Thermodynamics of Aqueous Solutions Containing Volatile Weak Electrolytes

A thermodynamic framework has been established to calculate equilibrium vapor-liquid compositions for dilute aqueous solutions of one or more volatile weak electrolytes: ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide, in the temperature range 0° to 100°C and for liquid-phase concentrations from 10^{-4} to 1 or 2 molal.

Binary electrolyte-water parameters are obtained from reduction of experimental data for single-solute solutions. Additional parameters required for multi-solute systems are estimated from correlations. These parameters, coupled with chemical equilibria, are used to predict multicomponent vapor-liquid equilibria. At a fixed temperature, either liquid-phase or vapor-phase compositions may be calculated if the composition of the other phase is known. Although the framework has no adjustable parameters for multisolute systems, predicted and observed equilibria are in good agreement for two ternary systems: ammonia-hydrogen sulfide-water and ammonia-carbon dioxide-water.

THOMAS J. EDWARDS
JOHN NEWMAN
and
JOHN M. PRAUSNITZ

Chemical Engineering Department
University of California
Berkeley, California 94720

SCOPE

Stringent limits on allowable emissions of aqueous pollutants are now commonly observed. Since many industrial wastewaters contain volatile solutes such as ammonia and hydrogen sulfide, attention must be given to vapor-liquid equilibria of volatile weak electrolytes in aqueous solutions. Upon searching the literature, the designer of pollution abatement equipment finds only severely limited information. In contrast to extensive theoretical and experimental work reported for strong-electrolyte aqueous solutions, little attention has been given to aqueous weak-electrolyte systems.

Literature data for single-solute systems are mostly old, and in general, they are limited to a minimum concentration of 10^{-1} molal and to a temperature range of 10° to 50°C. Only a few multisolute systems have been studied, notably by Van Krevelen et al. (1949), who studied the NH_3-CO_2-H_2O, NH_3-H_2S-H_2O, and NH_3-CO_2-H_2S-H_2O systems. Van Krevelen's experimental work pertains only to ammonia-rich systems and does not include very dilute solutions. His theoretical studies also apply only to ammonia-rich systems; they are limited by simplifying assumptions to restricted ranges of ammonia/acid ratios and, for some cases, require experimental information which is not available.

The purpose of this work is to establish a molecular thermodynamic framework for calculating equilibrium vapor-liquid compositions of dilute solutions containing one or more volatile weak electrolytes as commonly encountered in chemical industry. The electrolytes examined are ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide for the temperature range 0° to 100°C and for liquid-phase concentrations covering four orders of magnitude, from 10^{-4} to 1 or 2 molal (moles per 1000 g of water).

CONCLUSIONS AND SIGNIFICANCE

A molecular thermodynamic framework has been constructed for calculation of vapor-liquid equilibria in aqueous solutions containing one or more weak electrolytes. This framework gives satisfactory results in the temperature range 0° to 100°C for multisolute systems with total solute concentration less than 2 molal and ionic strength not more than 0.5 molal.

The framework is so constructed that the equilibrium compositions of multisolute systems can be predicted using only binary parameters; no ternary (or higher) parameters are required.

Binary parameters are presented for aqueous solutions of ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide. For a multisolute calculation, it is necessary to solve simultaneously a set of equations reflecting material balances, charge balances, chemical equilibria, and phase equilibria. An efficient computer program for this purpose has been established.

The principal significance of this work is that it provides a convenient, thermodynamically consistent method for calculation of multisolute vapor-liquid equilibria in dilute aqueous solutions of volatile weak electrolytes.

Molecular thermodynamics provides a useful approach toward obtaining phase-equilibrium relations in a system containing one or more weak electrolytes.

The system we wish to describe is represented by Figure 1. At a given temperature and pressure, the weak electrolyte and water equilibrate between the vapor phase V and

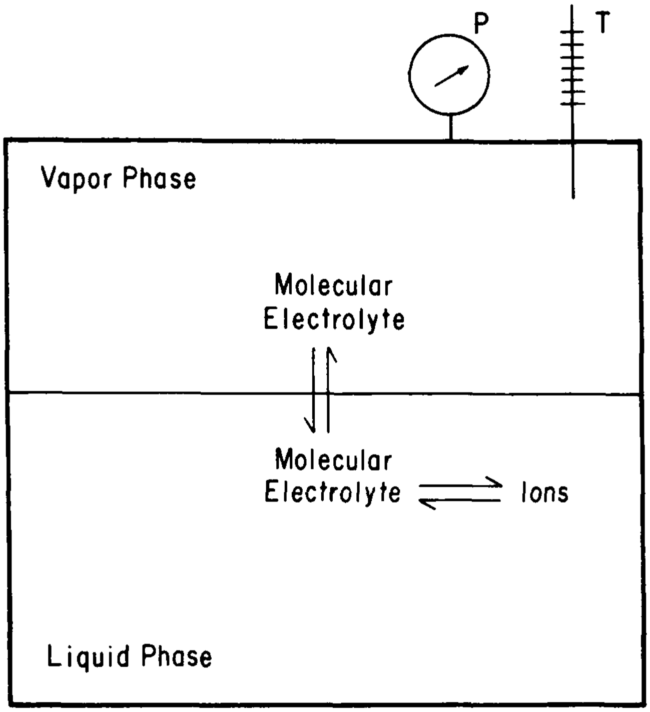

Fig. 1. Vapor-liquid equilibrium in a single-solute system.

the liquid phase L. Since industrial interest is primarily in the stripping of weak electrolytes from aqueous streams, the temperature and the liquid-phase composition are usually known; the vapor-phase mole fraction y and total pressure P are to be calculated.

The weak electrolyte in the liquid phase exists in two forms: molecular and ionic. A chemical equilibrium between these two forms is described by dissociation equilibrium constant K; and at high dilution, vapor-liquid equilibrium is characterized by Henry's constant H. Vapor-phase dissociation of the electrolyte is appreciable only at very high temperatures and is therefore neglected.

A thermodynamic analysis of this system may be based on two descriptions: a macroscopic (bulk) basis and a microscopic (molecular) basis.

The macroscopic basis describes the system only in terms of bulk properties; any molecular process, such as dissociation, is neglected. Deviations from ideality are described by a gross, or stoichiometric, activity coefficient without any discussion of its molecular significance. The bulk property that characterizes the liquid phase is the total, or stoichiometric, electrolyte concentration. This concentration is that reported by standard quantitative-analysis techniques and is the sum of the molecular and ionic concentrations. In the subsequent discussion, this macroscopic description is denoted by the subscript A.

The second description, the microscopic, deals with the solution on a molecular level. The properties that characterize the liquid phase are the concentrations of the molecular solutes and those of the ions. This description, which recognizes dissociation in the liquid phase, is denoted by the subscript a.

It would be advantageous to describe the system in terms of the bulk (stoichiometric) concentration which is available from chemical analysis. However, to interpret and correlate the data it is necessary to use molecular and ionic concentrations. A well-constructed thermodynamic framework must be able to describe the system on either the macroscopic or the microscopic basis.

SINGLE SOLUTE SYSTEMS

Thermodynamic analysis of aqueous weak-electrolyte phase equilibria is based on four principles. (Although the following equations are written for univalent electrolytes, similar equations may be written for other electrolyte types.)

The first principle is an overall mass balance in the liquid phase:

$$m_A = m_a + \frac{1}{2}(m_+ + m_-) \tag{1}$$

where m_A is the stoichiometric concentration of the weak electrolyte, m_a is the molecular concentration of the weak electrolyte, and m_+ and m_- are the concentrations of the cation and anion, respectively.

The second principle is a charge balance in the liquid phase

$$m_+ = m_- \tag{2}$$

Those concentrations of H^+ and OH^- ions which result from the dissociation of water are neglected since the ion concentrations resulting from solute dissociation are of much greater magnitude.

The third principle is the chemical equilibrium between the undissociated and dissociated forms of the weak electrolyte

$$K = \frac{a_+ a_-}{a_a} \tag{3}$$

where K is the dissociation equilibrium constant and a_+, a_-, a_a represent the activity of the cation, anion, and molecular (hydrated)[†] form of the weak electrolyte.

The fourth principle is the equilibrium between the vapor and liquid phases. The chemical potential of the electrolyte must be the same in both phases:

$$\mu_a{}^V = \mu_a{}^L \tag{4}$$

To use Equation (4), we must relate the activities in Equation (3) to concentrations. Therefore, the equilibrium constant K for a 1:1 electrolyte is rewritten

$$K = \frac{m_+ m_-}{m_a} \cdot \frac{\gamma_\pm{}^2}{\gamma_a} \tag{5}$$

where $\gamma_\pm$ is the mean ionic activity coefficient and γ_a is the activity coefficient of the molecular form of the weak electrolyte.

The mean ionic activity coefficient is defined by

$$\gamma_\pm \equiv \sqrt{\gamma_+ \gamma_-} \tag{6}$$

Both activity coefficients are normalized in the manner customary for dilute solutions:

$$\begin{matrix} \gamma_\pm \rightarrow 1 \\ \gamma_a \rightarrow 1 \end{matrix} \quad \text{as} \quad \sum_i m_i \rightarrow 0 \tag{7}$$

where i stands for all solute species.

[†] When the molecular solute enters solution, some of it is hydrated by water, for example,

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

Few data, however, are available for this hydration of weak electrolytes. In thermodynamic descriptions, a convention is used as suggested by Lewis et al. (1961). The standard states of the molecular and hydrated forms are defined such that the above reaction occurs with no change in Gibbs free energy.

Thus

$$K = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3} a_{H_2O}} = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_4OH}}$$

By convention, $a_{H_2O} = 1$ for dilute aqueous solution. The molecular and hydrated forms of the solute are then thermodynamically equivalent.

TABLE 1. EFFECT OF TEMPERATURE ON DISSOCIATION CONSTANTS OF WEAK ELECTROLYTES IN WATER

$$\ln K = C_1 + C_2/T + C_3 \ln T + C_4 T$$
$$K = \text{moles/kg of water}$$
$$T = {}^\circ\text{K}$$

Electrolyte	C_1	C_2	C_3	C_4	Range of experimental data, °K
NH_3	191.97	−8,451.61	−31.4335	0.0152123	273-398
CO_2	2,767.92	−80,063.5	−478.653	0.714984	273-338
H_2S	−45.453	−5,322.37	11.952	−0.07000	278-363
SO_2	1,958.84	−50,481.0	−344.331	0.563442	273-323
HCN	−6,034.04	150,387.0	1,061.49	−1.80964	283-323

The dissociation equilibrium constant defined in Equation (5) has units of molality, or moles of solute per kilogram of water.

The dissociation equilibrium constants of the weak electrolytes were obtained from the literature[†] for the data ranges indicated in Table 1. These data were fit to a semi-empirical equation derived in Appendix A:

$$\ln K = C_1 + C_2/T + C_3 \ln T + C_4 T \tag{8}$$

where the parameters C_1, C_2, C_3, C_4 are shown in Table 1. Extrapolations based on this equation are approximately valid for the range 0° to 100°C.

Assuming for the moment that $\gamma_\pm^2/\gamma_a = 1$ in Equation (5), Equations (1), (2), and (5) give

$$m_a = \frac{2(m_A)^2}{K + 2m_A + \sqrt{K^2 + 4m_A K}} \tag{9}$$

Equation (9) gives the molecular electrolyte concentration as a function of the stoichiometric (total) electrolyte concentration.

For use in Equation (4), the vapor-phase chemical potential can be related to the vapor-phase mole fraction y by

$$(\mu_a{}^V - \mu_a{}^*) = RT \ln y_a \phi_a P \tag{10}$$

where ϕ is the fugacity coefficient and the superscript $*$ denotes the vapor-phase standard state chosen to be the pure ideal gas at system temperature and one atmosphere. The pressure P in Equation (10) must be written in units of atmospheres.

For the liquid phase we write

$$(\mu_a{}^L - \mu_a{}^\theta) = RT \ln m_a \gamma_a \tag{11}$$

where $\mu_a{}^\theta$ is the chemical potential of a at the conditions implied in Equation (7), that is, a hypothetical ideal dilute solution of a at system temperature and pressure and at unit molality. To achieve consistency with standard nomenclature used in electrolyte theory, we introduce two standard state activities, defined by

$$\lambda_i{}^\theta = \exp\left(\frac{\mu_i{}^\theta}{RT}\right) \tag{12}$$

$$\lambda_i{}^* = \exp\left(\frac{\mu_i{}^*}{RT}\right) \tag{13}$$

where $\lambda_i{}^\theta$ has units of (molality)$^{-1}$ or (kg of water) (moles)$^{-1}$, and $\lambda_i{}^*$ has units of (atm)$^{-1}$.

Combination of Equations (4), (10), (11), (12), and (13) gives the equation of phase equilibrium:

$$y_a \phi_a P = m_a \gamma_a \mathbf{H}_a \tag{14}$$

where Henry's constant $\mathbf{H}_a$ is given by

$$\mathbf{H}_a = \lim_{m_a \to 0} \frac{y_a \phi_a P}{m_a} = \frac{\lambda_a{}^\theta}{\lambda_a{}^*}$$

Henry's constant is a function of temperature but is independent of composition; it is characteristic of the interaction of a given solute and solvent.

The weak electrolyte solution may be viewed from a macroscopic or microscopic basis. Thus the equation of phase equilibrium may be written either in terms of the microscopic view as in Equation (14) or in terms of the macroscopic view:

$$y_A \phi_A P = m_A \gamma_A \mathbf{H}_A \tag{15}$$

Since there is negligible dissociation in the vapor phase

$$\mu_A{}^V = \mu_a{}^V \tag{16}$$

or

$$\lambda_A{}^* = \lambda_a{}^* \tag{17}$$

and

$$y_A \phi_A P = y_a \phi_a P \tag{18}$$

We must now define the liquid-phase standard state for the stoichiometric species A. Since γ_A approaches zero at infinite dilution for any dissociating species, it is not possible to specify a standard state for A without taking dissociation into consideration. The liquid-phase standard state for the stoichiometric A is defined such that

$$\mu_A{}^\theta = \mu_a{}^\theta \tag{19}$$

or

$$\mathbf{H}_A = \mathbf{H}_a \tag{20}$$

An operational description of the stoichiometric standard state is a hypothetic ideal dilute aqueous solution of *undissociated* A at system temperature and pressure and at unit molality m_A.

Combining Equations (14), (15), (18), and (20) gives

$$\gamma_A = \frac{m_a \gamma_a}{m_A} \tag{21}$$

Using Equation (9) for the evaluation of m_a, we can relate the stoichiometric activity coefficient γ_A to the molecular activity coefficient γ_a:

$$\gamma_A = \frac{2 m_A \gamma_a}{K + 2m_A + \sqrt{K^2 + 4m_A K}} \tag{22}$$

An exact expression for γ_A is given later in Equation (22a).

[†] NH_3—Bates and Pinching (1949), Quist and Marshall (1968); Fisher and Barnes (1972).
CO_2—Clark (1966), Landolt-Bornstein (1960).
H_2S—Clark (1966), Ellis and Milestone (1967).
SO_2—Johnstone and Leppla (1934).
HCN—Izatt et al. (1962).

The stoichiometric activity coefficient γ_A depends on two quantities. The first is the molecular activity coefficient γ_a which describes the nonideality of the solution arising from interactions between dissolved species, ionic and molecular. The second is a function of the stoichiometric concentration; it arises from the dissociation of the weak electrolyte.

Since an electrolyte at infinite dilution tends to dissociate completely, as the stoichiometric concentration m_A approaches zero, so does the stoichiometric activity coefficient γ_A. Therefore, it is impossible to normalize the stoichiometric activity coefficient. As a result, a theoretical framework for the description of weak electrolyte solutions must be based on the normalized γ_a. The activity coefficient γ_A can only be predicted in terms of γ_a, as given by Equation (22).

To complete the thermodynamic analysis it is necessary also to consider the solvent. The equation of phase equilibrium for water is

$$\phi_w(1 - y_A)P = \gamma_w(1 - x_A)P_w^S \tag{23}$$

where subscript w refers to water. The vapor-phase fugacity coefficient is given by ϕ_w, and the pure-water saturation pressure is given by P_w^S. As discussed in detail elsewhere (Edwards, 1974), for the dilute solutions of interest here, the activity coefficient γ_w is approximately unity. Since we are concerned with the dilute range, $1 - x_A \approx 1$. The fugacity coefficient ϕ_w is set equal to unity since at the low total pressures of the experimental data considered here, the vapor phase behaves ideally. As a result Equation (23) simplifies to

$$(1 - y_A)P = P_w^S \tag{24}$$

VAPOR PHASE FUGACITY

The fugacity of the molecular electrolyte in the vapor phase is

$$f_a^V = y_a\phi_a P \tag{25}$$

For the conditions of interest, the total pressure is either very low or, if it is not, the vapor phase mole fraction of electrolyte y_a is near unity. We therefore use the Lewis fugacity rule

$$\phi_a = \phi_{\text{pure}\,a}\,(T, P) \tag{26}$$

Coupling the Lewis fugacity rule with the virial equation of state (truncated after the second-term) we find that

$$\phi_a = \exp\frac{B_a P}{RT} \tag{27}$$

where B_a is the second virial coefficient of the weak electrolyte at system temperature. Values of B_a were obtained from the compilation of Dymond and Smith (1969). At temperatures higher than those considered here, when the vapor pressure of water becomes large, the Lewis rule may no longer provide a good assumption.

LIQUID PHASE FUGACITY

The fugacity of the weak electrolyte in the liquid phase is

$$f_a^L = m_a\gamma_a\mathbf{H}_a \tag{28}$$

The activity coefficient γ_a is obtained from an expression for the Gibbs energy of the liquid phase as shown in Appendix B:

$$\ln\gamma_i = -\frac{\alpha z_i^2\sqrt{I}}{1 + \sqrt{I}} + 2\sum_{k\neq w}\beta_{ik}m_k \tag{29}$$

where w stands for water, α is the Debye-Hückel proportionality factor†, z_i is the ionic charge of species i, I is the ionic strength of the solution defined by

$$I \equiv \frac{1}{2}\sum_j z_j^2\, m_j \tag{30}$$

and β_{ik} is the specific interaction parameter for species i and k in units of kg of water/mole.

The first term in Equation (29) is the Debye-Hückel term of classical electrolyte theory.

The second term of Equation (29) describes short range (van der Waals) interactions between solute species. These interactions may be divided into three classes: (1) *molecule-molecule;* (2) *molecule-ion;* and (3) *ion-ion.*

Coulombic forces between like-charged ions do not allow the ions to approach each other closely enough for short-range van der Waals forces to become appreciable. We therefore adopt the Brönsted specific interaction assumption that for ions i and j of like charge, $\beta_{ij} = 0$.

For a single weak electrolyte in aqueous solution, the concentration of the ions is so small that Equation (29) simplifies to

$$\ln\gamma_a = 2\,\beta_{a\text{-}a}m_a \tag{31}$$

For sulfur dioxide, the strongest electrolyte of interest here, the molecule-ion term becomes significant only near the highest concentration considered in this work, 1 molal.

Henry's constant is a weak function of pressure as expressed by

$$\ln\mathbf{H}^{(P)} = \ln\mathbf{H}^{(P^S)} + \frac{\overline{v}_a^{\infty}(P - P^S)}{RT} \tag{32}$$

where P^S is the saturation pressure of the solvent at the system temperature, $\mathbf{H}^{(P^S)}$ is Henry's constant evaluated at that saturation pressure, and $\overline{v}_a^{\infty}$ is the partial molar volume of the solute at infinite dilution (Krichevsky and Kasarnovsky, 1935).

The correlation of Lyckman et al. (1965) was used to estimate $\overline{v}_a^{\infty}$ at 25°C for NH_3, CO_2, H_2S, SO_2, and HCN: 30.0, 37.6, 34.0, 45.5, and 72.8 (cm^3) $(\text{g-mole})^{-1}$ respectively. An alternate method is given by Brelvi and O'Connell (1972). For our purposes, $\overline{v}_a^{\infty}$ is taken independent of temperature. At the modest pressures considered here, calculated results are not sensitive to $\overline{v}_a^{\infty}$.

DATA REDUCTION

Combining Equations (14), (31), and (32) and noting that $P >> P_w^S$, we may write the equation of phase equilibrium

$$\ln\left[\frac{y_a\phi_a P}{m_a}\right] - \frac{\overline{v}_a^{\infty}P}{RT} = \ln\mathbf{H} + 2\beta_{aa}m_a \tag{33}$$

where it is understood that $\mathbf{H}$ stands for $\mathbf{H}^{(P^S)}$. For a given weak electrolyte in water, all the variables of the left-hand side may be calculated as discussed above. Plotting that group versus m_a for each isothermal set of data gives a straight line with intercept ln H and slope $2\beta_{a\text{-}a}$. Figure 2 *shows an example of data reduction for the ammonia-water system.*

Vapor-liquid equilibrium data were taken from the literature†† and reduced by a computer program NATLOG

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† A Debye-Hückel parameter A_γ is tabulated as a function of temperature in Appendix 4 of Lewis et al. (1961); $\alpha = 2.303\,A_\gamma$.

†† NH_3—Sherwood (1925), Clifford and Hunter (1933), Morgan and Maass (1931).
CO_2—Houghton et al. (1957).
H_2S—Clarke and Glew (1971); Wright and Maass (1932).
SO_2—Sherwood (1925), Morgan and Maass (1931).
HCN—Siegle (1973).

Table 2. Effect of Temperature on Henry's Constants of Weak Electrolytes in Water

$$\ln \mathbf{H} = D_1 + D_2/T + D_3 \ln T + D_4 T$$
$$\mathbf{H} = \text{kg-atm/mole}$$
$$T = {}^\circ\text{K}$$

Electrolyte	D_1	D_2	D_3	D_4	Range of validity, °K
NH_3	160.559	−8,621.06	−25.6767	0.035388	273-373
CO_2	1,082.37	−34,417.2	−182.28	0.25159	273-373
H_2S	−403.658	7,056.07	74.6926	−0.14529	273-373
SO_2	1,135.63	−32,143.3	−198.14	0.33836	273-373
HCN	7,605.09	−212,343	−1,319.22	2.08347	283-343

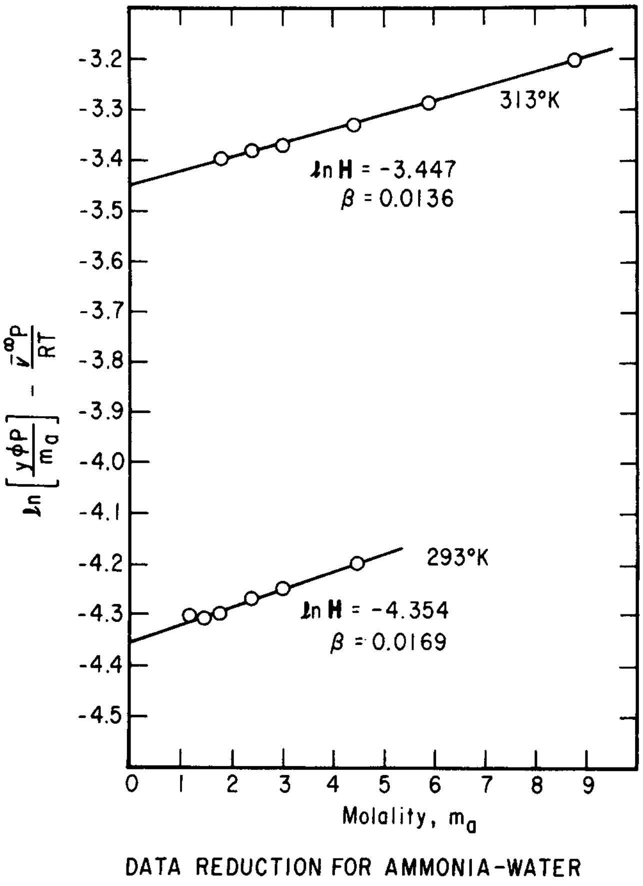

Fig. 2. Data reduction for ammonia-water.

given elsewhere (Edwards, 1974).

Henry's constants were fit to the semiempirical equation

$$\ln \mathbf{H} = D_1 + D_2/T + D_3 \ln T + D_4 T \qquad (34)$$

where **H** has units of kg-atm/mole. The parameters and their temperature range are given in Table 2. Figure 3 shows Henry's constants for five weak electrolytes in water.

Although $\beta_{a\text{-}a}$ is a weak function of temperature, the accuracy of the experimental data does not allow a satisfactory description of the temperature dependence. The fugacity of the liquid phase is primarily a function of m_a and **H**, the specific interaction coefficient $\beta_{a\text{-}a}$ provides only a small correction.

Table 3 gives specific interaction coefficients obtained from experimental data at 20°C.

We may now relax one of the assumptions made in deriving Equation (9). We can rederive Equation (9) assuming only that $\gamma_\pm^2 = 1$:

Table 3. Molecule-Molecule Specific Interaction Parameter for Single Solutes

Solute	β, kg water/mole
NH_3	0.017
CO_2	0.010
H_2S	0.005
SO_2	−0.277
HCN	−0.018

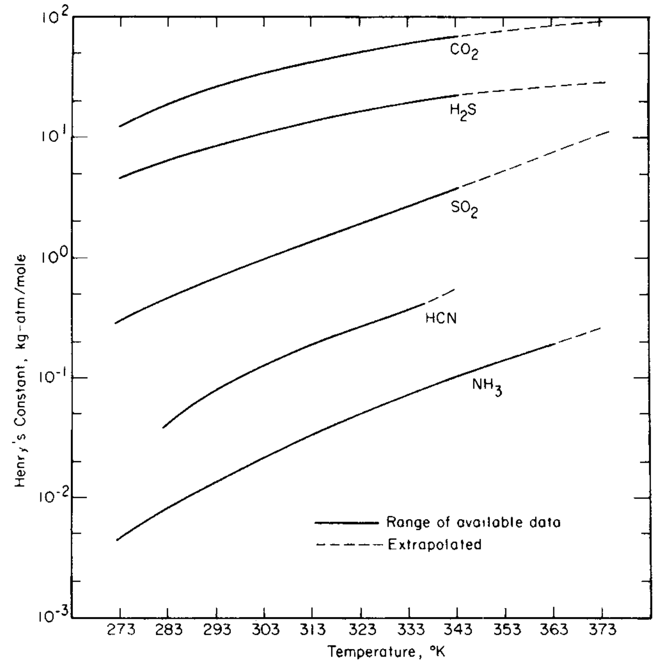

Fig. 3. Henry's constant in water.

$$m_a = \frac{2(m_A)^2}{K\gamma_a + 2m_A + \sqrt{(K\gamma_a)^2 + 4m_A K\gamma_a}}$$

$$\gamma_A = \frac{2\, m_A\, \gamma_a}{K\gamma_a + 2m_A + \sqrt{(K\gamma_a)^2 + 4m_A K\gamma_a}}$$

Moreover, the assumption that $\gamma_\pm^2 = 1$ may also be relaxed. For dilute solutions, Debye-Hückel theory states that

$$\ln \gamma_\pm = -\frac{\alpha\, z_+ z_- \sqrt{I}}{1 + \sqrt{I}} \qquad (35)$$

Using Equations (9), (31), and (35), m_a can be found from

Table 4. Vapor-Liquid Equilibria for SO_2-H_2O at 10°C

m_A	m_a	γ_A	γ_a	ϕ_a	$y_{SO_2}P$ (atm)
1.0×10^{-3}	4.56×10^{-5}	4.56×10^{-2}	1.00	1.00	1.90×10^{-5}
1.0×10^{-2}	2.50×10^{-3}	2.50×10^{-1}	1.00	1.00	1.04×10^{-3}
1.0×10^{-1}	5.88×10^{-2}	6.09×10^{-1}	1.04	1.00	2.53×10^{-2}
7.0×10^{-1}	5.38×10^{-1}	1.02	1.33	0.99	2.98×10^{-1}

$$m_a = \frac{2(m_A)^2}{K\dfrac{\gamma_a}{\gamma_\pm^2} + 2m_A + \sqrt{\left(K\dfrac{\gamma_a}{\gamma_\pm^2}\right)^2 + \dfrac{4m_AK\gamma_a}{\gamma_\pm^2}}} \tag{9a}$$

Similarly, γ_A [Equation (22)] becomes

$$\gamma_A = \frac{2m_A\gamma_a}{K\dfrac{\gamma_a}{\gamma_\pm^2} + 2m_A + \sqrt{\left(K\dfrac{\gamma_a}{\gamma_\pm^2}\right)^2 + \dfrac{4m_AK\gamma_a}{\gamma_\pm^2}}} \tag{22a}$$

This $\gamma_\pm$ correction to Equations (9) and (22) becomes appreciable only for solutions of moderate ionic strength, for example, solutions of sulfur dioxide at higher concentrations.

CALCULATIONS FOR SINGLE-SOLUTE SYSTEMS

To calculate liquid-vapor equilibria for a binary system at fixed temperature, the following sequence is used:

1. Find m_a as a function of m_A from Equation (9), using the dissociation equilibrium constant K as determined by Equation (8).
2. Calculate γ_a using Equation (31).
3. Evaluate $\gamma_\pm$ using Equations (1), (30), and (35).
4. Calculate m_a using Equation (9a).
5. Iterate on steps 2, 3, 4 until values converge. Two iterations are usually sufficient.
6. Calculate γ_A from Equation (22a).
7. Evaluate $y_a\phi_aP$ as a function of m_A from Equation (15), using the Henry's constant H determined by Equation (34).
8. Calculate P from $P = P_w^S + y_aP$.
9. Find ϕ_a at the pressure P from Equation (27).
10. Calculate y_aP as a function of m_A using Equation (33).
11. Iterate on steps 7, 8, 9, and 10 until convergence on y_aP is achieved.

This sequence of calculations was made for all the solutes of interest in the range 0° to 100°C and 10^{-4} to 1 molal by the computer program WEKELEC given elsewhere (Edwards, 1974). Table 4 gives results for sulfur dioxide-water at 10° with $\beta_{a\text{-}a}$ evaluated at that temperature.

The total (stoichiometric) concentration m_A approaches the molecular concentration m_a at higher concentrations. At lower concentrations, however, an increasingly larger fraction of the solute is in ionic, rather than molecular, form. The effect of dissociation is also evident in the difference in behavior of stoichiometric γ_A and molecular γ_a. As the solution becomes more dilute, γ_a becomes a very small fraction of unity.

Figure 4 illustrates the importance of considering weak-electrolyte dissociation in vapor-liquid equilibrium calculations. The broken curve gives results calculated with the erroneous assumption that sulfur dioxide is a nonelectrolyte in an ideal dilute solution. The solid curve gives calculated results taking dissociation into account. Both curves are calculated with the same Henry's constant, given by Equation (34) with parameters shown in Table 2. At high concentrations the agreement between the curves is fair, but it becomes increasingly worse at lower concentrations.

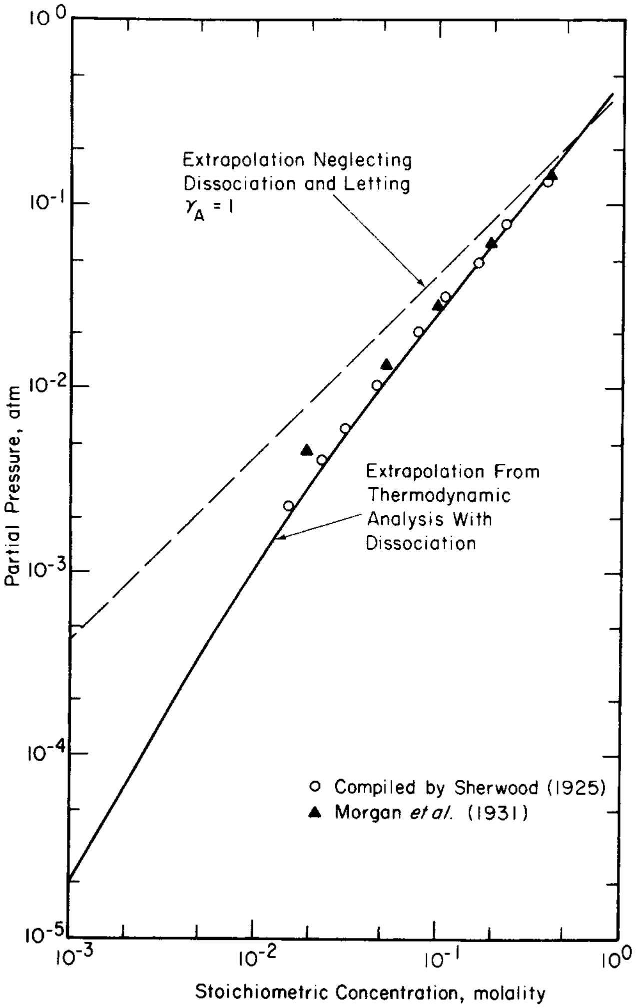

Fig. 4. Solubility of sulfur dioxide in water at 10°C.

MULTISOLUTE SYSTEM

Although vapor-liquid equilibria are of importance for a single weak electrolyte in aqueous solution, primary industrial interest is in systems containing more than one solute. A general thermodynamic analysis for a multisolute system is given below.

When a single weak electrolyte is placed into solution, the only chemical reaction occurring is that of ionic dissociation. For very dilute concentrations this effect is appreciable. At more moderate concentrations, however, only a relatively small fraction of the weak electrolyte is in ionic form.

As an example, when ammonia is placed in solution as a single solute, the dissociation reaction is

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad (36)$$

Similarly, for hydrogen sulfide, the reaction is

$$H_2S \rightleftarrows H^+ + HS^- \qquad (37)$$

The great majority of each electrolyte exists in the solution in molecular, rather than ionic, form. (The *p*H of the hydrogen sulfide solution is such that the second dissociation to the sulfide ion is negligible.)

However, if ammonia and hydrogen sulfide are both present in the solution, the relative concentrations of the molecular and ionic forms of the electrolyte change drastically. In addition to Equations (36) and (37), we must also consider

$$\begin{aligned} NH_3 + H_2S &\rightleftarrows NH_4^+ + HS^- \\ NH_3 + HS^- &\rightleftarrows NH_4^+ + S^= \end{aligned} \qquad (38)$$

Since these acid-base reactions occur much more readily than the simple dissociation reactions, the ionic concentrations are greatly increased even at moderate concentrations. Depending on the concentration of the weak acid and weak base in solution, the fraction of weak electrolyte in molecular form may be greatly reduced. Since it is the molecular species which is in equilibrium with the vapor phase, the partial pressure of the weak electrolyte in the vapor phase may also be greatly reduced.

For each electrolyte, the equation of phase equilibrium is given by Equation (14). The standard states for species a in the liquid and vapor phases in the multisolute system are the same as those in the single-solute system. Thus, the value of H_a is identical for both single and multisolute cases.

To calculate the composition of a vapor phase in equilibrium with a liquid phase of known stoichiometric concentrations, it is necessary to determine m_a and γ_a. Due to chemical reactions between the two electrolytes [Equation (38)], a simple relation among the stoichiometric and molecular values of m and γ does not exist, in contrast to the single-solute case [Equations (9) and (22)].

Equation (29) gives γ_i. In the single-solute case the only species whose concentration is of significant magnitude is the molecular species. In multisolute systems, however, the ionic concentrations are of sufficient magnitude that molecule-ion and ion-ion interactions must also be considered. Since the specific interaction parameters for these interactions are not available in the literature and since they cannot be obtained from reduction of single-solute systems, they must be estimated.

THERMODYNAMIC ANALYSIS FOR MULTISOLUTE SYSTEMS

The four general principles used in the analysis of single-solute systems are used as before: dissociation equilibria, mass balances, solution electroneutrality, and vapor-liquid equilibria. However, the dissociation equilibrium for water, neglected in the single-solute case, is now required to relate the acid and base concentrations to each other.

To illustrate, consider the equations needed to describe the NH_3-H_2S-H_2O system. In this system, seven molecular species (in addition to water) are present in solution: NH_3 (molecular), H_2S (molecular), NH_4^+, HS^-, $S^=$, H^+, OH^-. Thus we have 14 unknowns (m_i and γ_i for each of these species) and in solving for them we must write 14 independent equations. These equations are

Dissociation equilibria:

(I) $K_1 = \dfrac{a_{NH_4^+}\, a_{OH^-}}{a_{NH_3}}$ where $a_i = m_i \gamma_i$

(II) $K_2 = \dfrac{a_{HS^-}\, a_{H^+}}{a_{H_2S}}$

(III) $K_3 = \dfrac{a_{S^=}\, a_{H^+}}{a_{HS^-}}$

(IV) $K_w = a_{H^+}\, a_{OH^-}$

Mass balances:

(V) Total $NH_3 = m_{NH_3} + m_{NH_4^+}$

(VI) Total $H_2S = m_{H_2S} + m_{HS^-} + m_{S^=}$

Electroneutrality:

(VII) $m_{NH_4^+} + m_{H^+} = m_{HS^-} + 2m_{S^=} + m_{OH^-}$

Activity coefficients for each of seven species:

(VIII-XIV) $\ln \gamma_i = \dfrac{-\alpha\, z_i^2 \sqrt{I}}{1 + \sqrt{I}} + 2 \sum\limits_{k \neq w} \beta_{ik} m_k$

The above equations are written for the case where the liquid-phase stoichiometric concentrations are known and the vapor-phase composition is desired. If, however, the opposite is true, then Equations (V) and (VI) are replaced by

(Va) $y_{NH_3} \phi_{NH_3} P = m_{NH_3} \gamma_{NH_3} H_{NH_3}$

(VIa) $y_{H_2S} \phi_{H_2S} P = m_{H_2S} \gamma_{H_2S} H_{H_2S}$

Although not explicitly listed, the acid-base reaction is inherent in the given equations through the interaction of H^+ and OH^- ion in the water dissociation equation.

To evaluate the activity coefficients, a method of estimating β_{ik} must be selected. Fortunately, the equilibrium calculations are not sensitive to this estimation method because the important parameters are H and K, not β_{ik}.

Molecule-molecule interaction parameters between like species are listed in Table 3. For the interaction parameters for unlike molecular species, we use the mixing rule

$$\beta_{12} = \frac{1}{2}(\beta_{11} + \beta_{22}) \qquad (39)$$

In estimating the molecule-ion (salting out) and ion-ion specific interaction parameters, we use a procedure described by Bromley (1972) in his work on strong electrolytes.

In examining β's for ion-ion interactions, Bromley observed that, to a good approximation,

$$\beta_{+-} = \beta_+ + \beta_- \qquad (40)$$

where β_{+-} is the interaction parameter of the particular cation-anion pair and β_+ and β_- are characteristic of the specific ions. Bromley has taken the experimentally determined β_{+-} values of a number of strong electrolytes and found the best common values of β_+ (or β_-) for a number of ions. To accomplish this separation, β_{H^+} is set equal to 0.1 as a base value.

Bromley assumes that the factors that influence β_+ also determine the entropy of the ion in solution. When β_+ or β_-) is plotted versus $z_i \bar{S}_i^0$, a straight line results; here z_i is the charge of the ion and $\bar{S}_i^0$ is the partial molar entropy of the ion in an infinitely dilute solution as tabulated by Latimer (1952). Due to insufficient data, $\bar{S}^0_{NH_2COO^-}$ was assumed equal to $\bar{S}^0_{CH_3COO^-}$.

To obtain values for β_+ and β_- for the ions of interest, the appropriate values of $z_i \bar{S}_i^0$ were interpolated on Bromley's plot. The estimated values of ion-ion β's are given in Table 5.

We assume that the molecular-ion interaction parameter can also be separated into two parts

$$\beta_{m\text{-ionic}} = \beta_{\text{molecule}} + \beta_{\text{ion}} \qquad (41)$$

Thus, if plots of $\beta_{m\text{-}i}$ versus $z_i\overline{S}_i^0$ for each particular molecular species are made, a correlation between the two quantities should be observed since the β_m contribution of the given molecular species should be constant for every molecule-ion interaction. Molecular-ionic interaction (salting out) parameters are presented for H_2S in salt solutions by McLauchlan (1903) and for the other weak electrolytes by Long and McDevit (1952). Again interpolation of $z_i\overline{S}_i^0$ for the ions of interest on the appropriate plots was performed, with values of molecular-ion parameters shown in Table 6.

Due to lack of data for hydrogen cyanide, the molecular-ion parameters for that system are set equal to zero.

The 14 equations describing the system NH_3-H_2S-H_2O are nonlinear. To solve the equations simultaneously, an iterative method must be used. The method chosen for this work is the multidimensional Newton-Raphson iteration. In this method, an initial estimate of the individual species concentration is made, the activity coefficients are calculated, and an iteration is made on those values until convergence is achieved. Once m_i and γ_i have been determined, Equation (14) is used to calculate the partial pressure of the weak electrolytes in the vapor phase.

TABLE 5. ESTIMATED ION-ION SPECIFIC INTERACTION PARAMETERS

$\beta = \beta_+ + \beta_-$

Ion	β_+ or β_-† (kg of water/mole)
NH_4^+	−0.12
HCO_3^-	0.25
$CO_3^=$	−0.12
HS^-	0.20
$S^=$	0.05
HSO_3^-	0.24
$SO_3^=$	−0.05
CN^-	0.30
NH_2COO^-	0.33
H^+	0.10
OH^-	0.15

† Specific interaction parameters between ions of like sign are assumed to be zero.

TABLE 6. ESTIMATED MOLECULE-ION (SALTING-OUT) SPECIFIC INTERACTION PARAMETERS

Molecule-ion	$\beta_{m\text{-ion}}$ (kg of water/mole)	Molecule-ion	$\beta_{m\text{-ion}}$ (kg of water/mole)
NH_3-HCO_3^-	−0.031	CO_2-OH^-	0.039
NH_3-$CO_3^=$	0.068	H_2S-NH_4^+	0.082
NH_3-HS^-	−0.015	H_2S-HCO_3^-	−0.037
NH_3-$S^=$	0.032	H_2S-$CO_3^=$	0.077
NH_3-HSO_3^-	−0.038	H_2S-HSO_3^-	−0.045
NH_3-$SO_3^=$	0.044	H_2S-$SO_3^=$	0.051
NH_3-CN^-	0.043	H_2S-CN^-	−0.049
NH_3-NH_2COO^-	−0.028	H_2S-NH_2COO^-	−0.032
NH_3-H^+	0.015	H_2S-H^+	0.017
NH_3-OH^-	0.021	H_2S-OH^-	0.023
CO_2-NH_4^+	0.0	SO_2-NH_4^+	−0.05
CO_2-HS^-	0.0	SO_2-HCO_3^-	−0.86
CO_2-$S^=$	0.053	SO_2-$CO_3^=$	0.94
CO_2-HSO_3^-	−0.03	SO_2-HS^-	−0.58
CO_2-$SO_3^=$	0.068	SO_2-$S^=$	0.28
CO_2-CN^-	−0.036	SO_2-CN^-	−1.06
CO_2-NH_2COO^-	0.017	SO_2-NH_2COO^-	−0.79
CO_2-H^+	0.033	SO_2-H^+	0.0
		SO_2-OH^-	0.08

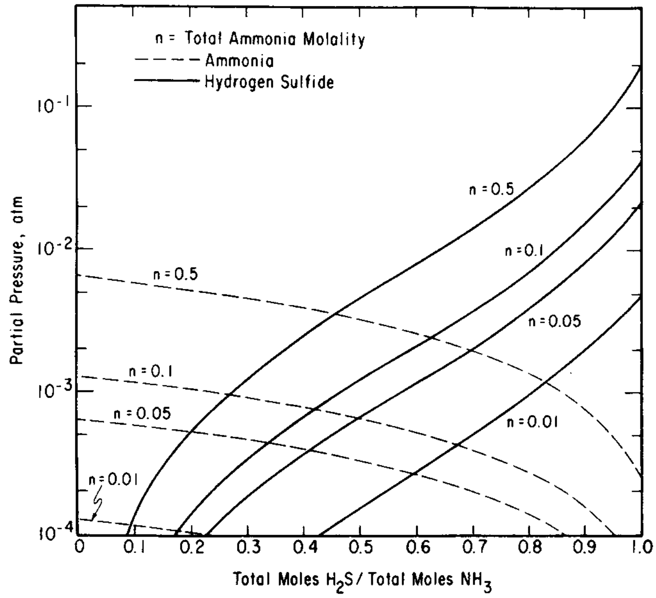

Fig. 5. Vapor-liquid equilibria at 20°C for ammonia-hydrogen sulfide-water containing excess ammonia.

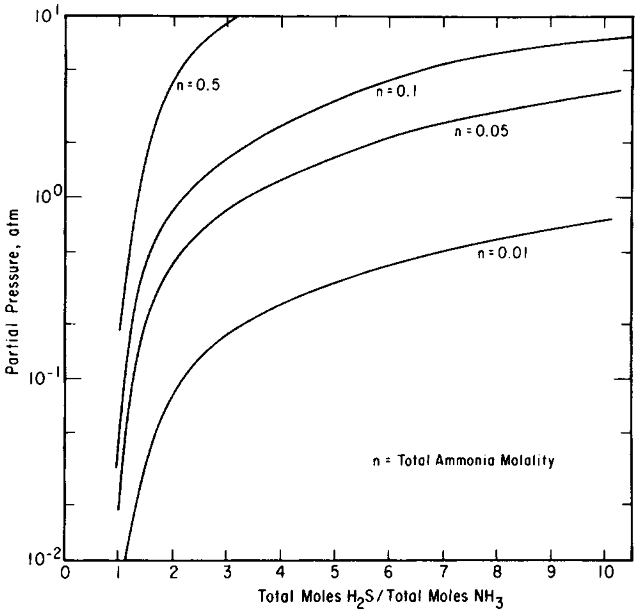

Fig. 6. Partial pressure of hydrogen sulfide at 20°C for ammonia-hydrogen sulfide-water containing excess hydrogen sulfide.

CALCULATED MULTISOLUTE EQUILIBRIA

Calculations were performed utilizing a computer program, WAVES, given elsewhere (Edwards, 1974). Results for the NH_3-H_2S-H_2O system at 20°C are shown in Figures 5 and 6.

As the H_2S/NH_3 ratio in the aqueous phase increases, the partial pressure of NH_3 becomes less than that corresponding to the single-solute case. This is due to the acid-base reaction reducing the amount of molecular NH_3 in equilibrium with the vapor phase, even though the total concentration of NH_3 is constant. As the H_2S/NH_3 ratio exceeds unity, the plot of partial pressure of H_2S changes slope and approaches an asymptote. The amount of H_2S converted by the acid-base reaction to the ionic form is a smaller and smaller fraction of the total amount of H_2S. At high ratios, then, the partial pressure of H_2S in the multisolute systems approaches that in the single-solute system.

The theoretical framework described above allows prediction of the behavior of systems with $H_2S/NH_3 \geqq 1$. This region cannot be treated using Van Krevelen's equation.

To show the accuracy of the multisolute calculation, predicted values for vapor-liquid equilibria of the NH_3-H_2S-H_2O system are compared with experimental values at three temperatures in Table 7. In view of the complexity of the system, agreement is satisfactory.

Calculations were also performed for the system NH_3-CO_2-H_2O. These calculations included consideration of the carbamate equilibrium

$$NH_2COO^- + H_2O \rightleftarrows NH_3 + HCO_3^- \qquad (42)$$

The equilibrium constant is estimated by (Faurholt, 1925)

$$\ln K = -1.22 - 1998 \left(\frac{1}{T} - 0.00341\right) \qquad (43)$$

Predicted and observed vapor-liquid equilibria are shown at 20°C in Figure 7 and at 90°C in Table 8. The results are satisfactory. The agreement at 90°C is remarkable considering the extrapolation of parameters necessary for this calculation.

LIMITATIONS OF THEORY

Three considerations limit the region of concentration for which the framework presented here is valid.

TABLE 7. VAPOR-LIQUID EQUILIBRIA FOR THE NH_3-H_2S-H_2O SYSTEM

Solute and concentration	Partial pressure, torr 20°C	40°C	60°C
NH_3 (0.3 molal)	1.15	2.8	6.2
H_2S (0.185 molal)	4.4	15.7	49.9
Observed H_2S†	4.2	13.3	39.6
NH_3 (0.585 molal)	3.00	7.3	15.9
H_2S (0.285 molal)	3.66	13.2	42.7
Observed H_2S†	3.0	12.7	35.5

† Van Krevelen et al. (1949).

TABLE 8. VAPOR-LIQUID EQUILIBRIA AT 90°C FOR THE NH_3-CO_2-H_2O SYSTEM

Total concentration, molal		Partial pressure of NH_3, torr	
NH_3	CO_2	Observed†	Calculated
1.09	0.005	193	157
0.635	0.036	103	84
1.26	0.115	192	157
1.44	0.165	203	172
0.38	0.051	51	45
1.65	0.265	214	179
1.70	0.33	205	172
1.43	0.365	152	128
1.20	0.32	128	106

† Badger and Wilson (1947).

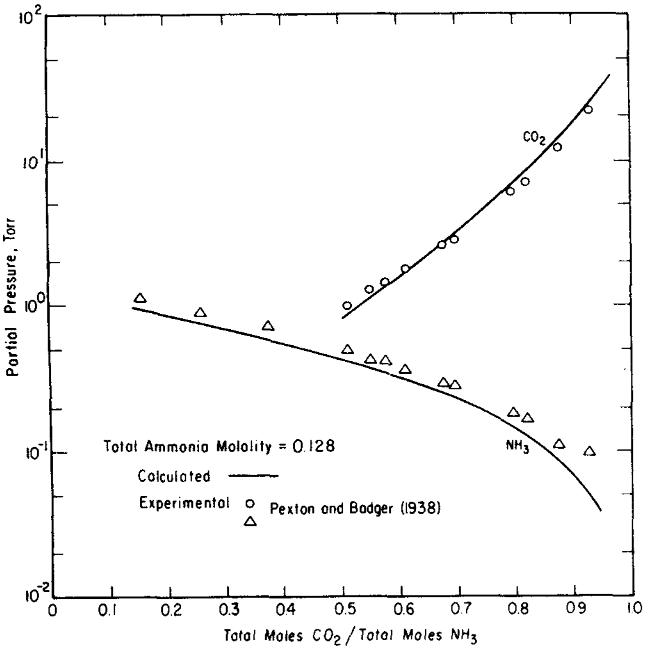

Fig. 7. Vapor-liquid equilibria at 20°C for ammonia—carbon dioxide-water containing excess ammonia.

1. The assumption that the activity of the water is unity. Examination of data for strong and nonelectrolyte solutions shows that the weak electrolyte concentration necessary to decrease the activity of water to 0.95 is between 1.5 molal and 2.3 molal.
2. The concentration at which three-body (and higher) interactions become important. The interaction parameters β_{ik} reflect only two-body interactions. Assuming 10 nearest neighbors in the solution, a molecular concentration of more than 2 molal is required before three-body interactions become appreciable.
3. The concentration range for which Equation (29) is valid. Although the activity coefficients of the ionic species do not appear explicitly in the equation of equilibrium, Equation (14), they do influence the concentrations of the molecular species through the dissociation equilibria. Our experience suggests that satisfactory agreement is achieved between calculated and experimental values for ionic strengths up to 0.5 molal.

Thus the upper limits of concentration for which the model is valid is approximately 2 molal molecular concentration and an ionic strength of 0.5 molal. Since the solution approaches ideality for dilute solutions, there is no lower concentration limit.

The accuracy of the extrapolations for K and $\mathbf{H}$ determine the limits on temperature.

CONCLUSION

In this work a thermodynamic framework has been presented for the calculation of vapor-liquid equilibria for weak electrolytes in aqueous solution. Parameters for the multisolute case are obtained from binary data and from approximations based on correlations. One advantage of this framework over that of Van Krevelen is the absence of limits for the relative amounts of two (or more) weak electrolytes. In contrast to previous work, for which the accuracy became worse for more dilute concentrations, the theory presented here should be more accurate in that range than at higher concentrations.

The multisolute equations are so arranged that either the vapor *or* the liquid phase composition may be calculated if the other phase composition is known.

Upon request to the authors, computer programs are available for calculation of vapor-liquid equilibria of aqueous solutions containing one or more of the following weak electrolytes: ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation and to the American Petroleum Institute for financial assistance and to the Computer Center, University of California, Berkeley, for the use of its facilities.

NOTATION

a = activity = f/f^0
f = fugacity, atm
m = concentration, molality, moles per kilogram of water
n = number of moles
$\bar{v}$ = partial molar volume
x_a = liquid-phase mole fraction = $n_i \Big/ \sum_i n_i$
x_A = liquid-phase mole fraction = $n_A/(n_A + n_w)$
y = vapor-phase mole fraction = $n_A/(n_A + n_w)$
z = charge number
A_{ij} = Margules interaction parameter
B = second virial coefficient
$\mathbf{B}$ = Debye-Hückel parameter
C_P = heat capacity
C_1, C_2, C_3, C_4 = parameters for Equation (8)
D_1, D_2, D_3, D_4 = parameters for Equation (34)
G = Gibbs energy
H = enthalpy
$\mathbf{H}$ = Henry's constant = λ^θ/λ^* (kg-atm/mole)
I = ionic strength $\equiv \frac{1}{2}\sum_i m_i z_i^2$
K = dissociation equilibrium constant (molality)
M_0 = molecular weight of solvent
P = pressure, atm
R = gas constant
$\bar{S}$ = partial molar entropy
T = temperature

Greek Letters

α = Debye-Hückel proportionality factor
β = specific interaction parameter, kg water/mole
γ = molal activity coefficient
λ = molal standard state activity
μ = chemical potential
ϕ = vapor-phase fugacity coefficient
Γ = mole-fraction activity coefficient
Λ = mole-fraction standard-state activity

Superscript

L = liquid phase
0 = standard state
S = saturation
V = vapor phase
θ = liquid-phase standard state
$*$ = vapor-phase standard state
∞ = infinite dilution

Subscript

a = molecular
m = molecule
0 = solvent
w = water
A = stoichiometric
$+$ = cation
$-$ = anion
$\pm$ = mean ionic

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APPENDIX A. TEMPERATURE DEPENDENCE OF THERMODYNAMIC EQUILIBRIUM CONSTANTS

The van't Hoff equation describes the dependence of the dissociation constant on temperature

$$\frac{d \ln K}{dT} = \frac{\Delta H_R}{RT^2} \qquad \text{(A1)}$$

where ΔH_R is the enthalpy of dissociation at temperature T. We define

$$\Delta C_P \equiv C_{P_{\text{ions}}} - C_{P_{\text{molecular electrolyte}}}$$

A second-order Taylor expansion for ΔH_R is

$$\Delta H_R{}^T = \Delta H_R{}^{298} + \Delta C_P{}^{298}\,(T - 298) + \frac{d\Delta C_P{}^{298}}{2dT}\,(T - 298)^2 \qquad \text{(A2)}$$

The expansion is based on 298°K since enthalpies of dissociation can be calculated at this temperature from the NBS tables (Wagman et al., 1968).

Equation (A2) is substituted into Equation (A1) and, following integration, yields

$$\ln K = C_1' + C_2'/T + C_3'\left(\frac{298}{T} - \ln 1/T\right) + C_4'\left(T/2 + 298 \ln 1/T - \frac{(298)^2}{2T}\right) \qquad \text{(A3)}$$

where

$$C_1' = \text{integration constant}$$

$$C_2' = -\Delta H^{298}/R$$

$$C_3' = \Delta C_P{}^{298}/R$$

$$C_4' = \frac{1}{R}\,\frac{d\Delta C_P{}^{298}}{dT}$$

Gathering common terms in Equation (A3) gives Equation (8) in the text where

$$C_1 = C_1'$$

$$C_2 = C_2' + C_3'\,(298) - \frac{(298)^2 C_4'}{2}$$

$$C_3 = C_3' - C_4'\,(298)$$

$$C_4 = C_4'/2$$

Constants for this equation are given in Table 1.

A similar derivation holds for Equation (34).

APPENDIX B. AN EXPRESSION FOR THE GIBBS ENERGY OF A SOLUTION CONTAINING ELECTROLYTES

The Gibbs energy of a solution containing one or more electrolytes can be expressed by an equation similar to that proposed by Guggenheim (1959).

For a dissolved electrolyte i, the chemical potential is given by

$$\mu_i = RT \ln \gamma_i\, m_i\, \lambda_i{}^\theta = RT \ln \Gamma_i\, x_i\, \Lambda_i{}^\theta \qquad \text{(B1)}$$

where

$$x_i = \frac{n_i}{n_0 + \sum\limits_{i \neq 0} n_i} = \frac{M_0 m_i}{1 + M_0 \sum\limits_{i \neq 0} m_i} \qquad \text{(B2)}$$

and x_i is the mole fraction of i, m_i is the molality of i, M_i is the molecular weight of i (kg/mole), and subscript 0 represents the solvent species.

The standard state activities are denoted by $\lambda_i{}^\theta$ and $\Lambda_i{}^\theta$. These standard states are specified by

$$\begin{matrix} \gamma_i \rightarrow 1 \\ \Gamma_i \rightarrow 1 \end{matrix} \quad \text{as} \sum_{i \neq 0} m_i \rightarrow 0 \qquad \text{(B3)}$$

For dilute solutions

$$\ln m_i\, \lambda_i{}^\theta = \ln M_0\, m_i\, \Lambda_i{}^\theta$$

and therefore

$$\Lambda_i{}^\theta = \frac{\lambda_i{}^\theta}{M_0} \qquad \text{(B4)}$$

The total Gibbs energy of the solution, expressed in mole fractions, is

$$\frac{G}{RT} = \frac{n_0 \mu_0{}^0}{RT} + \sum_{i \neq 0} n_i \ln \Lambda_i{}^\theta + n_T \sum_i x_i \ln x_i + \text{electrical terms} + n_T \sum_{i \neq 0} \sum_{j \neq 0} A_{ij}\, x_i\, x_j \qquad \text{(B5)}$$

where

$\mu_0{}^0$ = chemical potential of a mole of pure solvent at system temperature and pressure

$\Lambda_i{}^\theta$ = mole fraction standard state activity

A_{ij} = Margules parameter characterizing the *i-j* interaction

n_i = number of moles of species i

$n_T = n_0 + \sum\limits_{i \neq 0} n_i$

The first three terms of Equation (B5) represent the Gibbs energy of the ideal dilute solution. The first term gives the standard state contribution of the solvent and the second the standard state contributions of all solute species. The third term represents the ideal entropy of mixing of the solution.

The observed Gibbs energy of the electrolyte solution differs from the ideal value due to specific interactions between the components of the solution. These interactions are of two origins: long range (Coulombic) forces and short range (Van der Waals) forces. The terms describing these nonidealities constitute the excess Gibbs energy.

The fourth term represents the contribution of electrostatic interaction between charged ions. This term is based on the Debye-Hückel theory for very dilute solutions of electrolytes.

The fifth term is essentially empirical; a Margules-type term has been chosen to describe the short-range interactions between the components of the solution. It represents the contributions of interactions between molecular species, between molecules and ionic species (salting-out terms), and those short-range interactions between ion pairs not accounted for by Debye-Hückel theory.

Equations (B2), (B4), and (B5) are combined and the approximation $\ln(1 + \delta) = \delta - \frac{1}{2}\delta^2$ (for $\delta << 1$) is used to obtain

$$\frac{G}{RT} = \frac{n_0\mu_0}{RT} + \sum_{j\neq 0} n_j\,[\ln m_j\lambda_j^\theta - 1] + \text{D.H.}$$
$$+ \sum_{i\neq 0}\sum_{j\neq 0} n_i\, m_j\left[M_0 A_{ij} - \frac{1}{2} M_0\right] \quad \text{(B6)}$$

The Debye-Hückel term can now be used in its familiar form. Thus

$$\text{D.H.} = -\frac{2}{3}\alpha\sqrt{I}\,\tau(\mathbf{B}a\sqrt{I})\sum_j z_j^2\, n_j \quad \text{(B7)}$$

where

$$\tau(\delta) = \frac{3}{\delta^3}\left[\ln(1+\delta) - \delta + \frac{1}{2}\delta^2\right]$$

Taking the partial derivative with respect to the number of moles species i, we obtain the activity coefficient

$$\ln\gamma_i = \frac{\partial(G/RT)}{\partial n_i} - \ln m_i\,\lambda_i^\theta$$
$$= \frac{-\alpha\, z_i^2\sqrt{I}}{1 + \mathbf{B}a\sqrt{I}} + 2\sum_{j\neq 0}\beta_{ij}\, m_j \quad \text{(B8)}$$

where $\beta_{ij} = M_0(A_{ij} - 0.5)$.

For all practical purposes the product **B***a* is unity when I is expressed in units of molality.

Manuscript received September 11, 1974; revision received November 12 and accepted November 13, 1974.

Wall Mass Transfer in Laminar Pulsatile Flow in a Tube

Wall mass transfer was measured in fully developed pulsating laminar flow in a tube using the diffusion-controlled electrode technique. The average Reynolds number, pulsating frequency and amplitude, and length of the mass transfer surface were the independent variables studied. The results are given in the form of the amplitude ratio and phase angle of the pulsating wall transfer rate. At lower frequencies the amplitude and phase were found to be correlated by the variable $\omega_d^2\, Gz^{-2/3}$ in accordance with theory. At higher frequencies an empirical correlation with the variable $\omega_d^2\, Gz^{-1/3}(L/D)^{1/3}$ was found. While this may show some deficiency in the usual theoretical model, it is also possible that other causes such as non-development of the flow are responsible. Time-averaged transfer rates were found to be only slightly different from the corresponding steady flow transfer rates in the range of variables investigated.

RUTTON D. PATEL
JOHN J. MCFEELEY
Department of Chemical Engineering
Polytechnic Institute of New York
Brooklyn, New York 11201

and

KENNETH R. JOLLS
Department of Chemical Engineering
Iowa State University
Ames, Iowa 50010

SCOPE

Mass or heat transfer in pulsatile flow is of importance in many areas. Examples are pulsed operation of extraction columns and heat exchangers, transport in the cardiovascular system, etc. When the velocity of a fluid flowing past a surface transferring mass has superimposed on it a time-varying component, then the mass transfer rate is also found to vary with time around some mean value. This mean or time averaged value is often, but not always, found to be greater than that for the corresponding steady flow. Such effects are of obvious interest since they offer the possibility of improving the performance of process equipment. Another question of interest is the relation between the fluctuating transfer rate (or equivalently, the mass transfer coefficient) and the fluctuating velocity. More specifically, we wish to know how rapidly the transfer rate varies upon the inception of a velocity perturbation, and how the magnitude of the fluctuation in mass transfer rate depends on the magnitude of the velocity fluctuation. These questions are answered if the phase difference and the amplitude ratio of the fluctuating transfer rate to the fluctuating velocity field are known.

There has been extensive work in this area, both theoretical and experimental, dealing with questions such as local fluctuating transfer rates, time-averaged transfer rates, etc. in various geometries, such as pulsed extraction columns, flow in tubes, flow past plates, etc. Conflicting results have been reported. Some authors find the time-

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Correspondence concerning this paper should be addressed to R. D. Patel. J. J. McFeeley is with Polaroid Corporation, Cambridge, Massachusetts.