Part II. Thermodynamic Analysis

P. L. CHUEH, N. K. MUIRBROOK, and J. M. PRAUSNITZ

University of California, Berkeley, California

Thermodynamic analysis is applied to high-pressure vapor-liquid equilibria in binary and multicomponent mixtures containing one or more noncondensable components. A thermodynamic consistency test is described, and a modification of van Laar's model is given for representing adjusted activity coefficients in binary and multicomponent liquid solutions up to the critical composition. With only experimental data used on the two binaries at 0°C., vapor-liquid equilibria are calculated for the carbon dioxide–nitrogen–oxygen ternary at high pressures. Brief reference is made to the possibility of air separation by high-pressure absorption in liquid carbon dioxide.

Thermodynamic analysis is a tool for interpreting phase-equilibrium data; such interpretation is necessary for interpolating or extrapolating data to new conditions and for correlating phase behavior in terms of physicochemical parameters. While thermodynamic analysis of phase-equilibrium data at low pressures is common, such analysis for mixtures at high pressures, approaching the critical of the system, is still rare primarily because thermodynamic techniques for performing such analysis are still in a state of development. In this work we consider the thermodynamic analysis of vapor-liquid equilibria for the carbon dioxide–nitrogen–oxygen system at 0°C. up to the critical pressure. First, we present a thermodynamic consistency test applicable to the two binary systems carbon dioxide–nitrogen and carbon dioxide–oxygen. We then present a modified van Laar model for representing the activity coefficients of the two binaries and proceed to show how this model is easily extended to multicomponent mixtures containing two or more noncondensable components. Finally, we discuss the calculation of ternary high-pressure vapor-liquid equilibria using only data obtained from two binary mixtures. This calculation is illustrated with results for the carbon dioxide–nitrogen–oxygen system with brief reference to the problem of air separation by high-pressure absorption in liquid carbon dioxide.

THERMODYNAMIC CONSISTENCY OF BINARY SYSTEMS

Vapor-liquid equilibrium data are said to be thermodynamically consistent when they satisfy the Gibbs-Duhem equation. When the data satisfy this equation, it is likely, but by no means guaranteed, that they are correct; however, if they do not satisfy this equation, it is certain that they are incorrect.

Thermodynamic consistency tests for binary vapor-liquid equilibria at low pressures have been described by many authors; a good review is given in the monograph by Van Ness (*12*). Extension of these methods to isothermal high-pressure equilibria presents two difficulties: first, it is necessary to have experimental data for the density of the liquid mixture along the saturation line and second, since the ideal gas law is not valid, it is necessary to calculate vapor-phase fugacity coefficients either from volumetric data for the vapor mixture or else from an equation of state. In an attempt to simplify the second requirement, Adler and co-workers (*1*) used the Lewis fugacity rule to calculate vapor-phase fugacities; however, since the errors in this approximation are often very large, it is not possible to come to any meaningful conclusions concerning the thermodynamic consistency of experimental equilibrium data when this approximation is used as an essential part of the consistency test.

The consistency test described here is an extension to isothermal high-pressure data of the integral (area) test given by Redlich and Kister (*8*) and by Herington (*2*) for isothermal low-pressure data. For a binary system at constant temperature, the Gibbs-Duhem equation is written

$$x_1\, d \ln f_1 + x_2\, d \ln f_2 = v^L dP/RT \qquad (1)$$

When one uses the identity $x_1\, d \ln x_1 + x_2\, d \ln x_2 = 0$, Equation (1) can be rearranged to read

$$\ln \frac{f_2/x_2}{f_1/x_1}\, dx_2 + \frac{v^L dP}{RT} = d\left(\ln \frac{f_1}{x_1} + x_2 \ln \frac{f_2/x_2}{f_1/x_1}\right) \qquad (2)$$

Introducing fugacity coefficients ϕ and K factors ($K_i = y_i/x_i$) into Equation (2), one obtains

$$\left(\ln \frac{\phi_2}{\phi_1} + \ln \frac{K_2}{K_1}\right) dx_2 + \frac{v^L dP}{RT} =$$
$$d\left[\ln K_1 + \ln \phi_1 P + x_2\left(\ln \frac{\phi_2}{\phi_1} + \ln \frac{K_2}{K_1}\right)\right] \qquad (3)$$

In Equations (1), (2), and (3) subscript 2 refers to the light component. Equation (3) is now integrated from $x_2 = 0$ to some arbitrary upper limit x_2. The following boundary conditions apply:

when $x_2 = 0$: $\phi_1 = \phi_1^s$; $P = P_1^s$; $K_1 = 1$

The integrated form of Equation (3) can be most conveniently written as

Area I + *Area II* + *Area III* =

$$\left[\ln K_1 + \ln \frac{\phi_1 P}{\phi_1^s\, P_1^s} + x_2\left(\ln \frac{\phi_2}{\phi_1} + \ln \frac{K_2}{K_1}\right)\right] \text{at } x_2 \qquad (4)$$

where

$$\textit{Area I} = \int_{x_2=0}^{x_2} \ln \frac{K_2}{K_1}\, dx_2 \qquad (5)$$

$$\textit{Area II} = \int_{x_2=0}^{x_2} \ln \frac{\phi_2}{\phi_1}\, dx_2 \qquad (6)$$

$$\textit{Area III} = \frac{1}{RT} \int_{x_2=0}^{x_2} v^L dP \qquad (7)$$

The three areas are found by graphical integration. The thermodynamic consistency test consists of comparing the sum of the three areas [left-hand side of Equation (4)] with the right-hand side of Equation (4).† The three areas

---

N. K. Muirbrook is with Humble Oil and Refining Company, Linden, New Jersey.

† We noticed a consistency test similar to ours described by Richard E. Thompson and Wayne C. Edmister in the *A.I.Ch.E. J.*, 11, No. 3, 457 (1965), after this work was completed.

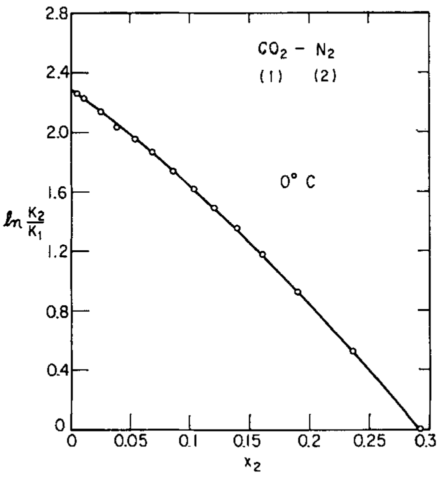

Fig. 1. First area in thermodynamic consistency test.

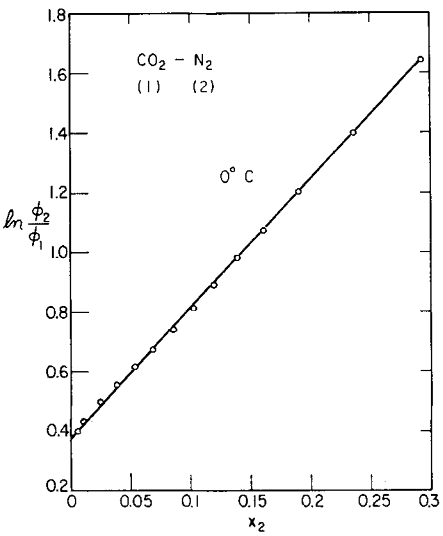

Fig. 2. Second area in thermodynamic consistency test.

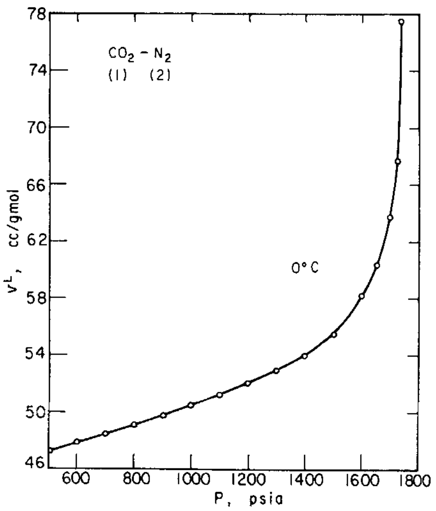

Fig. 3. Third area in thermodynamic consistency test.

depend upon equilibrium data for the composition range $x_2 = 0$ to $x_2 = x_2$. However, the right-hand side of Equation (4) depends only on equilibrium data at the upper limit $x_2 = x_2$. The comparison indicated by Equation (4) should be made for several values of x_2 up to and including the critical composition.

To illustrate this thermodynamic consistency test, Figures 1, 2, and 3 show plots of the appropriate functions needed to calculate *Areas I, II,* and *III* for the nitrogen–carbon dioxide system at 0°C.; the data are taken from the preceding paper (Part I). Fugacity coefficients were calculated with the modified Redlich-Kwong equation (9).

A comparison of the left-hand side (LHS) and the right-hand side (RHS) of Equation (4) is given in Table 1 for the two systems nitrogen–carbon dioxide and oxygen–carbon dioxide at 0°C. with data reported in the preceding paper. For each system the comparison is made at three different values of x_2 including the critical point. In order to assess their relative importance, values of all the individual terms in Equation (4) are reported in Table 1. It is apparent that all the terms contribute significantly and that none may be neglected except that $\ln K_1$ must necessarily vanish at the critical mole fraction.

The final column in Table 1 reports the absolute value of the difference between LHS and RHS divided by their arithmetic mean. For the two systems considered here, the percent inconsistency is always less than about 5%. In view of the uncertainties in the fugacity coefficients (resulting from a good but still approximate equation of state) it is probably fair to judge the thermodynamic consistency of these data as very good.

The thermodynamic consistency test for binary systems described above can be extended to ternary (and higher) systems with techniques similar to those described by Herington (3) and others (*7, 11*). The necessary calculations become quite tedious, and unless extensive multicomponent data are available, they are usually not worthwhile.

THERMODYNAMIC REPRESENTATION OF PHASE EQUILIBRIA IN BINARY SYSTEMS

The purpose of this thermodynamic analysis is to describe how the fugacity of a component in a mixture depends on the independent variables temperature, pressure, and composition. For a component in the vapor phase, this dependence is given by the fugacity coefficient, which in turn is directly related to the equation of state. For a component in the liquid phase, it is given by the activity coefficient.

For isothermal data, the activity coefficient depends on the liquid-phase composition and also on the total pressure. It is desirable to separate these two coefficients as described previously (7):

$$\gamma_1^{(P_1^s)} \equiv \frac{f_1}{x_1 f_{1\text{pure}}^{(P_1^s)}} \exp - \int_{P_1^s}^{P} \frac{\bar{v}_1^L dP}{RT} \qquad (8)$$

Table 1. Thermodynamic Consistency Test [Equation (4)]

x_2	Area I	Area II	Area III	LHS	$\ln K_1$	$\ln \frac{\phi_1 P}{\phi_1^s P_1^s}$	$x_2\left(\ln \frac{K_2}{K_1} + \ln \frac{\phi_2}{\phi_1}\right)$	RHS	% inconsistency
Carbon dioxide(1)-Nitrogen(2) at 0°C.:									
0.1030	0.2024	0.0618	0.1042	0.369	—0.3496	0.4855	0.2505	0.386	4.5
0.1902	0.3142	0.1500	0.1703	0.635	—0.2562	0.5044	0.404	0.652	2.6
0.2926^c	0.3618	0.2965	0.1968	0.855	0	0.3974	0.482	0.879	2.8
Carbon dioxide(1)-Oxygen(2) at 0°C.:									
0.0997	0.1910	0.0519	0.0878	0.331	—0.3439	0.4415	0.2305	0.328	0.9
0.1980	0.3227	0.1354	0.1516	0.610	—0.3011	0.4762	0.407	0.582	4.7
0.3120^c	0.3720	0.2599	0.223	0.855	0	0.3336	0.491	0.825	3.6

Note: c = critical.

$$\gamma_2^{*(P_1^s)} \equiv \frac{f_2}{x_2 H_{2,1}^{(P_1^s)}} \exp - \int_{P_1^s}^{P} \frac{\bar{v}_2^L dP}{RT} \tag{9}$$

The adjusted activity coefficients are independent of pressure; they refer to an (arbitrary) reference pressure here taken as P_1^s, the saturation pressure of the pure heavy component. At constant temperature these adjusted activity coefficients are functions only of liquid composition, and therefore they must satisfy the isothermal, isobaric Gibbs-Duhem equation

$$x_1 \, d \ln \gamma_1^{(P_1^s)} + x_2 \, d \ln \gamma_2^{*(P_1^s)} = 0 \tag{10}$$

Since there are many useful integrated forms of Equation (10) (for example, the van Laar and Margules equations), the definitions given by Equations (8) and (9) make it possible to represent high-pressure vapor-liquid equilibria in a manner essentially identical to that used for low-pressure vapor-liquid equilibria.

The asterisk (*) in Equation (9) is to serve as a reminder that the unsymmetric convention has been used in the normalization of the adjusted activity coefficients. For component 1, the standard state fugacity is the fugacity of pure liquid 1 at the temperature of the solution and at P_1^s, the saturation pressure of pure 1. For component 2, the standard state fugacity is its Henry's constant in solvent 1, at the temperature of the solution and at P_1^s. As a result both adjusted activity coefficients approach unity as the liquid solution becomes infinitely dilute with respect to the light component:

$$\gamma_1^{(P_1^s)} \rightarrow 1 \quad \text{as} \quad x_1 \rightarrow 1 \tag{11}$$

$$\gamma_2^{*(P_1^s)} \rightarrow 1 \quad \text{as} \quad x_2 \rightarrow 0 \tag{12}$$

The unsymmetric normalization convention has the advantage that it avoids the use of any hypothetical liquid standard state for the pure noncondensable component.

Adjusted activity coefficients were calculated for the carbon dioxide–nitrogen system and for the carbon dioxide–oxygen system at 0°C. Henry's constants were determined by plotting $\ln f_2/x_2$ vs. $P - P_1^s$ (where subscript 2 refers to the light component) and extrapolating to $P - P_1^s = 0$. Henry's constants are 5,740 and 4,450 lb./sq. in. abs. for nitrogen and oxygen, respectively. Fugacity coefficients for the vapor phase were calculated from the modified Redlich-Kwong equation (9). Partial molar volumes for the liquid phase were computed from the measured liquid molar volumes (with Equation A.III.12 in reference 7 used) and were assumed to be independent of pressure.

For both systems complete sets of partial molar volumes, fugacity coefficients, and adjusted activity coefficients are given elsewhere (*4*). A brief summary, to indicate the values obtained, is given in Table 2.

EXCESS GIBBS ENERGY

Following Scatchard (*10*), we define the excess Gibbs energy per mole of solution by

$$\frac{g^E}{RT} = x_1 \ln \gamma_1^{(P_1^s)} + x_2 \ln \gamma_2^{*(P_1^s)} \tag{13}$$

In view of the unsymmetric normalization, g^E vanishes at infinite dilution with respect to component 2 but not with respect to component 1; that is

$$g^E \rightarrow 0 \quad \text{as} \quad x_2 \rightarrow 0$$

but

$$g^E \neq 0 \quad \text{as} \quad x_1 \rightarrow 0 \tag{14}$$

As defined here, the ideal solution ($g^E = 0$) is one where the fugacity of the light component is given by Henry's law (with suitable pressure correction); physically, this means that g^E is zero whenever the concentration of component 2 in the liquid phase is sufficiently small to prevent molecules of component 2 from interacting with one another. In a manner analogous to that used by Wohl (*13*), the excess Gibbs energy can be represented by a power series in the effective volume fraction of the solute

$$\frac{g^E}{RT(x_1 q_1 + x_2 q_2)} = -\alpha_{22} \Phi_2^2 - \alpha_{222} \Phi_2^3 - \ldots\ldots \tag{15}$$

where

$$\Phi_2 = \frac{q_2 x_2}{q_1 x_1 + q_2 x_2} \tag{16}$$

The activity coefficients can be found from the exact relations

$$\left(\frac{\partial n_T g^E}{\partial n_1} \right)_{T,P,n_2} = RT \ln \gamma_1^{(P_1^s)} \tag{17}$$

$$\left(\frac{\partial n_T g^E}{\partial n_2} \right)_{T,P,n_1} = RT \ln \gamma_2^{*(P_1^s)} \tag{18}$$

A DILATED VAN LAAR MODEL FOR LIQUID MIXTURES

When Equation (15) is truncated after the first term, Equations (17) and (18) yield the classical van Laar equations (for unsymmetric normalization) as reported previously (*7*). These equations, containing two adjustable parameters, were shown to be satisfactory for fitting adjusted activity coefficients for the butane–carbon dioxide system; however, they are not satisfactory for describ-

TABLE 2. SUMMARY OF THERMODYNAMIC FUNCTIONS FOR TWO SATURATED BINARY SYSTEMS AT 0°C.

P, lb./sq. in. abs.	x_2	$\bar{v}^L$, cc./g.-mole		y_2	ϕ_1	ϕ_2	$\gamma_1^{(P_1^s)}$	$\gamma_2^{*(P_1^s)}$
		1	2					
			Carbon dioxide(1)-Nitrogen(2):					
800	0.0390	47.9	76.7	0.2360	0.661	1.156	1.025	0.911
1,200	0.1030	47.9	87.8	0.3675	0.532	1.198	1.035	0.743
1,500	0.1607	46.7	101.0	0.3842	0.440	1.290	1.071	0.594
1,740^c	0.2926	20.8	215.0	0.2926	0.336	1.743	1.377	0.236
			Carbon dioxide(1)-Oxygen(2):					
800	0.0455	47.9	62.3	0.2520	0.660	1.093	1.008	1.03
1,200	0.1205	48.3	73.2	0.3838	0.523	1.112	1.010	0.819
1,500	0.1980	46.7	90.8	0.4065	0.422	1.187	1.035	0.625
1,703^c	0.3120	6.05	230.0	0.3120	0.322	1.552	1.365	0.257

Note: c = critical.

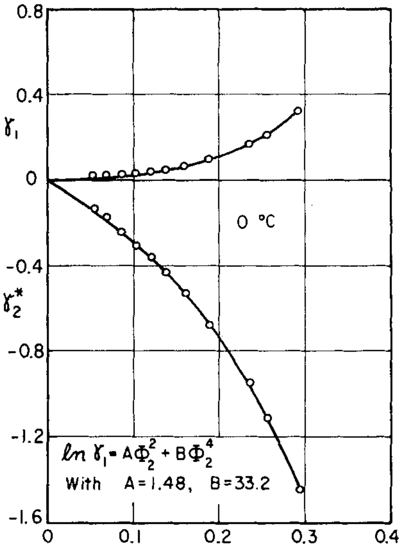

Fig. 4. Adjusted activity coefficients for the carbon dioxide (1)–nitrogen (2) system.

ing the properties of the two systems investigated in Part I. In addition, the three-suffix Margules equations were found to be unsatisfactory.

The probable reason for the failure of the classical van Laar treatment is due to Van Laar's assumption that q_1 and q_2 are constants, independent of composition. The q's are parameters which reflect the cross sections, or sizes, or spheres of influence of the molecules; at conditions remote from critical, where the liquid molar volume is close to a linear function of the mole fraction, it is reasonable to assume that the q's are composition independent. However, for a concentrated mixture of a noncondensable component 2 with a subcritical liquid 1, the molar volume is a highly nonlinear function of the mole fraction, especially in the vicinity of the critical composition. The liquid solution dilates as x_2 rises, and van Laar's model must be modified to take this effect into account.

For practical reasons (since experimental data are usually not plentiful), it is desirable to derive equations for the adjusted activity coefficients which contain no more than two parameters. Because of this limitation, we assume that whereas q_1 and q_2 depend on composition, their ratio does not. Since the van Laar treatment is a two-body (quadratic) theory we assume that q_1 and q_2 are given by a quadratic function of the effective volume fraction:

$$q_1 = v_1^c\,[1 + \eta_{12}\,\Phi_2^2] \tag{19}$$

$$q_2 = v_2^c\,[1 + \eta_{12}\,\Phi_2^2] \tag{20}$$

In Equations (19) and (20) we have arbitrarily used the pure-component critical volumes as our measure of the molecular cross sections at infinite dilution, when $\Phi_2 = 0$. Some other constant (for example, van der Waal's b or Lennard-Jones' σ^3) could just as easily be used. The *dilation constant* η_{12} is a measure of how effectively the light component swells the liquid solution.

When Equations (19) and (20) are substituted into the truncated Equation (15), the adjusted activity coefficients are

$$\ln \gamma_1^{(P_1^s)} = A\,\Phi_2^2 + B\,\Phi_2^4 \tag{21}$$

$$\ln \gamma_2^{*(P_1^s)} = A\left(\frac{v_2^c}{v_1^c}\right)(\Phi_2^2 - 2\Phi_2) + B\left(\frac{v_2^c}{v_1^c}\right)\left(\Phi_2^4 - \frac{4}{3}\Phi_2^3\right) \tag{22}$$

where

$$A \equiv \alpha_{22}\,v_1^c \tag{23}$$

$$B \equiv 3\eta_{12}\,\alpha_{22}\,v_1^c \tag{24}$$

Equations (21) and (22) are the desired two-parameter equations. These equations provide an excellent fit of the adjusted activity coefficients for the two systems investigated in Part I. The correlation for the carbon dioxide–nitrogen system is shown in Figure 4; Figure 5 shows that these equations also provide an excellent fit of the adjusted activity coefficients of the butane–carbon dioxide system reported previously (7).†

THERMODYNAMIC REPRESENTATION OF EQUILIBRIA FOR MULTICOMPONENT SYSTEMS

The dilated Van Laar model is easily extended to solutions containing two or more noncondensable components. Consider a ternary solution containing one subcritical component, designated by subscript 1, and two supercritical (noncondensable) components, designated by subscripts 2 and 3. (Extension to systems containing three or more noncondensable components will then be self-evident.) Adjusted activity coefficients for components 1 and 2 are given by Equations (8) and (9). The adjusted activity coefficient for component 3 is given by an expression analogous to Equation (9):

$$\gamma_3^{*(P_1^s)} \equiv \frac{f_3}{x_3 H_{3,1}^{(P_1^s)}} \exp - \int_{P_1^s}^{P} \frac{\bar{v}_3^L\,dP}{RT} \tag{25}$$

The excess Gibbs energy is written as an expansion in the effective volume fractions Φ_2 and Φ_3:

$$\frac{g^E}{RT(x_1q_1 + x_2q_2 + x_3q_3)} = -\,\alpha_{22}\,\Phi_2^2 - \alpha_{33}\,\Phi_3^2 - 2\alpha_{23}\,\Phi_2\,\Phi_3 + \text{higher terms} \tag{26}$$

where

$$\Phi_2 = \frac{x_2q_2}{x_1q_1 + x_2q_2 + x_3q_3} \tag{27}$$

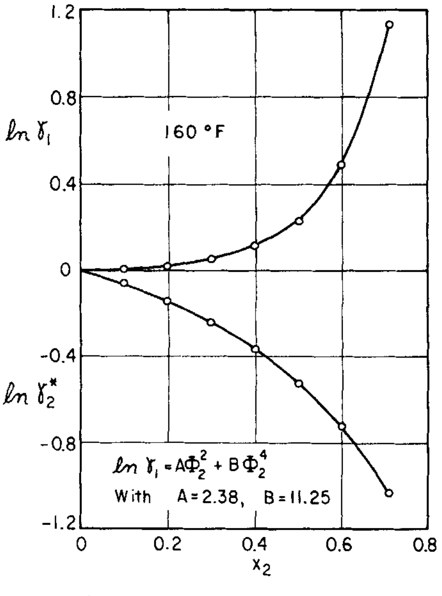

Fig. 5. Adjusted activity coefficients for the butane (1)–carbon dioxide (2) system.

---

† In Figure 3 of reference 7 there is a misprint. The value for A should be 22.7, not 27.7.

and

$$\Phi_3 = \frac{x_3 q_3}{x_1 q_1 + x_2 q_2 + x_3 q_3} \tag{28}$$

For each component i the parameter q_i is related to the liquid composition by

$$q_i = v_i^c \left[1 + \eta_{12}\Phi_2^2 + 2\eta_{1,23}\Phi_2\Phi_3 + \eta_{13}\Phi_3^2\right] \tag{29}$$

Equation (26) contains six parameters. The self-interaction coefficient α_{22} and the dilation constant η_{12} can be found from binary data for the 1-2 system; similarly α_{33} and η_{13} can be found from the binary data for the 1-3 system. The interaction coefficient α_{23} and the dilation constant $\eta_{1,23}$ are properties of the ternary system. (Strictly, α_{23} is a property determinable from the 2-3 binary, but since components 2 and 3 are both noncondensable at the system temperature, binary phase equilibria for this binary system cannot be obtained at the temperature of interest.)

To simplify matters, it is desirable to relate the constants α_{23} and $\eta_{1,23}$ to constants which may be obtained from data for the 1-2 and 1-3 binaries. For nonpolar systems we propose the relations

$$\eta_{1,23} = (\eta_{12}\eta_{13})^{1/2} \tag{30}$$

and

$$\alpha_{23} = (\alpha_{22}\alpha_{33})^{1/2} \tag{31}$$

When these equations are introduced into Equation (26), we obtain

$$\frac{g^E}{RT} = -(x_1 q_1 + x_2 q_2 + x_3 q_3)\left(\sqrt{\alpha_{22}}\,\Phi_2 + \sqrt{\alpha_{33}}\,\Phi_3\right)^2 \tag{32}$$

and

$$q_i = v_i^c\left[1 + \left(\sqrt{\eta_{12}}\,\Phi_2 + \sqrt{\eta_{13}}\,\Phi_3\right)^2\right] \tag{33}$$

The activity coefficients for the three components can be found by appropriate differentiation of Equation (32):

$$\ln \gamma_1^{(P_1^s)} = v_1^c\,\Phi_\alpha^2\,(1 + 3\Phi_\eta^2) \tag{34}$$

$$\ln \gamma_2^{*(P_1^s)} = v_2^c\left[\Phi_\alpha^2\,(1 + 3\Phi_\eta^2 - 2\sqrt{\eta_{12}}\Phi_\eta) - 2\sqrt{\alpha_{22}}\,\Phi_\alpha\,(1 + \Phi_\eta^2)\right] \tag{35}$$

$$\ln \gamma_3^{*(P_1^s)} = v_3^c\left[\Phi_\alpha^2\,(1 + 3\Phi_\eta^2 - 2\sqrt{\eta_{13}}\Phi_\eta) - 2\sqrt{\alpha_{33}}\,\Phi_\alpha\,(1 + \Phi_\eta^2)\right] \tag{36}$$

where

$$\Phi_\alpha \equiv \sqrt{\alpha_{22}}\,\Phi_2 + \sqrt{\alpha_{33}}\,\Phi_3 \tag{37}$$

$$\Phi_\eta \equiv \sqrt{\eta_{12}}\,\Phi_2 + \sqrt{\eta_{13}}\,\Phi_3 \tag{38}$$

Equations (34), (35), and (36) have been used to predict adjusted activity coefficients for nitrogen, oxygen, and carbon dioxide in the ternary system at 0°C. The predicted results are shown in Figure 6. We find that the predicted activity coefficients are in very good agreement with those calculated from the experimental ternary data reported in Part I. Parameters used in Equations (34), (35), and (36) are given in Table 3.

PREDICTION OF TERNARY VAPOR-LIQUID EQUILIBRIA AT HIGH PRESSURES

Finally, we describe the prediction of ternary vapor-liquid equilibria using only binary data for the carbon dioxide–oxygen–nitrogen system at 0°C. In the case under consideration here, two components are noncondensables, and therefore data for only two binaries (1-2 and 1-3) can be used, since the remaining binary (2-3) cannot exhibit vapor-liquid equilibria at the temperature of interest. We consider the problem where the temperature (0°C.) and the liquid-phase composition are given, and we want to find the pressure and the vapor-phase composition.

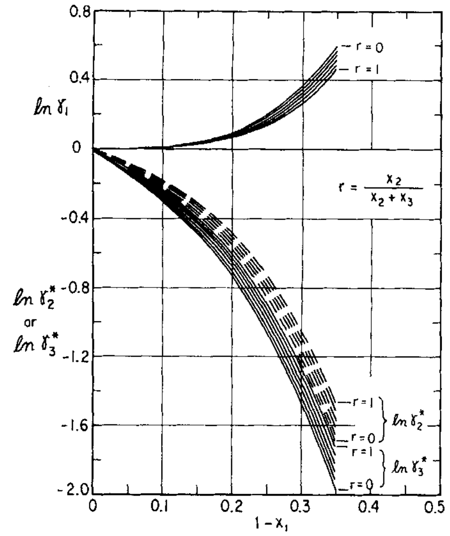

Fig. 6. Adjusted activity coefficients for the ternary system carbon dioxide(1)–oxygen(2)–nitrogen (3).

The three equations of equilibrium are

$$\text{CO}_2\text{:}\quad \gamma_1^{(P_1^s)} x_1 f_{1_{\text{pure}}}^{(P_1^s)} \exp \int_{P_1^s}^{P} \frac{\bar{v}_1^L dP}{RT} = \phi_1 y_1 P \tag{39}$$

$$\text{N}_2\text{:}\quad \gamma_2^{*(P_1^s)} x_2 H_{2,1}^{(P_1^s)} \exp \int_{P_1^s}^{P} \frac{\bar{v}_2^L dP}{RT} = \phi_2 y_2 P \tag{40}$$

$$\text{O}_2\text{:}\quad \gamma_3^{*(P_1^s)} x_3 H_{3,1}^{(P_1^s)} \exp \int_{P_1^s}^{P} \frac{\bar{v}_3^L dP}{RT} = \phi_3 y_3 P \tag{41}$$

The constants $f_{1_{\text{pure}}}^{(P_1^s)}$, P_1^s, $H_{2,1}^{(P_1^s)}$, and $H_{3,1}^{(P_1^s)}$ are, respectively, 393, 505.5, 5,740 and 4,450 lb./sq.in.abs. The three activity coefficients can be calculated as a function of liquid phase composition from Equations (34) to (36). The three fugacity coefficients can be found from the modified Redlich-Kwong equation but depend on the unknown y's and P.

An approximation must be used to calculate the partial molar volumes of the three components in the ternary. Since the total concentration of the light components in the liquid phase is never more than about 30 mole %, we assume that the liquid molar volume of the ternary solution is given by

$$v^L_{\text{ternary}} = \frac{x_2}{x_2 + x_3}\,v^L_{12_{\text{binary}}} + \frac{x_3}{x_2 + x_3}\,v^L_{13_{\text{binary}}} \tag{42}$$

We then use this calculated liquid molar volume to compute partial molar volumes by employing an extension to ternary systems of Equation (A.III.12) given in reference 7.

TABLE 3. PARAMETERS FOR CALCULATION OF TERNARY ACTIVITY COEFFICIENTS FOR THE $CO_2(1)$-$O_2(2)$-$N_2(3)$ AT 0°C.

	Critical volume, v_c, liter/g.-mole	Self-interaction constant, α, g.-mole/liter	Dilation constant, η_{1i}
1	0.0956	—	—
2	0.0744	13.2	12.4
3	0.0901	15.5	7.48

TABLE 4. RELATIVE VOLATILITIES AND K FACTORS OF OXYGEN AND NITROGEN IN CARBON DIOXIDE AT 0°C.

P, lb./sq. in. abs.	$K_{O_2} = y_{O_2}/x_{O_2}$	$K_{N_2} = y_{N_2}/x_{N_2}$	$\alpha = K_{N_2}/K_{O_2}$*
600	7.02	8.44	1.20
650	6.65	7.63	1.15
700	6.27	7.10	1.13
750	5.91	6.55	1.11
800	5.54	6.05	1.09
850	5.15	5.67	1.10
900	4.81	5.30	1.10
950	4.48	5.00	1.12
1,000	4.17	4.70	1.13
1,100	3.63	4.06	1.12
1,200	3.19	3.57	1.12
1,300	2.78	3.15	1.13
1,400	2.40	2.77	1.16
1,500	2.05	2.39	1.16
1,600	1.69	1.96	1.16
1,675	1.35	1.59	1.17

* The reliability of α varies from ±0.02 at 600 lb./sq. in. abs. to ±0.01 at 1,600 lb./sq. in. abs.

Simultaneous solution of Equations (39), (40), and (41) is tedious and was therefore programmed for solution by an electronic digital computer.

Using the equations presented immediately above, we have calculated K factors for nitrogen and oxygen in liquid carbon dioxide because we were interested in the possibility of air separation by high-pressure absorption. Our calculations show that the K factors for these two gases are essentially independent of the relative liquid-phase concentrations of the two gases at a fixed temperature and pressure. (The small variations which we observed are less than the accuracy of the calculations.) As a consequence it is possible to calculate at 0°C. the relative volatility of nitrogen with respect to oxygen as a function of pressure only. The results of this calculation are given in Table 4.

The relative volatilities do not vary very much with pressure, but the capacity of the solvent to dissolve gas increases very much with pressure. At 1,300 lb./sq. in. abs. the molar ratio of total dissolved gas to solvent is about 14%, whereas at 600 lb./sq. in. abs. it is only about 1.4% Therefore, when the pressure is increased from 600 to 1,300 lb./sq. in. abs. (only slightly more than a factor of 2), the required solvent-to-gas ratio for a fixed production rate is reduced by a factor of 10. In this particular system this very favorable improvement in capacity appears to be possible with no significant reduction in solvent selectivity.

CONCLUSION

A method for testing for thermodynamic consistency of vapor-liquid equilibrium data along an isotherm up to the critical pressure was discussed. The method is rigorous except for the assumption of a suitable equation of state which is required to calculate vapor-phase fugacity coefficients. In addition to x-y-P data, it is also essential to have data on the liquid-phase density along the saturation curve.

Furthermore, a modified van Laar model has been presented, which appears to be useful for representing adjusted activity coefficients of binary and multicomponent mixtures with only two parameters per binary at a given temperature. We have used this model to calculate ternary vapor-liquid equilibria for the carbon dioxide–nitrogen–oxygen system. In this work we have restricted ourselves to those high-pressure multicomponent solutions which contain only one condensable component but any number of noncondensables. The case where there is only one noncondensable component with two or more condensable components has recently been discussed by O'Connell (5).

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation and to the donors of the Petroleum Research Fund for financial support, to the Computer Center of the University of California for the use of their facilities, and to J. S. Newman for helpful advice.

NOTATION

A = parameter defined by Equation (23)
B = parameter defined by Equation (24)
f = fugacity
g = molar Gibbs energy
H = Henry's constant
K = y/x
n = number of moles
P = total pressure
q = effective size parameter
R = gas constant
T = absolute temperature
v = molar volume
$\bar{v}$ = partial molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
α = interaction constant
γ = activity coefficient
η = dilation constant
ϕ = fugacity coefficient
Φ = effective volume fraction

Subscripts

1, 2, 3 = components (1 refers to condensable component)
T = total

Superscripts

c = critical
E = excess
L = liquid phase
P_1^s = saturation pressure of component 1
s = saturation
* = normalization by unsymmetric convention

LITERATURE CITED

1. Adler, S. B., Leo Friend, R. L. Pigford, and G. M. Rosselli, *A.I.Ch.E. J.*, **6**, 104 (1960).
2. Herington, E. F. G., *Nature*, **160**, 610 (1947).
3. ———, *J. Appl. Chem.*, **2**, 11 (1952).
4. Muirbrook, N. K., Ph.D. dissertation, Univ. California, Berkeley (1964).
5. O'Connell, J. P., and J. M. Prausnitz, *Ind. Eng. Chem. Fundamentals Quart.*, **3**, 347 (1964).
6. Prausnitz, J. M., and G. D. Snider, *A.I.Ch.E. J.*, **5**, 7S (1959).
7. Prausnitz, J. M., *Chem. Eng. Sci.*, **18**, 613 (1963).
8. Redlich, O., and A. T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).
9. Redlich, O., F. J. Ackerman, R. D. Gunn, M. Jacobson, and S. Lau, *Chem. Eng. Data*, to be published (also *UCRL-11968*).
10. Scatchard, G., *Trans. Faraday Soc.*, **33**, 160 (1937).
11. Tao, L. C., *Ind. Eng. Chem. Fundamentals Quart.*, **1**, 119 (1962).
12. Van Ness, H. C., "Classical Thermodynamics of Non Electrolyte Solutions," Pergamon Press, New York (1964).
13. Wohl, K., *Trans. Am. Inst. Chem. Engrs.*, **42**, 215 (1946).

Manuscript received June 1, 1965; revision received August 30, 1965; paper accepted September 1, 1965.