

2 FUNDAMENTAL CONSIDERATIONS

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2.1 INTRODUCTION

This chapter provides a thermodynamic toolbox and contains most of the important basic relations that are used in other chapters. The scope is restricted almost exclusively to the second law of thermodynamics and its consequence, but the treatment is still intended to be exemplary rather than definitive. New results are not presented as befits a discussion of fundamentals which are necessarily invariant with time.

2.2 BASIC THERMODYNAMICS

The state of a system may be described in terms of a small number of variables. For a phase in the absence of any external field, the second law of thermodynamics may be written as

$$dU = TdS - pdV + \sum_i \mu_i dn_i \quad (2.1)$$

This equation shows that the change dU in the energy U may be described in terms of simultaneous changes dS in the entropy S , dV in the volume V , and dn_i in the amounts n_i of the C components. It is often convenient to eliminate the size of the phase by writing Equation (2.1) in terms of intensive variables. For example, division by the total amount

$$N = \sum_i n_i \quad (2.2)$$

gives

$$dU_m = TdS_m - pdV_m + \sum_i \mu_i dx_i \quad (2.3)$$

where the subscript $_m$ denotes a molar quantity and the mole fraction of component i is defined by

$$x_i = n_i/N \quad (2.4)$$

Equation (2.1), or Equation (2.3) for intensive variables, is the most fundamental expression of the second law of thermodynamics. However, entropy, in particular, is not a very convenient experimental variable and, consequently, alternative forms have been derived from the fundamental equation (2.1). Introduction of the following characteristic functions:

$$\text{Enthalpy} \quad H = U + pV \quad (2.5)$$

$$\text{Hemholtz energy} \quad A = U - TS \quad (2.6)$$

$$\text{Gibbs energy} \quad G = U + pV - TS = H - TS = A + pV \quad (2.7)$$

and use of Legendre transformations (1,2) with the fundamental equation (2.1) gives the following alternative forms of the second law

$$dH = TdS + Vdp + \sum_i \mu_i dn_i \quad (2.8)$$

$$dA = -SdT - pdV + \sum_i \mu_i dn_i \quad (2.9)$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i \quad (2.10)$$

Another modification of Equation (2.1), frequently used in statistical mechanics, is

$$d(pV) = SdT + pdV + \sum_i n_i d\mu_i \quad (2.11)$$

or, as the Gibbs-Duhem equation, in the study of phase equilibria

$$0 = SdT - Vdp + \sum_i n_i d\mu_i \quad (2.12)$$

From Equation (2.1) and Equations (2.8) - (2.10) it can be seen that

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,\hat{n}_i} = \left(\frac{\partial H}{\partial n_i} \right)_{S,p,\hat{n}_i} = \left(\frac{\partial A}{\partial n_i} \right)_{T,V,\hat{n}_i} = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,\hat{n}_i} \quad (2.13)$$

where the subscripted \hat{n}_i means that the amounts n_j of all the components are constant except for component i . The quantity μ_i is the chemical potential of species i . In terms of intensive variables these equations are

$$dH_m = TdS_m + V_m dp + \sum_i \mu_i dx_i \quad (2.14)$$

$$dA_m = -S_m dT - p dV_m + \sum_i \mu_i dx_i \quad (2.15)$$

$$dG_m = -S_m dT + V_m dp + \sum_i \mu_i dx_i \quad (2.16)$$

$$d(pV_m) = S_m dT + p dV_m + \sum_i n_i d\mu_i \quad (2.17)$$

$$0 = S_m dT - V_m dp + \sum_i x_i d\mu_i \quad (2.18)$$

For a system of constant composition, Equation (2.1) and Equations (2.8) - (2.10) reduce to

$$dU = TdS - pdV \quad (2.19)$$

$$dH = TdS + Vdp \quad (2.20)$$

$$dA = -SdT - pdV \quad (2.21)$$

$$dG = -SdT + Vdp \quad (2.22)$$

A large number of thermodynamic relations may be derived from the above equations by conventional manipulations. Table 2.1 summarizes the most frequently used equations.

Table 2.1 Frequently used thermodynamic relationships with general validity.

$$dU = TdS - pdV$$

$$dA = -SdT - pdV$$

$$dH = TdS + Vdp$$

$$dG = -SdT + Vdp$$

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

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

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

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

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 p}{\partial T^2} \right)_V$$

$$\left(\frac{\partial C_P}{\partial p} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$$

$$C_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = -T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial p}{\partial V} \right)_T$$

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial p}{\partial V} \right)_S$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

$$\kappa_T - \kappa_S = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial p} \right)_S = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial T}{\partial S} \right)_P$$

Maxwell:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

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

Helmholtz:

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p \quad \left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p$$

Gibbs-Helmholtz:

$$\left\{ \frac{\partial(A/T)}{\partial T} \right\}_V = - \frac{U}{T^2} \quad \left\{ \frac{\partial(G/T)}{\partial T} \right\}_p = - \frac{H}{T^2}$$

2.2.1 Homogeneous Functions

A homogeneous function F of the first order in any number of the variables x, y, z, \dots is defined by:

$$F(\lambda x, \lambda y, \lambda z, \dots) = \lambda F(x, y, z, \dots) \quad (2.21)$$

where λ is an arbitrary number. If each independent variable is made λ times larger, the function F increases λ times. For large enough systems, all extensive thermodynamic properties are homogeneous and of the first order in amounts n_i at fixed temperature and pressure. For homogeneous functions of the first order, Euler's theorem applies:

$$\lambda F(x, y, z, \dots) = x \left(\frac{\partial F}{\partial x} \right)_{y,z,\dots} + y \left(\frac{\partial F}{\partial y} \right)_{x,z,\dots} + z \left(\frac{\partial F}{\partial z} \right)_{x,y,\dots} + \dots \quad (2.22)$$

Equation (2.22) relates the value of the function to the values of its derivatives. For $\lambda = 1$, Equation (2.22) reduces to:

$$F(x, y, z, \dots) = x \left(\frac{\partial F}{\partial x} \right)_{y,z,\dots} + y \left(\frac{\partial F}{\partial y} \right)_{x,z,\dots} + z \left(\frac{\partial F}{\partial z} \right)_{x,y,\dots} + \dots \quad (2.23)$$

By applying Euler's theorem to the various characteristic functions $U = U(S, V, n_1, n_2, \dots)$, $H = H(S, p, n_1, n_2, \dots)$, $A = A(V, T, n_1, n_2, \dots)$ and $G = G(p, T, n_1, n_2, \dots)$, respectively, the following expressions result

$$U = TS - pV + \sum_i n_i \mu_i \quad (2.24)$$

$$H = TS + \sum_i n_i \mu_i \quad (2.25)$$

$$A = -pV + \sum_i n_i \mu_i \quad (2.26)$$

$$G = \sum_i n_i \mu_i \quad (2.27)$$

For further details on Euler's theorem see references 1-3.

2.2.2 Thermodynamic Properties from Differentiation of Fundamental Equations

The quantities $U(S, V, n_1, n_2, \dots)$, $H(S, p, n_1, n_2, \dots)$, $A(T, V, n_1, n_2, \dots)$, and $G(T, p, n_1, n_2, \dots)$ are examples of thermodynamic potentials from which all properties of a system can be obtained without the need for integration. For example, Equation (2.10) gives directly the heat capacity at constant pressure

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{p,n} = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{p,n}$$

and the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,n} = - \left(\frac{\partial^2 G}{\partial p^2} \right)_{T,n} \bigg/ \left(\frac{\partial G}{\partial p} \right)_{T,n}$$

The avoidance of integration is often an advantage in theoretical applications of thermodynamics because there are no troublesome constants of integration. On the other hand, very often the derivatives needed involve variables that are difficult to measure experimentally. Even with the Gibbs energy surface, which is closely linked to the convenient experimental variables of temperature, pressure and composition, differences in the Gibbs energy can be studied only at equilibrium. At constant composition the characteristic functions $U = U(S, V, n_1, n_2, \dots)$,

$H = H(S, p, n_1, n_2, \dots)$, $A = A(V, T, n_1, n_2, \dots)$ and $G = G(p, T, n_1, n_2, \dots)$ reduce to $U = U(S, V)$, $H = H(S, p)$, $A = A(V, T)$ and $G = G(p, T)$. By differentiation of these functions and use of the fundamental equations (2.5) and (2.18) - (2.20), the value of any thermodynamic property can be expressed in terms of the derivatives of each characteristic function. Table 2.2 summarizes the most relevant results. Further details can be found elsewhere (3).

2.3 Deviation Functions

Almost all definitions of molar properties for mixtures lack an unambiguous definition in the sense that they can be related directly to measurable properties. Therefore, it is common practice to compare an actual mixture property with its corresponding value obtained from an arbitrary model, for instance, an equation of state. This approach leads to the introduction of deviation functions. For a general mixture molar property M_m the deviation function is defined by (4):

$$M_m^D = M_m^{\text{actual}} - M_m^{\text{model}} \quad (2.28)$$

An important aspect in this definition is the choice of the independent variables. Almost all analytical equations of state are expressions explicit in pressure: that is, temperature, molar volume (or density) and composition $x = x_1, x_2, \dots$ are the natural independent variables. Therefore, Equation (2.28) can be rewritten into:

$$M^D(T, V, n) = M^{\text{actual}}(T, V, n) - M^{\text{model}}(T, V, n) \quad (2.29)$$

where n denotes the amounts n_1, n_2, \dots . The value of M obtained from the model is evaluated at the same values of the independent variables as used for the actual mixture property. Alternatively, although not of direct interest for equation-of-state models, temperature, pressure and composition may be a suitable choice as independent variables for deviation functions, *i.e.*:

$$M^D(T, p, n) = M^{\text{actual}}(T, p, n) - M^{\text{model}}(T, p, n) \quad (2.30)$$

In this case the value of M obtained from the model is evaluated at the same values of T, p , and n as used for the actual mixture property. Both approaches are interrelated as follows (4):

$$M^D(T, V, n) = M^D(T, p, n) + \int_{p_r}^p \left(\frac{\partial M^{\text{model}}}{\partial p} \right)_{T, n} dp \quad (2.31)$$

In this equation p_r is the reference pressure at which the molar volume of the mixture obtained from the model is equal to molar volume of the actual mixture at the same temperature and composition as the mixture. A necessary feature of the model is that such a p_r exists.

Table 2.2 Thermodynamic properties expressed in derivatives of the characteristic functions.

	$U(S,V)$	$H(p,S)$	$A(T,V)$	$G(T,p)$
p	$-\left(\frac{\partial U}{\partial V}\right)_S$		$-\left(\frac{\partial A}{\partial V}\right)_S$	
V		$\left(\frac{\partial H}{\partial p}\right)_S$		$\left(\frac{\partial G}{\partial p}\right)_T$
T	$\left(\frac{\partial U}{\partial S}\right)_V$	$\left(\frac{\partial H}{\partial S}\right)_p$		
S			$-\left(\frac{\partial A}{\partial T}\right)_V$	$-\left(\frac{\partial G}{\partial T}\right)_p$
U		$H - p\left(\frac{\partial H}{\partial p}\right)_S$	$A - T\left(\frac{\partial A}{\partial T}\right)_V$	$G - p\left(\frac{\partial G}{\partial p}\right)_T - T\left(\frac{\partial G}{\partial T}\right)_p$
H	$U - V\left(\frac{\partial U}{\partial V}\right)_S$		$A - T\left(\frac{\partial A}{\partial T}\right)_V - V\left(\frac{\partial A}{\partial V}\right)_S$	$G - T\left(\frac{\partial G}{\partial T}\right)_p$
A	$U - S\left(\frac{\partial U}{\partial S}\right)_V$	$H - S\left(\frac{\partial H}{\partial S}\right)_p - p\left(\frac{\partial H}{\partial p}\right)_S$		$G - p\left(\frac{\partial G}{\partial p}\right)_T$

Table 2.2 Thermodynamic properties expressed in derivatives of the characteristic functions (cont.)

G	$U - V\left(\frac{\partial U}{\partial V}\right)_S - S\left(\frac{\partial U}{\partial S}\right)_V$	$H - S\left(\frac{\partial H}{\partial S}\right)_p$	$A - V\left(\frac{\partial A}{\partial V}\right)_S$
C_p		$\frac{(\partial H/\partial S)_p}{(\partial^2 H/\partial S^2)_p}$	$-T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$
C_v	$\frac{(\partial U/\partial S)_V}{(\partial^2 U/\partial S^2)_V}$		$-T\left(\frac{\partial^2 A}{\partial T^2}\right)_V$
κ_T			$\left\{V\left(\frac{\partial^2 A}{\partial V^2}\right)_T\right\}^{-1}$
κ_S	$\left\{V\left(\frac{\partial^2 U}{\partial V^2}\right)_S\right\}^{-1}$	$-\frac{(\partial^2 H/\partial p^2)_S}{(\partial H/\partial p)_S}$	$-\frac{(\partial^2 G/\partial p^2)_T}{(\partial G/\partial p)_T}$

2.3.1 Residual Functions

As pointed out in the previous section, the calculation of deviation functions requires a choice of an appropriate model. If the model system is chosen to be an ideal gas mixture, which is an obvious choice for fluid mixtures, then the deviation functions are called *residual functions*. With temperature, volume, and composition as independent variables Equation (2.29) becomes

$$M^D(T, V, n) = M^R(T, V, n) = M^{\text{actual}}(T, V, n) - M^{\text{ig}}(T, V, n) \quad (2.32)$$

or with T and p as independent variables

$$M^D(T, p, n) = M^R(T, p, n) = M^{\text{actual}}(T, p, n) - M^{\text{ig}}(T, p, n) \quad (2.33)$$

which is a particular form of Equation (2.30). The two sets of residual functions are related by Equation (2.31) in the form:

$$M^R(T, V, n) = M^R(T, p, n) + \int_{p_r}^p \left(\frac{\partial M^{\text{ig}}}{\partial p} \right)_{T, n} dp \quad (2.34)$$

where the reference pressure $p_r = RT/V_m$ is sufficiently low for the thermodynamic property M of the real fluid to have the ideal-gas value.

Some thermodynamic properties (U , H , C_v and C_p) of an ideal gas are independent of pressure, while, others like S , A and G are not. Consequently, from Equation (2.33), it can be seen easily that the following equations hold:

$$U^R(T, V, n) = U^R(T, p, n) \quad (2.35)$$

$$H^R(T, V, n) = H^R(T, p, n) \quad (2.36)$$

$$C_v^R(T, V, n) = C_v^R(T, p, n) \quad (2.37)$$

$$C_p^R(T, V, n) = C_p^R(T, p, n) \quad (2.38)$$

$$S^R(T, V, n) = S^R(T, p, n) = R \ln Z \quad (2.39)$$

$$A^R(T, V, n) = A^R(T, p, n) + RT \ln Z \quad (2.40)$$

$$G^R(T, V, n) = G^R(T, p, n) + RT \ln Z \quad (2.41)$$

with $Z = pV/nRT$ as the compression factor.

2.3.2 Evaluation of Residual Functions

With temperature, molar volume and composition as the independent variables, general expressions for the residual functions of thermodynamic properties are readily obtained from Equation (2.32). Abbott and Nass (4) have given a definitive list of expressions for various properties as residual functions and these are summarised in Table 2.3.

For temperature, pressure and compositions as the independent variables, Abbott and Nass (4) also evaluated general expressions for the residual functions. Table 2.4 summarizes the results. For further details see references 2 and 4.

2.4 Mixing and Departure Functions

In terms of the independent variables, temperature, pressure and composition, departure functions compare the value of a general thermodynamic property $M(T, p, n)$ with the corresponding property in the ideal-gas state and at a reference pressure p_r , that is $M^{\text{ig}}(T, p_r, n)$. According to the ideal gas law, the reference pressure p_r is related to the reference volume $V_r = nRT/p_r$. Similarly, as was the case for the residual functions, the independent variables, temperature, molar volume and composition can also be used to define departure functions. Based on these independent variables, the general thermodynamic property $M(T, V, n)$ is compared with the corresponding ideal-gas property $M^{\text{ig}}(T, V, n)$.

2.4.1 Departure Functions with Temperature, Molar Volume and Composition as the Independent Variables

The following equality can be derived for the departure function of a general thermodynamic property $M(T, V, n)$:

$$M(T, V, n) - M^{\text{ig}}(T, V_r, n) = \int_{\infty}^V \left\{ \left(\frac{\partial M}{\partial V} \right)_{T, n} - \left(\frac{\partial M^{\text{ig}}}{\partial V} \right)_{T, n} \right\} dV + \int_{V_r}^V \left(\frac{\partial M^{\text{ig}}}{\partial V} \right)_{T, n} dV \quad (2.42)$$

Applying conventional thermodynamic manipulations on Equation (2.42), the following relations can be obtained:

$$U - U^{\text{ig}} = \int_{\infty}^V \left\{ T \left(\frac{\partial p}{\partial T} \right)_{V, n} - p \right\} dV \quad (2.43)$$

$$H - H^{\text{ig}} = \int_{\infty}^V \left\{ T \left(\frac{\partial p}{\partial T} \right)_{V, n} - p \right\} dV + nRT(Z-1) \quad (2.44)$$

Table 2.3 Residual functions with volume or density as an independent variable. $(\rho = n/V \text{ and } Z = pV/nRT).$

$M^R(T, V, n)$	Residual Function
$U^R =$	$- nRT^2 \int_0^{\rho} \left(\frac{\partial Z}{\partial T} \right)_{\rho, n} \frac{d\rho}{\rho}$
$H^R =$	$- nRT^2 \int_0^{\rho} \left(\frac{\partial Z}{\partial T} \right)_{\rho, n} \frac{d\rho}{\rho} + nRT(Z - 1)$
$S^R =$	$- nR \int_0^{\rho} \left\{ T \left(\frac{\partial Z}{\partial T} \right)_{\rho, n} + Z - 1 \right\} \frac{d\rho}{\rho}$
$A^R =$	$nRT \int_0^{\rho} (Z-1) \frac{d\rho}{\rho}$
$G^R =$	$nRT \int_0^{\rho} (Z-1) \frac{d\rho}{\rho} + nRT(Z - 1)$
$C_V^R =$	$- RT \int_0^{\rho} \left\{ T \left(\frac{\partial^2 Z}{\partial T^2} \right)_{\rho, n} + 2 \left(\frac{\partial Z}{\partial T} \right)_{\rho, n} \right\} \frac{d\rho}{\rho}$
$C_P^R =$	$C_V^R - R + R \left\{ Z + T \left(\frac{\partial Z}{\partial T} \right)_{\rho, n} \right\}^2 \left\{ Z + \rho \left(\frac{\partial Z}{\partial \rho} \right)_{T, n} \right\}^{-1}$
$p^R =$	$\rho RT(Z - 1)$

Table 2.4 Residual functions with pressure as the independent variable. ($\rho = n/V$ and $Z = pV/nRT$).

$M^R(T, p, n)$	Residual Function
$U^R =$	$- nRT^2 \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_{p,n} \frac{dp}{p} - nRT(Z - 1)$
$H^R =$	$- nRT^2 \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_{p,n} \frac{dp}{p}$
$S^R =$	$- nR \int_0^\rho \left\{ T \left(\frac{\partial Z}{\partial T} \right)_{p,n} + Z - 1 \right\} \frac{dp}{p}$
$A^R =$	$nRT \int_0^\rho (Z - 1) \frac{dp}{p} - nRT(Z - 1)$
$G^R =$	$nRT \int_0^\rho (Z - 1) \frac{dp}{p}$
$C_V^R =$	$- RT \int_0^\rho \left\{ T \left(\frac{\partial^2 Z}{\partial T^2} \right)_{p,n} + 2 \left(\frac{\partial Z}{\partial T} \right)_{p,n} \right\} \frac{dp}{p}$
$C_p^R =$	$C_V^R - R + R \left\{ Z + T \left(\frac{\partial Z}{\partial T} \right)_{p,n} \right\}^2 \left\{ Z + \rho \left(\frac{\partial Z}{\partial \rho} \right)_{T,n} \right\}^{-1}$
$p^R =$	$\frac{RT}{p}(Z - 1)$

$$S - S^{\text{ig}} = \int_{\infty}^V \left\{ \left(\frac{\partial p}{\partial T} \right)_{V,n} - \frac{nR}{V} \right\} dV + nR \ln \left(\frac{V}{V_r} \right) \quad (2.45)$$

Note, that if the reference volume V_r is replaced by the actual volume V of the system, then the corresponding residual functions are recovered (Table 2.3).

$$A - A^{\text{ig}} = \int_{\infty}^V \left(p - \frac{nRT}{V} \right) dV - nRT \ln \left(\frac{V}{V_r} \right) \quad (2.46)$$

$$G - G^{\text{ig}} = - \int_{\infty}^V \left(p - \frac{nRT}{V} \right) dV - nRT \ln \left(\frac{V}{V_r} \right) + nRT(Z - 1) \quad (2.47)$$

The thermodynamic properties for the reference state are defined by the following relations:

$$U^{\text{ig}} = \sum_i n_i U_i^{\text{ig}} = \sum_i n_i H_i^{\text{ig}} - nRT \sum_i n_i \quad (2.48)$$

$$S^{\text{ig}} = \sum_i n_i S_i^{\text{ig}} - R \sum_i n_i \ln n_i \quad (2.50)$$

$$H^{\text{ig}} = \sum_i n_i H_i^{\text{ig}} \quad (2.49)$$

$$A^{\text{ig}} = \sum_i n_i A_i^{\text{ig}} + RT \sum_i n_i \ln n_i = \sum_i n_i H_i^{\text{ig}} - T \sum_i n_i S_i^{\text{ig}} - RT \sum_i n_i + RT \sum_i n_i \ln n_i \quad (2.51)$$

$$G^{\text{ig}} = \sum_i n_i G_i^{\text{ig}} + RT \sum_i n_i \ln n_i = \sum_i n_i H_i^{\text{ig}} - T \sum_i n_i S_i^{\text{ig}} + RT \sum_i n_i \ln n_i \quad (2.52)$$

From Equations (2.48) through (2.52), the following mixture properties for ideal gases are obtained:

$$\Delta_{\text{mix}} U = U^{\text{ig}} - \sum_i n_i U_i^{\text{ig}} = 0 \quad (2.53)$$

$$\Delta_{\text{mix}} H = H^{\text{ig}} - \sum_i n_i H_i^{\text{ig}} = 0 \quad (2.54)$$

$$\Delta_{\text{mix}} S = S^{\text{ig}} - \sum_i n_i S_i^{\text{ig}} = - R \sum_i n_i \ln n_i \quad (2.55)$$

$$\Delta_{\text{mix}} A = A^{\text{ig}} - \sum_i n_i A_i^{\text{ig}} = RT \sum_i n_i \ln n_i \quad (2.56)$$

$$\Delta_{\text{mix}} G = G^{\text{ig}} - \sum_i n_i G_i^{\text{ig}} = RT \sum_i n_i \ln n_i \quad (2.57)$$

Departure functions are conveniently evaluated from Equation (2.46) as the generating

function. The following calculation procedure is the appropriate route to follow:

1. Equation (2.46) gives $(A - A^{\text{ig}})$

$$2. (S - S^{\text{ig}}) = - \left(\frac{\partial(A - A^{\text{ig}})}{\partial T} \right)_{V,n} \quad (2.58)$$

$$3. (U - U^{\text{ig}}) = (A - A^{\text{ig}}) + T(S - S^{\text{ig}}) \quad (2.59)$$

$$4. (H - H^{\text{ig}}) = (A - A^{\text{ig}}) + T(S - S^{\text{ig}}) + nRT(Z - 1) \quad (2.60)$$

$$5. (G - G^{\text{ig}}) = (A - A^{\text{ig}}) + nRT(Z - 1) \quad (2.61)$$

2.4.2 Departure Functions with temperature, Pressure and Composition as the Independent Variables

In this case, the general thermodynamic property is $M(T, p, x)$ and the following equality for the departure function can be derived:

$$M(T, p, n) - M^{\text{ig}}(T, p_r, n) = \int_0^p \left\{ \left(\frac{\partial M}{\partial p} \right)_{T,n} - \left(\frac{\partial M^{\text{ig}}}{\partial p} \right)_{T,n} \right\} dp + \int_{p_r}^p \left(\frac{\partial M^{\text{ig}}}{\partial p} \right)_{T,n} dp \quad (2.62)$$

The following relations can be obtained from Equation (2.62):

$$U - U^{\text{ig}} = \int_0^p \left\{ V - T \left(\frac{\partial V}{\partial T} \right)_{p,n} \right\} dp - nRT(Z - 1) \quad (2.63)$$

$$H - H^{\text{ig}} = \int_0^p \left\{ V - T \left(\frac{\partial V}{\partial T} \right)_{p,n} \right\} dp \quad (2.64)$$

$$S - S^{\text{ig}} = \int_0^p \left\{ \frac{nR}{p} - T \left(\frac{\partial V}{\partial T} \right)_{p,n} \right\} dp - nR \ln \left(\frac{p}{p_r} \right) \quad (2.65)$$

$$A - A^{\text{ig}} = \int_0^p \left\{ V - \frac{nRT}{p} \right\} dp - nRT(Z - 1) + nRT \ln \left(\frac{p}{p_r} \right) \quad (2.66)$$

$$G - G^{\text{ig}} = \int_0^p \left\{ V - \frac{nRT}{p} \right\} dp + nRT \ln \left(\frac{p}{p_r} \right) \quad (2.67)$$

Note, if the reference pressure p_r is replaced by the actual pressure p of the system, then the corresponding residual functions are recovered (Table 2.4).

Again, the thermodynamic properties for the reference state can be obtained from the Equations (2.48) - (2.52). In order to obtain the departure functions for this set of independent variables, the following procedure is recommended:

1. Equation (2.67) gives $(G - G^{ig})$

$$2. (S - S^{ig}) = - \left\{ \frac{\partial(G - G^{ig})}{\partial T} \right\}_{p,n} \quad (2.68)$$

$$3. (U - U^{ig}) = (G - G^{ig}) + T(S - S^{ig}) - nRT(Z - 1) \quad (2.69)$$

$$4. (H - H^{ig}) = (G - G^{ig}) + T(S - S^{ig}) \quad (2.70)$$

$$5. (A - A^{ig}) = (G - G^{ig}) - nRT(Z - 1) \quad (2.71)$$

Further details on departure functions can be found elsewhere (5).

2.5 Mixing and Excess Functions

Deviation functions for mixtures are concerned mainly with variation in composition rather than pressure or density. Consequently, it is convenient to use molar quantities. Molar excess functions are defined by

$$M_m^E = M_m^D = M_m^{\text{actual}} - M_m^{\text{id}} \quad (2.72)$$

where M_m^{id} is the molar value for the ideal mixture at the same temperature and pressure. If, for example, $M^{\text{id}} = V^{\text{id}}$ then the molar volume of the ideal mixture (id) is given by

$$V_m^{\text{id}} = \sum_i x_i V_i^* \quad (2.73)$$

where V_i^* is the molar volume of pure component i .

Other thermodynamic properties for ideal mixtures are defined by:

$$U_m^{\text{id}} = \sum_i x_i U_i^* \quad (2.74)$$

$$H_m^{\text{id}} = \sum_i x_i H_i^* \quad (2.75)$$

$$S_m^{\text{id}} = \sum_i x_i S_i^* - R \sum_i x_i \ln x_i \quad (2.76)$$

$$A_m^{\text{id}} = \sum_i x_i A_i^* + RT \sum_i x_i \ln x_i \quad (2.77)$$

$$G_m^{\text{id}} = \sum_i x_i G_i^* + RT \sum_i x_i \ln x_i \quad (2.78)$$

From Equations (2.73) through (2.78), it readily can be seen that for the mixing properties

the following expressions hold:

$$\Delta_{\text{mix}} V_m = V_m^{\text{id}} - \sum_i x_i V_i^* = 0 \quad (2.79)$$

$$\Delta_{\text{mix}} U_m = U_m^{\text{id}} - \sum_i x_i U_i^* = 0 \quad (2.80)$$

$$\Delta_{\text{mix}} H_m = H_m^{\text{id}} - \sum_i x_i H_i^* = 0 \quad (2.81)$$

$$\Delta_{\text{mix}} S_m = S_m^{\text{id}} - \sum_i x_i S_i^* = -R \sum_i x_i \ln x_i \quad (2.82)$$

$$\Delta_{\text{mix}} A_m = A_m^{\text{id}} - \sum_i x_i A_i^* = RT \sum_i x_i \ln x_i \quad (2.83)$$

$$\Delta_{\text{mix}} G_m = G_m^{\text{id}} - \sum_i x_i G_i^* = RT \sum_i x_i \ln x_i \quad (2.84)$$

Again an important aspect in this definition is the choice of the independent variables. From Equation (2.72) two different definitions of excess functions can be obtained:

$$M^{\text{E}}(T, V, n) = M(T, V, n) - M^{\text{id}}(T, V, n) \quad (2.85)$$

$$M^{\text{E}}(T, p, n) = M(T, p, n) - M^{\text{id}}(T, p, n) \quad (2.86)$$

The two approaches are related by

$$M_m^{\text{E}}(T, V, n) = M_m^{\text{E}}(T, p, n) + \int_{p_r}^p \left(\frac{\partial M_m^{\text{id}}}{\partial p} \right)_{T, x} dp \quad (2.87)$$

Abbott and Nass (4) pointed out that in this case p is the pressure for which the molar volume of the ideal solution is the same as that of the real solution at given temperature and composition. This pressure is obtained by solving

$$V_m(T, p, x) = \sum_i x_i V_i^*(T, p_r) \quad (2.88)$$

A required feature of the model is that Equation (2.88) can be solved for the pressure. For Equation (2.87), Abbott and Nass (4) proposed an approximate relation suitable for practical purposes:

$$M_m^{\text{E}}(T, V, n) = M_m^{\text{E}}(T, p, n) + \left(\frac{\partial M_m^{\text{id}}}{\partial p} \right)_{T, x} \left(\frac{V_m^{\text{E}}}{\sum_i x_i \kappa_i^* V_i^*} \right) \quad (2.89)$$

In Equation (2.89), κ_i^* is the isothermal compressibility of pure i :

$$\kappa_i^* = - \frac{1}{V_i^*} \left(\frac{\partial V_i^*}{\partial p} \right)_T \quad (2.90)$$

Based on Equation (2.89), Abbott and Nass (4) summarize expressions for the various thermodynamic properties.

Excess functions and residual functions are related. From Equations (2.33) and (2.86), it can be seen that the following equality holds:

$$M^E(T, p, n) = M^R(T, p, n) - \{M^d(T, p, n) - M^ig(T, p, n)\} \quad (2.91)$$

Considering Equations (2.48) to (2.52) and (2.74) to (2.78), one can see readily that for an arbitrary extensive thermodynamic property the following relation holds:

$$M^E(T, p, n) = M^R(T, p, n) - \left\{ \sum_i x_i M_i(T, p, n) - \sum_i x_i M_i^{ig}(T, p, n) \right\} \quad (2.92)$$

2.6 Partial Molar Properties

A partial molar property M_i of an arbitrary extensive thermodynamic property $M = M(T, p, n_1, n_2, \dots)$ is defined by the equation:

Partial molar properties give information about the change of the total property due to addition of

$$M_i = \left(\frac{\partial M}{\partial n_i} \right)_{T, p, \hat{n}_i} \quad (2.93)$$

an infinitely small amount of species i to the mixture. From Equation (2.17) it becomes apparent that, by definition, the chemical potential is the partial molar Gibbs energy, *i.e.*, $\mu_i = G_i$. For this arbitrary thermodynamic property M the following expressions can be derived (2):

$$dM = \left(\frac{\partial M}{\partial p} \right)_{T, n} dp + \left(\frac{\partial M}{\partial T} \right)_{p, n} dT + \sum_i M_i dn_i \quad (2.94)$$

where $M = \sum_i n_i M_i$, or equivalently,

$$M_m = \sum_i x_i M_i \quad (2.95)$$

From Equations (2.94) and (2.95) the generalized Gibbs-Duhem equation is readily obtained:

$$\left(\frac{\partial M}{\partial p} \right)_{T, n} dp + \left(\frac{\partial M}{\partial T} \right)_{p, n} dT - \sum_i n_i dM_i = 0 \quad (2.96)$$

In the case, when $M = G$, Equation (2.12) is recovered.

2.7 Fugacity and Fugacity Coefficients

The fugacity of a real fluid mixture with constant composition and at constant temperature is defined by the equation:

$$dG = RT \ln f \quad (2.97)$$

Combination of this equation with its ideal gas equivalent leads to:

$$d(G - G^{\text{ig}}) = dG^{\text{R}} = RT \ln \left(\frac{f}{p} \right) = RT d \ln \phi \quad (2.98)$$

In this equation G^{R} is the residual Gibbs energy and ϕ is the fugacity coefficient. Integration of Equation (2.98) yields:

$$G^{\text{R}} = RT \ln \phi \quad (2.99)$$

Comparison of Equation (2.97) and its equivalent in Table 2.4 leads to:

$$\ln \phi = \int_0^p (Z-1) d \frac{f}{p} \quad (2.100)$$

This expression shows that an equation of state can be used to evaluate the fugacity coefficient. Similar expressions hold for an arbitrary pure component i :

$$dG_i = RT \ln f_i \quad (2.101)$$

and:

$$G_i^{\text{R}} = RT \ln \phi_i \quad (2.102)$$

In a real solution for species i the defining equation reads:

$$dG_i = RT \ln \hat{f}_i \quad (2.103)$$

From the definition of the residual Gibbs energy $G^{\text{R}} = G - G^{\text{ig}}$, it follows that:

$$G_i^{\text{R}} = G_i - G_i^{\text{ig}} \quad (2.104)$$

and for an ideal gas at constant temperature it holds that:

$$\mu_i = G_i^{\text{ig}} + RT \ln y_i \quad (2.105)$$

From Equations (2.103) through (2.105) the following expression results:

$$d(G_i - G_i^{\text{ig}}) = dG_i^{\text{R}} = RT \ln \left(\frac{\hat{f}_i}{y_i p} \right) = RT d \ln \hat{\phi}_i \quad (2.106)$$

Note that from Equation (2.106) the relationship between the fugacity \hat{f}_i and the fugacity-coefficient $\hat{\phi}_i$ in the mixture for component i follows:

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i p} \quad (2.107)$$

Integration of Equation (2.106) leads to a similar expression as represented by Equation (2.102):

$$G_i^R = RT \ln \hat{\phi}_i \quad (2.108)$$

For $M = G$, Equation (2.93) can be rewritten into:

$$G_i^R = \left(\frac{\partial(nG^R)}{\partial n_i} \right)_{T,p,\hat{n}_i} \quad (2.109)$$

Substitution of Equations (2.102) and (2.108) into Equation (2.109) gives:

$$\ln \hat{\phi}_i = \left(\frac{\partial(\ln \phi)}{\partial n_i} \right)_{T,p,\hat{n}_i} \quad (2.110)$$

Since $\ln \hat{\phi}_i$ is related to $\ln \phi_i$ as a partial molar property, from Equation (2.95) the following relation holds:

$$\ln \phi = \sum_i x_i \ln \hat{\phi}_i \quad (2.111)$$

At constant temperature and pressure, the following Gibbs-Duhem equation can be obtained from Equation (2.96):

$$\sum_i x_i d(\ln \hat{\phi}_i) = 0 \quad (2.112)$$

Fugacities and/or fugacity-coefficients in mixtures are easily evaluated from all kinds of equation-of-state models. In case the equation of state has pressure and temperature as the independent variables, the following, generally valid, relationship can be applied:

$$RT \ln \hat{\phi}_i = RT \ln \left(\frac{\hat{f}_i}{y_i p} \right) = \int_0^p \left(V_i - \frac{RT}{p} \right) dp \quad (2.113)$$

In this equation the partial molar volume V_i is to be evaluated from the equation of state and Equation (2.93). For a pure substance the partial molar volume V_i becomes equivalent to the molar volume V_i^* and Equation (2.113) simplifies to Equation (2.100). Most equation-of-state models have temperature and volume as the independent variables. In that case the following, generally valid, expression can be used for evaluation of the fugacity and/or fugacity-coefficient in mixtures at constant temperature and composition:

$$RT \ln \hat{\phi}_i = RT \ln \left(\frac{\hat{f}_i}{y_i p} \right) = \int_V^\infty \left[\left(\frac{\partial p}{\partial n_i} \right)_{T, V, \hat{n}_i} - \frac{RT}{V} \right] dV - RT \ln Z \quad (2.114)$$

In this equation $Z = pV/nRT$ is the compressibility factor of the mixture; the partial derivative in Equation (2.114) can be obtained from the equation of state under consideration. For a pure substance Equation (2.114) reduces to:

$$RT \ln \phi_i = RT \ln \frac{f}{p} = \int_V^\infty \left[\frac{p}{n_i} - \frac{RT}{V} \right] dV - RT \ln Z + RT(Z - 1) \quad (2.115)$$

For an extensive treatment of the fugacity concept, one is referred elsewhere (1,2,6).

2.8 Activity Coefficients

Although activity coefficients, in general, are most conveniently evaluated from models which are specifically designed for the condensed phase only, this section demonstrates how the concept of activity is related to a similar formalism introduced for the fugacity concept. Equation (2.102) in Section 2.7 relates the residual Gibbs energy and the fugacity. In a similar way the excess Gibbs energy (Section 2.5) is related to the activity-coefficient formalism, which may be useful in describing the non-ideality of a condensed phase.

From Equation (2.86) the following equation is readily obtained by applying Equation (2.93):

$$G_i^E = G_i - G_i^{\text{id}} \quad (2.116)$$

Integration of Equation (2.102) at constant temperature and pressure from the pure state of component i , where $G_i = G_i^*$ and $\hat{f}_i = f_i$, to an arbitrary composition in the solution

yields:

$$G_i - G_i^* = RT \ln \left(\frac{\hat{f}_i}{f_i} \right) \quad (2.117)$$

Application of Equation (2.93) to Equation (2.78) gives:

$$G_i^{\text{id}} = G_i^* + RT \ln x_i \quad (2.118)$$

Consequently, from the latter two equations the following result is obtained:

$$G_i - G_i^{\text{id}} = RT \ln \left(\frac{\hat{f}_i}{x_i f_i} \right) = RT \ln \gamma_i \quad (2.119)$$

where, by definition, $\gamma_i = \hat{f}_i/(x_i f_i)$ is called the activity coefficient of component i in the solution.

In a similar way, as fugacity coefficients are related to the residual Gibbs energy, identical expressions for the activity coefficient can be related to the excess Gibbs energy. For instance, the partial molar excess Gibbs energy of species i is related to the activity coefficient by:

$$G_i^E = RT \ln \gamma_i \quad (2.120)$$

Since G_i^E is the partial molar property of G^E , consequently, $\ln \gamma_i$ is also a partial molar property of G , the following two relations of general validity can be derived:

$$G^E = RT \sum_i x_i \ln \gamma_i \quad (2.121)$$

$$RT \ln \gamma_i = \left(\frac{\partial(nG^E)}{\partial n_i} \right)_{T,P,\hat{n}_i} \quad (2.122)$$

Additionally, at constant temperature and pressure, from Equation (2.96) it follows that:

$$\sum_i x_i d(\ln \gamma_i) = 0 \quad (2.123)$$

For further details one is referred elsewhere (1-3,5,6).

2.9 The Phase Rule

For a system consisting of C components and P phases in equilibrium the number of intensive variables required to specify the state of the system (that is the number of degrees of freedom F) is given by the Gibbs phase rule:

$$F = C - P + 2 - R \quad (2.124)$$

In this equation R represents the number of restrictions imposed on the system. While the value for isothermal, isobaric or isochoric changes is obvious, the restrictions imposed by chemical reactions are often more subtle. For example, liquid water will exist as a mixture of H_2O , H^+ , H_3O^+ , and OH^- but, if C is taken as 4, then the requirements of electroneutrality and the ionic equilibria lead to $R = 3$ and the system still behaves, quite correctly, as a pure component. Two restrictions are particularly important when studying phases in equilibrium. If P_{az} phases have the same composition, then there are $(P_{az} - 1)$ phase boundaries across which the $(C-1)$ compositions must be the same and the additional restriction is:

$$R = (P_{az} - 1)(C - 1) \quad (2.125)$$

and the number of degrees of freedom is:

$$F = C(2 - P_{az}) + 1 \quad (2.126)$$

This makes it clear that 3 phases can have the same composition only in the special case of a pure component, *i.e.*, at its triple point. If $P_{az} = 2$, then $F = 1$, and an azeotropic line always results irrespective of the number of components.

The second special case applies to the critical state. Here the P_c phases that become identical at the critical state are considered separately from the P_{nc} phases that behave normally. In this case, the additional restriction is $R = 2P_c - 1$, and the number of degrees of freedom becomes:

$$F = C - P_{nc} + 2 - (2P_c - 1) \quad (2.127)$$

Consequently, a critical point ($F = 0$) is unique for a pure component while, for a binary mixture, a critical line ($F = 1$) is the simplest case and critical endpoints ($P_{nc} = 1, P_{nc} = 2$) are unique points. We note also that since F cannot be negative:

$$C \geq 2P_c - 3 \quad (2.128)$$

As a consequence, a tricritical point cannot exist in a binary mixture. The combination of the restrictions for an azeotrope and a critical state shows that it is not possible for two azeotropic phases to become identical in a critical state, *i.e.*, the critical and the azeotropic composition must be different. The restrictions that follow from the phase rule are simple consequences of geometry and are useful because they reduce the number of variables that must be used to describe the state of a system: small values of F should result in simple equations of state. However, the phase rule gives no guidance as to which variables should be chosen.

2.10 Equilibrium Conditions

For a closed system with an arbitrary number of components and phases in which the temperature and pressure are uniform, the following combined statement of the first and second law is applicable (2,6):

$$dU^t + pdV^t - TdS^t \leq 0 \quad (2.129)$$

In this equation t refers to the total value of the various properties. The inequality symbol applies for infinite small changes between non-equilibrium states and the equality symbol holds for infinite small changes between equilibrium states, *i.e.*, reversible processes.

For practical purposes, from Equation (2.129), the following alternative equation in terms of the Gibbs energy can be obtained:

$$dG^t + S^tdT - V^tdp \leq 0 \quad (2.130)$$

Since in this equation temperature and pressure, which are easily controlled in experiments, are the independent variables, Equation (2.130) is the most useful representation of Equation (2.129). At constant temperature and pressure, Equation (2.130) reduces to:

$$(dG^t)_{p,T} \leq 0 \quad (2.131)$$

This equation states that at constant temperature and pressure any irreversible process proceeds in such a direction that the total Gibbs energy of a closed system will decrease. At equilibrium the Gibbs energy has reached a minimum value for the given temperature and pressure.

2.10.1 Phase Equilibria

For a closed multi-component system, Equation (2.131) can be used to derive the equilibrium conditions between two or more phases in a system at constant temperature and pressure. If we indicate the various phases by $\alpha, \beta, \gamma, \dots, \pi$, and the various species by $1, 2, 3, \dots, C$, the following

equilibrium conditions in terms of the chemical potential result:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots = \mu_i^\pi, \quad i = 1, 2, 3, \dots, C \quad (2.132)$$

Alternatively, it easily can be shown (2,6) that phase equilibrium can also be defined in terms of the fugacity:

$$\hat{f}_i^\alpha = \hat{f}_i^\beta = \hat{f}_i^\gamma = \dots = \hat{f}_i^\pi, \quad 1, 2, 3, \dots, C \quad (2.133)$$

For a simple vapor-liquid equilibrium Equation (2.133) reads:

$$\hat{f}_i^v = \hat{f}_i^l, \quad i = 1, 2, 3, \dots, C \quad (2.134)$$

Substitution of Equations (2.107) and (2.119) into this equilibrium condition gives:

$$\gamma_i \hat{\phi}_i^v p = x_i \gamma_i f_i^l, \quad i = 1, 2, 3, \dots, C \quad (2.135)$$

This formalism is the gamma-phi approach for calculating vapor-liquid equilibria. The fugacity coefficient $\hat{\phi}_i^v$ of each component that accounts for the non-ideality of the vapor phase can be evaluated from an equation of state model, while the activity coefficient γ_i to describe the non-ideal behavior of the liquid phase can be obtained from an excess Gibbs energy model.

The fugacity f_i^l of pure species i can be obtained from the relation (2,6,7):

$$RT \ln \left(\frac{f_i}{f_i^*} \right) = \int_{p_i^*}^p V_i dp \quad (2.136)$$

In case the temperature is appreciably below critical and for not too high pressures, Equation (2.136) can be approximated by:

$$\ln \frac{f_i}{f_i^*} = \frac{V_i^l(p - p_i^*)}{RT} \quad (2.137)$$

Substitution of $f_i^* = \phi_i^* p_i^*$ gives:

$$f_i^l = \phi_i^* p_i^* \exp \left[\frac{V_i^l(p - p_i^*)}{RT} \right] \quad (2.138)$$

In the latter expression the exponential is the Poynting factor. The contribution of this term becomes significant only at higher pressures. For an ideal vapor phase ($\hat{\phi}_i^v=1$), the liquid phase is an ideal solution ($\gamma_i = 1$) and if the Poynting factor does not contribute (low pressures), Equation (2.135) reduces to Raoult's law.

Equations of state, in principle, are able to describe the vapor and liquid phase simultaneously, i.e., both the $\hat{\phi}_i^v$ and $\hat{\phi}_i^l$ can be evaluated from an equation of state model. Substitution of Equation (2.107) for both the vapor and liquid phase into Equation (2.134) leads to the phase equilibrium conditions:

$$y_i \hat{\phi}_i^v = x_i \hat{\phi}_i^l, \quad i = 1, 2, 3, \dots, C \quad (2.139)$$

Details of the various approaches to model vapor-liquid equilibria from equations of state can be found elsewhere (2,3,5-9).

2.10.2 Chemical Equilibria

Application of Equation (2.131), the general criterion for chemical equilibrium, is conveniently expressed in terms of the chemical potential of each species present in the equilibrium mixture:

$$\sum_i \nu_i \mu_i = 0, \quad i = 1, 2, 3, \dots, C \quad (2.140)$$

In this equation ν_i are the stoichiometric coefficients, which for products are taken with a positive sign and for reactants are taken with a negative sign. At constant temperature and composition, Equation (2.103) reads:

$$d\mu_i = dG_i = RT d \ln \hat{f}_i \quad (2.141)$$

Integration of this equation from a standard state of pure species i to its actual state in solution gives:

$$\mu_i = \mu_i^0 + RT \ln \left(\frac{\hat{f}_i}{f_i^0} \right) = \mu_i^0 + RT \ln \hat{a}_i \quad (2.142)$$

In this equation \hat{a}_i is the activity of component i in the mixture. Substitution of this expression into the condition for chemical equilibrium gives the important relation:

$$\prod_i (\hat{a}_i)^{\nu_i} = \exp \left[\frac{-\sum_i \nu_i \mu_i^0}{RT} \right] \quad (2.143)$$

Since the right-hand side of Equation (2.143) is a function of temperature only, this term can be written as:

$$\Delta_r G^0 = \sum_i \nu_i \mu_i^0 = -RT \ln K(T) \quad (2.144)$$

Equation (2.144) defines the thermodynamic equilibrium constant, which is a function of temperature only. From Equations (2.143) and (2.144) it can be seen how the equilibrium constant is related to the activities of the various species in the mixture. Since the activities of the reacting

species are related to their fugacities, equations of state can be used for their evaluation. Further details on chemical equilibria can be found elsewhere (1,3,7).

2.11 STABILITY AND THE CRITICAL STATE

2.11.1 Densities and Fields

Griffiths and Wheeler (11) divided thermodynamic properties into two classes: *fields* f (for example T , p , and μ) that must be uniform throughout a system at equilibrium; and *densities* ρ (for example S , V , and n) which, in general, are discontinuous across a phase boundary although they are uniform throughout each phase. With this nomenclature, the fundamental equation (2.1) for the second law of thermodynamics can be written, very compactly, in the form:

$$dU = \sum_j f_j d\rho_j \quad (2.145)$$

where the density $U(S, V, n_1, \dots, n_C)$ is the thermodynamic surface and it should be noted that the hydrostatic field is $-p$ rather than p . Equation (2.145) shows that conjugate densities and fields are related by

$$f_j = (\partial U / \partial \rho_j)_{\hat{\rho}_j} \quad (2.146)$$

where the subscript $\hat{\rho}_j$ indicates that all the densities except ρ_j are held constant. Griffiths and Wheeler used an equivalent definition

$$\rho_j = - (\partial f_0 / \partial f_j)_{\hat{f}_j} \quad (2.147)$$

where f_0 is a thermodynamic potential.

2.11.2 Stability

Just as the fields, which are the first derivatives $(\partial U / \partial \rho)$, characterise equilibrium, the curvature of the thermodynamics surface, which depends on the second derivatives $(\partial^2 U / \partial \rho_j \partial \rho_k)$, determines the stability of the system. The stability determinant for a system with C components may be written as

$$D(S, V, n_1, \dots, n_{C-1}) = \begin{vmatrix} U_{SS} & U_{SV} & U_{Sn_1} & \dots \\ U_{VS} & U_{VV} & U_{Vn_1} & \dots \\ U_{n_1S} & U_{n_1V} & U_{n_1n_1} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \quad (2.148)$$

where the elements of the determinant are given by

$$U_{\rho_j \rho_k} = \left(\frac{\partial^2 U}{\partial \rho_j \partial \rho_k} \right)_{\hat{\rho}_j \hat{\rho}_k} \quad \text{with} \quad \rho_j, \rho_k = S, V, n_1, \dots, n_C \quad (2.149)$$

In a stable system with C components, the thermodynamic surface $U(S, V, n_1, \dots, n_{C-1})$ lies above its tangent plane and has positive curvature and, consequently, all the $(C + 1)$ determinants $D(S), D(S, V), D(S, V, n_1), \dots, D(S, V, n_1, \dots, n_{C-1})$ are positive. Furthermore, since the variables may be chosen in any order, many more determinants may be formed and they are all positive. However, with C components there are only $(C + 1)$ independent variables and a set of $(C + 1)$ determinants is sufficient to establish the conditions for stability. For example, the system is stable provided

$$D(S) = \left(\frac{\partial T}{\partial S} \right)_{V, n} = \frac{T}{C_V} \geq 0 \quad (2.150)$$

$$D(S, V) = \frac{D(S, V)}{D(S)} D(S) = - D(S) \left(\frac{\partial p}{\partial V} \right)_{T, n} = D(S) \frac{1}{V \kappa_T} \geq 0 \quad (2.151)$$

$$D(S, V, n_1) = \frac{D(S, V, n_1)}{D(S, V)} D(S, V) = D(S, V) \left(\frac{\partial \mu}{\partial n_1} \right)_{T, p, n_1} \geq 0 \quad (2.152)$$

and so on. The ratios of the determinants are obtained from

$$\frac{D(\rho_1, \dots, \rho_j)}{D(\rho_1, \dots, \rho_{j-1})} = \left(\frac{\partial f_j}{\partial \rho_j} \right)_{f_i, \rho_k, k \neq j} \quad (2.153)$$

which was derived by Gibbs (12).

2.11.3 Critical State

The critical state is the limit of stability at which all the determinants that were positive in Section 2.11.2 become zero. However, in the usual case where a transition between two phases is terminated, the critical state imposes only 3 additional restrictions, irrespective of the number of components. Similarly, although all the discontinuities in the densities vanish because the phases become identical, it is sufficient to consider the behaviour of the system with respect to a single density and to formulate the restrictions in terms of higher-order derivatives

$$(\partial^2 U / \partial \rho_j^2)_{\rho_j} = 0; \quad (\partial^3 U / \partial \rho_j^3)_{\rho_j} = 0; \quad (\partial^4 U / \partial \rho_j^4)_{\rho_j} > 0; \quad (2.154)$$

The conditions are often defined in other thermodynamic surfaces where the variables more closely match an equation of state or the experimental conditions. For example, a gas-liquid critical point in a pure fluid is usually defined by

$$(\partial p/\partial V)_{T,n} = 0; \quad (\partial^2 p/\partial V^2)_{T,n} = 0; \quad (\partial^3 p/\partial V^3)_{T,n} < 0 \quad (2.155)$$

which may be written in terms of the $A(T, V, n)$ surface as where the notation introduced in Equation (2.149) has been extended in an obvious way.

$$A_{2V} = \left(\frac{\partial^2 A}{\partial V^2} \right)_{T,n} = \frac{1}{V\kappa_T} = 0; \quad A_{3V} = \left(\frac{\partial^3 A}{\partial V^3} \right)_{T,n} = 0; \quad A_{4V} = \left(\frac{\partial^4 A}{\partial V^4} \right)_{T,n} > 0 \quad (2.156)$$

Temperature is assumed to be uniform and constant for both Equations (2.155) and (2.156). However, if the $H(S, p, n)$ surface is used, then an entirely equivalent set of conditions is obtained

$$H_{2S} = \left(\frac{\partial^2 H}{\partial S^2} \right)_{p,n} = \frac{T}{C_p} = 0; \quad H_{3S} = \left(\frac{\partial^3 H}{\partial S^3} \right)_{p,n} = 0; \quad H_{4S} = \left(\frac{\partial^4 H}{\partial S^4} \right)_{p,n} > 0 \quad (2.157)$$

but now pressure is assumed to be uniform and constant. Equation (2.153) shows the relation between these surfaces and $U(S, V, n)$, since $A_{2V} = D(S, V)/D(S)$ and $H_{2S} = D(V, S)/D(V)$. Conditions equivalent to Equations (2.156) or (2.157) are obtained from the $U(S, V, n)$ surface and Equation (2.154) with $\rho_j = V$ or S . While Equation (2.155) is more familiar through its use of (p, V, T) variables and association with gas-liquid critical points in pure fluids, each set of conditions can be used to describe the same critical state. For example Equation (2.157) or $\rho_j = S$ in Equation (2.154) might be very appropriate for a calorimetric study of a gas-liquid critical point.

The experimental conditions of a critical state in a binary mixture are closely matched by the Gibbs energy $G(T, p, n_1, n_2)$ and the relation with the $U(S, V, n_1, n_2)$ surface is established with Equation (2.153) in the form

$$D(S, V, n_1)/D(S, V) = (\partial \mu_1/\partial n_1)_{T,p,n_2} \quad (2.158)$$

which leads to the following conditions for the critical state:

$$(\partial \mu_1/\partial n_1)_{T,p,n_2} = 0; \quad (\partial^2 \mu_1/\partial n_1^2)_{T,p,n_2} = 0; \quad (\partial^3 \mu_1/\partial n_1^3)_{T,p,n_2} \geq 0 \quad (2.159)$$

The Gibbs-Duhem Equation (2.18) allows these conditions to be expressed (1,10) in terms of the molar Gibbs energy G_m and a mole fraction x

$$G_{2x} = (\partial^2 G/\partial x^2)_{T,p} = 0; \quad G_{3x} = (\partial^3 G/\partial x^3)_{T,p} = 0; \quad G_{4x} = (\partial^4 G/\partial x^4)_{T,p} \geq 0 \quad (2.160)$$

Since most equations of state have temperature, molar volume, and composition as independent variables, while the Gibbs energy is explicit in temperature, pressure, and composition; a formulation of the critical conditions in terms of the Helmholtz energy is required. The following equations allow a transformation between $G(T, p, x)$ and $A(T, V, x)$ (1,10):

$$G_{2x} = A_{2x} - (A_{Vx})^2/A_{2V} \quad (2.161)$$

$$G_{3x} = A_{3x} - 3A_{V2x}(A_{Vx}/A_{2V}) + 3A_{2Vx}(A_{Vx}/A_{2V})^2 - A_{3V}(A_{Vx}/A_{2V}) \quad (2.162)$$

The Helmholtz energy $A(T, V, x)$ and the derivatives required for Equations (2.161) and (2.162) may be obtained from any Equation of state that gives the pressure through

$$A(V,T,x) = (1-x)A_1^*(V^\circ,T) + xA_2^*(V^\circ,T) + RT\{(1-x)\ln(1-x) + x\ln x\} - \int_{V^*}^V p dV \quad (2.163)$$

In this equation $A_1^*(V^\circ,T)$ and $A_2^*(V^\circ,T)$ are the molar Helmholtz energies of the pure components and V° is a reference volume.

Multicomponent systems are handled in a similar way. For example, a ternary mixture can be described in terms of four variables and Equation (2.153) gives

$$D(S,V,n_1,n_2)/D(S,V,n_1) = (\partial\mu_2/\partial n_2)_{T,p,\mu_1,\mu_3} \quad (2.164)$$

and the conditions for a critical state are therefore

$$(\partial\mu_2/\partial n_2)_{T,p,\mu_1,\mu_3} = 0; \quad (\partial^2\mu_2/\partial n_2^2)_{T,p,\mu_1,\mu_3} = 0; \quad (\partial^3\mu_2/\partial n_2^3)_{T,p,\mu_1,\mu_3} > 0 \quad (2.165)$$

The defining equations for higher-order critical points are straightforward in terms of the Gibbs energy and the composition variables. For instance, for a tricritical point in a (pseudo) binary mixture the following $2P_c - 1 = 5$ conditions have to be satisfied (1,10):

$$G_{2x} = 0; \quad G_{3x} = 0; \quad G_{4x} = 0; \quad G_{5x} = 0; \quad G_{6x} > 0 \quad (2.166)$$

For higher-order critical points, the transformation equations from the Gibbs into the Helmholtz energy become extremely complex.

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