T$ unknown, neither the vapor pressures nor the activity coefficients can initially be calculated. An iteration scheme or a solve routine with starting values for the unknowns is required. For $y_1 = 0.60$ and $P = 101.33$ kPa, results are listed in the accompanying table.

#### d. DEW T calculation:

Find $x_1$ and $T$, given $y_1$ and $P$. Again, an iteration scheme or a solve routine with starting values for the unknowns is required. For $y_1 = 0.60$ and $P = 101.33$ kPa, results are listed in the accompanying table.

#### a. Azeotropic calculations:

As noted in Example 1a, only a single degree of freedom exists for this special case. The most sensitive quantity for identifying the azeotropic state is the relative volatility, defined as

$$ \alpha_{12} = \frac{y_2 / x_2}{y_1 / x_1} $$

Because $y_2 = x_2$ for the azeotropic state, $\alpha_{12} = 1$. Substitution for the two ratios by Eq. (4-307) provides an equation for calculation of $\alpha_{12}$ from the thermodynamic functions:

$$ \alpha_{12} = \frac{\gamma_1 P_i^{sat}}{\gamma_2 P_i^{sat}} $$

Because $\alpha_{12}$ is a monotonic function of $x_1$, the test of whether an azeotrope exists at a given T or P is provided by values of $\alpha_{12}$ in the limits of $x_1 = 0$ and $x_1 = 1$. If both values are either $> 1$ or $< 1$, no azeotrope exists. But if one value is $< 1$ and the other $> 1$, an azeotrope necessarily exists at the given T or P. Given T, the azeotropic composition and pressure is found by seeking the value of $P$ that makes $x_2 = y_2$ or that makes $\alpha_{12} = 1$. Similarly, given P, one finds the azeotropic composition and temperature. Shown in the accompanying table are calculated azeotropic states for a temperature of 46°C and for a pressure of 101.33 kPa. At 46°C, the limiting values of $\alpha_{12}$ are 8.289 at $x_1 = 0$ and 0.223 at $x_1 = 1$. 
Data Reduction  Correlations for $G^*$ and the activity coefficients are based on VLE data taken at low to moderate pressures. Group-contribution methods, such as UNIFAC, depend for validity on parameters evaluated from a large base of such data. The process of finding a suitable analytic relation for $g = (G^*/RT)$ as a function of its independent variables $T$ and $x_i$, 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. Thermodynamics 27: 113–134 (1995); Pure Appl. Chem. 67: 879–872 (1995)].

Presumed in all that follows is the existence of an equation inherently capable of correlating values of $G^*$ for the liquid phase as a function of $x_i$:

$$g = G^*/RT = G^*(x_i; \alpha, \beta, \ldots)$$  \hspace{1cm} (4-310)

where $\alpha$, $\beta$, etc., represent adjustable parameters.

The measured variables of binary VLE are $x_i$, $y_i$, $T$, and $P$. Experimental values of the activity coefficient of species $i$ in the liquid are related to these variables by Eq. (4-303), written as

$$y_i^* = \frac{y_i^* P_i}{x_i P} \Phi_i \quad i = 1, 2$$  \hspace{1cm} (4-311)

where $\Phi_i$ is given by Eq. (4-305) and the asterisks denote experimental values. A simple summability relation analogous to Eq. (4-252) defines an experimental value of $g^*$:

$$g^* = x_1 \ln y_1^* + x_2 \ln y_2^*$$  \hspace{1cm} (4-312)

Moreover, Eq. (4-263), the Gibbs-Duhem equation, may be written for experimental values in a binary system at constant $T$ and $P$ as

$$x_1 \frac{d \ln y_1^*}{dx_1} + x_2 \frac{d \ln y_2^*}{dx_1} = 0$$  \hspace{1cm} (4-313)

Because experimental measurements are subject to systematic error, sets of values of $\ln y_1^*$ and $\ln y_2^*$ may not satisfy, i.e., may not be consistent with, the Gibbs-Duhem equation. Thus Eq. (4-313) applied to sets of experimental values becomes a test of the thermodynamic consistency of the data, rather than a valid general relationship.

Values of $g$ provided by the equation used to correlate the data, as represented by Eq. (4-310), are called derived values, and produce derived values of the activity coefficients by Eqs. (4-180) with $M = g$:

$$\ln y_i = g + x_i \frac{dg}{dx_i}$$  \hspace{1cm} (4-314a)

$$\ln y_i = g - x_i \frac{dg}{dx_i}$$  \hspace{1cm} (4-314b)

These two equations combine to yield

$$\frac{dg}{dx_i} = \ln \frac{y_i}{y_i^*}$$  \hspace{1cm} (4-315)

This equation is valid for derived property values. The corresponding experimental values are given by differentiation of Eq. (4-312):

$$\frac{dg^*}{dx_i} = x_1 \frac{d \ln y_1^*}{dx_1} + x_2 \frac{d \ln y_2^*}{dx_1} - \ln y_i^*$$

or

$$\frac{dg^*}{dx_i} = \ln \frac{y_i^*}{y_i^*} + x_1 \frac{d \ln y_1^*}{dx_1} + x_2 \frac{d \ln y_2^*}{dx_1}$$  \hspace{1cm} (4-316)

Subtraction of Eq. (4-316) from Eq. (4-315) gives

$$\frac{dg}{dx_i} - \frac{dg^*}{dx_i} = \ln \frac{y_i}{y_i^*} - \ln \frac{y_i^*}{y_i^*} - \left( \frac{x_1 d \ln y_1^*}{dx_1} + x_2 d \ln y_2^* dx_1 \right)$$

The differences between like terms represent residuals between derived and experimental values. Defining these residuals as

$$\delta g = g - g^* \quad \text{and} \quad \delta \ln \frac{y_i}{y_i^*} = \ln \frac{y_i}{y_i^*} - \ln \frac{y_i^*}{y_i^*}$$

puts this equation into the form

$$\frac{d \delta g}{dx_i} = \delta \ln \frac{y_i}{y_i^*} = \left( x_1 \frac{d \ln y_1^*}{dx_1} + x_2 \frac{d \ln y_2^*}{dx_1} \right)$$  \hspace{1cm} (4-317)

If a data set is reduced so as to yield parameters—$\alpha$, $\beta$, etc.—that make the $\delta g$ residuals scatter about zero, then the derivative on the left is effectively zero, and the preceding equation becomes

$$\delta \ln \frac{y_i}{y_i^*} = x_1 \frac{d \ln y_1^*}{dx_1} + x_2 \frac{d \ln y_2^*}{dx_1}$$  \hspace{1cm} (4-317)

The right side of this equation is the quantity required by Eq. (4-313), the Gibbs-Duhem equation, 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 $\delta g$ 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 $y_i$. Equation (4-303) is solved for $P$ and written for species 1 and for species 2. Adding the two equations gives

$$P = \frac{x_1 y_1^* P^*}{\Phi_1} + \frac{x_2 y_2^* P^*}{\Phi_2}$$  \hspace{1cm} (4-318)

whence by Eq. (4-303),

$$y_i = \frac{x_i y_i^* P^*}{\Phi_i P}$$  \hspace{1cm} (4-319)

These equations allow calculation of the primary residuals:

$$\delta P = P - P^* \quad \text{and} \quad \delta y_i = y_i - y_i^*$$

If the experimental values $P^*$ and $y_i^*$ are closely reproduced by the correlating equation for $g$, then these residuals, evaluated at the experimental values of $x_i$, scatter about zero. This is the result obtained when the data approach thermodynamic consistency. When they do not, these residuals fail to scatter about zero and the correlation for $g$ does not properly reproduce the experimental values $P^*$ and $y_i^*$.

Such a correlation is unnecessarily divergent. An alternative is to base data reduction on just the $P$-$x_i$ data subset; this is possible because the full $P$-$x_i$-$y_i$ data set includes redundant information. Assuming that the correlating equation is appropriate to the data, one merely searches for values of the parameters $\alpha$, $\beta$, etc., that yield pressures by Eq. (4-318) that are as close as possible to the measured values. The usual procedure is to minimize the sum of squares of the residuals $\delta P$ known as Barker’s method [Austral. J. Chem. 6: 207–210 (1953)], it provides the best possible fit of the experimental pressures. When experimental $y_i^*$ values are not consistent with the $P$-$x_i$ data, Barker’s method cannot lead to calculated $y_i$ values that closely match the experimental $y_i^*$ values. With experimental error usually concentrated in the $y_i^*$ values, the calculated $y_i$ values are likely to be more nearly correct. Because Barker’s method requires only the $P$-$x_i$ data subset, the measurement of $y_i^*$ values is not usually worth the extra effort, and the correlating parameters $\alpha$, $\beta$, etc., are usually best determined without them. Hence, many $P$-$x_i$ data subsets appear in the literature; 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. 1, parts 1–8, DEHEMA, 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. (4-302).

Equations (4-303) and (4-304) are applicable to species 2, designated the solvent, but not to the solute, for which an alternative approach is required. Figure 4-7 shows a typical plot of the liquid-phase fugacity of the solute \(f_1\) versus its mole fraction \(x_1\), at constant temperature. Since the curve representing \(f_1\) 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

\[
k_1 = \lim_{x_1 \to 0} \frac{f_1}{x_1} \tag{4-320}
\]

This is the definition of \(k_1\) for temperature \(T\) and for pressure equal to the vapor pressure of the pure solvent \(P^\text{sat}_1\).

The activity coefficient of the solute at infinite dilution is

\[
\lim_{x_1 \to 0} \gamma_1 = \lim_{x_1 \to 0} \frac{f_1}{x_1 f_1} = \frac{1}{k_1} \lim_{x_1 \to 0} \frac{f_1}{x_1} \tag{4-321}
\]

In view of Eq. (4-320), this becomes \(\gamma_1^\infty = k_1 f_1\), or

\[
f_1 = \frac{k_1}{\gamma_1} \tag{4-321}
\]

where \(\gamma_1^\infty\) represents the infinite dilution value of the activity coefficient of the solute. Because both \(k_1\) and \(\gamma_1^\infty\) are evaluated at \(P^\text{sat}_1\), 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 then becomes

\[
\gamma_1 = \frac{f_1}{x_1 f_1} = \frac{y_1 P \phi_1 - y_2 P \gamma_1^\infty}{x_1 f_1} = \frac{x_1 k_1}{\phi_1 P} \tag{4-322}
\]

For the solute, this equation takes the place of Eqs. (4-303) and (4-304). Solution for \(y_1\) gives

\[
y_1 = \frac{x_1 (y_1 / y_2) \gamma_1^\infty k_1}{\phi_1 P} \tag{4-323}
\]

For the solvent, species 2, the analog of Eq. (4-319) is

\[
y_2 = \frac{x_2 (y_1 / y_2) \gamma_2^\infty k_2}{\phi_2 P} \tag{4-324}
\]

Because \(y_1 + y_2 = 1\),

\[
P = \frac{x_1 (y_1 / y_2) k_1}{\phi_1} + \frac{x_2 (y_1 / y_2) k_2}{\phi_2} \tag{4-325}
\]

The same correlation that provides for the evaluation of \(\gamma_2^\infty\) also allows evaluation of \(\gamma_1^\infty\).

There remains the problem of finding Henry’s constant from the available VLE data.

For equilibrium

\[
\frac{f_1}{x_1} = \frac{P \phi_1 y_1}{\gamma_1} \tag{4-326}
\]

Division by \(x_1\) gives

\[
k_1 = \frac{P \phi_1 y_1}{\phi_1} \lim_{x_1 \to 0} \frac{y_1}{x_1} \tag{4-327}
\]

The limiting value of \(y_1 / x_1\) can be found by plotting \(y_1 / x_1\) versus \(x_1\) and extrapolating to zero.

**K Values, VLE, and Flash Calculations** A measure of the distribution of a chemical species between liquid and vapor phases is the **K value**, defined as the equilibrium ratio:

\[
K_i = \frac{y_i}{x_i} \tag{4-328}
\]

It has no thermodynamic content, but may make for computational convenience through elimination of one set of mole fractions in favor of the other. It does characterize “lightness” of a constituent species. A “light” species, with \(K > 1\), tends to concentrate in the vapor phase whereas a “heavy” species, with \(K < 1\), tends to concentrate in the liquid phase.

The rigorous evaluation of a **K value** follows from Eq. (4-299):

\[
K_i = \frac{y_i}{x_i} = \frac{y_1}{x_1} = \frac{y_1 / y_2}{\phi_1 / \phi_2 P} \tag{4-329}
\]

When Raoult’s law applies, Eq. (4-326) reduces to \(K_i = P^\text{sat}_i / P\). For modified Raoult’s law, \(K_i = P^\text{sat}_i / P\). However, Eq. (4-326) shows that they are in general functions of \(T\), \(P\), \(x_i\), and \(y_i\), making convenient and accurate correlation impossible. Those correlations that do exist are approximate and severely limited in application. The nomographs for \(K\) values of light hydrocarbons as functions of \(T\) and \(P\), prepared by DePriester [Chem. Eng. Progr. Symp. Ser. No. 7, 49: 1–43 (1953)], do allow for an average effect of composition, but their essential basis is Raoult’s law.

The defining equation for \(K\) can be rearranged as \(y_1 = K x_1\). The sum \(\Sigma y_1 = 1\) then yields

\[
\sum_i K_i x_i = 1 \tag{4-327}
\]

With the alternative rearrangement \(x_i = y_i / K_i\), the sum \(\Sigma x_i = 1\) yields

\[
\sum_i \frac{y_i}{K_i} = 1 \tag{4-328}
\]

Thus for bubble point calculations, where the \(x_i\) are known, the problem is to find the set of \(K\) values that satisfies Eq. (4-327), whereas for dew point calculations, where the \(y_i\) are known, the problem is to find the set of \(K\) values that satisfies Eq. (4-328).

The flash calculation is a very common application of VLE. Considered here is the \(P, T\) flash, in which are calculated the quantities and compositions of the vapor and liquid phases in equilibrium at known \(T\), \(P\), and overall composition. This problem is determined on the basis of Duhem’s theorem: *For any closed system formed initially from*
The initial step in solving a given mass of prescribed chemical species, the equilibrium state is completely determined when any two independent variables are fixed. The independent variables are here \( T \) and \( P \), and systems are formed from given masses of nonreacting chemical species.

For a real fluid of a system with overall composition represented by the set of mole fractions \( \{x_i\} \), let \( L \) represent the molar fraction of the system that is liquid (mole fractions \( \{x_i\} \)) and let \( V' \) represent the molar fraction that is vapor (mole fractions \( \{y_i\} \)). The material balance equations are

\[
L + V' = 1 \quad \text{and} \quad z_i = x_iL + y_iV' \quad i = 1, 2, \ldots, N
\]

Combining these equations to eliminate \( L \) gives

\[
z_i = x_i(1 - V') + y_iV' \quad i = 1, 2, \ldots, N \tag{4-329}
\]

Substitute \( x_i = y_i/K_i \) and solve for \( y_i \):

\[
y_i = \frac{z_iK_i}{1 + y_i(K_i - 1)} \quad i = 1, 2, \ldots, N
\]

Because \( \Sigma y_i = 1 \), this equation, summed over all species, yields

\[
\sum_{i=1}^{N} \frac{z_iK_i}{1 + y_i(K_i - 1)} = 1 \tag{4-330}
\]

The initial step in solving a \( P, T \) flash problem is to find the value of \( V' \) which satisfies this equation. Note that \( V' = 1 \) is always a trivial solution.

**Example 4: Flash Calculation**

The system of Example 3 has the overall composition \( z_1 = 0.4000 \) at \( T = 325.15 \text{ K} \) and \( P = 101.33 \text{ kPa} \). Determine \( V', x_1, \) and \( y_1 \).

The BUBL \( P \) and DEW \( P \) calculations at \( T = 325.15 \text{ K} \) of Example 3a and 3b show that for \( x_1 = z_1 \), \( P_{sat} = 108.134 \text{ kPa} \), and for \( y_1 = z_1 \), \( P_{sat} = 87.939 \text{ kPa} \). Because \( P \) here lies between these values, the system is in two-phase equilibrium, and a flash calculation is appropriate.

The modified Raoult’s law \( K \) values are given by

\[
K_i = \frac{(y_i/P_i)(P/P_i)}{P} \quad \text{and} \quad K_i = \frac{(y_i/P_i)(P/P_i)}{P}
\]

Equation (4-329) may be solved for \( V' \):

\[
\frac{(z_i)(K_i)}{1 + (y_i)(K_i)} + \frac{(z_i)(K_i)}{1 + (y_i)(K_i)} = 1
\]

A trial calculation illustrates the nature of the solution. Vapor pressures are taken from Example 3a or 3b, a trial value of \( x_1 \), thus allowing calculation of \( \hat{y}_i \), and \( \gamma_i \). By Eqs. (B) and (C) of Example 3. The values of \( K_i \), \( K_i \), and \( y_i \) that result are substituted into the summation equation. In the unlikely event that the sum is indeed unity, the chosen value of \( x_1 \) is correct. If not, then successive trials easily lead to this value. Note that the trivial solution giving \( V' = 1 \) must be avoided. More elegant solution procedures can of course be employed. The answers are

\[
x_1 = 0.2573, \quad y_1 = 0.5190, \quad V' = 0.5775
\]

with \( \gamma_1 = 2.5297, \gamma_2 = 1.0997, \quad K_1 = 2.1873, \quad K_2 = 0.6306 \)

**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 \( G^* \) is included only for the local composition equations, and it is at best 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. (4-204), may be applied to each phase:

**Liquid:** \( \hat{f}_i = \hat{\phi}_i x_i P \) \n
**Vapor:** \( \hat{f}_i = \hat{\phi}_i y_i P \)

By Eq. (4-298),

\[
x_i \hat{\phi}_i = y_i \hat{\phi}_i \quad i = 1, 2, \ldots, N \tag{4-331}
\]

This introduces 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. (4-331) represents \( N \) complex relationships connecting \( T, P, \{x_i\}, \) and \( \{y_i\} \).

Two widely used cubic equations of state appropriate for VLE calculations, both special cases of Eq. (4-100) [with Eqs. (4-101) and (4-102)], are the Soave-Redlich-Kwong (SRK) equation and the Peng-Robinson (PR) equation. The present treatment is applicable to both. The pure numbers, \( e, \sigma, \Psi, \) and \( \Omega \) and expressions for \( \alpha(T_i) \) specific to these equations are listed in Table 4-2. The associated expression for \( \hat{\phi}_i \) is given by Eq. (4-246).

The simplest application of equations of state in vapor/liquid equilibrium is to the calculation of vapor pressures \( P_{sat} \) of pure liquids. Vapor pressures can of course be measured, but values are also implicit in cubic equations of state.

A subcritical PV isotherm, generated by a cubic equation of state, is shown in Fig. 4-8. Three segments are evident. The very steep one on the left \((x)\) is characteristic of liquids. Note that as \( P \to \infty \), vapor \( V \to b \), where \( b \) is a constant in the cubic equation. The gently sloping segment on the right \((u)\) is characteristic of vapors; here \( P \to 0 \) as \( V \to \infty \). The middle segment \((d)\), with both a minimum (note \( P < 0 \)) and a maximum, provides a transition from liquid to vapor, but has no physical meaning. The actual transition occurs along a horizontal line, such as connects points \( M \) and \( W \).

For pure species \( i \), Eq. (4-331) reduces to \( \hat{\phi}_i = \hat{\phi}_i \), which may be written as

\[
\ln \hat{\phi}_i = \ln \hat{\phi}_i \tag{4-332}
\]

For given \( T \), line \( MW \) lies at the vapor pressure \( P_{sat} \) and if only if the fugacity coefficients for points \( M \) and \( W \) satisfy Eq. (4-332). These points then represent saturated liquid and vapor phases in equilibrium at temperature \( T \).

The fugacity coefficients in Eq. (4-332) are given by Eq. (4-245):

\[
\ln \hat{\phi}_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i P, \quad p = l, v \tag{4-333}
\]

Expressions for \( Z_i' \) and \( Z_i' \) come from Eqs. (4-104):

\[
Z_i = 1 + \beta_i - q_i P, \quad Z_i' = \frac{Z_i - \beta_i}{(Z_i + e\beta_i)(Z_i + \sigma\beta_i)} \tag{4-334}
\]

and \( I_\ell' \) comes from Eq. (4-112):

\[
I_\ell' = \frac{1}{\alpha - \epsilon} \ln \frac{Z_i' + \sigma\beta_i}{Z_i' + e\beta_i}, \quad p = l, v \tag{4-336}
\]
The equation-of-state parameters are independent of phase. As defined by Eq. (4-105), $\beta$ is a function of $P$ and here becomes

$$\beta = \frac{b P_v}{RT}$$  \hspace{1cm} (4-337)

The remaining equation-of-state parameters, given by Eqs. (4-101), (4-102), and (4-106), are functions of $T$ only and are written here as

$$a_i(T) = \psi \left( \frac{a(T_1)R T_i^2}{P_v} \right)$$  \hspace{1cm} (4-338)

$$b_i = \Omega \left( \frac{RT_i}{P_v} \right)$$  \hspace{1cm} (4-339)

$$q_i = \frac{a_i(T)}{b_i RT}$$  \hspace{1cm} (4-340)

The eight equations (4-332) through (4-337) may be solved for the eight unknowns $P_v$, $\beta$, $Z_i$, $Z_i'$, $I_i$, $I_i'$, ln $\phi_i$, and ln $\phi_i'$. Perhaps more useful is the reverse calculation whereby an equation-of-state parameter is evaluated from a known vapor pressure. Thus, Eqs. (4-332) and (4-333) may be combined and solved for $q_i$, yielding

$$q_i = \frac{Z_i - Z_i' + \ln [(Z_i - \beta)/(Z_i - \beta_i)]}{I_i - I_i'}$$  \hspace{1cm} (4-341)

Expressions for $Z_i$, $Z_i'$, $I_i$, $I_i'$, and $\beta_i$ are given by Eqs. (4-334) through (4-337). Because $Z_i$ and $Z_i'$ depend on $q_i$, an iterative procedure is indicated, with a starting value for $q_i$ from a generalized correlation as given by Eqs. (4-338), (4-339), and (4-340).

For mixtures the presumption is that the equation of state has exactly the same form as when written for pure species. Equations (4-104) are therefore applicable, with parameters $\beta$ and $q$ given by Eqs. (4-105) and (4-106). Here, these parameters, and therefore $b$ and $a(T)$, are functions of composition. Liquid and vapor mixtures in equilibrium in general have different compositions. The PV isotherms generated by an equation of state for these different compositions are represented in Fig. 4-9 by two similar lines: the solid line for the liquid-phase composition and the dashed line for the vapor-phase composition. They are displaced from each other because the equation-of-state parameters are different for the two compositions.

Each line includes three segments as described for the isotherm of Fig. 4-8: the leftmost segment representing a liquid phase and the rightmost segment, a vapor phase, both with the same composition. Each left segment contains a bubble point (saturated liquid), and each right segment contains a dew point (saturated vapor). Because these points for a given line are for the same composition, they do not represent phases in equilibrium and do not lie at the same pressure. Shown in Fig. 4-9 is a bubble point $B$ on the solid line and a dew point $D$ on the dashed line. Because they lie at the same $P$, they represent phases in equilibrium, and the lines are characterized by the liquid and vapor compositions.

For a BUBL $P$ calculation, the temperature and the liquid composition are known, and this fixes the location of the PV isotherm for the composition of the liquid phase (solid line). The problem then is to locate a second (dashed) line for a vapor composition such that the line contains a dew point $D$ on its vapor segment that lies at the pressure of the bubble point $B$ on the liquid segment of the solid line. This pressure is the phase equilibrium pressure, and the composition for the dashed line is that of the equilibrium vapor. This equilibrium condition is shown by Fig. 4-9.

The absence of a theory to prescribe the composition dependence of parameters for cubic equations of state, empirical mixing rules are used to relate mixture parameters to pure-species parameters. The simplest realistic expressions are a linear mixing rule for parameter $b$ and a quadratic mixing rule for parameter $a$, as shown by Eqs. (4-113) and (4-114). A common combining rule is given by Eq. (4-115). The general mole fraction variable $x_i$ is used here because application is to both liquid and vapor mixtures. These equations, known as van der Waals prescriptions, provide for the evaluation of mixture parameters solely from parameters for the pure constituent species. They find application primarily for mixtures comprised of simple and chemically similar molecules.

Useful in the application of cubic equations of state to mixtures are partial equation-of-state parameters. For the parameters of the generic cubic, represented by Eqs. (4-104), (4-105), and (4-106), the definitions are

$$\bar{a}_i = \left[ \frac{\partial (na)}{\partial n_i} \right]_{T,a}$$  \hspace{1cm} (4-342)

$$\bar{b}_i = \left[ \frac{\partial (nb)}{\partial n_i} \right]_{T,b}$$  \hspace{1cm} (4-343)

$$\bar{q}_i = \left[ \frac{\partial (nq)}{\partial n_i} \right]_{T,q}$$  \hspace{1cm} (4-344)

These are general equations, valid regardless of the particular mixing or combining rules adopted for the composition dependence of mixture parameters.

Parameter $q$ is defined in relation to parameters $a$ and $b$ by Eq. (4-106). Thus,

$$nq = \frac{n(\bar{a}a + \bar{b}b)}{RT}$$

whence

$$\bar{q}_i = \left[ \frac{\partial (nq)}{\partial n_i} \right]_{T,q} = q \left( 1 + \bar{a}_i + \frac{\bar{b}_i}{\bar{b}} \right)$$  \hspace{1cm} (4-345)

Any two of the three partial parameters form an independent pair, and any one of them can be found from the other two. Because $q$, $a$, and $b$ are not linearly related, $\bar{q}_i = a_i/b_i/RT$.

Values of $\phi_i$ and $\phi_i'$ as given by Eq. (4-246) are implicit in an equation of state and with Eq. (4-331) allow calculation of mixture VLE. Although more complex, the same basic principle applies as for pure-species VLE. With $\phi_i$ a function of $T$, $P$, and $[x_i]$, and $\phi_i'$ a function of $T$, $P$, and $[y_i]$, Eq. (4-331) represents $N$ relations among the $2N$ variables: $T$, $P$, $(N-1)$ $x_i$s, and $(N-1)$ $y_i$s. Thus, specification of $N$ of these variables, usually either $T$ or $P$ and either the liquid- or vapor-phase composition, allows solution for the remaining $N$ variables by BUBL $P$, DEW $P$, BUBL $T$, and DEW $T$ calculations.
Because of limitations inherent in empirical mixing and combining rules, such as those given by Eqs. (4-113) through (4-115), the equation-of-state approach has found primary application to systems exhibiting modest deviations from ideal solution behavior in the liquid phase, e.g., to systems containing hydrocarbons and cryogenic fluids. However, since 1990, extensive research has been devoted to developing mixing rules that incorporate the excess Gibbs energy or activity coefficient data available for many systems. The extensive literature on this subject is reviewed by Valderrama [Ind. Eng. Chem. Res. 42: 1603–1618 (2003)] and by Twu, Sim, and Tassone [Chem. Eng. Progress 98(11): 58–65 (Nov. 2002)]

The idea here is to exploit the connection between fugacity coefficients and activity coefficients provided by their definitions:

\[
\gamma_i = \frac{f_i}{x_i} = \frac{f_i \xi_i P}{\phi_i}
\]

Therefore,

\[
\ln \gamma_i = \ln \phi_i - \ln \phi_i
\]

Because \( \gamma_i \) is a liquid-phase property, this equation is written for the liquid phase. Substituting for \( \ln \phi_i \) and \( \ln \phi_i \) by Eqs. (4-245) and Eq. (4-246) gives

\[
\ln \gamma_i = \frac{b_i}{b} (Z - 1) - Z + 1 - \ln \frac{Z - \beta}{Z - \beta} - \tilde{\gamma} q_i + q_i
\]

Symbols without subscripts are mixture properties. Solution for \( \tilde{\gamma} \) yields

\[
\tilde{\gamma} = \frac{1}{I} \left[ 1 - Z_i + \frac{b_i}{b} (Z - 1) - \ln \frac{Z - \beta}{Z - \beta} + q_i \ln I - \ln \gamma_i \right]
\]

Because \( \tilde{\gamma} \) is a partial property, the summability equation provides an exact mixing rule:

\[
q = \sum_i x_i \tilde{\gamma}_i
\]


**Extrapolation of Data with Temperature** Liquid-phase excess-property data for binary systems at near-ambient temperatures appear in the literature. They provide for the extrapolation of \( C^E \) correlations with temperature. The key relations are Eq. (4-250), written as

\[
d \left( \frac{C^E}{RT} \right) = - \frac{H^E}{RT^2} dT \quad \text{constant } P, x
\]

and the excess-property analog of Eq. (4-26):

\[
d H^E = C^E f dT \quad \text{constant } P, x
\]

Integration of the first equation from \( T_0 \) to \( T \) gives

\[
\frac{C^E}{RT} = \left( \frac{C^E}{RT} \right)_{T_0} - \int_{T_0}^{T} \frac{H^E}{RT^2} dT
\]

Integration of the second equation from \( T_0 \) to \( T \) yields

\[
H^E = H^E_{T_0} + \int_{T_0}^{T} \frac{C^E f}{RT} dT
\]

In addition,

\[
d C^E = \left( \frac{\partial C^E}{\partial T} \right)_{F} dT
\]

Integrate from \( T_0 \) to \( T \):

\[
C^E = C^E_{T_0} + \int_{T_0}^{T} \left( \frac{\partial C^E}{\partial T} \right)_{F} dT
\]

Combining this equation with Eqs. (4-349) and (4-350) leads to

\[
\frac{C^E}{RT} = \left( \frac{C^E}{RT} \right)_{T_0} - \left( \frac{H^E}{RT} \right)_{T_0} \left\{ \frac{T}{T_0} - 1 \right\} \frac{T_1}{T}
\]

\[
- \frac{C^E}{R} \int \frac{T}{T_0} - \left\{ \frac{T}{T_0} - 1 \right\} \frac{T_1}{T} - I
\]

where

\[
I = \int_{T_0}^{T} \frac{1}{T^2} \left( \int_{T_0}^{T} \frac{\partial C^E}{\partial T} \right)_{F} dT dT dT
\]

This general equation employs excess Gibbs energy data at temperature \( T_0 \), excess enthalpy (heat-of-mixing) data at \( T_1 \), and excess heat capacity data at \( T_2 \). Integral \( I \) depends on the temperature dependence of \( C^F \). Excess heat capacity data are uncommon, and the \( T \) dependence is rarely known. Assuming \( C^E \) independent of \( T \) makes the integral zero, and the closer \( T_0 \) and \( T_1 \) are to \( T_2 \) the less the influence of this assumption. When no information is available for \( C^F \) and excess enthalpy data are available at only a single temperature, \( C^E \) must be assumed zero. In this case only the first two terms on the right side of Eq. (4-351) are retained, and it more rapidly becomes imprecise as \( T \) increases.

For application of Eq. (4-351) to binary systems at infinite dilution of one of the constituent species, it is divided by the product \( x_i x_2 \).

\[
\frac{C^E}{x_i x_2 RT} = \left( \frac{C^E}{x_i x_2 RT} \right)_{T_0} - \left( \frac{H^E}{x_i x_2 RT} \right)_{T_0} \left\{ \frac{T}{T_0} - 1 \right\} \frac{T_1}{T}
\]

The assumption here is that \( C^F \) is independent of \( T \), making \( I = 0 \). As shown by Smith, Van Ness and Abbott [Introduction to Chemical Engineering Thermodynamics, 7th ed., p. 437, McGraw-Hill, New York (2005)],

\[
\ln \gamma_i = \left( \frac{C^E}{x_i x_2 RT} \right)_{T_2} = \ln \gamma_i
\]

The preceding equation may therefore be written as

\[
\ln \gamma_i = \left( \frac{C^E}{x_i x_2 RT} \right)_{T_2} = \ln \gamma_i
\]

**Example 5: VLE at Several Temperatures** For the methanol(1)/acetic acid(2) system at a base temperature of \( T_s = 323.15 \) K (50°C), both VLE data [Van Ness and Abbott, Int. DATA SER., Ser. A, Sel. Data Mixtures, 1978: 67 (1978)] and excess enthalpy data [Morrise et al., J. Chem. Eng. Data 20: 403–405 (1975)] are available. The VLE data are well correlated by the Margules equations. As noted in connection with Eq. (4-270), parameters \( A_{21} \) and \( A_{12} \) relate directly to infinite-dilution values of the activity coefficients. Thus, we have from the VLE data at 323.15 K:

\[
A_{21} = \ln \gamma_1 = 0.6281 \quad \text{and} \quad A_{12} = \ln \gamma_2 = 0.6557
\]

These values allow calculation of equilibrium pressures through Eqs. (4-270) and (4-308) for comparison with the measured pressures of the data set. Values of \( P_{\text{meas}} \) required in Eq. (4-308) are the measured values reported with the data set. The root-mean-square (rms) value of the pressure differences is given in Table 4-7 as 0.08 kPa, thus confirming the suitability of the Margules equation for this system. Vapor-phase mole fractions were not reported; hence no value can be given for \( \partial \gamma_i / \partial x_i \).

Experimental VLE data at 372.8 and 397.7 K are given by Wilkak et al. [Fluid Phase Equilib. 28: 13–37 (1986)]. Values of \( \ln \gamma_i \) and hence of the Margules parameters for these higher temperatures are found from Eq. (4-352) with \( C^E = 0 \). The required excess enthalpy values at \( T_0 \) are

\[
\left( \frac{H^E}{x_1 x_2 RT} \right)_{T_2} = 1.3636 \quad \text{and} \quad \left( \frac{H^E}{x_1 x_2 RT} \right)_{T_2} = 1.0362
\]
the $\{v\}$ are stoichiometric coefficients and the $A_j$ stand for chemical formulas. The $v_i$ 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 are represented by the equations

$$0 = \sum_i v_{ij} A_i \quad j = 1, \ldots, r$$

(4-357)

where $\text{sign}(v_{ij}) = -$ for a reactant species and $+$ for a product species.

If species $i$ does not participate in reaction $j$, then $v_{ij} = 0$.

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 $j$

$$\frac{\Delta n_{1j}}{v_{1j}} = \frac{\Delta n_{2j}}{v_{2j}} = \cdots = \frac{\Delta n_{Nj}}{v_{Nj}}$$

(4-358)

All these terms are equal, and they can be equated to the change in a single quantity $\varepsilon_j$, called the reaction coordinate for reaction $j$, thereby giving

$$\Delta n_i = \sum_j v_{ij} \Delta \varepsilon_j \quad i = 1, 2, \ldots, N$$

(4-360)

If the initial number of moles of species $i$ is $n_i$, and if the reaction is adopted that $\varepsilon_j = 0$ for each reaction in this initial state, then

$$n_i = n_i + \sum_j v_{ij} \varepsilon_j \quad i = 1, 2, \ldots, N$$

(4-361)

Equation (4-361) 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 $\varepsilon_j$ are capable of independent variation. It is not an equilibrium relation, but merely an accounting scheme, valid for tracking the progress of the reactions to arbitrary levels of conversion. The reaction coordinate has units of moles. A change in $\varepsilon_j$ of 1 mol 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. (4-296). For a system in which just a single reaction occurs, Eq. (4-361) becomes

$$n_i = n_i + v_i \varepsilon \quad \text{whence} \quad d_n = v_i \, d\varepsilon$$

(4-361a)

Substitution for $d_n$, in Eq. (4-296) leads to

$$\sum_i v_i \mu_i = 0$$

(4-362)

Generalization of this result to multiple reactions produces

$$\sum_i v_i \mu_i = 0 \quad j = 1, 2, \ldots, r$$

(4-363)

**Standard Property Changes of Reaction**

For the reaction

$$aA + bB \rightarrow IL + mM$$

a standard property change is defined as the property change resulting when $a$ mol of $A$ and $b$ mol of $B$ in their standard states at temperature

TABLE 4-7 VLE Results for Methanol(1)/Acetone(2)

<table>
<thead>
<tr>
<th>T, K</th>
<th>$A_{2i}$</th>
<th>$A_{2j}$</th>
<th>RMS $\delta P$</th>
<th>RMS $% \delta P$</th>
<th>RMS $\delta g_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>323.15</td>
<td>0.6281</td>
<td>0.6557</td>
<td>0.08</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>372.8</td>
<td>0.4465</td>
<td>0.5177</td>
<td>0.85</td>
<td>0.22</td>
<td>0.004</td>
</tr>
<tr>
<td>397.7</td>
<td>0.3725</td>
<td>0.4615</td>
<td>2.46</td>
<td>0.32</td>
<td>0.014</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T, K</th>
<th>$A_{2i}$</th>
<th>$A_{2j}$</th>
<th>RMS $\delta P$</th>
<th>RMS $% \delta P$</th>
<th>RMS $\delta g_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>323.15</td>
<td>0.6281</td>
<td>0.6557</td>
<td>0.08</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>372.8</td>
<td>0.4465</td>
<td>0.5177</td>
<td>0.85</td>
<td>0.22</td>
<td>0.004</td>
</tr>
<tr>
<td>397.7</td>
<td>0.3725</td>
<td>0.4615</td>
<td>2.46</td>
<td>0.32</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Results of calculations with the Margules equations are displayed as the primary entries at each temperature in Table 4-7. The values in parentheses are from the gamma/phi approach as reported in the papers cited.

Results for the 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. Extrapolations based on the same data to still higher temperatures can be expected to become progressively less accurate.

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 a binary system.

**LIQUID/LIQUID AND VAPOR/LIQUID/ LIQUID EQUILIBRIA**

Equation (4-295) is the basis for both liquid/liquid equilibria (LLE) and vapor/liquid/liquid equilibria (VLL). Thus for LLE with superscripts $\alpha$ and $\beta$ denoting the two phases, Eq. (4-295) is written as

$$f_i^\alpha = f_i^\beta$$

(4-353)

Eliminating fugacities in favor of activity coefficients gives

$$x_i^\alpha y_i^\alpha = x_i^\beta y_i^\beta$$

(4-354)

For most LLE applications, the effect of pressure on the $\gamma_i$ can be ignored, and Eq. (4-354) then constitutes a set of $N$ equations relating equilibrium compositions to one another and to temperature. For a given temperature, solution of these equations requires a single equilibrium compositions to one another and to temperature. For a

$$\sum_i v_i A_i = 0$$

(4-361)

Chemical reaction stoichiometry

For a phase in which a chemical reaction occurs according to the equation

$$\{v\}_1 A_1 + \{v\}_2 A_2 + \cdots \rightarrow \{v\}_1 A_1 + \{v\}_2 A_2 + \cdots$$

As for LLE, an expression for $C^G$ capable of representing liquid/liquid phase splitting is required; as for VLE, a vapor-phase equation of state for computing the $\phi_i$ is also needed.

**CHEMICAL REACTION STOICHIOMETRY**

For a phase in which a chemical reaction occurs according to the equation

$$\{v\}_1 A_1 + \{v\}_2 A_2 + \cdots \rightarrow \{v\}_1 A_1 + \{v\}_2 A_2 + \cdots$$

the $\{v\}$ are stoichiometric coefficients and the $A_j$ stand for chemical formulas. The $v_i$ 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 are represented by the equations

$$0 = \sum_i v_{ij} A_i \quad j = 1, II, \ldots, r$$

(4-357)

where $\text{sign}(v_{ij}) = -$ for a reactant species and $+$ for a product species.

If species $i$ does not participate in reaction $j$, then $v_{ij} = 0$.

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 $j$

$$\frac{\Delta n_{1j}}{v_{1j}} = \frac{\Delta n_{2j}}{v_{2j}} = \cdots = \frac{\Delta n_{Nj}}{v_{Nj}}$$

(4-358)

All these terms are equal, and they can be equated to the change in a single quantity $\varepsilon_j$, called the reaction coordinate for reaction $j$, thereby giving

$$\Delta n_i = \sum_j v_{ij} \Delta \varepsilon_j$$

(4-360)

If the initial number of moles of species $i$ is $n_i$, and if the reaction is adopted that $\varepsilon_j = 0$ for each reaction in this initial state, then

$$n_i = n_i + \sum_j v_{ij} \varepsilon_j$$

(4-361)

Equation (4-361) 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 $\varepsilon_j$ are capable of independent variation. It is not an equilibrium relation, but merely an accounting scheme, valid for tracking the progress of the reactions to arbitrary levels of conversion. The reaction coordinate has units of moles. A change in $\varepsilon_j$ of 1 mol 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. (4-296). For a system in which just a single reaction occurs, Eq. (4-361) becomes

$$n_i = n_i + v_i \varepsilon \quad \text{whence} \quad d_n = v_i \, d\varepsilon$$

(4-361a)

Substitution for $d_n$, in Eq. (4-296) leads to

$$\sum_i v_i \mu_i = 0$$

(4-362)

Generalization of this result to multiple reactions produces

$$\sum_i v_i \mu_i = 0 \quad j = 1, II, \ldots, r$$

(4-363)

**Standard Property Changes of Reaction**

For the reaction

$$aA + bB \rightarrow IL + mM$$

a standard property change is defined as the property change resulting when $a$ mol of $A$ and $b$ mol of $B$ in their standard states at temperature...
The application of Eq. (4-369) requires explicit introduction of composition variables. For gas-phase reactions this is accomplished through the fugacity coefficient

\[ \hat{a}_i = \frac{f_i}{f_i^0} = y_i \phi_i P_P^0 \]

However, the standard state for gases is the ideal gas state at the standard state pressure, for which \( f_i = P_P^0 \). Therefore,

\[ \hat{a}_i = \frac{y_i \phi_i P_P^0}{P_P^0} \]

and Eq. (4-369) becomes

\[ \prod_i \left( y_i \phi_i \right)^{y_i} \left( \frac{P}{P_P^0} \right)^{y_i} = K_y \quad \text{all } j \quad (4-371) \]

where \( y_i = \Sigma y_i \) and \( P_P^0 \) is the standard state pressure of 100 kPa, expressed in the same units used for \( P \). The \( y_i \)'s may be eliminated in favor of equilibrium values of the reaction coordinates \( \xi_i \), see (Equation 6). Then, for fixed temperature Eqs. (4-371) relate the \( \xi_i \) to \( P \). In principle, specification of the pressure allows solution for the \( \xi_i \). However, the problem may be complicated by the dependence of the \( \phi_i \) on composition, i.e., on the \( \xi_i \). If the equilibrium mixture is assumed an ideal solution then [Eq. (4-218)] each \( \phi_i \) becomes \( \phi_i \), 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. (4-371) results for gas-phase reactions when the phase is assumed an ideal gas. In this event \( \phi_i = 1 \), and

\[ \prod_i \left( y_i \phi_i \right)^{y_i} \left( \frac{P}{P_P^0} \right)^{y_i} = K_y \quad \text{all } j \quad (4-372) \]

In the general case the evaluation of the \( \phi_i \) requires an iterative process. An initial step is to set each \( \phi_i \) equal to unity and to solve the problem by Eq. (4-372). This provides a set of \( y_i \) values, allowing evaluation of the \( \phi_i \) by, for example, Eq. (4-243) or (4-246). Equation (4-371) can then be solved for a new set of \( y_i \) values, with the process continued to convergence.

For liquid-phase reactions, Eq. (4-369) is modified by introduction of the activity coefficient \( \gamma = f_i / \nu_i f_i \), where \( \nu_i \) is the liquid-phase mole fraction. The activity is then

\[ \hat{a}_i = \hat{f}_i = \gamma \nu_i \left( \frac{f_i}{f_i^0} \right) \]

Both \( f_i \) and \( f_i^0 \) represent fugacity of pure liquid \( i \) at temperature \( T \), but at pressures \( P \) and \( P_P^0 \), respectively. Except in the critical region, pressure has little effect on the properties of liquids, and the ratio \( f_i / f_i^0 \) is often taken as unity. When this is not acceptable, this ratio is evaluated by the equation

\[ \ln \frac{f_i}{f_i^0} = \frac{1}{RT} \int V_i dP = \frac{V_i (P - P_P^0)}{RT} \]

When the ratio \( f_i / f_i^0 \) is taken as unity, \( \hat{a}_i = \gamma \nu_i \), and Eq. (4-369) becomes

\[ \prod_i \left( \gamma_i \nu_i \right)^{y_i} = K_y \quad \text{all } j \quad (4-373) \]

Here the difficulty is to determine the \( \gamma_i \)'s, which depend on the \( x_i \)'s. 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. (4-373) reduces to

\[ \prod_i (x_i y_i)^{y_i} = K_y \quad \text{all } j \quad (4-374) \]

the "law of mass action." The significant feature of Eqs. (4-372) and (4-374), the simplest expressions for gas- and liquid-phase reaction...
equilibrium, is that the temperature-, pressure-, and composition-dependent terms are distinct and separate.

The effect of temperature on the equilibrium constant follows from Eq. (4-41) written for pure species $j$ in its standard state (wherein the pressure $P^*$ is fixed):

$$\frac{d(G^0_j/RT)}{dT} = -\frac{H_j^0}{RT^2}$$

With Eqs. (4-365) and (4-366) this equation easily extends to relate standard property changes of reaction:

$$\frac{d(\Delta G^0_j/RT)}{dT} = -\Delta H_j^0/RT^2$$ (4-375)

In view of Eq. (4-370) this may also be written as

$$\frac{d \ln K}{dT} = \frac{\Delta H_j^0}{RT^2}$$ (4-376)

For an endothermic reaction, $\Delta H_j^0$ is positive and $K_j$ increases with increasing $T$; for an exothermic reaction, it is negative and $K_j$ decreases with increasing $T$.

Because the standard state pressure is constant, Eq. (4-28) may be extended to relate standard properties of reaction, yielding

$$d(\Delta T)_j = (\Delta C_j)_j dT \quad \text{and} \quad d(\Delta S)_j = (\Delta C_j)_j \frac{dT}{T}$$

Integration of these equations from reference temperature $T_0$ (usually 298.15 K) to temperature $T$ gives

$$\Delta H^0 = \Delta H_j^0 + R \int_{T_0}^{T} \frac{(\Delta C_j)_j}{T} dT$$ (4-377)

$$\Delta S^0 = \Delta S_j^0 + R \int_{T_0}^{T} \frac{(\Delta C_j)_j}{T} dT$$ (4-378)

where for simplicity subscript $j$ has been suppressed. The definition of $G$ leads directly to $\Delta G^0 = \Delta H^0 - T \Delta S^0$. Combining this equation with Eqs. (4.370), (4.377), and (4.378) yields

$$\ln K = \frac{-\Delta G^0}{RT} = \frac{-\Delta H_j^0}{RT} - \frac{1}{T} \int_{T_0}^{T} \frac{(\Delta C_j)_j}{T} dT + \int_{T_0}^{T} \frac{(\Delta C_j)_j}{T} dT$$

Substituting $\Delta S_j = (\Delta G_j - \Delta H_j)/T_0$, rearranging, and defining $\tau = T/T_0$ give finally

$$\ln K = \frac{-\Delta G_j^0}{RT_0} + \frac{\Delta H_j^0}{RT_0} \left( \frac{\tau - 1}{\tau} \right)$$

When heat capacity equations have the form of Eq. (4.52), the integrals are evaluated by equations of exactly the form of Eqs. (4.53) and (4.54), but with parameters $A$, $B$, $C$, and $D$ replaced by $\Delta A$, $\Delta B$, $\Delta C$, and $\Delta D$, in accord with Eq. (4.364). Thus for the ideal gas standard state

$$\int_{T_0}^{T} \frac{(\Delta C_j)_j}{T_0} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^{3/2} (\tau^{3/2} - 1) + \frac{\Delta C}{3} T_0 (\tau^{3/2} - 1)$$

$$+ \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right)$$ (4-380)

$$\int_{T_0}^{T} \frac{(\Delta C_j)_j}{T} dT = \Delta A \ln \tau + \left[ \frac{\Delta B}{2} T_0^{3/2} (\tau^{3/2} - 1) + \frac{\Delta C}{3} T_0 (\tau^{3/2} - 1) \right] (\tau - 1)$$ (4-381)

Equations (4.379) through (4.381) together allow an equation to be written for $\ln K$ as a function of $T$ for any reaction for which appropriate data are available.

In the more extensive compilations of data, values of $\Delta G^0$ and $\Delta H^0$ for formation reactions are given for a wide range of temperatures, rather than just at the reference temperature $T_0 = 298.15$ K. [See in particular TRC Thermodynamic Tables—Hydrocarbons and TRC Thermodynamic Tables—Non-hydrocarbons, serial publications of the Thermodynamics Research Center, Texas A & M Univ. System, College Station, Tex.; “The NBS Tables of Chemical Thermodynamic Properties,” J. Phys. Chem. Ref. Data 11, supp. 2 (1982).] Where data are lacking, methods of estimation are available; these are reviewed by Poling, Prausnitz, and O’Connell, The Properties of Gases and Liquids, 5th ed., chap. 6. McGraw-Hill, New York, 2000. For an estimation procedure based on molecular structure, see Constantinou and Gani, Fluid Phase Equilib. 103: 11–22 (1995). See also Sec. 2.

**Example 6: Single-Reaction Equilibrium** The hydrogenation of benzene to produce cyclohexane by the reaction

$$\text{C}_6\text{H}_6 + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}$$

is carried out over a catalyst formulated to repress side reactions. Operating conditions cover a pressure range from 10 to 35 bar and a temperature range from 450 to 670 °C. Reaction rate increases with increasing $T$, but because the reaction is exothermic the equilibrium conversion decreases with increasing $T$. A comprehensive study of the effect of operating variables on the chemical equilibrium of this reaction has been published by J. Carrero-Manilla and M. Llano-Restrepo, Fluid Phase Equilib. 219: 181–193 (2004). Presented here are calculations for a single set of operating conditions, namely, $T = 600$ K, $P = 15$ bar, and a molar feed ratio $H_2/C_6H_6 = 3$, the stoichiometric value. For these conditions we determine the fractional conversion of benzene to cyclohexane. Carrero-Manilla and Llano-Restrepo express ln $K$ as a function of $T$ by an equation which for 600 K yields the value $K = 0.02874$.

A feed stream containing 3 mol H$_2$ for each 1 mol C$_6$H$_6$ is the basis of calculation, and for this single reaction, Eq. (4.361) becomes $n_i = n_i^n + n_x^n$, yielding

$$n_B = 1 - \varepsilon$$ benzene

$$n_H = 3 - 3\varepsilon$$ hydrogen

$$n_C = \varepsilon$$ cyclohexane

$$\sum n_i = 4 - 3\varepsilon$$

Each mole fraction is therefore given by $y_i = n_i/(4 - 3\varepsilon)$.

Assume first that the equilibrium mixture is an ideal gas, and apply Eq. (4.372), written for a single reaction, with subscript $j$ omitted and $v = 3$.

$$\prod_j y_j^{v_j} \left( \frac{P}{P^*} \right)^{v_j} = \left( \frac{1}{4 - 3\varepsilon} \right) \left( \frac{3}{4 - 3\varepsilon} \right)^3$$

whence

$$\prod_j y_j^{v_j} \left( \frac{P}{P^*} \right)^{v_j} = K = 0.02874$$ and $\varepsilon = 0.815$

Thus, the assumption of ideal gases leads to a calculated conversion of 81.5 percent.

An alternative assumption is that the equilibrium mixture is an ideal solution. This requires application of Eq. (4.371). However, in the case of an ideal solution Eq. (4.215) indicates that $\phi^x = \phi$, in which case Eq. (4.371) for a single reaction becomes

$$\prod_j y_j^{v_j} \left( \frac{P}{P^*} \right)^{v_j} = K$$

For purposes of illustration we evaluate the pure-species fugacity coefficients by Eq. (4.206), written here as

$$\phi = \exp(B_i + \omega_i B_i^B) \frac{P_i}{T_i}$$

The following table shows values for the various quantities in this equation. Note that $T_i$ and $P_i$ for hydrogen are effective values as calculated by Eqs. (4.124) and (4.125) and used with $\omega = 0$.

<table>
<thead>
<tr>
<th>$\text{C}_6\text{H}_6$</th>
<th>$T_i$</th>
<th>$P_i$</th>
<th>$P_i^*$</th>
<th>$\omega$</th>
<th>$B_i$</th>
<th>$B_i^B$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>562.2</td>
<td>1.067</td>
<td>48.98</td>
<td>0.306</td>
<td>0.21</td>
<td>0.2972</td>
<td>0.0078</td>
<td>0.891</td>
</tr>
<tr>
<td>4.28</td>
<td>14.009</td>
<td>19.78</td>
<td>0.758</td>
<td>0.00</td>
<td>0.139</td>
<td>1.004</td>
<td></td>
</tr>
<tr>
<td>553.6</td>
<td>1.084</td>
<td>40.73</td>
<td>0.368</td>
<td>0.21</td>
<td>0.2880</td>
<td>0.016</td>
<td>0.908</td>
</tr>
</tbody>
</table>
The equilibrium equation now becomes:

\[
\prod_i (\gamma_i \phi_i)^n \left( \frac{P}{P^0} \right)^{\gamma_i} = \left( \frac{\varepsilon}{4 - 3e} \right)^{0.919} \left( \frac{3 - 3e}{4 - 3e} \right)^{1.004} \left( \frac{15}{1} \right) = K = 0.02874
\]

Solution yields 
\[\varepsilon = 0.816\]

This result is hardly different from that based on the ideal gas assumption. The fugacity coefficients in the equilibrium equation clearly cancel one another. This result is hardly different from that based on the ideal gas assumption. The equilibrium equation now becomes:

\[
\sum_i \gamma_i \phi_i \mu_i = 0 \quad i = 1, 2, \ldots, N
\]  (4-383)

However, the chemical potential is given by Eq. (4-368); for gas-phase reactions and standard states as the pure ideal gases at \(P^0\), this equation becomes

\[
\mu_i = \Delta G_i^\circ + RT \ln \frac{\hat{f}_i}{P^0}
\]

If \(\Delta G_i^\circ\) is arbitrarily set equal to zero for all elements in their standard states, then for compounds \(\Delta G_i = \Delta G_i^\circ\), the standard Gibbs energy change of formation of species \(i\). In addition, the fugacity is eliminated—in favor of the fugacity coefficient by Eq. (4-204), \(\hat{f}_i = y_i \phi_i\). With these substitutions, the equation for \(\mu_i\) becomes

\[
\mu_i = \Delta G_i^\circ + RT \ln \frac{\hat{f}_i P}{P^0}
\]

Combination with Eq. (4-383) gives

\[
\Delta G_i^\circ + RT \ln \frac{\hat{f}_i P}{P^0} + \sum_k \lambda_k \phi_k = 0 \quad i = 1, 2, \ldots, N
\]  (4-384)

If species \(i\) is an element, \(\Delta G_i^\circ\) is zero. There are \(N\) equilibrium equations [Eqs. (4-384)], one for each chemical species, and there are \(\nu\) material balance equations [Eqs. (4-382)], one for each element—a total of \(N + \nu\) equations. The unknowns in these equations are the \(n_i\) (note that \(y_i = n_i/\Sigma n_i\)), of which there are \(N\), and the \(\lambda_k\), of which there are \(\nu\)—a total of \(N + \nu\) unknowns. Thus the number of equations is sufficient for the determination of all unknowns.

Equation (4-384) is derived on the presumption that the set \(\{\phi_i\}\) is known. If the phase is an ideal gas, then each \(\phi_i\) is unity. If the phase is an ideal solution, each \(\phi_i\) becomes \(\delta_i\) and can at least be estimated. For real gases, each \(\phi_i\) is a function of the set \(\{y_i\}\), the quantities being calculated. Thus an iterative procedure is indicated, initiated with each \(\phi_i\) set equal to unity. Solution of the equations then provides a preliminary set \(\{y_i\}\). For low pressures or high temperatures this result is usually adequate. Where it is not satisfactory, an equation of state with the preliminary set \(\{y_i\}\) gives a new and more nearly correct set \(\{\phi_i\}\) for use in Eq. (4-384). Then a new set \(\{y_i\}\) 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.


**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 wasted energy 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 obtained when the specific change of state is accomplished completely reversibly. The implications of this requirement are that

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 $T_a$. This may require Carnot engines or heat pumps internal to the system that provide for the reversible transfer of heat from the temperatures of the flowing fluid to that of the surroundings. Because Carnot engines and heat pumps are cyclic, they undergo no net change of state.

These conditions are implicit in the entropy balance of Eq. (4-156) when $\dot{S}_G = 0$. If in addition there is but a single surrounding temperature $T_o$, this equation becomes

$$\Delta(Sn)_o - \frac{\dot{Q}}{T_o} = 0 \quad (4-385)$$

The energy balance for a steady-state steady-flow process as given by Eq. (4-150) is

$$\Delta \left[ (H + \frac{1}{2} u^2 + zg) \dot{m} \right]_{ls} = \dot{Q} + W_s \quad (4-150)$$

Combining this equation with Eq. (4-385) to eliminate $\dot{Q}$ yields

$$\Delta \left[ (H + \frac{1}{2} u^2 + zg) \dot{m} \right]_{ls} = T_a \Delta(Sn)_o + W_s,(rev) \quad (4-386)$$

where $W_s,(rev)$ indicates that the shaft work is for a completely reversible process. This work is called the ideal work $W_{ideal}$. Thus

$$W_{ideal} = \Delta \left[ (H + \frac{1}{2} u^2 + zg) \dot{m} \right]_{ls} - T_a \Delta(Sn)_o \quad (4-386)$$

In most applications to chemical processes, the kinetic and potential energy terms are negligible compared with the others; in this event Eq. (4-386) is written as

$$W_{ideal} = \Delta(Hn)_o - T_a \Delta(Sn)_o \quad (4-387)$$

For the special case of a single stream flowing through the system, Eq. (4-387) becomes

$$W_{ideal} = \dot{m} (\Delta H - T_a S) \quad (4-388)$$

Division by $\dot{m}$ puts this equation on a unit-mass basis:

$$W_{ideal} = \Delta H - T_a S \quad (4-389)$$

A completely reversible process 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 (4-386) through (4-389) 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 $W_s$ (or $W_s,(rev)$) is given by an energy balance, and comparison can be made of the actual work with the ideal work. When $W_{ideal}$ (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 it is smaller than $W_s$. In this case a thermodynamic efficiency $\eta$ is defined as the ratio of the ideal work to the actual work:

$$\eta_{(work required)} = \frac{W_{ideal}}{W_s} \quad (4-390)$$

When $W_{ideal}$ (or $W_{ideal}$) is negative, $|W_{ideal}|$ is the maximum work obtainable from a given change in the properties of the flowing streams, and it is larger than $|W_s|$. In this case, the thermodynamic efficiency is defined as the ratio of the actual work to the ideal work:

$$\eta_{(work produced)} = \frac{W_s}{W_{ideal}} \quad (4-391)$$

**LOST WORK**

Work that is wasted as the result of irreversibilities in a process is called lost work $W_{lost}$, and it is defined as the difference between the actual work of a process and the ideal work for the process. Thus, definition,

$$W_{lost} = W_s - W_{ideal} \quad (4-392)$$

The rate form is

$$W_{lost} = \dot{m} (-\dot{W}_s) \quad (4-393)$$

The actual work rate comes from Eq. (4-150):

$$\dot{W}_s = \Delta \left( H + \frac{1}{2} u^2 + zg \right) \dot{m} - \dot{Q} \quad (4-394)$$

Subtracting the ideal work rate as given by Eq. (4-386) yields

$$W_{lost} = \dot{m} T_a \Delta(Sn)_o - \dot{Q} \quad (4-394)$$

For the special case of a single stream flowing through the control volume,

$$W_{lost} = \dot{m} T_a \Delta S - \dot{Q} \quad (4-395)$$

Division of this equation by $\dot{m}$ gives

$$W_{lost} = T_a \Delta S - Q \quad (4-396)$$

where the basis is now a unit amount of fluid flowing through the control volume.

The total rate of entropy generation (in both system and surroundings) as a result of a process is

$$\dot{S}_G = \Delta(Sn)_o - \frac{\dot{Q}}{T_a} \quad (4-397)$$

Division by $\dot{m}$ provides an equation based on a unit amount of fluid flowing through the control volume:

$$\dot{S}_G = \Delta S - \frac{Q}{T_a} \quad (4-398)$$

Equations (4-397) and (4-398) are special cases of Eqs. (4-156) and (4-157).

Multiplication of Eq. (4-397) by $T_a$ gives

$$T_a \dot{S}_G = T_a \Delta(Sn)_o - \dot{Q} \quad (4-399)$$

Because the right sides of this equation and of Eq. (4-394) are identical, it follows that

$$W_{lost} = T_a \dot{S}_G \quad (4-399)$$

For flow on the basis of a unit amount of fluid, this becomes

$$W_{lost} = T_a S_G \quad (4-400)$$

Because the second law of thermodynamics requires

$$\dot{S}_G \geq 0 \quad \text{and} \quad S_G \geq 0$$

therefore

$$W_{lost} \geq 0 \quad \text{and} \quad W_{lost} \geq 0$$

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, i.e., 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 generation 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. (4-399) for each step of the process and summing give

$$\sum W_{lost} = T_a \sum S_G$$
Dividing Eq. (4-399) by this result yields
\[ W_{\text{lost}} = S_g \sum W_{\text{lost}} = S_g \sum W_{\text{lost}} \]

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. (4-393), written as
\[ \sum W_{\text{lost}} = W_r - W_{\text{ideal}} \]  
(4-401)

For a work-requiring process, all these work quantities are positive and \( W_r > W_{\text{ideal}} \). The preceding equation is then expressed as
\[ W_r = W_{\text{ideal}} + \sum W_{\text{lost}} \]  
(4-402)

A work analysis then gives each of the individual work terms in the summation on the right as a fraction of \( W_r \).

For a work-producing process, \( W_r \) and \( W_{\text{ideal}} \) are negative, and \( |W_{\text{ideal}}| > |W_r| \). Equation (4-401) in this case is best written as
\[ |W_{\text{ideal}}| = |W_r| + \sum W_{\text{lost}} \]  
(4-403)

A work analysis here expresses each of the individual work terms on the right as a fraction of \( |W_{\text{ideal}}| \). A work analysis cannot be carried out in the case where a process is so inefficient that \( |W_{\text{ideal}}| \) is negative, indicating that the process should produce work, but \( W_r \) is positive, indicating that the process in fact requires work. A lost-work or entropy generation analysis is always possible.

Example 7: Lost-Work Analysis A work analysis follows for a simple Linde system for the separation of air into gaseous oxygen and nitrogen, as depicted in Fig. 4-10. Table 4-8 lists a set of operating conditions for the number of stages, here taken as 3.

Calculation of ideal work: If changes in kinetic and potential energies are neglected, Eq. (4-387) is applicable. From the tabulated data,
\[ \Delta(H)_{\text{in}} = (13,460)(0.1364) + (12,046)(0.8636) - (12,407)(1) = -144 \text{ J/K} \]
\[ \Delta(S)_{\text{in}} = (114.8)(0.1364) + (114.34)(0.8636) - (117.35)(1) = -2.4453 \text{ J/K} \]

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:
\[ W_r = \frac{m\gamma R T_1}{0.8(\gamma-1)} \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \]

where \( n \) = number of stages, here taken as 3
\( \gamma = \) ratio of heat capacities, here taken as 1.4
\( T_1 = \) initial absolute temperature, equal to 300 K
\( P_2/P_1 = \) overall pressure ratio, equal to 54.5
\( R = \) universal gas constant, equal to 8.314 J/(mol·K)

The efficiency factor of 0.8 is already included in the equation. Substitution of the remaining values gives
\[ W_r = \frac{(3)(1.4)(8.314)(300)}{(0.8)(0.4)} \left[ (54.5)^{4/3/1.4} - 1 \right] = 15,171 \text{ J} \]
The heat transferred to the surroundings during compression as a result of intercooling and aftercooling to 300 K is found from the first law:
\[ Q = n\Delta H - W_r = (12,046 - 12,407) = -15,171 = -15,532 \text{ J} \]

Calculation of lost work: Equation (4-394) may be applied to each of the major units of the process. For the compressor/cooler,
\[ W_{\text{lost}} = (300)([(82.98)(1) - (117.35)(1)] - (-15,532)) = 5221.0 \text{ J} \]

For the exchanger,
\[ W_{\text{lost}} = (300)([(114.34)(0.8636) + (52.08)(1)] - (75.82)(0.8636) - (83.69)(0.1364) - (82.98)(1)) = 2063.4 \text{ J} \]

Finally, for the rectifier,
\[ W_{\text{lost}} = (300)([(75.82)(0.8636) + (83.69)(0.1364) - (52.08)(1)] = 147 = 7297.0 \text{ J} \]

Work analysis: Because the process requires work, Eq. (4-402) 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.

<table>
<thead>
<tr>
<th>Point</th>
<th>( P, \text{ bar} )</th>
<th>( T, \text{ K} )</th>
<th>Composition</th>
<th>State</th>
<th>( H, \text{ J/mol} )</th>
<th>( S, \text{ J/(mol·K)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55.22</td>
<td>300</td>
<td>Air</td>
<td>Superheated</td>
<td>12,046</td>
<td>82.98</td>
</tr>
<tr>
<td>2</td>
<td>1.01</td>
<td>295</td>
<td>Pure O(_2)</td>
<td>Superheated</td>
<td>13,460</td>
<td>118.48</td>
</tr>
<tr>
<td>3</td>
<td>1.01</td>
<td>295</td>
<td>91.48% N(_2)</td>
<td>Superheated</td>
<td>12,074</td>
<td>114.34</td>
</tr>
<tr>
<td>4</td>
<td>55.22</td>
<td>147.2</td>
<td>Air</td>
<td>Superheated</td>
<td>5,650</td>
<td>52.08</td>
</tr>
<tr>
<td>5</td>
<td>1.01</td>
<td>79.4</td>
<td>91.48% N(_2)</td>
<td>Saturated vapor</td>
<td>5,773</td>
<td>75.82</td>
</tr>
<tr>
<td>6</td>
<td>1.01</td>
<td>90</td>
<td>Pure O(_2)</td>
<td>Saturated vapor</td>
<td>7,483</td>
<td>83.69</td>
</tr>
<tr>
<td>7</td>
<td>1.01</td>
<td>300</td>
<td>Air</td>
<td>Superheated</td>
<td>12,407</td>
<td>117.35</td>
</tr>
</tbody>
</table>


Thus, by Eq. (4-387),
\[ W_{\text{ideal}} = -144 - (300)(-2.4453) = 589.6 \text{ J} \]

The thermodynamic efficiency of this process as given by Eq. (4-390) is only 3.9 percent. Significant inefficiencies reside with each of the primary units of the process.