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Hypothetical Standard States and the Thermodynamics of High-Pressure Phase Equilibria

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Thermodynamic analysis of phase-equilibrium data is necessary for testing such data, for extension to new conditions, and for purposes of correlation and prediction of phase-equilibrium behavior. While such analysis is common for low-pressure systems, it is rare for high-pressure systems owing to difficulties encountered in the definition of standard states. For a gaseous solute in the liquid phase it is proposed that the standard state be taken as the hypothetical liquid at the temperature and total pressure of the solution. The properties of this standard state are specified by the temperature and total pressure and by the specific volume which the substance would have if it did not experience a phase change. This standard state is useful since it is not a function of the solution but only of the substance being considered. For a condensable component in the gas phase it is convenient for most purposes to define the standard state as the ideal gas at the temperature and total pressure of the solution, but to separate the effect of composition on the activity coefficient from that of pressure, it is proposed to define the standard state as the real hypothetical gas at the solution conditions. To illustrate these ideas, activity coefficients are computed for several high-pressure systems, and it is shown how these activity coefficients may be used in the correlation, testing, and extension of high-pressure phase-equilibrium data.

Thermodynamic analysis of phase-equilibrium data is needed for testing and correlating such data and especially for extension to new conditions and to other systems for which no data are available. It is not reasonable to expect that good data for a very large number of systems will ever be obtained over wide ranges of temperature and pressure, and it is therefore essential that available data for representative systems be carefully scrutinized and interpreted with the aid of suitable thermodynamic functions. Such thermodynamic analysis, coupled with the theory of intermolecular forces and aided by techniques like the molecular theory of corresponding states, forms the basis for a useful generalization of phase-equilibrium data. The primary justification for thermodynamic analysis is that it is the first important step toward the ultimate aim of solution theory: prediction of the properties of a mixture from those of the pure components.

In the technical literature it has been customary to subject to thermodynamic analysis equilibrium data for solutions taken at or near atmospheric pressure, but there has been a notable absence of such analyses for phase-equilibrium data obtained at higher pressures in the vicinity of 100 atm. or more. For example some of the excellent experimental studies of Sage and Lacey and W. B. Kay and their co-workers on hydrocarbon mixtures have been in the literature for many years but have received very little thermodynamic scrutiny. A major reason for the lack of thermodynamic attention to high-pressure systems is that when the customary thermodynamic functions of the high-pressure mixture are referred to those of the pure components, these components exist in physically unattainable (hypothetical) states. Thermodynamic analysis of high-pressure systems therefore requires precise definitions of hypothetical standard states as well as methods of evaluating the thermodynamic functions corresponding to those states. This paper presents techniques for the calculation of hypothetical standard-state functions and in a few examples illustrates their applicability to thermodynamic analysis of high-pressure phase equilibria.

STANDARD STATES

The activity coefficient of a component is defined as the ratio of the activity of that component to its mole fraction; the activity in turn is defined as the ratio of the fugacity of that component in the solution to its fugacity in some standard (arbitrary) state. An activity coefficient therefore always refers to some standard state, and the numerical value of an activity coefficient is meaningless unless the standard state is also specified. While the choice of a standard state is completely arbitrary, it has been customary to use as standard states either the pure component (in the same state of aggregation as that of the solution) or the state corresponding to infinite dilution; in addition, Mauser and Kortüm (7) recently showed that for sparingly soluble solutes it is convenient to use the state corresponding to saturation. These three standard states, designated respectively by *a*, *b*, and *c*, all serve the same function of normalization whereby the activity coefficient approaches a definite limit as the standard state is approached:

$$\begin{aligned}&(a)\quad \gamma_i \to 1 \text{ as } x_i \to 1\\ &(b)\quad \gamma_i \to 1 \text{ as } x_i \to 0 \qquad\qquad (1)\\ &(c)\quad \gamma_i \to \frac{1}{x_i} \text{ as } x_i \to x_i \quad \text{(saturated)}\end{aligned}$$

Normalization (*a*), sometimes called the symmetric convention, is most commonly used for solutions of liquids at low pressures; normalization (*b*), sometimes called the *unsymmetric convention*, is used for solutions of electrolytes in liquids; normalization (*c*) is useful only in equilibria where one of the phases is a pure component. From the viewpoint of classical thermodynamics all three standard states are equally acceptable, but from the viewpoint of the theory of solutions standard state (*a*) is highly preferable to the other two. The activity coefficient of a component shows the effect of composition on the activity of that component relative to its activity in the standard state; since the aim of solution theory is to predict the properties of components in solution from those of the pure components, the most meaningful standard state is necessarily the pure component itself. When standard states (*b*) or (*c*) are used, the activity coefficient gives information about the activity relative to that at some other concentration; in other words in cases (*b*) and (*c*) the standard state is itself a function of the solution. While standard states (*b*) and (*c*) have certain mathematical advantages which appeal to the pure thermodynamicist, for chemical engineering purposes standard state (*a*) is by far the most useful since it is consistent with the aim of correlating and predicting the thermodynamic properties of solutions. Of the three types of standard states, method (*a*) alone permits meaningful comparisons to be made of the activity coefficient of a given solute in different solvents. Unfortunately, however, using the pure material for the standard state frequently necessitates the use of physically unattainable or hypothetical standard states.

HYPOTHETICAL STANDARD STATES

When a gaseous light component is dissolved in a heavier liquid component, and if the symmetric convention is to be used, the standard state of the gaseous solute is the pure solute as a hypothetical liquid at the temperature of the liquid solution. Similarly the standard state for a heavy component dissolved in a gaseous light component is the pure solute as a gas at the temperature of the gaseous solution; if the standard state is taken at the total pressure of the solution and if that pressure exceeds the vapor pressure of the heavy component, then that component cannot exist as a gas and hence the standard state is hypothetical. In each case, that is in gaseous and in liquid solution, it is desirable to have as the standard state the pure material in the same state of aggregation (gas or liquid) as that of the solution to which it refers. How are the properties of the hypothetical standard states to be computed? Any method is necessarily somewhat arbitrary, but some methods appear to be physically more reasonable than others. The difference between a gas and a liquid is indicated by the size of the specific volume. Hence in specifying the properties of a hypothetical liquid or a hypothetical gas it seems most reasonable to specify the volume which, together with the temperature, is sufficient to compute all other properties. Thus the fugacity of a hypothetical standard state is fixed by the temperature of the pure material (which must be the same as that of the solution) and by its specific volume, which can be determied by a reasonable extrapolation and which is subject only to the restriction that $\gamma_i \to 1$ as $x_i \to 1.0$.

CONDENSABLE COMPONENTS IN THE GAS PHASE

A gaseous solution containing one light component and one heavy component is considered. The activity coefficient of the heavy component in the gaseous solution is given by

$$\gamma_h = \bar{f}_h / y_h f_h^\circ \qquad (2)$$

The pressure to which f_h° refers is arbitrary. It has therefore been customary in many cases to use as the reference state the ideal hypothetical vapor at the total pressure, in which case f_h° is equal to the total pressure. Then the

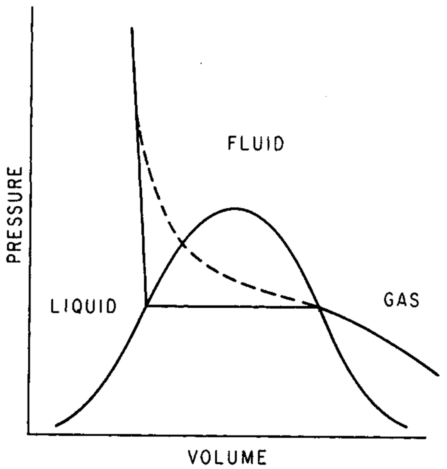

Fig. 1. Isotherm for hypothetical gas.

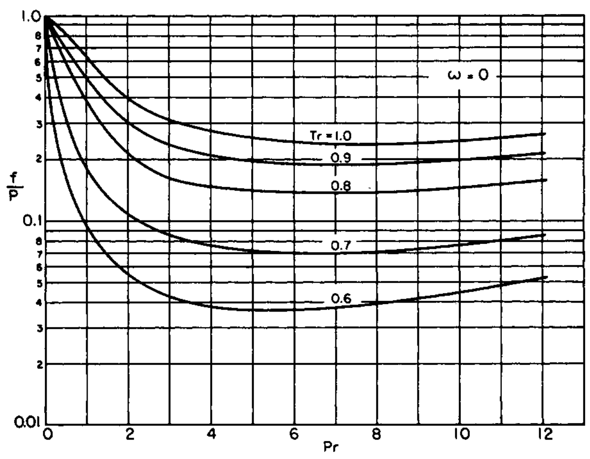

Fig. 2. Fugacity coefficients for hypothetical gases.

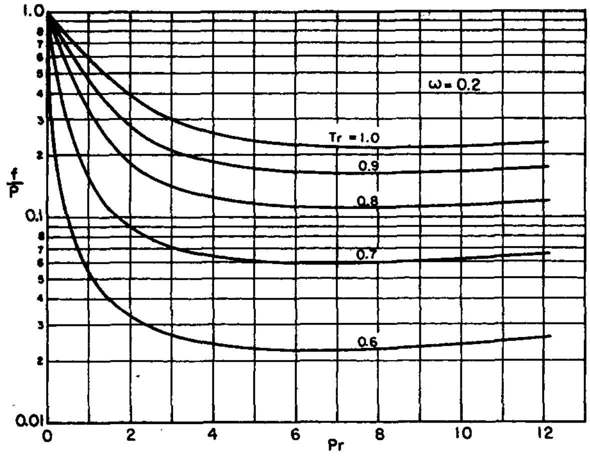

Fig. 3. Fugacity coefficients for hypothetical gases.

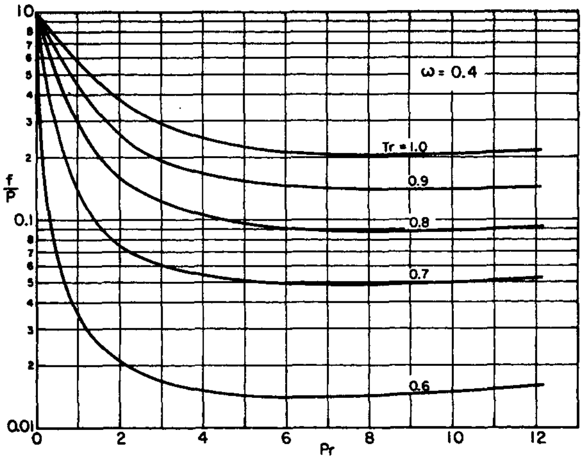

Fig. 4. Fugacity coefficients for hypothetical gases.

activity coefficient is really a fugacity coefficient defined by

$$\phi_h = \frac{\bar{f}_h}{y_h P} \qquad (3)$$

For most calculational purposes the fugacity coefficient is perfectly satisfactory. It performs the important function of relating the fugacity of a component in the gas phase to its mole fraction, and thus it takes care of half the problem in phase equilibria. (The other half, of course, is to use a similar coefficient for performing the same function for the liquid phase.) However while ϕ is very useful, its physical significance is less clear than that of γ, because the fugacity coefficient is really the product of two terms, each of which has a separate physical significance; the relationship between the activity coefficient and the fugacity coefficient is

$$\phi = \nu \gamma \qquad (4)$$

where $v = f/P$ for the pure component in the standard state.

As indicated by Equation (4), the fugacity coefficient ϕ is a single factor which takes into account deviations from ideality of the pure component (due to pressure) and deviations from ideal solution (due to the presence of a second component). ϕ can readily be calculated from an equation of state for the gaseous mixture (*1, 8*). To interpret its physical meaning, however, it is sometimes desirable to separate the nonideality effects due to nonideal solution from those due to nonideality of the pure vapor. In that case it is necessary to use as the standard state the pure hypothetical vapor at the temperature and total pressure of the solution. If the activity coefficient of component h is to reflect solely the effect of solution with the other component l, then it is necessary to have the limiting relation at constant temperature $\gamma_h \rightarrow 1$ as $y_h \rightarrow 1$ and to have the pressure to which f_h° refers be the total pressure of the solution. If that pressure is greater than the vapor pressure of the heavy component, then the reference state is a hypothetical one, since pure vapor h cannot exist at a pressure exceeding the vapor pressure. The calculation of hypothetical f_h° is necessarily arbitrary, but a reasonable procedure is to compute it in such a way as to reflect the properties that the heavy component would have if instead of condensing at the vapor pressure it remained a vapor. This calculation is best performed by continuing the gas-phase isotherm on a pressure vs. volume diagram through the two-phase region to the liquid portion of the isotherm in a manner shown schematically in Figure 1. At high pressures there is no distinction between gas and liquid, both states of aggregation being designated by the word *fluid*. At high pressures, therefore, the extrapolated hypothetical gas isotherm must become identical with the real liquid isotherm. While this fact does not uniquely determine the shape of the extrapolated isotherm, it gives at least some direction on how such an isotherm may be reasonably constructed. Once this hypothetical isotherm is available, the fugacity at any pressure is computed from

$$\ln f/P = \int_0^P \left(\frac{Pv}{RT} - 1 \right) \frac{dP}{P} \qquad (5)$$

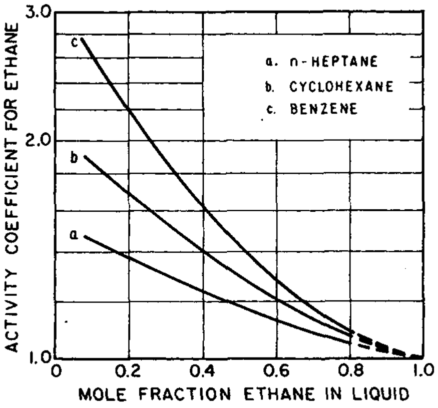

Fig. 5. Liquid-phase activity coefficient for ethane in three systems at 168°F.

Hypothetical gas-phase fugacities have been calculated in the manner described for several representative nonpolar gases having different acentric factors and the results plotted on reduced coordinates for different ω. Figures 2, 3, and 4 give the fugacities of hypothetical gases as a function of reduced temperature, reduced pressure, and acentric factor. These charts are quite different from those presented earlier by Hougen and Watson and others (*2, 13*). The earlier charts were extrapolated by use of gas-phase equilibrium data; hence they include a generalized composition effect. Such an effect cannot of course be generalized in terms of the properties of the condensable solute alone. The charts presented here do not include composition effects but are based only on pure-component extrapolations. Hence they serve merely as a basis for calculating gas-phase activity coefficients. Fugacities calculated from these charts should never be used for the prediction of phase equilibria unless it is also possible to estimate γ [see Equation (1)]. The assumption that $\gamma = 1$ (Lewis fugacity rule) can lead to very large errors. (*8*).

The fugacity as calculated from Figures 2, 3, or 4 refers to the fugacity that a substance would have if it existed in the pure state as a vapor at the prescribed conditions of temperature and pressure. As an illustration of the physical significance of this fugacity, the fugacity of hypothetical decane vapor at 75°C. and 60 atm. (the vapor pressure of decane at 75°C. is 0.0329 atm.) is considered. The fugacity coefficient of decane in various gaseous solvents has been measured experimentally (9); in hydrogen it is 1.45, in nitrogen 0.620, and in carbon dioxide 0.231. These data indicate that the fugacity coefficient falls with the molecular weight of the gaseous solvent. Therefore it is to be expected that the fugacity coefficient for pure decane is much less than unity. From the generalized charts it is estimated to be 0.012.

Once f/P for the pure hypothetical vapor is known, γ_h can be calculated from Equation (4). For decane in hydrogen, nitrogen, and carbon dioxide at 75°C. and 60 atm. the activity coefficients are, respectively, 121, 51.6, and 19.3.

For most computational purposes the fugacity coefficient ϕ is satisfactory, and it is not necessary to calculate γ. It is only when one wishes to compare the effect of different gaseous solvents that it is instructive to separate ϕ into the pressure and into the composition effect. For example it is sometimes found at advanced pressure (especially in systems containing hydrogen) that ϕ is close to unity. One might therefore erroneously conclude that the gas phase is ideal. In fact, however, it is not ideal at all, but because of two compensating nonidealities ($\nu << 1$ and $\gamma >> 1$) the over-all effect gives an apparent ideality.

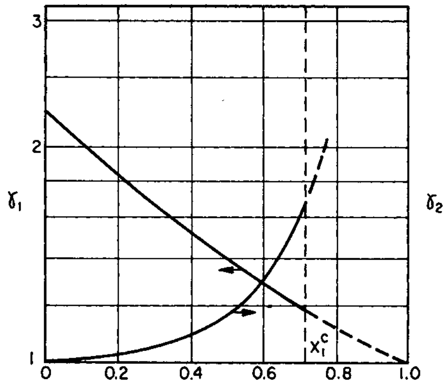

Fig. 6. Activity coefficients for carbon dioxide (1)—butane (2)—system at 160°F.

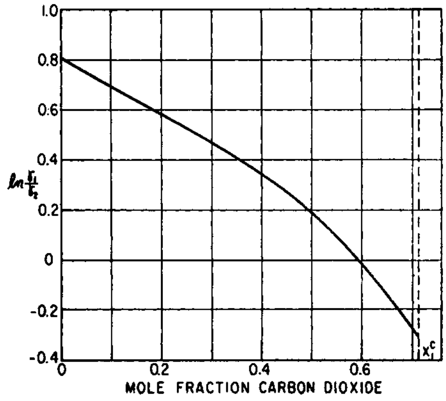

Fig. 7. Activity-coefficient ratio vs. composition for carbon dioxide-butane system at 160°F.

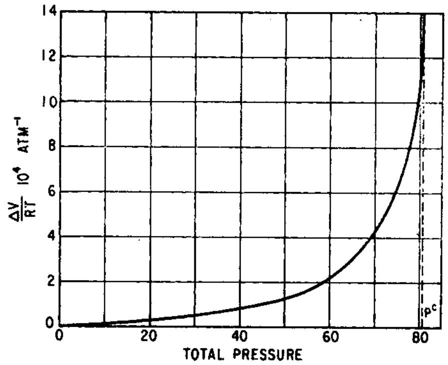

Fig. 8. Volume change vs. pressure for carbon dioxide-butane system at 160°F.

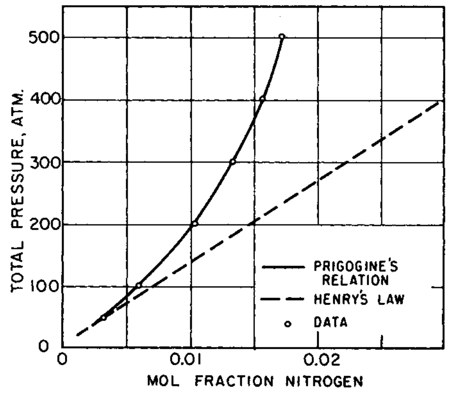

Fig. 9. Solubility of nitrogen in liquid ammonia at 0°C.

GASEOUS SOLUTES IN THE LIQUID PHASE

The hypothetical standard-state fugacity of a gaseous solute is determined by the temperature and pressure of the solution and by the molar liquid volume of the pure solute. Several estimates of this volume may have to be made before the right one is found; the test is only that upon extrapolation $\gamma_i \to 1$ as $x_i \to 1$. Once it is found, however, it can be used for that solute in all solvents, since the standard state as used here is a function only of the pure material and not of the solution.

To fix ideas, the binary data at 75°C. for ethane in benzene, cyclohexane and n-heptane reported by Kay and co-workers (*5, 4, 6*) are considered. The activity coefficient of the ethane, given by γ_e, must for all three cases obey the relation $\gamma_e \to 1$ as $x_e \to 1$. The activity coefficient is given by

$$\gamma_e = \frac{\bar{f}_e}{x_e f_e^\circ} \qquad (6)$$

The pressure of the standard state is arbitrary, but it is convenient to choose the total pressure as the standard-state pressure. In that case f_e° is the fugacity of pure (hypothetical) ethane liquid at the temperature and total pressure of the solution. The system temperature, 75°C., is well above the critical for ethane. To determine the fugacity of pure liquid ethane, therefore, it is necessary to specify the molar volume which ethane would have at 75°C. if instead of becoming a gas it had remained a liquid. This can be estimated from the volumetric data for pure ethane at lower temperature. If the volume estimated is v_e, then the standard-state fugacity is found by

$$f_e^\circ = f(v_e,T) \exp \frac{v_e(P - P_e^*)}{RT} \qquad (7)$$

In this case the hypothetical standard state is considered to be pure, incompressible ethane at the volume and the temperature. The properties $f(v_e, I)$ and P_e^* are found from a Mollier diagram for pure ethane. The check on having chosen the right value for v_e is the condition that when $\ln \gamma_e$ is extrapolated to $x_e = 1$, the extrapolation leads to $\ln \gamma_e = 0$.

The results of such calculations for ethane in three solvents are shown in Figure 5. In these calculations $v_e = 84$ cc./g.-mole. This value was found by extrapolating with respect to temperature the molar liquid volumes of ethane in the vicinity of the normal boiling point where its molar volume is 55 cc./g.-mole. Figure 5 shows that the activity coefficient of ethane in all three solvents tends to unity as pure ethane is approached. Since the activity coefficient is a measure of the unlikeness between solute and solvent, one would expect a definite trend in the activity coefficients of ethane in the three solvents. As expected, the activity coefficient of ethane is highest in the aromatic and lowest in the paraffinic solvent, the results for the naphthenic solvent falling between these two. From these results it would not be difficult to make good predictions of the activity of ethane in other hydrocarbon solvents at 75°C.

GIBBS-DUHEM EQUATION AND THERMODYNAMIC CONSISTENCY

In a binary system at constant temperature it is not possible to vary the composition without also changing the total pressure. The Gibbs-Duhem equation for an isothermal binary system is (3)

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2} + \frac{\Delta v}{RT}\frac{\partial P}{\partial x_1} \qquad (8)$$

where the volume change is given by

$$\Delta v = v(\text{mixture}) - x_1 v_1^\circ - x_2 v_2^\circ$$

In condensed phases at low pressures the last term on the right-hand side of Equation (8) is negligible compared with the other terms. At high pressures, however, this last term is important and may not be neglected, especially when tests for thermodynamic consistency are applied. The most useful test is that proposed by Redlich and Kister (*11*), who define a function Q

$$Q \equiv x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (9)$$

In the symmetric convention $Q = 0$ at $x_1 = 0$ and $x_2 = 0$.

Differentiating Q with respect to x_1 and substituting

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2} \qquad (10)$$

Redlich and Kister obtain

$$\int_0^1 \ln \gamma_1/\gamma_2 \, dx_1 = 0 \qquad (11)$$

For high-pressure systems, however, Equation (8) must be used instead of Equation (10). Also it is not possible to integrate the activity coefficients from $x_1 = 0$ to $x_1 = 1$, since high-pressure systems will show a critical point $0 < x_1^c < 1$. The test for thermodynamic consistency for high-pressure systems therefore is

$$\int_0^{x_1^c} \ln \gamma_1/\gamma_2 \, dx_1 + \int_{P(x_1=0)}^{P^c} \frac{\Delta v}{RT} dP = x_1^c \ln \gamma_1^c + x_2^c \ln \gamma_2^c \qquad (12)$$

This test for thermodynamic consistency is illustrated with data for the carbon dioxide–butane system at 160°F. reported by Sage and Lacey (*12*). The critical temperature of carbon dioxide is 87.8°F.; the standard state for carbon dioxide in the liquid phase is therefore hypothetical. If the standard state for carbon dioxide is taken as the hypothetical incompressible liquid at 160°F. with a volume of 71 cc./g.-mole, the activity coefficient γ_1 of carbon dioxide obeys the relation $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$. Activity coefficients for this binary system are shown in Figure 6. Since Sage and Lacey also reported volumetric data for the liquid solution, it is a simple matter to calculate the volume change, which is small for low carbon dioxide concentrations but becomes large near the critical point. Figure 7 shows a plot of $\ln \gamma_1/\gamma_2$ vs. x_1 for the range $x_1 = 0$ to the critical point which occurs at $x_1^c = 0.713$. Figure 8 gives a plot of $\Delta v/RT$ vs. the pressure up to the critical point. From the areas under these plots the values of the integrals in Equation (12) are found. The left-hand side of Equation (12) gives a value of 0.2708; the right-hand side has a value of 0.2690. The thermodynamic consistency of these data is therefore very good.

EFFECT OF PRESSURE ON GAS SOLUBILITY

The effect of pressure on the solubility of a gas in a liquid is commonly expressed in the form of Henry's law, which states that the partial pressure of a gas is proportional to the mole fraction of the solute in the liquid solvent. Henry's law is essentially equivalent to assuming that the activity coefficient of the solute is a constant independent of the composition of the liquid solution. While Henry's law is frequently a very good approximation, better results can sometimes be obtained by making a more reasonable assumption about the variation of activity coefficient with solute concentration. To do this it is necessary to utilize some technique, such as that discussed above, for computing activity coefficients of gaseous solutes. To illustrate, one should consider the nitrogen-ammonia system at 0°C. The solubility of nitrogen in liquid ammonia at 0°C. and 50 atm. is $x_{N_2} = 0.0031$. It is desired to predict the solubility of nitrogen in ammonia at higher pressures up to 500 atm. First the activity coefficient of nitrogen in the liquid ammonia at 50 atm. is computed with a standard state hypothetical liquid nitrogen at a temperature of 0°C. and a volume of 79 cc./g.-mole. Second it is necessary to utilize some suitable expression for the variation of activity coefficient with mole fraction. It has been shown by Prigogine and Defay (*10*) that for dilute solutions of a nonpolar substance in an associating solvent the activity coefficient is given by

$$\gamma_1 = \frac{1}{\dfrac{x_2}{\Psi_2} + x_1} \qquad (13)$$

Using the previously calculated activity coefficient at 50 atm. one can evaluate Ψ_2. Equation (13), coupled with the excellent assumption that Ψ_2 does not change over the concentration interval considered here, is then used to predict the solubility at higher pressures. The results, shown in Figure 9, are compared with Henry's law and with the experimental data of Wiebe and Gaddy (*12*). In this case Henry's law leads to appreciable error in the pressure range above 200 atm.

ACKNOWLEDGMENT

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NOTATION

f = fugacity
f_h^o = fugacity of pure heavy component as a vapor at the temperature of the solution and at a fixed pressure
f_e^o = fugacity of pure (hypothetical) ethane liquid at the temperature of the solution and at a fixed pressure
P = total pressure
Q = defined by Equation (8)
R = gas constant
T = absolute temperature
v = molar volume
x_i = mole fraction of species i in the liquid phase
y_i = mole fraction of species i in the gas phase
γ_i = activity coefficient of species i

Greek Letters

ϕ = fugacity coefficient
Δv = volume change
ν = fugacity coefficient for the pure component
Ψ = average degree of association
ω = acentric factor

Superscripts

– (bar) = component in solution
o = standard state
* = equilibrium
c = critical

Subscripts

h = heavy component
e = ethane
l = light component

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