Rapid Estimation of Minimum Solubility of Solids in Gases

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Prausnitz (*8*) and Rowlinson (*11, 12*) have derived equations to estimate the fugacity of a component in a nonideal gas mixture; that is

$$\ln\phi_j = \ln\bar{f_j}/Py_j = \frac{2}{V}\sum_k y_k B_{jk} + \frac{3}{2V^2}\sum_i\sum_k y\, y_k C_{ijk} - \ln Z \quad (1)$$

One of the more useful applications of this relation is to calculate the solubility of low-volatile solids in a high-pressure gas. If the solubility of the inert gas in the solid phase is negligible and if the solubility of the solid in the gas is small then it is easy to show that the mole fraction of the solid component in the gas phase is given as

$$\ln y_j = \ln P_{VPj}/P + \ln Z - \frac{2}{V}B_{jh} - \frac{3}{2V^2}C_{jhh} + \int_{P_{VP}}^{P}(v_j^s/RT)\,dP \quad (2)$$

In Equation (2), all terms on the right-hand side except $\ln P_{VPj}/P$, are correction terms owing to either the Poynting effect or to the nonideality of the gas phase. For ideal gases and small Poynting effects, Equation (2) predicts that y is inversely proportional to pressure at constant temperature. However, owing to the nonideal terms, especially

$$\left(-\frac{2}{V}B_{jh}\right)$$

a plot of y_j against pressure at constant temperature will usually show a definite minimum in composition, and at high pressures the mole fraction increases with increasing pressure. Prausnitz (*8*) shows several such plots and the applicability of Equation (2) to predict y-P data.

One very practical application of Equation (2) is to predict the minimum concentration of the less volatile component in a high-pressure, low-temperature purification system. For example, a convenient way to remove the impurity carbon dioxide from air is to cool the high-pressure air and separate the solid dry-ice from the air by filters or deposition on the tubes of a heat exchanger. Owing to the phenomenon referred to above, there should be an optimum pressure to operate such a system at any given temperature.

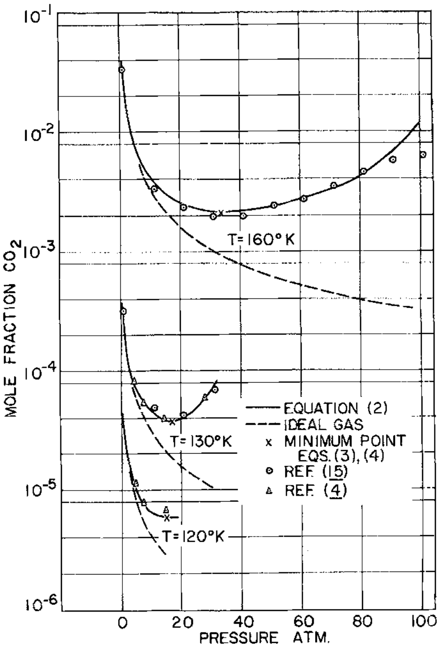

Fig. 1. Calculated and experimental values of vapor composition carbon dioxide-air system.

In a study of experimental data for all such systems investigated to date (*1, 2, 3, 4, 6, 7, 13, 14, 15, 16*), it became obvious that the pressure minimum occurred at a low enough pressure that terms [in Equation (2)] involving the third interaction virial and the Poynting correction are of negligible importance. Thus it is only necessary to consider the first three terms in the right-hand side of Equation (2). When Equation (2) is differentiated with respect to pressure and equated to zero, it follows that the minimum mole fraction and corresponding pressure are expressed simply as

$$y_{j(\min)} = -\frac{2eB_{jh}P_{VPj}}{RT} \quad (3)$$

$$P(\text{at } y_{\min}) = \frac{-RT}{B_{hh} + 2B_{jh}} \quad (4)$$

Similar types of equations were obtained by Reuss and Beenakker, but these were expressed in terms of the density of the pure components and of the mixtures (*10*).

For example, when Equations (3) and (4) are applied for the carbon dioxide-air system at three temperatures,

TABLE 1. COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL COMPOSITION PRESSURE POINTS AT MINIMUM COMPOSITION

System	T, °K.	B_{jh},* cc./g. mole	B_{hh},* cc./g. mole	$P_{VP,j}$,* atm.	Minimum mole fraction contaminant: Equation (3)	Minimum mole fraction contaminant: Exper.	Pressure at minimum mole fraction, atm.: Equation (4)	Pressure at minimum mole fraction, atm.: Exper.
CO-H_2	60	−98	−21.5	2.5×10^{-2}	2.7×10^{-3}	2.6×10^{-3} (*2*)	23	21 (*2*)
	50	−134	−32.4	1.1×10^{-3}	1.9×10^{-4}	1.8×10^{-4}	14	15
	40	−198	−49.5	3.1×10^{-5}	1.0×10^{-5}	1.1×10^{-5}	7.4	8.5
N_2-H_2	60	−90	−21.5	6.2×10^{-2}	6.2×10^{-3}	6.5×10^{-3} (*2*)	24.5	22-24
	50	−125	−32.4	3.8×10^{-3}	6.3×10^{-4}	6.3×10^{-4}	14.6	16-17
	40	−184	−49.5	6.5×10^{-5}	2.0×10^{-5}	2.0×10^{-5}	7.9	8-9
	30	−306	−66	6.8×10^{-8}	4.6×10^{-8}	$<7 \times 10^{-7}$	3.6	<6
CO_2-air	190	−116	−35	6.77×10^{-1}	2.7×10^{-2}	—	59	—
	160	−160	−69	3.11×10^{-2}	2.0×10^{-3}	1.9×10^{-3} (*4, 15*)	34	35 (*4, 15*)
	140	−202	−98	1.83×10^{-3}	1.7×10^{-4}	1.9×10^{-4}	23	23
	130	−230	−115	3.15×10^{-4}	3.7×10^{-5}	4.0×10^{-5}	18.5	18-19
	125	−245	−123	1.20×10^{-4}	1.6×10^{-5}	1.6×10^{-5}	17	16
	120	−264	−128	4.3×10^{-5}	6.3×10^{-6}	7.6×10^{-6}	15	14

* j—contaminant, h—solvent gas.

120°, 130°, 160°K., the calculated minimum y and associated P agree well with experimental data as shown in Figure 1. Also shown in the figure are curves calculated from the complete form of Equation (2) and the ideal gas values ($y = P_{VP}/P$). Good results were obtained from Equations (3) and (4) with all other binary systems studied. Table 1 lists some of the representative results.

For the calculations shown here, the second virial coefficients were obtained from the Lennard-Jones potentials ϵ/k and σ and Table 1-B of Hirschfelder, Curtiss, and Bird (5). For the interaction coefficients, B_{jh}, the same technique was used employing the geometric mean of (ϵ/k) and the arithmetic mean of σ. Other methods of obtaining B_{hh} and B_{jh} were tried (8, 9) but the final calculation of $y_{\min}$ did not differ appreciably at the low pressures where the composition minimum was found. In Figure 1, the calculated curve was obtained from Equation (2) with the second virials determined as indicated above. The third virial coefficients were found from Table 1-C (5) with

$$(\epsilon/k)_{ijk} = [(\epsilon/k)_i\,(\epsilon/k)_j\,(\epsilon/k)_k]^{1/3}$$

$$\text{and } \sigma_{ijk} = (\sigma_i + \sigma_j + \sigma_k)/3$$

This technique for estimating the third virial coefficient is not satisfactory for estimating solubilities at high pressures; as shown in Figure 1, the agreement between experimental and calculated values of y_{CO_2} begin to differ appreciably at pressures exceeding 80 atm. It is interesting to note that in the system helium-oxygen (He-O_2), the interaction virial B_{O_2-He} is positive at the temperatures used in the experimental work and that Equation (3) would then be inapplicable; the physical significance seems to be that there is no minimum in composition for this system at any reasonable temperatures and pressures.

In summary, it has been shown that Equations (3) and (4) are convenient to use in estimating rapidly both the maximum purification attainable in a freeze-out purification system and the pressure level to be used to attain this purity.

NOTATION

B = second virial coefficient, volume/mole
C = third virial coefficient, (volume/mole)^2
e = natural logarithm base
f = fugacity
P = pressure
R = gas constant
T = temperature
v^s = specific volume of solid
V = specific volume of gas
y = mole fraction
Z = compressibility factor of gas

Subscripts

j = component present in both solid and gas phases
h = solvent component
VP = vapor pressure

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Diffusionally Controlled Surface Reactions in Tube-Wall Reactors

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The problem of obtaining kinetic information for reactions occurring on solid surfaces past which a fluid flows has received increasing attention in recent years. Of particular interest is the extraction of meaningful kinetic data for flow systems in which the observed rate of reaction is essentially the rate of transport to the reaction surface; that is, diffusionally controlled reactions. The literature on this subject has been devoted mainly to the development of mathematical schemes, operating on experimental data, to determine the values of parameters of the surface reaction; for example, surface concentrations.

Because chemical kinetics is largely an experimentally based science, it would seem appropriate to determine whether laboratory measurements of sufficiently high accuracy may be made for use in analytical schemes designed to yield kinetic information. It is the purpose of this note first to estimate surface concentrations in diffusionally controlled reactions of a particular type; and second, to show that simply determined laboratory data in such diffusionally controlled systems cannot be expected to yield estimates of these surface concentrations with any reasonable accuracy.

The simplest analysis of a surface reaction which is dependent upon a diffusional process involves the use of the quasi-stationary method developed by Frank-Kamenetskii (2). It is assumed in this method that the conditions of diffusional transport are independent of the course of the surface reaction. The fact that the diffusional and reaction processes are actually coupled by the surface boundary condition means that this method can only serve as an approximate model leading, in some cases, to large errors. These errors generally yield too low a surface concentration compared to more exact methods (1). For a first-order reaction, for example, errors of about 10% result which are small compared to other potential sources of error to be examined.

The quasi-stationary method assumes that the rate at which reactant is consumed at the surface equals the rate of diffusion of reactant to the sur-

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