Fugacities in High-Pressure Equilibria and in Rate Processes

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This work considers the importance of vapor-phase nonideal mixing in high-pressure equilibrium and rate-process calculations. New techniques are presented for calculating vapor-phase fugacity coefficients in nonideal mixtures.

The equilibrium properties of gaseous mixtures are represented by a virial equation of state which is adequate for the vast majority of chemical engineering problems. Techniques based on an extension of the corresponding-states theory are given for estimating the various coefficients appearing in the equation of state; these estimates appear to be reliable for a large variety of nonpolar or weakly polar systems. Techniques based on the theory of intermolecular forces are also presented for polar systems and for a limited class of mixtures containing hydrogen-bonding components. The proposed methods of calculation are illustrated by a large variety of problems occurring in common chemical engineering calculations, and it is shown that failure to correct for vapor-phase nonideal mixing can, in some cases, lead to very large errors.

The fugacity of a component in a vapor-phase mixture is needed in numerous chemical engineering computations (*2*, *4*). In simple cases the fugacity is equal to the partial pressure, but generally it is necessary to apply corrections for the nonideality of mixing as well as for the nonideality of the pure vapor. These two corrections are conveniently expressed in terms of one fugacity coefficient ϕ. In many common problems it is correct to assume that ϕ will not differ appreciably from unity unless the total pressure is at least moderately large; in some special cases, however, large deviations from ideality may occur even at a total pressure much less than 1 atm. This paper presents new techniques for calculating vapor-phase activity coefficients and through a variety of applications shows their relevance to typical chemical engineering problems.

RELATIONSHIP BETWEEN FUGACITIES AND VOLUMETRIC PROPERTIES IN MIXTURES

The fugacity coefficient of a component is defined (*27*) as the ratio of that component's fugacity in the mixture to its partial pressure. It is given precisely by

$$\ln \phi_i \equiv \ln \frac{\bar{f}_i}{y_i P} = \frac{1}{RT} \int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dP \qquad (1)$$

An alternate expression for the fugacity of a component in a mixture is given in terms of an activity coefficient (*15*), which measures the deviation from the Lewis fugacity rule. This activity coefficient is defined by

$$\ln \gamma_i \equiv \ln \frac{\bar{f}_i}{y_i f_i^0} = \frac{1}{RT} \int_0^P (\bar{V}_i - V_i^0)\, dP \qquad (2)$$

The relation between γ_i and ϕ_i is simply

$$\phi_i = \gamma_i \phi_i^0 \qquad (3)$$

The two coefficients ϕ and γ each have definite advantages and disadvantages. The latter is more useful when the component under consideration is a gas rather than a vapor; in that case γ usually does not differ greatly from unity and in fact obeys the limiting relation

$$\lim_{y_i \to 1} \gamma_i \to 1 \qquad (4)$$

Another way of expressing the advantage of γ is to say that the Lewis fugacity rule ($\gamma = 1$) is always a very good approximation for a component present in excess. A corresponding statement for ϕ can unfortunately not be made. A relation for ϕ analogous to Equation (4) is valid only at very low pressures.

However if the component under consideration is a vapor, it is advantageous to use the coefficient ϕ. For a vapor the fugacity in the pure state f^0 has physical significance only at pressures up to the vapor pressure of that component since the pure vapor cannot exist at higher pressures. The coefficient γ therefore, as indicated by Equation (2), has physical significance only under restricted conditions and is not convenient for condensable components.

EQUATIONS OF STATE FOR GAS MIXTURES

Numerous equations of state have been proposed for pure gases (*8*). As almost all are empirical or at best semiempirical in nature, it has not been possible to make an accurate assessment of the physical meaning which is associated with the various constants. It is this deficiency of equations of state for pure gases which has made it difficult to extend them to gas mixtures. Various empirical rules have been suggested for predicting the constants of a mixture from the constants of the pure components (*8*), but while some of these give good results in specific cases, they are generally not reliable. All mixing rules which relate the constants of a mixture to those of the pure components must in some way reflect the nature of the intermolecular forces acting between unlike molecules. These forces are sufficiently complex to render any particular mixing rule valid for only a restricted class of mixtures. Although the mixing rules that are recommended by Benedict give good results for mixtures of paraffinic and olefinic hydrocarbons (*1*), they are unsatisfactory for hydrocarbon mixtures containing aromatic components and have been shown to fail badly for a mixture of carbon dioxide and propane (*5*).

The material presented in this work indicates that for the vast majority of chemical engineering problems the virial equation is the most suitable equation of state for fugacity calculations in mixtures. At very high densities the virial equation is not useful, since a large number of virial coefficients are required, but at pressures and temperatures commonly encountered in chemical engineering work the virial equation is both adequate and convenient. This equation can be written in either a pressure- or a volume-explicit form. While the latter has some computational advantages, it is the pressure-explicit form which is more suitable for this work, since it requires a smaller number of terms and its coefficients have theoretical significance. It is given by

$$z = \frac{P_v}{RT} = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots \qquad (5)$$

B, C, and D are respectively the second, third, and fourth virial coefficients, which are functions of temperature and composition but not of density or pressure. When terminated after the third virial coefficient Equation (5) is valid up to almost the critical density and frequently beyond it, and if the series is terminated after the second virial coefficient, it is reliable up to about one half of the critical density.

Calculation of fugacity coefficients as indicated by the integral in Equation (1) requires a volume-explicit equation of state. Since Equation (5) is pressure-explicit, it is necessary to make a change of the independent variable, and it can be shown (*28*) that ϕ_i is related to the volumetric properties by

$$\ln \phi_i = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - \ln z \qquad (6)$$

VIRIAL COEFFICIENTS

Equation (5) can be derived by the methods of statistical thermodynamics (*11*) wherein the physical significance of the virial coefficients is related to the intermolecular forces. The temperature dependence of the virial coefficients can be found by calculations based on a suitable potential-energy function, but for most chemical engineering purposes it is much more convenient to use generalized plots or empirical equations within the framework of the theory of corresponding states. The concentration dependence of the virial coefficients however follows directly from their physical significance, and it is because of this feature that the virial equation is so valuable in calculating fugacities in gas-phase mixtures. Since each virial coefficient reflects the forces corresponding to the interaction of a particular number of molecules, it has been shown (*12*, *20*) that the *n*th virial coefficient is a polynomial of *n*th degree in the mole fraction. Thus the second virial coefficient of a mixture (B_m) is a quadratic function of the mole fraction; the third virial coefficient of a mixture (C_m) is a cubic function, etc.

$$B_m = \sum_i^n \sum_j^n y_i y_j B_{ij} \qquad (7)$$

$$C_m = \sum_i^n \sum_j^n \sum_k^n y_i y_j y_k C_{ijk} \qquad (8)$$

Whereas the virial coefficients B_m and C_m are functions of both temperature and composition, the various coefficients on the right side of Equations (7) and (8) are functions only of the temperature.

Much information (*13*) is available on the second virial coefficients of numerous gases, and a limited amount (*24*) is now known about the third virial coefficient; almost nothing is known about the fourth and higher virial coefficients. For all practical purposes therefore the series in Equation (5) must be cut off after the third term.

Equations (7) and (8), respectively, give the composition dependence of the second and third virial coefficients. When these equations are substituted into Equation (5) and the result is further substituted into Equation (6), the final result is

$$\ln \phi_i = 2\rho \sum_j^n y_j B_{ij} + \frac{3}{2}\rho^2 \sum_j^n \sum_k^n y_j y_k C_{ijk} - \ln z \qquad (9)$$

Equation (9) is an exact expression for the fugacity coefficient subject only to the restriction that the density be sufficiently small to permit neglect of terms involving the fourth and higher virial coefficients. For numerous chemical engineering problems (except those at very high densities) Equation (9) is the most suitable now available. Some applications of this equation are given later.

ESTIMATION OF VIRIAL COEFFICIENTS

Reliable volumetric studies have been reported for only a limited number of mixtures. However a considerable body of results is available for pure gases, and with the help of existing theory of intermolecular forces it is possible in many cases to make good estimates of virial coefficients for mixtures. Most experimental and theoretical work (*13*) has been concerned with the second virial coefficient, and at present much more is known about the second virial coefficient than about the third. Fortunately however Equation (9) is such that the fugacity coefficient is much more sensitive to the various B terms than to the C terms, and in many practical cases it is permissible to neglect the third virial coefficient entirely. Work on polar and hydrogen-bonded gases is much less plentiful than on nonpolar gases, and work on mixtures of polar gases is almost nonexistent. The initial discussion therefore excludes polar molecules. However even in systems containing polar gases fairly good estimates of virial coefficients can sometimes be made, and mixtures including one or more polar components will be considered later.

A comprehensive study of the volumetric properties of pure gases has been reported by Pitzer and associates (*24*, *25*) who found that the thermodynamic properties of nonpolar or weakly polar substances could be correlated within the framework of an extended theory of corresponding states by introducing an additional parameter called the *acentric factor*. However since Pitzer's work was concerned only with pure gases, his correlations can be used only for pure-gas coefficients. For the prediction of the so-called "cross coefficients", that is for those having different subscripts such as B_{ij} or C_{ijk} or C_{iik}, Pitzer's correlation by itself is insufficient.

Methods of estimating the second virial cross coefficients of simple gas mixtures have been proposed by Guggenheim and McGlashan (*14*), and very recently Prausnitz and Gunn (*26*) have shown how these methods can be modified to handle complex mixtures of a variety of nonpolar or slightly polar components. The principle of these methods lies in an extension of the theorem of corresponding states to mixtures. This extension consists of the definition of parameters which characterize the interactions responsible for the cross coefficients and which, with a suitable rearrangement of Pitzer's results for pure components, are sufficient to estimate the cross coefficients. These ideas can best be summarized by the equation below.

Second Virial Coefficients

For a pure component i the second virial coefficient B_{ii} is given by

$$\frac{B_{ii}}{V_{c_{ii}}} = \theta_B\left(\frac{T}{T_{c_{ii}}}, \omega_{ii}\right) \qquad (10)$$

For a mixture the cross coefficient B_{ij} is given by

$$\frac{B_{ij}}{V_{c_{ij}}} = \theta_B\left(\frac{T}{T_{c_{ij}}}, \omega_{ij}\right) \qquad (11)$$

The generalized function is tabulated in Table 1.* Estimation of B_{ij} therefore requires specification of the parameters $V_{c_{ij}}$, $T_{c_{ij}}$, and ω_{ij}.

An examination of reliable volumetric data (*26*) indicated that best results could be obtained by adopting a linear average for the characteristic volume and for the characteristic acentric factor; that is

$$V_{c_{ij}} = \tfrac{1}{2}(V_{c_i} + V_{c_j}) \qquad (12)$$

$$\omega_{ij} = \tfrac{1}{2}(\omega_i + \omega_j) \qquad (13)$$

The characteristic temperature $T_{c_{ij}}$ could not be correlated in a completely general way. Instead a correction term $\Delta T_{c_{ij}}$, characteristic of the $i - j$ interaction, was included:

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*The tabulated values are based on the correlating equation of Pitzer and Curl (*25*). Whereas these authors used the critical temperature and pressure to obtain the reduced virial coefficients, the tabulated values shown here are reduced with the critical volume.

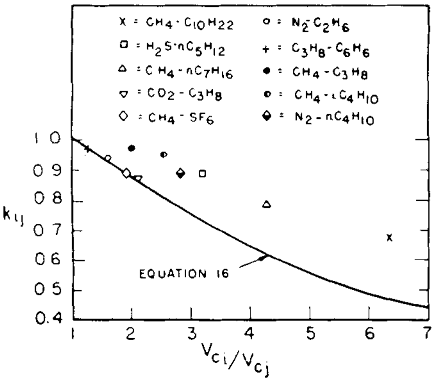

Fig. 1. Correction to the characteristic temperature

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{\frac{1}{2}} - \Delta T_{c_{ij}} \qquad (14)$$

For nonpolar components $\Delta T_{c_{ij}}$ is always positive and increases with the ratio $V_{c_{ii}}/V_{c_{jj}}$ (where component i is chosen such that $V_{c_{ii}}/V_{c_{jj}} \geq 1$). If the ratio of critical volumes is not very much different from unity, the correction is usually negligible; only for molecules of quite different size does $\Delta T_{c_{ij}}$ become important. The correlation given by Prausnitz and Gunn makes it possible to estimate $\Delta T_{c_{ij}}$ for a large number of systems.

Another way to write Equation (14) is

$$T_{c_{ij}} = k_{ij}(T_{c_i} T_{c_j})^{\frac{1}{2}} \qquad (15)$$

with $k_{ij} \leq 1$, since $\Delta T_{c_{ij}} \geq 0$.

Equation (15) is an inequality indicating that the geometric mean is a maximum value; this expression follows from the London theory of dispersion forces *(16)*. The geometric-mean rule for the critical temperatures is valid if the size of molecule i is approximately the same as that of molecule j; for molecules of different size however the geometric mean is too large. After making some simplifying assumptions one can show from the London formula that

$$k_{ij} = \left(\frac{4\beta}{(1+\beta)^2}\right)\left(\frac{2\zeta^{\frac{1}{2}}}{1+\zeta}\right) \qquad (16)$$

where

$$\beta = V_{c_i}/V_{c_j} \qquad (17)$$

$$\zeta = U_i/U_j \qquad (18)$$

In Equation (16) k_{ij} is always equal to or less than unity for all physically significant values of β and ζ.

It is gratifying that the analysis of experimental data as summarized by the empirically found relationship $k_{ij} \leq 1$ is in good qualitative agreement with theory; the quantitative agreement however is not very good, becoming progressively worse as β increases. Figure 1 shows a comparison between a few observed results and those calculated from Equation (16) with ζ equal to unity, and it is evident that the theoretical expression overcorrects for molecules of very different size. This is not surprising since the London expressions are valid only for spherical monatomic molecules, and while they serve as good approximations for small polyatomic molecules, they cannot be expected to hold for such large molecules as heptane or decane. Since no convenient theory for dispersion forces of polyatomic molecules has as yet been presented, it is necessary to make empirical modifications for systems having polyatomic components of high molecular weight. In many cases it is possible to make very good estimates of the small corrections required by interpolating the results given previously *(26)*. Where such interpolations cannot be reasonably made, it appears quite satisfactory for many nonpolar systems to use the approximate empirical relations:

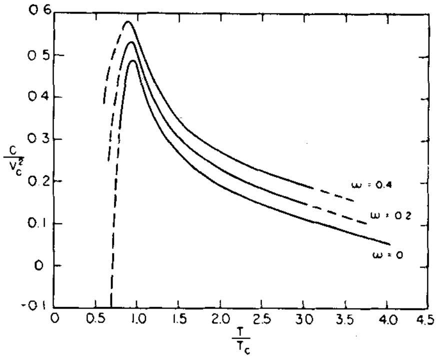

Fig. 2. Reduced third virial coefficients.

for the characteristic volume

for $\dfrac{V_{c_i}}{V_{c_j}} > 3.0,$

$$V_{c_{ij}} = \tfrac{1}{2}(0.9V_{c_i} + V_{c_j}) \qquad (19)$$

and for the characteristic temperature

for $\dfrac{V_{c_i}}{V_{c_j}} \leq 2.0$

k_{ij} as given by Equation (16)

for

$$3.0 > \frac{V_{c_i}}{V_{c_j}} > 2.0 \quad k_{ij} \approx 0.90$$

and for $\qquad (20)$

$$\frac{V_{c_i}}{V_{c_j}} > 3.0, \qquad k_{ij} \approx 0.85$$

Third Virial Coefficients

Very precise volumetric data are required for computing third virial coefficients. Such data are scarce, but, where available, third virial coefficients can be correlated by Pitzer's extended theory of corresponding states. The extension to mixtures can also be carried out in a manner analogous to that used for the second virial coefficient. Thus

$$\frac{C_{ijk}}{V_{c_{ijk}}^{\;2}} = \theta_c\left(\frac{T}{T_{c_{ijk}}}, \omega_{ijk}\right) \qquad (21)$$

Approximate values of the function θ_c are given in Figure 2. The plots are based on Pitzer's generalized compressibility tables and on volumetric data for

TABLE 1. COMPUTED VALUES OF THE GENERALIZED FUNCTION — θ_B

T_r/ω	0.0	0.1	0.2	0.3	0.4	0.5
0.50	4.008	5.412	6.897	8.473	10.144	11.923
0.55	3.388	4.237	5.135	6.088	7.099	8.175
0.60	2.908	3.497	4.121	4.783	5.484	6.231
0.65	2.526	2.945	3.388	3.858	4.356	4.887
0.70	2.216	2.526	2.855	3.203	3.572	3.966
0.75	1.960	2.194	2.441	2.704	2.982	3.278
0.80	1.746	1.925	2.114	2.315	2.528	2.754
0.85	1.564	1.701	1.845	1.999	2.162	2.335
0.90	1.408	1.512	1.623	1.740	1.864	1.996
0.95	1.273	1.352	1.436	1.524	1.618	1.718
1.00	1.155	1.213	1.274	1.339	1.408	1.481
1.05	1.051	1.093	1.138	1.185	1.235	1.289
1.10	0.959	0.985	1.014	1.043	1.075	1.109
1.15	0.877	0.893	0.909	0.926	0.945	0.965
1.20	0.803	0.808	0.813	0.818	0.823	0.829
1.25	0.736	0.733	0.730	0.727	0.724	0.720
1.30	0.676	0.665	0.653	0.640	0.627	0.613
1.40	0.571	0.548	0.524	0.498	0.471	0.442
1.50	0.483	0.451	0.418	0.382	0.345	0.304
1.60	0.408	0.370	0.329	0.286	0.240	0.192
1.70	0.344	0.301	0.256	0.208	0.157	0.102
1.80	0.288	0.241	0.190	0.137	0.080	0.020
1.90	0.238	0.187	0.133	0.076	0.016	−0.048
2.0	0.195	0.142	0.086	0.026	−0.037	−0.104
2.5	0.036	−0.023	−0.086	−0.153	−0.223	−0.298
3.0	−0.064	−0.125	−0.189	−0.258	−0.330	−0.407
3.5	−0.133	−0.194	−0.258	−0.327	−0.399	−0.475
4.0	−0.183	−0.243	−0.307	−0.374	−0.445	−0.522

argon, nitrogen, methane, *n*-butane, and *n*-heptane. These values for the third virial coefficient are less accurate than those for the second virial coefficients given in Table 1.

The theory of dispersion forces is insufficiently advanced, and experimental data on mixtures are not sufficiently precise to suggest definite mixing rules relating the characteristic parameters for the cross coefficients ($i \neq j \neq k$) to those of the pure components ($i = j = k$). However it is possible to extend to the third virial coefficient the mixing rules used for the second virial coefficient, and it has been shown by Rowlinson on theoretical grounds (*29*) that such extension is a very reasonable approximation. Thus

$$V_{c_{ijk}} = \tfrac{1}{3}(V_{c_i} + V_{c_j} + V_{c_k}) \qquad (22)$$

$$\omega_{ijk} = \tfrac{1}{3}(\omega_i + \omega_j + \omega_k) \qquad (23)$$

$$T_{c_{ijk}} = (T_{c_i}T_{c_j}T_{c_k})^{\frac{1}{3}} \qquad (24)$$

Empirical modifications of these mixing rules analogous to those given by Equations (16), (19) and (20) cannot as yet be made.

While the various C terms in Equation (9) cannot be estimated accurately, it should not be concluded that the accuracy of ϕ is seriously impaired. In many cases the density is sufficiently low to permit neglect of the third virial coefficient, and in any case in which Equation (9) may legitimately be used the second virial coefficient always plays a much more important role than the third. In a typical case where the third virial coefficient may not be neglected, an error of perhaps 20 or 30% in the various C terms may introduce an error of only 2 or 3% in the logarithm of ϕ.

APPLICATIONS IN NONPOLAR SYSTEMS

Phase Equilibria

One major use of fugacities is in the thermodynamic theory of phase equilibrium; if a vapor phase is in equilibrium with a condensed phase, then for any component i

$$\bar{f}_i^{\,c} = \bar{f}_i^{\,V} \qquad (25)$$

where the bar indicates that the component i is in a solution. Equation (25) is of little use until the fugacities can be related to the mole fractions; this relationship is established by the activity coefficients. Thus Equation (25) is rewritten

$$\gamma_i^{\,c} x_i f_i^{\,c} = \phi_i y_i P \qquad (25a)$$

Example 1

Consider the solubility of solid naphthalene in compressed ethylene gas at 35°C. Figure 3 shows various computed results as well as the experimental data of Diepen and Scheffer (*6*). The curves were computed by using Equation (25*a*) with the appropriate simplification that $\gamma_i^{\,c} x_i = 1$ (i refers to naphthalene), which follows from the fact that the solubility of ethylene in the solid naphthalene is negligible. Curve 1 was computed on the assumption of ideal gas, curve 2 assumes the Lewis fugacity rule, and curve 3 uses the Redlich and Kwong equation for the fugacity coefficient ϕ. Curve 4 is the virial equation (9), the coefficients having been evaluated as described earlier. In this particular case the solubility of naphthalene is so small that any terms proportional to y_i (or y_i^2) are negligible, causing further simplification. In this case Equation (9) reduces to

$$\ln \phi_1 = 2\rho B_{12} + \tfrac{3}{2}\rho^2 C_{122} - \ln z \qquad (25b)$$

where subscript 1 refers to naphthalene, 2 to ethylene.

Since the concentration of naphthalene in the vapor is very small, the quantities ρ and z have been evaluated from the properties of pure ethylene (*7*).

Figure 3, which is a semilogarithmic plot, shows that assumption of the validity of the Lewis fugacity rule or of ideal-gas behavior can introduce errors by a factor of 100 or 1,000. The Redlich and Kwong equation gives the correct trend but is still in error by a factor of about four, and thus the virial equation alone gives reliable results.*

The abnormally high solubility of condensed components in ethylene is due to the fact that in the vicinity of room temperature ethylene is only slightly above its critical temperature, a condition where gas-phase nonideality is a maximum.

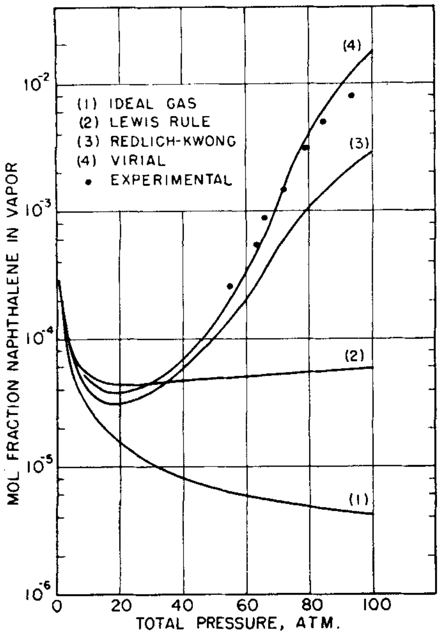

Fig. 3. Vapor-phase solubility of naphthalene in ethylene at 35°C.

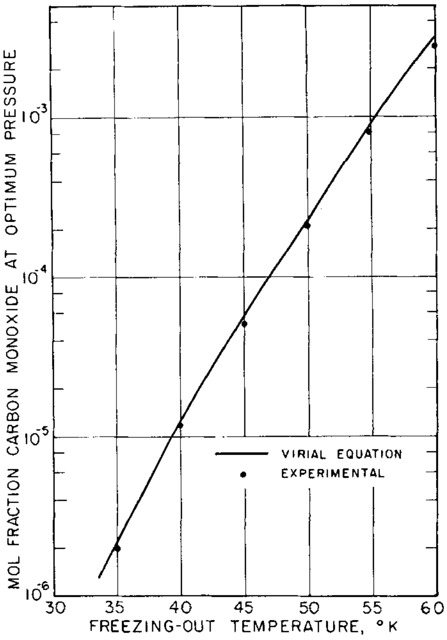

Fig. 4. Minimum carbon monoxide content in hydrogen purification.

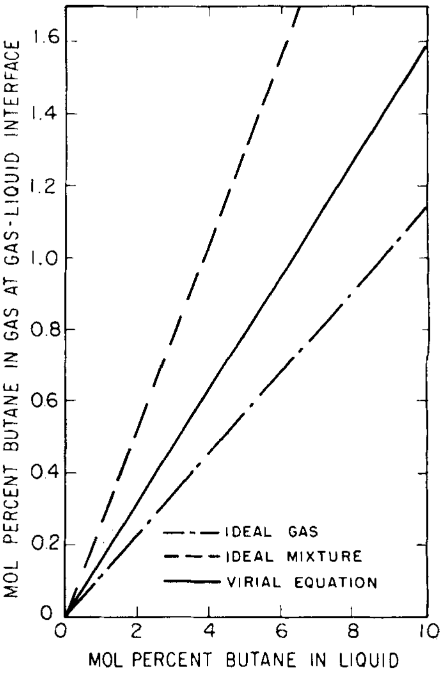

Fig. 5. High-pressure absorption of butane at 400 lb./sq. in. abs. and 20°C.

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*The data for this system were not included in the correlation of Prausnitz and Gunn (*26*). The coefficients B_{12} and C_{122} were estimated by the approximate methods described. They are $B_{12} = -600$ cc./g. mole and $C_{122} = 17{,}100$ (cc./g. mole)^2.

TABLE 2. K VALUES FOR DECANE AT 104°F. AND 294 LB./SQ. IN. ABS.

Second component	10^4K. Calculated [Equation (25*c*)]	Observed
Hydrogen	3.23	3.15
Methane	4.81	5.3
Ethylene	8.24	8.5
Generalized charts	5.0	

Example 2

An important application of vapor-phase fugacity coefficients is in the accurate specification of K values used in petroleum technology. From Equation (25*a*)

$$K_i \equiv y_i/x_i = \frac{\gamma_i{}^c f_i{}^c}{\phi_i P} \qquad (25c)$$

and thus K is strongly dependent on ϕ. The effect of vapor-phase nonideality is most pronounced when the volatility of a high-boiling component whose mole fraction in the vapor is small is considered. An example of this effect is shown in Table 2, where K values for *n*-decane at 104°F. and 294 lb./sq. in. abs. are given for mixtures of decane with hydrogen, methane, and ethylene. The calculated values were computed by use of Equation (25*b*) and neglect of the second term, together with Equation (25*c*) and with the very reasonable assumption that the liquid-phase activity coefficient for decane is unity in all cases. For comparison the data of Nederbragt (*23*)* are shown as well as the values given by the standard K charts for paraffins. The computed values are in good agreement with those observed; in this particular case all the nonideality of mixing is in the vapor phase. (If the K values for the light component were to be calculated for these mixtures, all the nonideality of mixing would be in the liquid phase.) Table 2 shows clearly that the K value is not only a function of the pressure and temperature but also of the nature of the other components which are present. The generalized values from the standard K charts therefore cannot be valid for all cases.

Example 3

For another practical application of vapor-phase fugacity coefficients, consider the production of hydrogen gas. Very pure hydrogen gas is needed in catalytic reactions (such as the synthesis of ammonia), since small amounts of impurities can act as catalyst poisons. The impurity most difficult to remove from hydrogen is carbon monoxide, and an effective purification procedure is to cool the impure hydrogen to very low temperatures and then by compression condense out the solid carbon monoxide. At a given temperature there is an optimum pressure which minimizes the equilibrium carbon monoxide content in the vapor phase. When the mole fraction of impurity in the vapor is plotted against the total pressure, a graph is obtained which resembles that shown for naphthalene in Figure 3; the plot first falls and then rises, going through a minimum which gives the coordinates of the optimum conditions. Equation (9) was used to calculate the minimum impurity content for the hydrogen–carbon monoxide system at several temperatures. Terms involving the third virial coefficient were neglected, and it was assumed that the solubility of hydrogen in solid carbon monoxide is negligible.* The results are shown in Figure 4 together with the experimental values reported by Dokoupil et al. (*10*). If the vapor phase in this problem were considered ideal, the mole fraction of carbon dioxide would be approximately inversely proportional to the pressure. Higher compression should therefore reduce the impurity concentration. Equation (10) however clearly shows that compression beyond the optimum pressure would actually increase rather than decrease the mole fraction of carbon monoxide in the vapor phase.

Chemical Equilibria and Kinetics

The equilibrium yield of a chemical reaction can be computed from the equilibrium constant for the reaction and from relationships between the fugacities of the components in the equilibrium mixture and their mole fractions. In the vapor phase these relationships are established by the fugacity coefficients. Thus for example for a reaction of the type

$$A + B \rightarrow AB \qquad (26)$$

$$K_a = K_{\bar{f}} = \frac{K_\phi K_y}{P}$$

where

$$K_\phi = \frac{\phi_{AB}}{\phi_A \phi_B}$$

and

$$K_y = \frac{y_{AB}}{y_A y_B}$$

provided that the standard state for all components is unit fugacity.

The equilibrium constant is computed from free energies of formation and is independent of the pressure. To compute the equilibrium yield it is necessary to estimate the fugacity coefficients of all the species in the solution; such a computation is necessarily of the trial-and-error type, since the equilibrium composition must be known to estimate the fugacity coefficients. However it is only in those cases where high accuracy is required and where the equilibrium constant is known with at least moderate accuracy that such a computation is worthwhile. In most common gas-phase reactions corrections due to nonideal mixing in the gas phase are of the same order as the uncertainties in the chemical equilibrium constant. Also at high temperatures it is frequently satisfactory to use the Lewis fugacity rule in this type of calculation as pointed out by Dodge (*9*). However if the temperature of the vapor mixture is below, at, or slightly above the critical temperature of one of the components, the Lewis fugacity rule is likely to be in severe error, and accurate calculation of the equilibrium composition will require the use of vapor-phase fugacity coefficients. Chemical equilibrium calculations at high pressure are discussed more fully by Comings (*4*).

At present chemical kinetic data in the gas phase are insufficiently precise to make an empirical test for whether or not fugacity coefficients are required in the kinetic rate expression; however theoretical considerations based on the activated complex theory suggest that fugacities should be used in expressing high-pressure reaction rates. As our understanding of chemical kinetics increases and as more precise kinetic data become available, it will probably become necessary to include fugacity coefficients in an exact formulation of chemical rate laws at advanced pressures.

Mass Transfer

The theory of mass transfer between phases requires information on the concentrations prevailing at the interface. The customary procedure is to assume that the interface is at equilibrium, and it is as a result of this assumption that fugacity coefficients enter into equations expressing the rate of interphase mass transfer. Fugacity coefficients therefore find application in such unit operations as high-pressure absorption as illustrated in the following.

Example 4

Consider the contacting of a natural gas with an absorbing oil at 68°F. and 400 lb./sq. in. abs. The initial composition of the gas is 20 mole % hydrogen, 75% methane, and 5% butane; the butane is to be absorbed, and its solubility in the oil is given by a Henry's law constant $H = 3.1$ atm. The equation for the rate of absorption N is

$$N_4 = k_g a p(y_4 - y_4{}^*) \qquad (27)$$

where subscript 4 refers to butane.

If equilibrium exists at the interface, the mole fraction of butane at the interface is given by

$$y_4{}^* = \frac{H x_4}{\phi_4 P} \qquad (28)$$

The fugacity coefficient can be computed from Equation (9). In this case virial coefficients beyond the second are not needed, and the expression for ϕ_4 is

$$\ln \phi_4 z = 2\rho[y_0 B_{04} + y_1 B_{14} + y_4 B_{44}] \qquad (29)$$

where subscript 0 refers to hydrogen and 1 to methane.

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*The data for these systems were not included in the correlation of Prausnitz and Gunn (*26*). The B_{12} coefficients were estimated by the approximate methods described.

*At the low temperatures considered here the actual rather than the pseudocritical parameters for hydrogen were used to compute B_{12}. No correction was made for V_{c12} and T_{c12}.

To obtain rapidly a value for z and ρ a modification of Kay's rule (*8*) was used with fictitious critical parameters for hydrogen. The cross coefficients were estimated by the methods described earlier yielding $\phi_4 = 0.71$. The mole fraction of butane in equilibrium with the liquid is shown as a function of liquid composition in Figure 5. For comparison, results are also shown for two other methods of calculation, ideal-gas behavior and ideal-vapor-phase mixing (Lewis fugacity rule). For the latter case the fugacity coefficient for pure butane was estimated from extrapolated curves on generalized plots (*17*). Figure 5 points out that in this case the assumption of ideal gas behavior actually gives results as good as or even slightly better than those obtained by assuming the Lewis fugacity rule. This is a result of compensating errors which frequently occur for a condensable component present in small concentrations in a gas which is remote from its critical conditions. In the example given here the deviation from nonideality for pure butane vapor tends to reduce ϕ, while the nonideality of mixing tends to raise ϕ (positive deviations from Raoult's law in the gaseous solution). Therefore the total effect of the two nonidealities is somewhat less than that obtained when either one is taken separately.

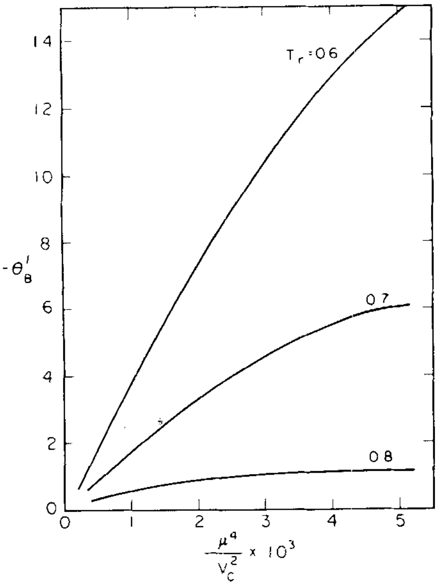

Fig. 6. Excess second virial coefficient for highly polar gases (V_c is in cc/g-mole, μ in Debyes).

POLAR MOLECULES

Reliable data on virial coefficients for polar molecules are scarce. The correlation of Pitzer and Curl for the second virial coefficients gives good results for weakly polar gases, but it is not valid for strongly polar gases, especially at reduced temperatures well below unity where the effect of polarity is most important. To augment the generalized second virial coefficients given in Table 1 data for a few polar but nonassociating molecules were analyzed. The theory of intermolecular forces of polar molecules (*22*) suggests that an approximate extension of Pitzer's treatment is to write the reduced, second virial coefficient (*30*)

$$\frac{B_{ii}}{V_{c_i}} = \theta_B\left(\frac{T}{T_{c_i}}, \omega_i^h\right) + \theta_B^1\left(\frac{T}{T_{c_i}}, \frac{\mu_i^4}{V_{c_i}^2}\right) \qquad (30)$$

The empirical function θ_B is given in Table 1; the empirical function θ_B^1 is shown in Figure 6. The plots in Figure 6 were obtained from data for ammonia, methyl chloride, acetone, and acetonitrile. This correlation is necessarily quite approximate and should be used only in the absence of other data. It is not valid for associating molecules like water or methyl alcohol.

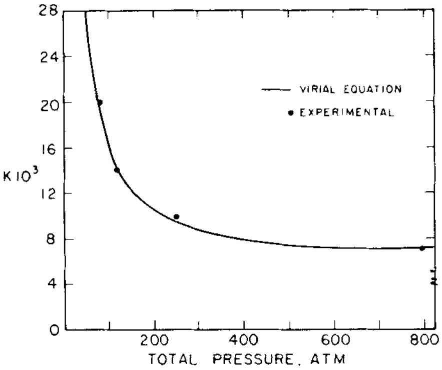

Fig. 7. *K* values for methanol in hydrogen at 75°C.

The second virial coefficient of a mixture containing one polar and one nonpolar component presents no difficulties. The polar molecule induces a dipole in the nonpolar (*22*), but the contribution of this induced polarity to the intermolecular forces is small compared to the much more important dispersion forces. The cross coefficient B_{12} for such a mixture can therefore be estimated by the same methods used for nonpolar mixtures, provided that the acentric factor of the polar component is replaced by that of its homomorph.

Example 5

Consider phase equilibrium in the system methanol-hydrogen at 75°C. The K value for methanol is given by Equation (25*c*), and the assumption of Henry's law for the solubility of hydrogen in methanol leads to $\gamma^c = 1.0$.

The fugacity coefficient is computed from Equation (25*b*) by neglecting the second term. At 75°C., T_{c12} is such that B_{12} is practically zero. The properties of pure hydrogen were used to estimate z. Computed K values for several pressures are shown in Figure 7 together with experimental results reported by Michels (*21*). This system is another example of a case where, because of compensating nonidealities, calculations based on ideal-gas behavior give better results than those based on the Lewis fugacity rule.

Virial coefficients for mixtures of weakly polar, nonassociating components can be estimated the same way as for nonpolar components. For such components Table 1 is applicable. For mixtures of highly polar, nonassociating components, however, Equation (30) should be used. For calculating B_{ij} Equation (30) becomes

$$\frac{B_{ij}}{V_{c_{ij}}} = \theta_B\left(\frac{T}{T_{c_{ij}}}, \omega_{ij}^h\right) + \theta_B^1\left(\frac{T}{T_{c_{ij}}}, \frac{\mu_i^2\mu_j^2}{V_{c_{ij}}^2}\right) \qquad (31)$$

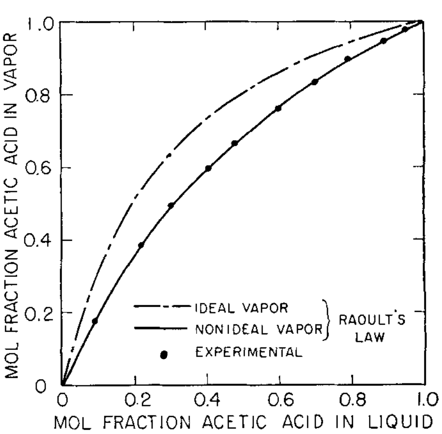

Fig. 8. Phase equilibria for acetic-acid–propionic acid at 20°C.

Unfortunately no data are available for testing this equation. In the absence of any experimental data it is probably best to use the arithmetic mean for ω_{ij}^h and $V_{c_{ij}}$ and the geometric mean for $T_{c_{ij}}$.

Prediction of the virial coefficients of mixtures of polar gases is particularly difficult because of hydrogen bonding resulting in association and solvation. Equations (30) and (31) are not valid for mixtures where hydrogen bonding is important either amongst molecules of the pure component (for example, water) or between molecules of different components (for example, chloroform-acetone).

If hydrogen bonding is significant, a different approach may sometimes be used to correct for vapor-phase imperfections (*18*). This approach considers all deviations from ideal behavior in the vapor phase to be due to the formation of dimers (or higher polymers). Thus for example the vapor of a hydrogen-bonding substance A is considered to be an ideal gas consisting of species A and A_2. The relative amount of each species is given by an equilibrium constant K_H; thus at moderate pressures

$$2A \rightleftarrows A_2 \quad \text{and} \quad K_H = \frac{p_{A_2}}{p_A^2}$$

The equilibrium constant is a function of temperature and must be determined experimentally. This technique is best illustrated by a numerical example as shown below.

Example 6

Consider the vapor-liquid equilibria of mixtures of acetic acid and propionic acid at 20°C. At this temperature the total pressure is in the neighborhood of 15 mm. Hg, and it would appear that at such a low pressure vapor-phase imperfections would be entirely negligible. However the dimerization of these acids in the vapor phase is so strong that large deviations from ideal behavior result. For each acid a dimerization equilibrium constant is defined:

$$K_{H_a} = \frac{p_{a_2}}{p_a^{\,2}} \quad \text{and} \quad K_{H_b} = \frac{p_{b_2}}{p_b^{\,2}}$$

where a refers to acetic acid and b to propionic acid.

In addition there is the solvation equilibrium

$$K_{H_{ab}} = \frac{p_{ab}}{p_a p_b}$$

K_{H_a} and K_{H_b} have been measured (*19*), and a reasonable assumption for $K_{H_{ab}}$ is to set it equal to $(K_{H_a}K_{H_b})^{\frac{1}{2}}$. In this procedure the nonideal binary vapor phase is now considered to be equivalent to an ideal five-component mixture consisting of two monomers and three dimers. When this treatment of the vapor phase (*3*) is combined with the assumption that Raoult's law holds for the liquid phase, a $y - x$ diagram can be constructed as shown in Figure 8, which also shows the curve computed without vapor-phase corrections as well as the experimental data of Christian (*3*). The results suggest the rather surprising conclusion that in this system, in spite of the very low total pressure, the deviations from ideality are predominantly in the vapor rather than in the liquid phase.

This approach to vapor-phase nonideality is necessarily limited to the few systems where the polymerization constants have been measured and where, because of chemical similarity, a geometric mean may be a good approximation for the cross dimerization constant.

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NOTATION

B = second virial coefficient
C = third virial coefficient
D = fourth virial coefficient
$\bar{f}_i$ = fugacity of component i in gaseous solution
f_i^0 = fugacity of pure component i as a gas or vapor
f_i^c = fugacity of pure condensed component i
$k_g a$ = mass transfer coefficient
k_{ij} = a characteristic parameter defined by Equation (16)
K = vaporization equilibrium constant = y/x
K_a = chemical equilibrium constant
K_H = dimerization constant
N = rate of mass transfer
p = partial pressure
P = total pressure
R = gas constant
T = absolute temperature
U = ionization potential
v = molar volume
V = volume
$\bar{V}_i$ = partial molar volume of component i
V_i^0 = volume of pure component i as a gas or vapor
x_i = mole fraction of component i in the condensed phase
y_i = mole fraction of component i in the gas phase
y_i^* = mole fraction of component i in the gas phase at the gas-liquid interface
z = compressibility factor, property of mixture

Greek Letters

γ = gas-phase activity coefficient [See Equation (2)]
γ^c = condensed phase activity coefficient
ϕ = vapor-phase fugacity coefficient [See Equation (1)]
ϕ° = vapor-phase fugacity coefficient for the pure component
ν = fugacity to pressure ratio for pure gas or vapors
ρ = molar density
θ_B = generalized function for the second virial coefficient
θ_c = generalized function for the third virial coefficient
ω = acentric factor
ω^h = acentric factor of homomorph; see Bondi, A., *A.I.C.H.E. Journal*, **3**, 4, 473 (1957).
β = ratio of critical volumes
ζ = ratio of ionization potentials
μ = dipole moment

Subscripts

c = critical (or characteristic)
$i, j, k \cdots$ = components
m = mixture
r = reduced
$1, 2 \cdots$ = components

Superscripts

v = vapor phase
c = condensed phase

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