

CLASSICAL THERMODYNAMIC BASIS OF ACTIVITY COEFFICIENTS: PREDICTIVE AND CONSISTENCY RULES FOR BINARY AND TERNARY MIXTURES BASED ON THE RELATION BETWEEN EXCESS GIBBS FREE ENERGIES OF (c)- AND ($c - 1$)-COMPONENT MIXTURES

G. ALI MANSOORI

*Department of Energy Engineering, University of Illinois at Chicago Circle,
Box 4348, Chicago, Illinois 60680 (U.S.A.)*

(Received September 3rd, 1979; accepted in revised form December 26th, 1979)

ABSTRACT

Mansoori, G.A., 1980. Classical thermodynamic basis of activity coefficients: Predictive and consistency rules for binary and ternary mixtures based on the relation between excess Gibbs free energies of (c)- and ($c - 1$)-component mixtures. *Fluid Phase Equilibria*, 4: 197–209.

A working equation in which the molar Gibbs free energy of a (c)-component mixture is related to that of a ($c - 1$)-component mixture, both at the same pressure and temperature, is developed. This working equation is applied to binary and ternary mixtures. For binary mixtures, a reformulated integral version of the Gibbs–Duhem equation for activity coefficients is derived which is readily applicable for consistency tests and calculation of one binary activity coefficient from another. In the case of ternary mixtures a number of rigorous equations are derived for relating ternary- and binary-mixture activity coefficients. It is concluded that, generally, a ternary-mixture activity coefficient can be calculated from the knowledge of another ternary coefficient, plus a binary-mixture activity coefficient. Also, the resulting equations allow us to perform consistency tests of ternary activity coefficients against the binary-mixture data. The limiting forms of the ternary-mixture activity coefficients, when the mole fraction of one of the three components approaches to unity or to its infinite dilution limit, are derived. The form of the ternary-mixture activity coefficients and the conditions under which they may be calculated, solely from the binary activity coefficient data, is presented.

INTRODUCTION

The practical application of fluid phase equilibria for problems of interest in science and engineering necessitates the use of a number of auxiliary functions (Prigogine and Defay, 1954; Rowlinson, 1969; Prausnitz, 1969; King, 1969). Among these functions, the activity coefficients of components of a liquid mixture are most needed, but not well understood. Classical thermodynamics have provided us, so far, with the relations between activity coefficients and excess thermodynamic properties, and the Gibbs–Duhem equation. According to the Gibbs–Duhem equation, one activity coefficient can be

expressed as a function of other activity coefficients of a mixture. There exists a large number of publications in the literature dealing with the empirical correlation of activity coefficients based on experimental measurements. There are also many attempts in deriving the activity coefficients from statistical thermodynamics. But as of yet, no fully satisfactory approach is available for the prediction of activity coefficients. Of course, molecular theories of statistical thermodynamics are very strong tools which may eventually provide us with the necessary information about activity coefficients (Rowlinson, 1969; Mansoori, 1980; Mansoori and Canfield, 1970). The technique presented in this report leads us to a new classical thermodynamic approach for inter-relating activity coefficients, in addition to the Gibbs—Duhem equation.

One of the important equations in thermodynamics of multicomponent systems is the Gibbs—Duhem equation (Gibbs, 1928; Duhem, 1899 and 1911). Probably the most extensive application of this equation is for the calculation or a consistency test of the activity coefficients of components of a mixture in one phase (Prigogine and Defay, 1954; Rowlinson, 1969; Prausnitz, 1969; King, 1969). According to the Gibbs—Duhem equation at constant pressure and temperature the following relation holds between the activity coefficients, γ_i , of the components of a mixture with (c) components

$$\sum_{i=1}^c x_i d \ln \gamma_i = 0 \quad (\text{constant } P \text{ and } T) \quad (1)$$

For a binary mixture eqn. (1) can also be shown in the following form

$$x_1 (d \ln \gamma_1 / dx_1) = x_2 (d \ln \gamma_2 / dx_2) \quad (\text{constant } P \text{ and } T) \quad (2)$$

In addition, one can derive the following integral relation for activity coefficients based on eqn. (1) for binary mixtures

$$\int_0^1 \ln(\gamma_1 / \gamma_2) dx_1 = 0 \quad (\text{constant } P \text{ and } T) \quad (3)$$

Equation (2) is used as a differential consistency test of the activity coefficient data, while eqn. (3) is for integral consistency test purposes. The Gibbs—Duhem equation is widely used in binary-mixture calculations for both the consistency test of activity coefficients data and calculation of one activity coefficient from another. Application of the Gibbs—Duhem equation for mixtures consisting of three or more components is of a lesser significance. In the latter case, in addition to the information which the Gibbs—Duhem equation provides us, we would also need to know relations between the activity coefficients of a multicomponent mixture and those of mixtures with less components. Specifically, there is a great deal of interest among scientists and engineers to relate ternary-mixture activity coefficients to those of binary mixtures at a given pressure and temperature. This is due to

the lack of ternary activity coefficient data and the difficulty which is associated with the collection of such data. This situation has led to a number of empirical equations relating ternary mixture activity coefficients to binary data.

In the present report, a rigorous thermodynamic technique is developed through which we are now able to derive relations between the activity coefficients of a multicomponent mixture and those of mixtures with less components. This technique is based on a working equation in which the molar Gibbs free energy of a (c)-component mixture is related to the molar Gibbs free energy of a ($c - 1$)-component mixture, both at the same pressure and temperature, through the definition of the activity coefficient. Application of the present technique to binary mixtures leads to a reformulated integral version of the Gibbs–Duhem equation which is readily applicable for consistency tests and the calculation of one binary activity coefficient from another. However, the utility of the present technique is best realized in the case of ternary mixtures by the development of rigorous equations relating ternary- and binary-mixture activity coefficients. The methodology presented here for binary and ternary mixtures can be extended to mixtures with four or more components in a similar fashion.

THE WORKING EQUATION

The chemical potential μ_i of a component of a mixture is defined with respect to the activity coefficient γ_i of that component through (Prigogine and Defay, 1954; Rowlinson, 1969; Prausnitz, 1969; King, 1969)

$$\mu_i(P, T, x_i\text{'s}) \equiv \mu_i^\circ + RT \ln \{x_i \gamma_i(P, T, x_i\text{'s})\} \quad (4)$$

In this equation μ_i° is commonly called the standard state chemical potential of i which may be chosen equal to the chemical potential of i in the pure state and at the same pressure and temperature as the mixture,

$$\mu_i^\circ \equiv g_i(P, T) \quad (5)$$

where g_i is the molar Gibbs free energy of pure component i . The chemical potential of a component of the mixture can be defined with respect to the molar Gibbs free energy of the mixture through (see Rowlinson, 1969, p. 108; King, 1969, p. 22)

$$\mu_i(P, T, x_i\text{'s}) = g(P, T, x_i\text{'s}) + (1 - x_i) \left[\frac{\partial g(P, T, x_i\text{'s})}{\partial x_i} \right]_{P, T, x_j/x_k} ; \quad (i \neq j \neq k) \quad (6)$$

The subscript x_j/x_k on the right hand side of eqn. (6) indicates that the partial differentiation with respect to x_i is performed by keeping the relative compositions of the other components of the mixture intact. By joining eqns. (4)–(6), we get the following differential equation

$$\left(\frac{\partial g}{\partial x_i} \right)_{P, T, x_j/x_k} + \left(\frac{1}{1 - x_i} \right) g = \left(\frac{1}{1 - x_i} \right) [g_i(P, T) + RT \ln \{x_i \gamma_i(P, T, x_i\text{'s})\}] \quad (7)$$

The general solution of the above differential equation is in the following form (Kamke, 1959; Coddington, 1961)

$$g = [B(x_i) + c] \exp[-A(x_i)] \quad (8)$$

such that

$$A(x_i) = \int_{x_i^0}^{x_i} \frac{dt}{1-t} = -\ln\left(\frac{1-x_i^0}{1-x_i}\right) \quad (9)$$

$$\begin{aligned} B(x_i) &= \int_{x_i^0}^{x_i} e^{A(t)} [g_i + RT \ln\{t\gamma_i(t)\}]_{x_j/x_k} \left(\frac{dt}{1-t}\right) \\ &= \left(\frac{x_i - x_i^0}{1 - x_i^0}\right) g_i + RT(1 - x_i^0) \int_{x_i^0}^{x_i} \left[\frac{\ln\{t\gamma_i(t)\}}{(1-t)^2} \right]_{x_j/x_k} dt \end{aligned} \quad (10)$$

and c is a constant. By substituting (9) and (10) in (8), the following relation for the Gibbs free energy of the mixture with respect to the activity coefficient of component i , γ_i , will be derived.

$$g = \left(\frac{x_i - x_i^0}{1 - x_i^0}\right) g_i + RT(1 - x_i^0) \int_{x_i^0}^{x_i} \left[\frac{\ln\{t\gamma_i(t)\}}{(1-t)^2} \right]_{x_j/x_k} dt + \left(\frac{1 - x_i^0}{1 - x_i}\right) C \quad (11)$$

This equation will be valid at constant P , T and x_j/x_k ; ($i \neq j \neq k$). In order to define x_i^0 and C , which appear in eqn. (11), the following boundary condition can be used:

$$g = g^{(-i)} \quad \text{at } x_i = 0 \quad (12)$$

where $g^{(-i)}$ is defined as the Gibbs free energy of a mixture excluding component i and at the same pressure, temperature and relative compositions of the remaining components as the original mixture. With the use of condition (12), eqn. (11) will be finally in the following form:

$$\begin{aligned} g &= (1 - x_i)g^{(-i)} + x_i g_i + RT\{(1 - x_i) \ln(1 - x_i) + x_i \ln x_i\} \\ &\quad + RT(1 - x_i) \int_0^{x_i} \left[\frac{\ln \gamma_i(t)}{(1-t)^2} \right]_{x_j/x_k} dt \end{aligned} \quad (13)$$

The subscript x_j/x_k on the integrand of the above equation indicates that integration will be performed over x_i by keeping the relative compositions of the other components of the mixture intact. Equation (13) is the working equation upon which the discussion presented in the remaining parts of this report will be based. In order to demonstrate applications of eqn. (13) for the calculation and consistency test of activity coefficients, it will be applied here for binary and ternary mixtures.

BINARY MIXTURES

In the case of a binary mixture and for $i = 1$, eqn. (13) can be written in the following form:

$$g^{(1,2)} = x_2 g_2 + x_1 g_1 + RT(x_2 \ln x_2 + x_1 \ln x_1) + RTx_2 \int_0^{x_1} [\ln \gamma_1^{(1,2)}(t)/(1-t)^2] dt \quad (14)$$

In this equation superscript (1, 2) indicates a binary mixture of components 1 and 2. Similarly, for $i = 2$, eqn. (13) will be in the following form for the same binary mixture

$$g^{(1,2)} = x_1 g_1 + x_2 g_2 + RT(x_1 \ln x_1 + x_2 \ln x_2) + RTx_1 \int_0^{x_2} [\ln \gamma_2^{(1,2)}(t)/(1-t)^2] dt \quad (15)$$

By comparing the above two equations with the definition of the excess molar Gibbs free energy,

$$g^E = g - \sum_{i=1}^c x_i (g_i + RT \ln x_i) \quad (16)$$

we conclude that

$$g^E/RT = x_2 \int_0^{x_1} \frac{\ln \gamma_2^{(1,2)}(t)}{(1-t)^2} dt = x_1 \int_0^{x_2} \frac{\ln \gamma_1^{(1,2)}(t)}{(1-t)^2} dt \quad (17)$$

This is an essential equation for binary-mixture activity coefficients by which calculation of one activity coefficient from another or the consistency test of the data can be performed.

By joining eqn. (17) with the relation between excess Gibbs free energy and activity coefficients,

$$g^E/RT = \sum_{i=1}^c x_i \ln \gamma_i \quad (18)$$

for a binary mixture it can be shown that

$$\ln \gamma_2^{(1,2)}(x_2) = -\frac{x_1}{x_2} \ln \gamma_1^{(1,2)}(x_1) + \int_0^{x_1} \frac{\ln \gamma_1^{(1,2)}(t)}{(1-t)^2} dt \quad (19)$$

This equation is originally derived from the Gibbs–Duhem equation (Wagner 1952, p. 16). Equation (19) is a very useful relation which can be used for the calculation of γ_2 when the relation for γ_1 is available. Equation (19) is

actually another form of the Gibbs–Duhem equation for binary mixtures which can be used for the same purposes as eqn. (1). The Gibbs–Duhem equation (1) can be derived from eqn. (19) when the latter equation is differentiated with respect to x_1 . However, eqn. (19) can be used more readily for the calculation of γ_2 from γ_1 than eqn. (1).

In order to use eqn. (17) for an integral consistency test of binary-mixture activity coefficients, it is enough to replace $x_1 = x_2 = 1/2$ in this equation. The resulting relation will be

$$\int_0^{1/2} \frac{\ln\{\gamma_1^{(1,2)}(t)/\gamma_2^{(1,2)}(t)\}}{(1-t)^2} dt = 0 \quad (20)$$

Equation (20) can be used the same way as eqn. (3) for integral consistency tests of activity coefficient data.

As is demonstrated above, through the use of the working equation (13) we have been able to derive a number of new forms for the Gibbs–Duhem equation of binary mixtures which give us a variety of new possibilities for consistency tests and calculations of activity coefficients. With the application of eqn. (13) for ternary mixtures and utilization of the binary-mixture equations presented above, we will be able to produce a number of interesting and useful relations between binary and ternary activity coefficients.

TERNARY MIXTURES

In the case of a ternary mixture and by choosing $i = 3$, eqn. (13) can be written in the following form

$$g^{(1,2,3)} = (1 - x_3)g^{(1,2)} + x_3 g_3 + RT\{(1 - x_3) \ln(1 - x_3) + x_3 \ln x_3\} \\ + RT(1 - x_3) \int_0^{x_3} \left[\frac{\ln \gamma_3^{(1,2,3)}(t, x_1/x_2)}{(1-t)^2} \right]_{x_1/x_2} dt \\ \text{(at constant } P, T \text{ and } x_1/x_2) \quad (21)$$

The binary molar Gibbs free energy, $g^{(1,2)}$, appearing in the above equation has a form exactly the same as in eqns. (14) or (15) except that x_1 and x_2 in these equations should be replaced with $x_1/(x_1 + x_2)$ and $x_2/(x_1 + x_2)$, respectively. For example, by the use of eqn. (14) for $g^{(1,2)}$

$$g^{(1,2)} = \left(\frac{x_2}{x_1 + x_2} \right) g_2 + \left(\frac{x_1}{x_1 + x_2} \right) g_1 + RT \left\{ \left(\frac{x_1}{x_1 + x_2} \right) \ln \left(\frac{x_1}{x_1 + x_2} \right) \right. \\ \left. + \left(\frac{x_2}{x_1 + x_2} \right) \ln \left(\frac{x_2}{x_1 + x_2} \right) \right\} + RT \left(\frac{x_2}{x_1 + x_2} \right) \int_0^{[x_1/(x_1+x_2)]} \frac{\ln \gamma_1^{(1,2)}(t)}{(1-t)^2} dt,$$

we get the following relation for $g^{(1,2,3)}$

$$\begin{aligned}
g^{(1,2,3)} &= \sum_{i=1}^3 x_i g_i + RT \sum_{i=1}^3 x_i \ln x_i + RT x_2 \int_0^{[x_1/(x_1+x_2)]} \frac{\ln \gamma_1^{(1,2)}(t)}{(1-t)^2} dt \\
&+ RT(1-x_3) \int_0^{x_3} \left[\frac{\ln \gamma_3^{(1,2,3)}(t, x_1/x_2)}{(1-t)^2} \right]_{x_1/x_2} dt \\
&\text{(at constant } P \text{ and } T) \tag{22}
\end{aligned}$$

Now, again, by comparison of this equation with eqn. (16), we derive the following relation for the ternary excess Gibbs free energy function

$$\begin{aligned}
g^E/RT &= x_2 \int_0^{[x_1/(x_1+x_2)]} \frac{\ln \gamma_1^{(1,2)}(t)}{(1-t)^2} dt \\
&+ (1-x_3) \int_0^{x_3} \left[\frac{\ln \gamma_3^{(1,2,3)}(t, x_1/x_2)}{(1-t)^2} \right]_{x_1/x_2} dt \quad \text{(at constant } P \text{ and } T) \tag{23}
\end{aligned}$$

In this equation, excess Gibbs free energy of the ternary mixture at constant temperature and pressure is expressed with respect to activity coefficients of binary and ternary mixtures. Equation (23) can be written in the following general form

$$\begin{aligned}
g^E/RT &= x_j \int_0^{[x_i/(x_i+x_j)]} \frac{\ln \gamma_i^{(i,j)}(t)}{(1-t)^2} dt \\
&+ (1-x_k) \int_0^{x_k} \left[\frac{\ln \gamma_k^{(1,2,3)}(t, x_i/x_j)}{(1-t)^2} \right]_{x_i/x_j} dt \tag{24a} \\
&= x_j \int_0^{[x_k/(x_j+x_k)]} \frac{\ln \gamma_k^{(j,k)}(t)}{(1-t)^2} dt \\
&+ (1-x_i) \int_0^{x_i} \left[\frac{\ln \gamma_i^{(1,2,3)}(t, x_j/x_k)}{(1-t)^2} \right]_{x_j/x_k} dt \quad \text{(at constant } P \text{ and } T) \tag{24b}
\end{aligned}$$

with $(i \neq j \neq k) = (1, 2, 3)$ and $x_i + x_j + x_k = 1$. Equation (24) is the essential equation for ternary-mixture activity coefficients and their relationships with binary-mixture activity coefficients. This equation can be transformed to a form in which one of the ternary activity coefficients can be calculated from another one and from the binary activity coefficients. Also, eqn. (24) can be transformed to a form which can be used for a consistency test of ternary activity coefficients with respect to binaries.

In order to demonstrate the utility of eqn. (24) for ternary activity coefficient calculation, we join eqn. (24a) with eqn. (18) for a ternary mixture, i.e.

$$g^E/RT = x_i \ln \gamma_i + x_j \ln \gamma_j + x_k \ln \gamma_k$$

in order to derive the following relation

$$\ln \gamma_j^{(1,2,3)} = -\frac{x_i}{x_j} \ln \gamma_i^{(1,2,3)} - \frac{x_k}{x_j} \ln \gamma_k^{(1,2,3)} + \int_0^{x_i/(x_i+x_j)} \frac{\ln \gamma_i^{(i,j)}(t)}{(1-t)^2} dt + \left(\frac{1-x_k}{x_j}\right) \int_0^{x_k} \left[\frac{\ln \gamma_k^{(1,2,3)}(t, x_i/x_j)}{(1-t)^2} \right] dt \quad (25)$$

At a given temperature and pressure the independent variables on the righthand side of this equation can be chosen as x_k and x_i/x_j . Partial differentiation of eqn. (25) with respect to x_k at constant x_i/x_j will produce

$$x_i d \ln \gamma_i + x_j d \ln \gamma_j + x_k d \ln \gamma_k = 0 \quad (i \neq j \neq k) = (1, 2, 3)$$

which is the Gibbs–Duhem equation, eqn. (1), for a ternary mixture. With the partial differentiation of x_i and x_j with respect to x_k we get

$$\left(\frac{\partial x_i}{\partial x_k}\right)_{x_i/x_j} = -\frac{x_i}{x_i + x_j}; \quad \left(\frac{\partial x_j}{\partial x_k}\right)_{x_i/x_j} = -\frac{x_j}{x_i + x_j} \quad (26)$$

because $x_i + x_j + x_k = 1$. Equation (25) can also be differentiated with respect to x_i/x_j at constant x_k . In this case, we use the following identities for ternary mixtures,

$$[\partial x_i / \partial (x_i/x_j)]_{x_k} = -\frac{x_i^2}{x_i + x_j}; \quad [\partial x_j / \partial (x_i/x_j)]_{x_k} = -\frac{x_j^2}{x_i + x_j} \quad (27)$$

and we derive the following relation

$$\ln \gamma_i^{(1,2,3)} = \ln \gamma_i^{(i,j)} \left(\frac{x_i}{x_i + x_j}\right) - \left(\frac{x_k}{1 - x_k}\right) \ln \gamma_k^{(1,2,3)} + \int_0^{x_k} \frac{\ln \gamma_k^{(1,2,3)}(t, x_i/x_j)}{(1-t)^2} dt - \frac{(1-x_k)}{x_j} \int_0^{x_k} \frac{1}{(1-t)^2} \left[\frac{\partial \ln \gamma_k^{(1,2,3)}(t, x_i/x_j)}{\partial (x_i/x_j)} \right]_t dt$$

The first term on the righthand side of this equation is the activity coefficient of component i in a binary mixture of i and j at the same pressure, temperature and relative compositions of i and j as in the ternary (i, j, k) mixture. This equation is a useful relation through which one may calculate $\gamma_i^{(1,2,3)}$ when $\gamma_k^{(1,2,3)}$ and $\gamma_i^{(i,j)}$ are available and they are all at the same pressure and temperature. This equation is also derived by Wagner (1952) using a different method. In the limit when $x_j = 0$, eqn. (28) reduces to eqn. (19) which holds for binary mixtures. In order to find the infinite dilution ternary activity coefficient $\gamma_{i\infty}^{(1,2,3)}$, it is sufficient to replace $x_i = 0$ in eqn. (28). The resulting equation will be

$$\gamma_{i\infty}^{(1,2,3)} / \gamma_{i\infty}^{(i,j)} = \gamma_j^{(j,k)}(x_j) \exp \left\{ - \int_0^{x_k} \frac{1}{(1-t)^2} \left[\frac{\partial \ln \gamma_k^{(1,2,3)}(t, x_i/x_j)}{\partial (x_i/x_j)} \right]_t dt \right\}_{t, x_i=0} \quad (29)$$

Equation (29) is a rigorous relation which provides us with the relationship between an infinite-dilution ternary activity coefficient and the binary activity coefficients. However, for the calculation of $\gamma_{i\infty}^{(1,2,3)}$, in addition to the knowledge of binary activity coefficients we also need to know

$$\lim_{x_i \rightarrow 0} \left(\frac{\partial \ln \gamma_k^{(1,2,3)}}{\partial (x_i/x_j)} \right)_{x_k}$$

which appears inside the integral on the righthand side of eqn. (29).

The essential relation for ternary-mixture activity coefficients, eqn. (24), can also be transformed to a form which would provide us with another interesting insight into the nature of ternary-mixture activity coefficients. For this, we perform partial differentiation on eqn. (24a) with respect to x_k at constant x_i/x_j , and join the resulting relation with eqn. (28). The final relation for partial derivative of g^E/RT with respect to x_k at constant x_i/x_j will be

$$\begin{aligned} \left[\frac{\partial (g^E/RT)}{\partial x_k} \right]_{x_i/x_j} &= - \left(\frac{x_i}{x_i + x_j} \right) \int_0^{[x_j/(x_i + x_j)]} \frac{\ln \gamma_j^{(i,j)}}{(1-t)^2} dt \\ &\quad - \ln \gamma_j^{(1,2,3)} + \ln \gamma_j^{(i,j)} \left(\frac{x_j}{x_i + x_j} \right) + \ln \gamma_k^{(1,2,3)} \\ &\quad + \frac{x_i(1-x_k)}{x_j^2} \int_0^{x_k} \frac{1}{(1-t)^2} \left[\frac{\partial \ln \gamma_k^{(1,2,3)}(t, x_i/x_j)}{\partial (x_i/x_j)} \right]_t dt \end{aligned} \quad (30)$$

This equation by itself does not reveal any new information about the nature of ternary-mixture activity coefficients. But, by switching the places of the dummy subscripts i and j in this equation, we will arrive at another equation which gives us $[\partial (g^E/RT)/\partial x_k]_{x_j/x_i}$. Now, due to the fact that

$$\left[\frac{\partial (g^E/RT)}{\partial x_k} \right]_{x_i/x_j} = \left[\frac{\partial (g^E/RT)}{\partial x_k} \right]_{x_j/x_i}$$

we may conclude from eqn. (30) the following interesting relation between the ternary- and binary-mixture activity coefficients.

$$\begin{aligned} \gamma_i^{(1,2,3)}/\gamma_j^{(1,2,3)} &= \left\{ \gamma_i^{(i,j)} \left(\frac{x_i}{x_i + x_j} \right) / \gamma_j^{(i,j)} \left(\frac{x_j}{x_i + x_j} \right) \right\} \\ &\quad \times \exp \left\{ - \frac{(1-x_k)^2}{x_j^2} \int_0^{x_k} \frac{1}{(1-t)^2} \left[\frac{\partial \ln \gamma_k^{(1,2,3)}(t, x_i/x_j)}{\partial (x_i/x_j)} \right]_t dt \right\} \end{aligned} \quad (31)$$

According to this equation, the ratio of two ternary activity coefficients of components i and j is equal to the ratio of two binary activity coefficients of a mixture of i and j times a correction factor. The binary-mixture composition should be chosen the same as the relative compositions of i and j in the

ternary mixture at the same pressure and temperature as the ternary mixture. The exponential correction factor appearing in (31) depends on the composition and activity coefficient of the third component (k) of the ternary mixture. From eqn. (31) it is clear that in the limits of infinite dilution and high concentrations of the third component (k) we may simplify this equation to the following form

$$\lim_{x_k \rightarrow 0 \text{ or } 1} (\gamma_i^{(1,2,3)}/\gamma_j^{(1,2,3)}) = \gamma_i^{(i,j)} \left(\frac{x_i}{x_i + x_j} \right) / \gamma_j^{(i,j)} \left(\frac{x_i}{x_i + x_j} \right) \quad (32)$$

This relation is an important conclusion which may be utilized for the calculation of ternary-mixture activity coefficients when the concentration of one of the components (k) is very high or very low.

Another observation which we could make about eqn. (31) is its limiting form when either components i or j are at the infinite dilution concentrations. In these two cases eqn. (31) will be identical with eqn. (29).

Another useful relation between ternary- and binary-mixture activity coefficients which may be utilized for an integral consistency test of ternary activity coefficient data can be derived by joining eqns. (3) and (31). By replacing $\gamma_i^{(i,j)}/\gamma_j^{(i,j)}$ from eqn. (31) in (3) we get

$$\int_0^1 \left\{ \ln \left(\frac{\gamma_i^{(1,2,3)}}{\gamma_j^{(1,2,3)}} \right) + \left(\frac{1 - x_k}{x_j} \right)^2 \int_0^{x_k} \frac{1}{(1-t)^2} \times \left[\frac{\partial \ln \gamma_k^{(1,2,3)}(t, x_i/x_j)}{\partial (x_i/x_j)} \right]_t dt \right\} d \left(\frac{x_i}{x_i + x_j} \right) = 0 \quad (33)$$

Now, by changing the variable in this equation from $x_i/(x_i + x_j)$ to x_i/x_j and integrating the second term of the equation over x_i/x_j , we derive the following relation

$$\int_0^\infty \left(\frac{x_j}{x_i + x_j} \right)^2 \ln \left(\frac{\gamma_i^{(1,2,3)}}{\gamma_j^{(1,2,3)}} \right) d(x_i/x_j) = - \int_0^{x_k} \frac{1}{(1-t)^2} \ln \left(\frac{\gamma_k^{(i,k)}(t)}{\gamma_k^{(j,k)}(t)} \right) dt$$

The latter equation can be further simplified by utilizing eqn. (19) for the integral appearing in its right hand side. The resulting relation will be

$$\int_0^\infty \left[\left(\frac{x_j}{x_i + x_j} \right)^2 \ln \left(\frac{\gamma_i^{(1,2,3)}}{\gamma_j^{(1,2,3)}} \right) \right]_{x_k} d(x_i/x_j) = \ln \left\{ \frac{\gamma_j^{(j,k)}(x_j^1 = x_i + x_j)}{\gamma_i^{(i,k)}(x_i^1 = x_i + x_j)} \right\} + \left(\frac{x_k}{1 - x_k} \right) \ln \frac{\gamma_k^{(j,k)}(x_k)}{\gamma_k^{(i,k)}(x_k)} \quad (34)$$

This equation is an important relation which may be used for an integral consistency test of ternary-mixture activity coefficient data provided that reliable binary-mixture activity coefficient data are available. The term $\gamma_j^{(j,k)}(x_j^1 =$

$x_i + x_j$) appearing on the righthand side of eqn. (34) stands for the activity coefficient of component j in the binary mixture of j and k at the same pressure and temperature as the ternary mixture and with a mole fraction of $x_j^1 = x_j + x_k$. Similar interpretations hold for the other binary activity coefficients appearing on the right hand side of eqn. (34). In the two limits when $x_k \rightarrow 0$ or 1 , eqn. (34) reduces to the following form

$$\lim_{x_k \rightarrow 0 \text{ or } 1} \int_0^1 \ln \left(\frac{\gamma_i^{(1,2,3)}}{\gamma_j^{(1,2,3)}} \right)_{x_k} d \left(\frac{x_i}{x_i + x_j} \right) = 0 \quad (35)$$

of course, in the limit of $x_k = 0$. This equation is identical with the Gibbs-Duhem equation for binary mixtures as shown by eqn. (3).

In the above discussion where we relate binary- and ternary-mixture activity coefficients, two of the three ternary coefficients always appear in every equation. This indicates that we may not be able to calculate a ternary activity coefficient solely from the knowledge of the binary data through the above equations. In order to investigate the conditions under which one may be able to do so we switch the places of subscripts i and k in eqn. (28) and subscripts j and k in eqn. (31). Then we eliminate $\gamma_k^{(1,2,3)}$ from the two resulting equations to derive a new equation. At this stage, we differentiate the new equation with respect to x_i at constant x_j/x_k and consequently derive the following equation

$$\begin{aligned} & \frac{\partial}{\partial x_i} \left\{ \ln \left[\gamma_i^{(i,j)} \left(\frac{x_i}{x_i + x_j} \right) / \gamma_j^{(i,j)} \left(\frac{x_j}{x_i + x_j} \right) \right] \right\}_{x_j/x_k} \\ &= \left(\frac{1}{1 - x_i} \right) \left(\frac{\partial \ln \gamma_i^{(1,2,3)}}{\partial x_i} \right)_{x_j/x_k} + \frac{x_k}{x_j(1 - x_i)} \left[\frac{\partial \ln \gamma_i^{(1,2,3)}}{\partial (x_j/x_k)} \right]_{x_i} \\ &+ \frac{2(1 - x_k)}{x_j^2(1 - x_i)} \int_0^{x_k} \frac{1}{(1 - t)^2} \left[\frac{\partial \ln \gamma_k^{(1,2,3)}}{\partial (x_i/x_j)} \right]_t dt \\ &- \frac{x_k}{x_j^2(1 - x_i)} \left[\frac{\partial \ln \gamma_k^{(1,2,3)}}{\partial (x_i/x_j)} \right]_{x_k} \\ &+ \frac{(1 - x_k)^2}{x_j^3(1 - x_i)} \int_0^{x_k} \frac{1}{(1 - t)^2} \left[\frac{\partial^2 \ln \gamma_k^{(1,2,3)}}{\partial (x_i/x_j)^2} \right]_t dt \end{aligned} \quad (36)$$

This equation as it stands is rather complex and does not provide us with any conclusion. However, in the limiting case when $x_k \rightarrow 0$, this equation may be reduced to a simpler form

$$\begin{aligned} & \lim_{x_k \rightarrow 0} \frac{\partial}{\partial x_i} \left\{ \ln \left[\gamma_i^{(i,j)} \left(\frac{x_i}{x_i + x_j} \right) / \gamma_j^{(i,j)} \left(\frac{x_j}{x_i + x_j} \right) \right] \right\}_{x_j/x_k} \\ &= \left(\frac{1}{1 - x_i} \right) \left(\frac{\partial \ln \gamma_i^{(1,2,3)}}{\partial x_i} \right)_{x_j/x_k} \end{aligned}$$

which after integration will become

$$\lim_{x_k \rightarrow 0} \gamma_i^{(1,2,3)} = \left\{ \gamma_i^{(i,j)} \left(\frac{x_i}{x_i + x_j} \right) / \gamma_j^{(i,j)} \left(\frac{x_j}{x_i + x_j} \right) \right\}^{(1-x_i)} \\ \times \exp \left\{ \int_0^{x_i} \ln \left[\gamma_i^{(i,j)} \left(\frac{t}{t + x_j} \right) / \gamma_j^{(i,j)} \left(\frac{x_j}{t + x_j} \right) \right] dt \right\} \quad (37)$$

For $x_k = 0$, this equation is consistent with the Gibbs—Duhem equation for binary mixtures. For small values of x_k , eqn. (37) can be used for prediction of $\gamma_i^{(1,2,3)}$ from binary-mixture activity coefficients data. In other words, in the limit of infinite dilution of a component of a ternary mixture, ternary activity coefficients of the other two components may be expressed with respect to their binary mixture as is demonstrated by eqn. (37). In the other limiting case when $x_k \rightarrow 1$ no clear result can be drawn from eqn. (36).

CONCLUSION

Through the rigorous classical thermodynamic technique presented in this report we have been able to introduce a number of new equations relating binary- and ternary-mixture activity coefficients. Application of the technique to binary mixtures presents us with a reformulated version of the Gibbs—Duhem equation. This reformulated version can be readily used for the consistency test of binary activity coefficient data and for calculation of one binary activity coefficient from another. Application of the present technique to the case of ternary mixtures provides us with a new insight into the nature of ternary-mixture activity coefficients and their relationships with binary data. According to eqn. (28), generally, a ternary-mixture activity coefficient can be calculated from the knowledge of another ternary coefficient plus the binary-mixture data, all at the same pressure and temperature. This conclusion is quite different from the Gibbs—Duhem equation. Through the Gibbs—Duhem equation for a ternary mixture, eqn. (1), we need to know two of the ternary activity coefficients in order to calculate the third. It should be pointed out that through the present technique we are also able to derive the Gibbs—Duhem equation without the application of the principle under which it was originally derived. Equation (34) is another significant conclusion of this technique. By the application of this equation we are now able to perform an integral consistency test of any two ternary activity coefficients with respect to binary activity coefficient data. Equations (29), (32), (35) and (37) reveal to us the limiting nature of ternary activity coefficients when the mole fraction of one of the three components approaches unity or its infinite dilution limit. Specifically, eqn. (37) provides us with an interesting form of the ternary activity coefficient and the condition under which it may be calculated, solely from the binary activity coefficient data. The working equation for the molar Gibbs free energy of a multicomponent mixture, eqn. (13), and

the analysis presented here can be similarly applied to mixtures with four or more components.

ACKNOWLEDGMENTS

The author appreciates the comments made by Dr. Marie-Louise Soboungi and Dr. Milton Blander in reviewing the manuscript. Support for this research is provided by the U.S. National Science Foundation, grant GK 43139, and the U.S. Department of Energy.

REFERENCES

- Coddington, E.A., 1961. *Ordinary Differential Equations*. Prentice-Hall, Englewood Cliffs, N.J.
- Duhem, P., 1899. *Traité élémentaire de Mécanique Chimique*, 4 Vols., Paris; and 1911. *Traité d'Energétique*, 2 Vols., Paris.
- Gibbs, J.W., 1928. *Collected Works*, 2 Vols., New York.
- Kamke, E., 1959. *Differentialgleichungen, Lösungsmethoden und Lösungen*. 6th edn., Leipzig.
- King, M.B., 1969. *Phase Equilibrium in Mixtures*. Pergamon Press, Oxford.
- Mansoori, G.A., 1980. Molecular basis of activity coefficients (isobaric-isothermal ensemble approach). *Fluid Phase Equilibria*, 4: 61-69.
- Mansoori, G.A. and Canfield, F.B., 1970. Perturbation and variational approaches to equilibrium thermodynamics of gases, liquids and phase transitions. *Ind. Eng. Chem.*, 62: 12-29.
- Prausnitz, J.M., 1969. *Molecular Theory of Fluid-Phase Equilibria*. Prentice-Hall, Englewood Cliffs, N.J.
- Prigogine, I. and Defay, R., 1954. *Chemical Thermodynamics*. Longman, London.
- Rowlinson, J.S., 1969. *Liquids and Liquid Mixtures*. 2nd edn., Butterworth & Co., London.
- Wagner, C., 1952. *Thermodynamics of Alloys*. Addison-Wesley Pub. Co., Inc., Reading, Mass.