Solutions of Glucose," *Trans. Faraday Soc.*, 51, 1186 (1955).
Voho, K., and P. Varo, "Chemical and Organoleptic Evaluation of Some Finnish Apple Varieties," *J. Sci. Agr. Soc. Finland*, 47, 445 (1975).
Wiebe, H. H., and H. A. Al-Saadi, "Matric Bound Water of Water Tissue from Succulents," *Physiol Plant.*, 36, 47 (1976).
Wilson, J. W., and C. W. Rose, "The Components of Leaf Water Potential. I. Osmotic and Matric Potentials," *Aust. J. Bio. Sci.*, 20, 239 (1967).
Wolf, M., J. E. Walker, and J. G. Kapsalis, "Water Vapor Sorption Hysteresis in Dehydrated Food," *J. Agr. Food Chem.*, 20, 1073 (1972).

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Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes

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A molecular-thermodynamic correlation is established for calculating vapor-liquid equilibria in aqueous solutions containing one or more volatile electrolytes: ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide. The correlation is similar to that presented in 1975, but the domain of application has been increased. The present correlation holds from about 0° to 170°C and for ionic strengths of about 6 molal; for the weak electrolytes considered here, this corresponds to total concentrations between 10 and 20 molal. To represent activities at these high concentrations, activity coefficients are expressed as a function of molality by Pitzer's equation. Required parameters are estimated from data reduction or from correlations.

Special attention is given to the ternary systems ammonia-carbon dioxide-water and ammonia-hydrogen sulfide-water. Calculated equilibria are in satisfactory agreement with the severely limited experimental data now available.

SCOPE

In response to ecological, economic, and political developments, the chemical and petroleum industries must more effectively recover weak electrolytes from plant effluent streams. Towards that end, it is necessary to examine the vapor-liquid equilibria of aqueous, volatile weak electrolytes.

The volatile weak electrolytes of greatest industrial importance are ammonia, carbon dioxide, and hydrogen sulfide, although sulfur dioxide and hydrogen cyanide are also of interest. Literature for the most commonly encountered industrial case (aqueous solutions containing two or more volatile weak electrolytes) is seriously limited. Most of the few available experimental data pertain to dilute solutions and to ambient temperatures.

In contrast to the large body of work published on nonelectrolyte and strong electrolyte solutions, theoretical or correlational work is sparse for aqueous, volatile weak electrolytes. Van Krevelen's (1949) studies apply only to ammonia rich systems; further, they are limited to restricted ranges of ammonia/acid ratios and, for some cases, require experimental information which is not available. The more recent work of Edwards et al. (1975) is limited to low concentrations of weak electrolytes and to temperatures below (about) 80°C. The present work extends Edwards' earlier efforts to higher concentrations and higher temperatures.

The purpose of this work is to extend a previously presented thermodynamic framework for calculating vapor-liquid equilibria for solutions containing volatile weak electrolytes as commonly encountered in the chemical and related industries. The electrolytes examined are ammonia, carbon dioxide, hydrogen sulfide, and sulfur dioxide for the temperature range 0° to 170°C; the composition range, depending on extent of ionization, may be as high as 10 to 20 molal. Limited information is also given for hydrogen cyanide.

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CONCLUSIONS AND SIGNIFICANCE

A molecular-thermodynamic framework has been established for calculation of vapor-liquid equilibria in aqueous solutions of one or more volatile weak electrolytes. This correlation holds from 0° to 170°C and for total ionic strengths of about 6 molal.

Required parameters are presented for solutions of ammonia, carbon dioxide, hydrogen sulfide, and sulfur dioxide. An engineering oriented computer program has been established, suitable for calculation of multicomponent vapor-liquid equilibria for aqueous solutions of volatile weak electrolytes.

The principal significance of this work is that it provides a convenient, thermodynamically consistent method for calculation of multisolute vapor-liquid equilibria of aqueous, volatile weak electrolytes at advanced temperatures and concentrations.

Molecular thermodynamics provides a useful method for interpreting and correlating vapor-liquid equilibria in aqueous solutions containing one or more volatile weak electrolytes. To establish the fundamental framework, we first describe a single-solute system and then extend that description to a multisolute system.

SINGLE-SOLUTE SYSTEM

As shown in Figure 1, the weak electrolyte, in water at a given temperature and pressure, distributes itself between the vapor and liquid phases. At very low concentration, the (vertical) phase equilibrium is determined primarily by Henry's constant $\underline{H}$ and the molality of molecular (not ionic) solute; that molality, in turn, is strongly influenced by the (horizontal) chemical dissociation equilibrium, characterized by dissociation constant $\underline{K}$. (Vapor phase dissociation of the electrolyte is appreciable only at very high temperatures and is therefore neglected here.)

Since ions are not volatile, the (vertical) phase equilibrium of the system is governed not by the total electrolyte concentration in the liquid phase, but only by that concentration of liquid phase electrolyte which exists in molecular (undissociated) form.

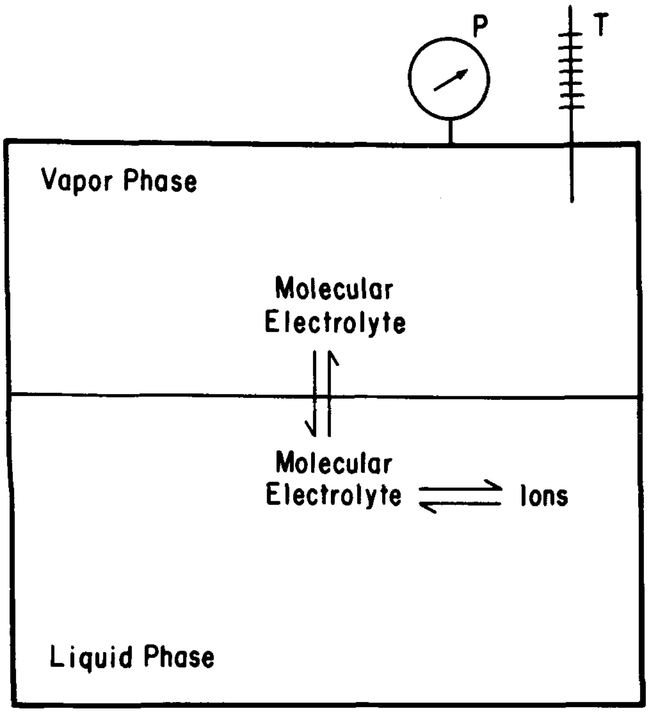

Fig. 1. Vapor-liquid equilibrium in a single-solute system.

As discussed elsewhere (Edwards et al., 1975), the molecular-thermodynamic model for aqueous weak electrolytes is based on four principles:

1. Mass balance for the weak electrolyte in the liquid phase gives

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

2. The ratio of molecular to ionic concentrations of the weak electrolyte is determined by the chemical dissociation equilibrium constant $\underline{K}$:

$$\underline{K} = \frac{a_+^{\nu_+} a_-^{\nu_-}}{a_a} \qquad (2)‡$$

The activity is related to molality through the activity coefficient γ^*

$$a_i = m_i \gamma_i^* \tag{3}$$

where $\gamma_i^* \to 1$ as $\sum_j m_j \to 0$. Subscript j refers to all solute species.

3. Bulk electroneutrality of the liquid phase gives

$$z_+ \cdot m_+ = z_- \cdot m_- \tag{4}$$

4. For the molecular solute, equilibrium between the vapor phase and the liquid phase is given by

$$y_a \phi_a P = m_a \gamma_a^* \underline{H}^{(P)} \tag{5}$$

To complete the thermodynamic framework, vapor-liquid equilibrium for the solvent (water) is given by

$$(1 - y_a)\phi_w P = a_w P^s{}_w \phi^s{}_w \exp \frac{\bar{v}_w (P - P_w^s)}{RT} \tag{6}$$

For Henry's constant, we use the units kilogram-atmosphere-(mole)$^{-1}$, and the activity coefficients are dimensionless. Therefore, for a 1-1 electrolyte, dissociation equilibrium constant $\underline{K}$ has units of molality, or moles of solute per kilogram of water. It is given as a function of temperature by

$$\ln \underline{K} = A_1/T + A_2 \ln T + A_3 T + A_4 \tag{7}$$

Parameters A_1, A_2, A_3, and A_4 are given in Table 1. Parameters for the first and second dissociation constants of carbon dioxide are based on data reported by Clark (1966); for hydrogen sulfide, ammonia, hydrogen cyanide, and water, the parameters are those given by Tsonopoulos

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‡ In some cases it is preferable to write instead of Equation (2) $\underline{K} = (a_+^{\nu_+} a_-^{\nu_-})(a_a a_w)^{-1}$.

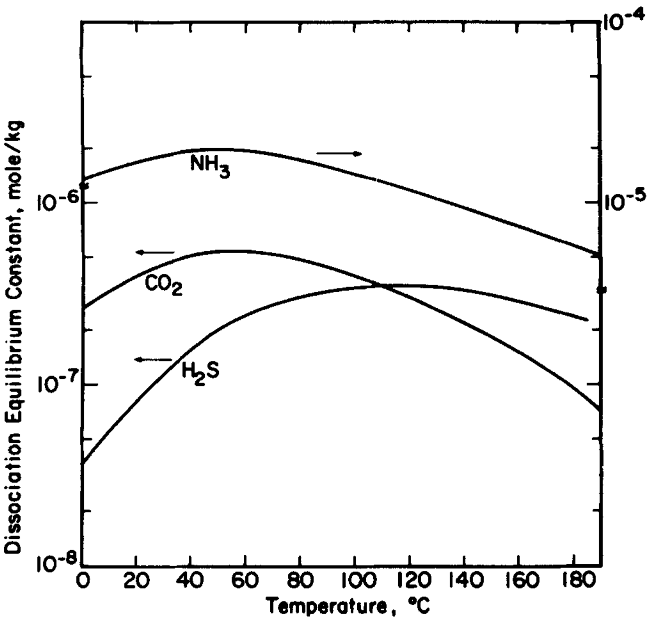

Fig. 2. First dissociation equilibrium constants in water.

et al. (1976).[†] For sulfur dioxide, dissociation-constant data are from Johnstone and Leppla (1934) and Landolt-Börnstein (1960). Figure 2 shows some dissociation equilibrium constants as a function of temperature.

VAPOR PHASE FUGACITY COEFFICIENTS

Owing to the strong polar character of the components, the fugacity coefficients may differ appreciably from unity even at moderate pressures. Fugacity coefficients were calculated using the method of Nakamura et al. (1976), where estimated vapor phase parameters are given for all fluids of interest here except hydrogen cyanide.

LIQUID PHASE ACTIVITY COEFFICIENTS

Activity coefficients $\underline{\gamma_i^*}$ describe physical interactions between solute species in the liquid phase; these are of three types: molecule-molecule, molecule-ion, and ion-ion. For the effect of liquid phase composition on the activity coefficient of the solute, we use an expression derived from Pitzer's theory (Pitzer, 1973; Pitzer and Kim, 1974):

$$\begin{aligned}\ln \gamma_i^* = {} & - A_\phi z_i^2 \left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2} \ln(1 + 1.2\sqrt{I}) \right] \\ & + 2 \sum_{j \neq w} m_j \left\{ \beta_{ij}^{(0)} + \frac{\beta_{ij}^{(1)}}{2I} [1 \right. \\ & \left. \qquad - (1 + 2\sqrt{I}) \exp(-2\sqrt{I})] \right\} \\ & - \frac{z_i^2}{4I^2} \sum_{j \neq w} \sum_{k \neq w} m_j \cdot m_k \cdot \beta_{jk}^{(1)} \{1 \\ & \qquad - (1 + 2\sqrt{I} + 2I) \exp(-2\sqrt{I})\} \qquad (8)^{\dagger}\end{aligned}$$

where I is the ionic strength of the solution

$$I = \frac{1}{2} \sum_j z_j^2 m_j \tag{9}$$

If i or j is a molecular species, we retain parameter $\beta_{ij}^{(0)}$ but, because experimental data are inadequate, we assume that parameter $\beta_{ij}^{(1)} = 0$. As written here, Equations (8) and (9) require that the units of m must be moles per kilogram of water.

Coulombic forces between like charged ions do not allow the ions to approach one another; therefore, following Brönsted (1922, 1923), we assume that for ions i and j of like charge, $\beta_{ij}^{(0)} = \beta_{ij}^{(1)} = 0$.

The activity of water is determined from the Gibbs-Duhem equation:

$$\begin{aligned}\ln a_w = M_w & \left\{ \frac{2A_\phi I^{3/2}}{1 + 1.2\sqrt{I}} - \sum_{i \neq w} \sum_{j \neq w} m_i m_j [\beta_{ij}^{(0)} \right. \\ & \left. + \beta_{ij}^{(1)} \exp(-2\sqrt{I})] \right\} - M_w \sum_{i \neq w} m_i \qquad (10)^{\dagger}\end{aligned}$$

For a single weak electrolyte with a very low dissociation constant, the concentration of the ions is so small that Equations (8) and (10) reduce to

$$\ln \gamma_a^* = 2\beta_{aa}^{(0)} m_a \tag{8a}$$

$$\ln a_w = [- \beta_{aa}^{(0)} m_a^2 - m_a] M_w \tag{10a}$$

HENRY'S CONSTANT

Henry's constant is a strong function of temperature and a weak function of pressure. The pressure dependence is given by (Krichevsky and Kasarnovsky, 1935)

$$\ln \underline{H}^{(P)} = \ln \underline{H}^{(P_w^s)} + \frac{\bar{v}_a^\infty (P - P^s_w)}{RT} \tag{11}$$

The correlation of Brelvi and O'Connell (1972) was used to estimate $\bar{v}_a^\infty$; in that correlation, the characteristic volume for ammonia and that for hydrogen sulfide was set at 90% of the critical volume. Some results are given in Table 2. In the following, the notation $\underline{H}$ is understood to represent $\underline{H}^{(P^s_w)}$.

Henry's constants as a function of temperature were obtained from binary data reduction.

DATA REDUCTION

From Equations (5), (8*a*), and (11), the equation of phase equilibrium for a single solute is

$$\ln \frac{y_a \phi_a P}{m_a} - \frac{\bar{v}_a^\infty (P - P^s_w)}{RT} = \ln \underline{H} + 2\beta_{aa}^{(0)} m_a \tag{12}$$

Henry's constant and molecule-molecule interaction parameters may be evaluated from Equation (12) as illustrated in Figure 3. The abscissa of Figure 3 is a function of the molecular concentration of the weak electrolyte; the effect of ionic dissociation is therefore implicity taken into account. The molecule-molecule interaction parameter is determined by the slope; the intercept determines the molecular Henry's constant H. The continuous line

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[†] The dissociation constant for ammonium hydroxide is related to the dissociation constant for the ammonium ion (as reported by Tsonopoulos et al.) by $K_{NH_4OH} = K_w / K_{NH_4^+}$.

[†] $A_\phi = 2.303 \, A_\gamma / 3$, where the Debye-Hückel parameter A_γ is tabulated from 0° to 100°C in Appendix 4 of Lewis et al. (1961). For higher temperatures, A_ϕ is given by

$$A_\phi = 1.4017 \cdot 10^{-6} \times \sqrt{\rho^s} / (D^s T)^{3/2}$$

The density ρ^s of saturated water (g cm^{-3}) is taken from the CRC Handbook of Chemistry and Physics (1970-71) and the dielectric constant D^s of saturated water from Akerlof and Oshny (1950).

[†] This follows from the definition of excess functions in electrochemical solutions as discussed by Newman (1973).

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

$$\ln \underline{K} = A_1/T + A_2 \ln T + A_3 T + A_4$$
$$\underline{K} = B_1/T + B_2 \ln T + B_3 T + B_4$$

Electrolyte	A_1	A_2	A_3	A_4	Range of validity, °C
NH_3	−3 335.7	1.4971	−0.0370566	2.76	0-225
CO_2	−12 092.1	−36.7816	0.0	235.482	0-225
HCO_3^-	−12 431.7	−35.4819	0.0	220.067	0-225
H_2S	−12 995.4	−33.5471	0.0	218.599	0-150
HS^-	$\underline{K} = 0.018\ K_w$				0-150
SO_2	−637.396	0.0	−0.0151337	−1.96211	0-50
HCN	−9 945.53	0.0	−0.0495786	26.9191	10-150
H_2O	−13 445.9	−22.4773	0.0	140.932	0-225
HSO_3^-	$\underline{K} = 1.02 \times 10^{-7}$				18

TABLE 2. PARTIAL MOLAR VOLUMES IN DILUTE AQUEOUS SOLUTION
(Calculated from Correlation of Brelvi and O'Connell)

Temp, °C	$\bar{v}_a^\infty$, cm³/mole NH_3	CO_2	H_2S	SO_2
0	28.7	32.4	34.8	40.3
50	30.0	34.0	36.5	42.3
100	33.9	38.3	41.1	47.6
150	40.4	45.6	48.8	56.5

gives results based on the data at 0°C. The dashed line gives results from two correlations, Equations (13) and (14).

Using literature data, Henry's constants were determined for ammonia (Clifford and Hunter, 1933; Sherwood, 1925; Wucherer 1932), carbon dioxide (Houghton et al., 1957; Stewart and Munjal, 1970; Malinin, 1959, 1975), hydrogen sulfide (Clarke and Glew, 1971; Miles and Wilson, 1975; Charmichael et al., 1952; Wright and Maass, 1932; Lee and Mather, 1977), sulfur dioxide (Sherwood, 1925; Morgan and Maass, 1931; Rabe and Harris, 1963; Beuschlein and Simenson, 1940), and hydrogen cyanide (E. I. du Pont de Nemours Co., personal communication). Figure 4 shows Henry's constants for the temperature range 0° to 170°C; they are represented by the semiempirical equation

$$\ln \underline{H} = B_1/T + B_2 \ln T + B_3 T + B_4 \qquad (13)$$

Table 3 gives parameters B_1, B_2, B_3, and B_4. Henry's constants have units of kilogram atmospheres per mole of solute.

The two-body, molecule-molecule interaction parameter $\beta_{aa}^{(0)}$ is a function of temperature. Within the limited accuracy of the data now available

$$\beta_{aa}^{(0)} = E + F/T \qquad (14)$$

Equation (14) provides an approximation for the same temperature range as that used for Henry's constants. Parameters E and F are given in Table 4.

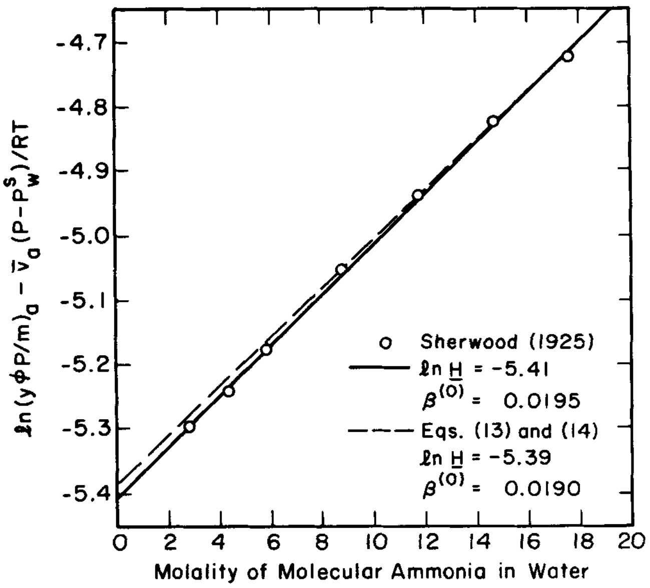

Fig. 3. Data reduction for ammonia-water at 0°C.

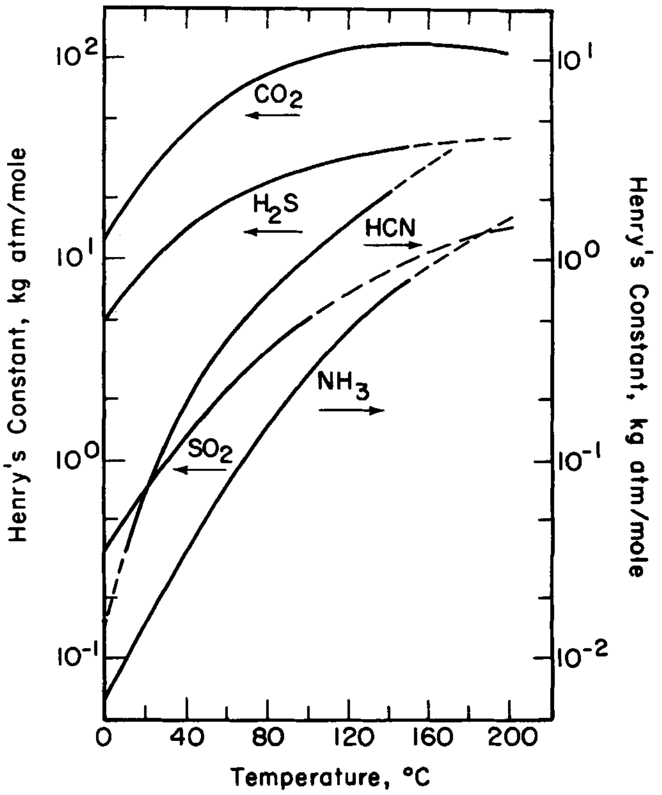

Fig. 4. Henry's constants in water.

TABLE 3. EFFECT OF TEMPERATURE ON HENRY'S CONSTANTS FOR WEAK ELECTROLYTES IN WATER

$$\ln \underline{H} = B_1/T + B_2 \ln T + B_3 T + B^4$$
$$\underline{H} = \text{kg-atm/mole};\ T,\ ^\circ\text{K}$$

Electrolyte	B_1	B_2	B_3	B_4	Range of validity, °C
NH_3	−157.552	28.1001	−0.049227	−149.006	0-150
CO_2	−6 789.04	−11.4519	−0.010454	94.4914	0-250
H_2S	−13 236.8	−55.0551	0.0595651	342.595	0-150
SO_2	−5 578.8	−8.76152	0.0	68.418	0-100
HCN	−49 068.8	−241.82	0.315014	1 446.005	10-140

TABLE 4. PARAMETERS E AND F IN EQUATION (14)

	E, kg/mole	F, (kg/mole) K
NH_3	−0.0260	12.29
CO_2*	−0.4922	149.20
H_2S	−0.2106	61.56
SO_2	+0.0275	0
HCN	−0.8919	278.86

* Temperature range 0° to 100°C.

RESULTS FOR SINGLE-SOLUTE SYSTEMS

Having determined parameters $\underline{H}$ and $\beta^{(0)}$ for single-solute systems, we can now calculate vapor-liquid equilibria for single-solute, weak electrolyte systems at a fixed temperature. Equations (1), (2), (4), (5), (6), (8*a*), (10*a*), and (11) must be solved simultaneously, using appropriate values of $\underline{K}$, $\underline{H}$, $\beta_{aa}^{(0)}$, and $\overline{v}_a^\infty$. Simultaneous solution of the equations is achieved by a multidimensional Newton-Raphson iteration technique using an initial estimate of the concentration of each individual species. Activity coefficients are calculated, and an iteration on solute concentrations proceeds until convergence is achieved. Once m_a and γ_a^* have been determined, Equation (5) is used to calculate the partial pressure of the weak electrolyte in the vapor phase.

Figures 5 and 6 show results for the systems ammonia-water and carbon dioxide-water at 60°C. In each figure, the two partial pressure curves indicate the effect of ionic dissociation on the vapor-liquid equilibria of dilute aqueous solutions of ammonia and carbon dioxide. In each figure, the broken curve gives results calculated assuming that the solute is a nonelectrolyte, while the solid curve gives calculated results taking dissociation into account. Both curves are calculated using the same Henry's constant, given by Equation (13). For each solute, significant deviation from nonelectrolyte behavior begins at a characteristic stoichiometric concentration owing to ionic dissociation as determined by chemical dissociation constant $\underline{K}$.

MULTISOLUTE SYSTEMS

Data for single-solute systems are of primary value for determining binary interaction parameters. However,

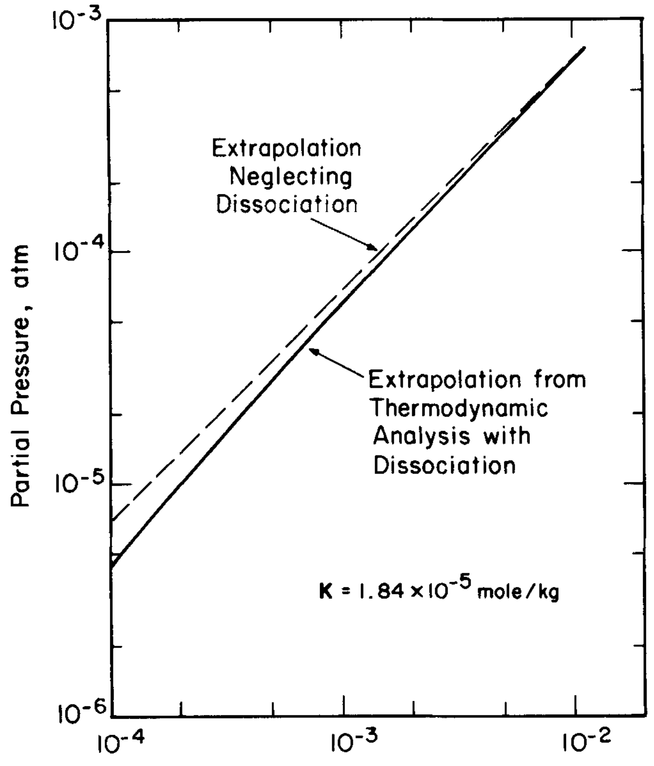

Fig. 5. Solubility of ammonia in water at 60°C.

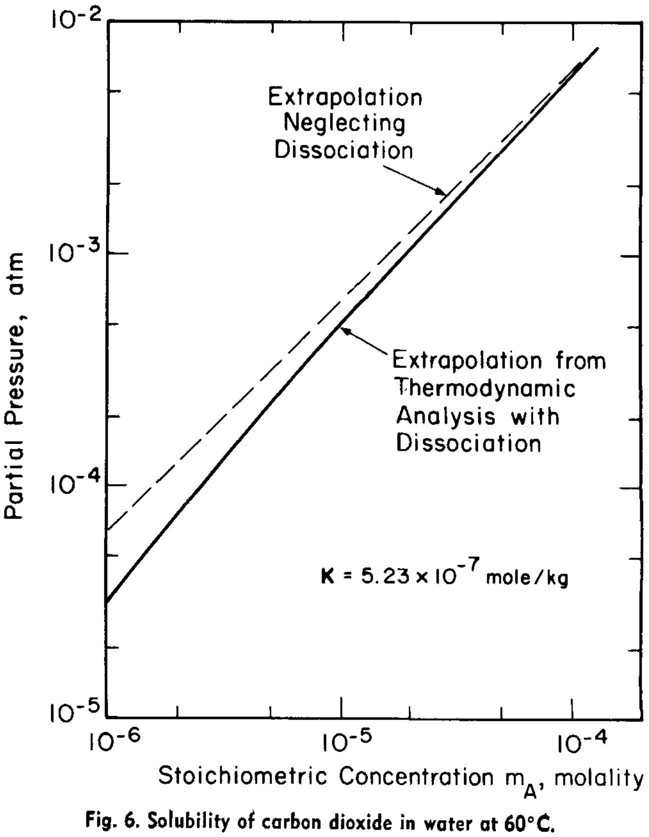

Fig. 6. Solubility of carbon dioxide in water at 60°C.

most systems confronting the design engineer are multisolute systems.

To illustrate the essential difference between a single-solute system and a multisolute system, consider the ammonia-carbon dioxide-water system.

In the multisolute system, we have two single-solute chemical dissociations:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (15)$$

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \qquad (16)$$

(The pH of the single-solute carbon dioxide system is such that the second dissociation to the carbonate ion is negligible.)

Since ammonia is a weak base and carbon dioxide a weak acid, in the multisolute system additional ionic equilibria must be considered:

$$NH_3 + CO_2 + H_2O \rightleftharpoons NH_4^+ + HCO_3^- \qquad (17a)$$

$$NH_3 + HCO_3^- \rightleftharpoons NH_4^+ + CO_3^= \qquad (17b)$$

Therefore, in addition to Equations (15) and (16), we must give consideration also to

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (18a)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad (18b)$$

Since multisolute acid-base equilibria [Equations (17*a*) and (17*b*)] are much more favorable toward ionization than the single-solute equilibria [Equations (15) and (16)], in the multisolute system the fractions of the weak electrolytes existing in ionic form are significantly larger than those in the single-solute systems. Since this shift to the ionic form reduces the molecular concentrations of the weak electrolytes, the vapor-liquid equilibria (which are determined primarily by the concentrations of molecular species) are profoundly affected, resulting in reductions of the partial pressures.

For the ammonia-carbon dioxide-water system, we must also consider the carbamate reaction

$$NH_3 + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O \qquad (19)$$

The equilibrium constant for this reaction is estimated (Faurholt, 1925; Harris, 1977; Mason, 1977) from

$$\ln \underline{K} = -8.6 + 2\,900/T \qquad (20)$$

for the temperature range 20° to 60°C. Since calculated results are not sensitive to the value of the carbamate equilibrium constant (for example, for the results given in Table 7 a decrease of $\underline{K}$ by a factor of two changes the calculated total pressure by less than 2%), we assume that Equation (20) provides also a sufficiently accurate estimate for higher temperatures.

The equilibria indicated by Equations (17*a*), (17*b*), and (19) produce ionic concentrations of such magnitude that we can no longer neglect the effect of molecule-ion and ion-ion interactions on the activity coefficients as expressed by Equation (8).

CALCULATIONS FOR MULTISOLUTE SYSTEMS

The four general principles used in the thermodynamic analysis of single-solute systems are used as before. However, the dissociation equilibrium for water, neglected in the single-solute case, is now required to interrelate the concentrations of hydrogen ion and hydroxyl ion.

In the example above, nine distinct species exist: NH_3 (molecular), CO_2 (molecular), NH_4^+, HCO_3^-, $CO_3^=$, H^+, OH^-, NH_2COO^-, and H_2O. Thus, we have seventeen unknowns (m_i and γ_i^* for all species except water, and a_w). To solve for these unknowns, we must have seventeen independent equations. These equations are:

Five chemical equilibria:

$$\underline{K}_1 = \frac{a_{NH_4^+}a_{OH^-}}{a_{NH_3}a_{H_2O}} \qquad \underline{K}_2 = \frac{a_{H^+}a_{HCO_3^-}}{a_{CO_2}a_{H_2O}}$$

$$\underline{K}_3 = \frac{a_{H^+}a_{CO_3^=}}{a_{HCO_3^-}} \qquad \underline{K}_4 = \frac{a_{NH_3}a_{HCO_3^-}}{a_{NH_2COO^-}a_{H_2O}}$$

$$\underline{K}_5 = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}}$$

Two mass balances:

Total $NH_3 = m_{NH_3} + m_{NH_4^+} + m_{NH_2COO^-}$

Total $CO_2 = m_{CO_2} + m_{HCO_3^-} + m_{CO_3^=} + m_{NH_2COO^-}$

Electroneutrality:

$$m_{NH_4^+} + m_{H^+} = m_{HCO_3^-} + 2m_{CO_3^=} + m_{NH_2COO^-} + m_{OH^-}$$

In addition, we use Equation (8) for eight activity coefficients, one for each species except water. Finally, we use Equation (10) for the activity of water.[†]

ESTIMATION OF INTERACTION PARAMETERS

To find activity coefficients γ_i^* and a_w, we require interaction parameters $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$.

Molecule-molecule interaction parameter $\beta_{ii}^{(0)}$ for like species is given by Equation (14) for ammonia, carbon dioxide, sulfur dioxide, and hydrogen cyanide.

To estimate the molecule-molecule interaction parameter between unlike species, we use the approximate rule

$$\beta_{ij}^{(0)} = \frac{1}{2}\left[\beta_{ii}^{(0)} + \beta_{ij}^{(0)}\right] \qquad (21)$$

There are insufficient experimental data for determining the necessary molecule-ion (salting out) and ion-ion interaction parameters. To estimate them, we use an approximation proposed by Bromley (1972):

$$\beta_{+-} = \beta_+ + \beta_- \qquad (22)$$

Edwards et al. (1975) extended Equation (22) to molecule-ion interaction parameters

$$\beta_{m-i} = \beta_{\text{molecule}} + \beta_{\text{ion}} \qquad (23)$$

β_{molecule} is characteristic of the molecular solute and where β_{ion} is characteristic of the ion.

Bromley also demonstrated that a rough correlation exists between β_i and the quantity $z_i\bar{S}_i^\infty$, where z_i is the charge on ion i, and $\bar{S}_i^\infty$ is the partial molar entropy of the ion in an infinitely dilute solution, as determined by Latimer (1952). To obtain β_+ and β_- for the ions of interest, Equation (22) was applied to the ion-ion interaction parameters $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$ given by Pitzer and Mayorga (1973) at 25°C for strong electrolytes; the best common value for each ion was determined. To accomplish this separation, $\beta^{(0)}_{Na^+}$ and $\beta^{(1)}_{Na^+}$ were arbitrarily

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[†] The above equations are written for the case where the liquid phase composition is given and the vapor phase composition is unknown. However, for the opposite case, the mass balances for ammonia and carbon dioxide are replaced by

$$y_{NH_3}\phi_{NH_3}P = m_{NH_3}\gamma^*_{NH_3}H_{NH_3} \exp \frac{\bar{v}_{NH_3}(P - P_w^s)}{RT}$$

$$y_{CO_2}\phi_{CO_2}P = m_{CO_2}\gamma^*_{CO_2}H_{CO_2} \exp \frac{\bar{v}_{CO_2}(P - P_w^s)}{RT}$$

yielding seventeen simultaneous, independent equations containing the known partial pressures.

Table 5. Estimated Values for Ion-Ion Interaction Parameter[*][†]

$$\beta(0) = \beta_+(0) + \beta_-(0)$$

Ion	$\beta_+^{(0)}$ or $\beta_-^{(0)}$ (kg/mole)
NH_4^+	−0.028
HCO_3^-	−0.049
$CO_3^=$	−0.034
HS^-	0.074
$S^=$	0.007
HSO_3^-	−0.035
$SO_3^=$	−0.017
CN^-	−0.025
NH_2COO^-	0.078
H^+	0.120
OH^-	0.088

[*] Interaction parameters between ions of like sign are assumed to be zero.

[†] These are preliminary results subject to change as more and better data become available.

set equal to zero. As proposed by Bromley, values so determined were plotted vs. $z_i\bar{S}_i^\infty$, and a satisfactory correlation was obtained.[*]

Following a suggestion by Pitzer and Mayorga (1973), $\beta_i^{(0)}$ and $\beta_i^{(1)}$ for ion-ion interactions are empirically interrelated by

$$\beta_i^{(1)} = 0.018 + 3.06\,\beta_i^{(0)} \tag{24}$$

Equation (24) significantly simplifies the calculation of activity coefficients in multisolute systems.

Table 5 presents estimated ion-ion interaction parameters $\beta_i^{(0)}$. The temperature dependence of these parameters is assumed to be negligible; this assumption is supported by data for $\beta_i^{(0)}$ for strong electrolytes at various temperatures (International Critical Tables, 1926; and Smithsonian Tables, 1954).

Molecule-ion interaction parameters determined by Equation (23) have been given previously (Edwards et al., 1975); they are shown in Table 6. The effect of temperature on $\beta_{m-i}^{(0)}$ is given by

$$\frac{d\beta_{m-i}^{(0)}}{dT} = -\frac{\bar{v}_a^\infty}{\beta_w RT}\,\frac{d\bar{v}_i^\infty}{dT} \tag{25}$$

The correlation of Brelvi and O'Connell (1972) is used to determine $\bar{v}_a^\infty$ and β_w, while $d\bar{v}_i^\infty/dT$ is found by the method of Helgeson and Kirkham (1974, 1976).

CALCULATED MULTISOLUTE RESULTS

Having determined all interaction parameters, we may calculate the vapor-liquid equilibria of the ammonia-carbon dioxide-water system. The seventeen equations must be solved simultaneously using the iterative Newton-Raphson technique.

Calculations were performed utilizing a computer program, SURFIMP.

To illustrate the importance of dissociation of weak electrolytes in calculating vapor-liquid equilibria, Figure 7 shows results first, using the methods discussed above and second, neglecting dissociation. When dissociation is not taken into consideration (that is, $\underline{K}_1$, $\underline{K}_2$, $\underline{K}_3 \cong 0$), the partial pressures of both carbon dioxide and ammonia are greatly overestimated.

Table 6. Estimated Values for Molecule-Ion (Salting Out) Interaction Parameters for 0 to 170°C[*]

Molecule-ion	$\beta_{m\text{-ion}}^{(0)}$ (kg/mole)
NH_3-NH_4^+	0
NH_3-HCO_3^-	$0.135\text{-}1.165 \times 10^{-3}T + 2.05 \times 10^{-6}T^2$
NH_3-$CO_3^=$	0.06
NH_3-HS^-	$0.16\text{-}1.24 \times 10^{-3}T + 2.20 \times 10^{-6}T^2$
NH_3-$S^=$	0.032
NH_3-HSO_3^-	−0.038
NH_3-$SO_3^=$	0.044
NH_3-CN^-	−0.043
NH_3-NH_2COO^-	0
NH_3-H^+	0.015
NH_3-OH^-	$0.227\text{-}1.47 \times 10^{-3}T + 2.6 \times 10^{-6}T^2$
CO_2-NH_4^+	$0.037\text{-}2.38 \times 10^{-4}T + 3.83 \times 10^{-7}T^2$
CO_2-HS^-	0
CO_2-$S^=$	0.053
CO_2-HSO_3^-	−0.03
CO_2-HCO_3^-	0
CO_2-$CO_3^=$	0
CO_2-$SO_3^=$	0.068
CO_2-CN^-	−0.036
CO_2-NH_2COO^-	0.017
CO_2-OH^-	$0.26\text{-}1.62 \times 10^{-3}T + 2.89 \times 10^{-6}T^2$
CO_2-H^+	0.033
H_2S-NH_4^+	$0.120\text{-}2.46 \times 10^{-4}T + 3.99 \times 10^{-7}T^2$
H_2S-HCO_3^-	−0.037
H_2S-$CO_3^=$	0.077
H_2S-HSO_3^-	−0.045
H_2S-$SO_3^=$	0.051
H_2S-CN^-	−0.049
H_2S-NH_2COO^-	−0.032
H_2S-H^+	0.017
H_2S-OH^-	$0.26\text{-}1.72 \times 10^{-3}T + 3.07 \times 10^{-6}T^2$
H_2S-HS^-	0
H_2S-$S^=$	0
SO_2-NH_4^+	−0.05
SO_2-HCO_3^-	−0.86
SO_2-$CO_3^=$	0.94
SO_2-HS^-	−0.58
SO_2-$S^=$	0.28
SO_2-CN^-	−1.06
SO_2-NH_2COO^-	−0.79
SO_2-H^+	0
SO_2-OH^-	0.08
SO_2-HSO_3^-	0
SO_2-$SO_3^=$	0

[*] These are preliminary results subject to change as more and better data become available. Owing to total lack of experimental data for hydrogen cyanide, all $\beta^{(0)}$ values for hydrogen cyanide-ion interactions are here set equal to zero.

Table 7 presents a comparison of experimental and predicted vapor-liquid equilibria for the ammonia-carbon dioxide-water system at 100°C. Experimental data are from Otsuka et al. (1960).

Table 8 shows calculated and experimental results for concentrated solutions of hydrogen sulfide and ammonia in water; experimental data are from Miles and Wilson (1975). While the total concentration of each solute is high, the molecular concentration is much smaller because of the neutralization reaction between the weak acid (hydrogen sulfide) and the weak base (ammonia).

To indicate how calculated multisolute results are affected by the binary parameters, Tables 7 and 8 present separate calculations, indicated by I and II. While Henry's constants $\underline{H}$ and chemical equilibrium constants $\underline{K}$ are known relatively well, there is much uncertainty in parameters $\beta^{(0)}$. It is important to keep in mind that the

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[*] Owing to insufficient data, $\bar{S}^\infty_{NH_2COO^-}$ was assumed equal to $\bar{S}^\infty_{CH_3COO^-}$.

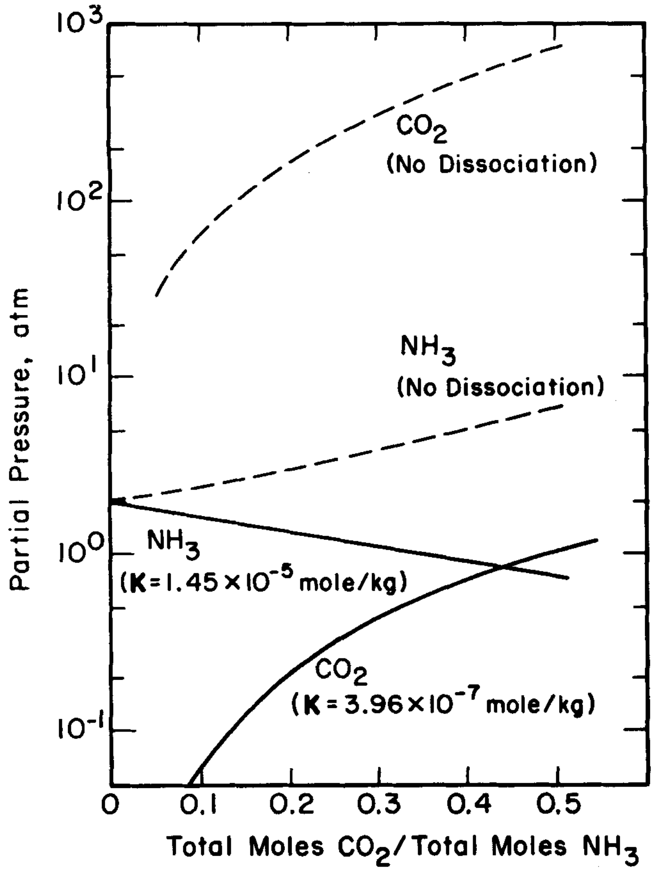

Fig. 7. Effect of dissociation on vapor-liquid equilibria. Ammonia-carbon dioxide-water system containing 6.75 molal ammonia at 100°C.

values of $\beta^{(0)}$ given here are only estimates, often based on extremely weak experimental evidence. More reliable and extensive binary data are needed to determine these parameters with confidence.

Calculated and experimental results show reasonable agreement, especially when we consider the probable experimental uncertainties.

It is difficult to estimate the reliability of the calculations because experimental data for multisolute systems are scarce, and experimental accuracy is often doubtful. While measurements of temperatures and pressure are likely to be accurate, liquid phase compositions may easily be in error because of experimental problems, especially at the dilute end. To indicate how errors in liquid composition may affect the pressure, Table 9 presents a sensitivity analysis for two systems. The two columns at the right show the changes in liquid composition which are required to obtain perfect agreement between calculated and observed pressures. For at least some cases, the changes indicated may easily lie within the experimental uncertainty.

LIMITATIONS OF PRESENT CORRELATION

The molecular-thermodynamic correlation presented in this work is primarily limited by the region of concentration for which Equations (8) and (10) are valid. Pitzer (1973) recommends an upper limit of 6 molal ionic strength; for typical cases studied here, this corresponds to a total solute concentration that is considerably higher, depending on the extent of ionization. For weak electrolytes, the total acceptable concentration may be as high as 10 or 20 molal. However, if ionization is extensive, the upper limit is necessarily lower.

Temperature limits are determined primarily by the accuracy of the extrapolations for $\underline{K}$ and $\underline{H}$. For aqueous systems containing ammonia, carbon dioxide, and hydrogen sulfide, the upper temperature limit is approximately 170°C.

CONCLUSION

This work presents a molecular-thermodynamic framework for the prediction of vapor-liquid equilibria in multisolute aqueous solutions of weak electrolytes. The framework covers ranges of temperature and concentration considerably larger than those considered in previous work. Necessary parameters may be obtained either from binary data reduction or else from empirical correlations; no

TABLE 7. EXPERIMENTAL* AND PREDICTED RESULTS FOR AMMONIA-CARBON DIOXIDE-WATER SYSTEM AT 100°C

			Concentration				
			Predicted molecular molality in liquid		Mole fraction in vapor		
	Total					Predicted	
Solute	molality in liquid		I	II	Exp'tl	I	II
NH_3	2.90		1.245	1.225	0.066	0.123	0.140
CO_2	1.45		0.014	0.015	0.506	0.494	0.481
		Ionic strength	1.50	1.55			
		Pressure, atm			3.15	2.51	2.53
NH_3	3.71		2.279	2.263	0.274	0.293	0.310
CO_2	1.14		0.0056	0.0065	0.202	0.230	0.242
		Ionic strength	1.26	1.24			
		Pressure, atm			2.08	1.98	2.10
NH_3	4.30		3.087	3.077	0.355	0.407	0.419
CO_2	0.907		0.0030	0.0038	0.095	0.116	0.135
		Ionic strength	1.01	0.98			
		Pressure, atm			2.00	1.97	2.10

* Otsuka et al. (1960).

I: All $\beta^{(0)}$ parameters as given in Tables 4 and 6.

II: As in I, except that

$$\beta^{(0)}_{NH_3,NH_4^+} = \tfrac{1}{2}\beta^{(0)}_{NH_3,NH_3} + \beta^{(0)}_{CO_2,NH_4^+} - \tfrac{1}{2}\beta^{(0)}_{CO_2,CO_2} = 0.051$$

and

$$\beta^{(0)}_{CO_2,HCO_3^-} = \beta^{(0)}_{CO_2,HSO_3^-} = -0.03; \quad \beta^{(0)}_{CO_2,CO_3^=} = \beta^{(0)}_{CO_2,SO_3^=} = 0.068$$

Table 8. Experimental* and Predicted Results for Ammonia-Hydrogen Sulfide-Water System at 80°C

			Concentration				
			Predicted molecular molality in liquid		Mole fraction in vapor		
	Total					Predicted	
Solute	molality in liquid		I	II	Exp'tl	I	II
NH_3	5.11		3.97	3.97	0.58	0.543	0.558
H_2S	1.14		0.0028	0.0034	0.095	0.064	0.076
		Ionic strength	1.14	1.14			
		Pressure, atm			1.30	1.08	1.16
NH_3	5.56		0.48	0.43	0.0058	0.0053	0.009
H_2S	5.30		0.22	0.17	0.970	0.961	0.948
		Ionic strength	5.08	5.13			
		Pressure, atm			16.50	12.91	10.05
NH_3	9.24		1.45	1.40	0.021	0.016	0.045
H_2S	7.93		0.14	0.087	0.950	0.953	0.910
		Ionic strength	7.79	7.84			
		Pressure, atm			13.20	12.64	8.10

* Miles and Wilson (1975).
I: $\beta^{(0)}$ parameters as given in Tables 4 and 6.
II: As in I, except that

$$\beta^{(0)}_{NH_3,NH_4^+} = \tfrac{1}{2}\beta^{(0)}_{NH_3,NH_3} + \beta^{(0)}_{CO_2,NH_4^+} - \tfrac{1}{2}\beta^{(0)}_{CO_2,CO_2} = 0.04$$

multisolute data are required. The calculational technique developed here is therefore readily applicable to chemical process design. Computer programs for that purpose are available.

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NOTE ADDED IN PROOF

After this work was completed, a similar study by Beutier and Renon [*Ind. Eng. Chem. Process Des. Dev.*, 17, 220 (1978)] came to our attention. These authors used a model essentially identical to that discussed here although they confined attention to temperatures below 100°C, whereas this work attempts to cover a larger temperature range, to 170°C.

For binary (single-solute) systems, calculations by Beutier and Renon show agreement with experiment which is essentially equal to that obtained by the calculations reported here.

Beutier and Renon however, show impressive agreement between calculated and experimental results for ternary (two-solute) systems; they quote several experimental studies which unfortunately were unknown to us. However, the good agreement for the two-solute aqueous systems shown by Beutier and Renon was obtained by fitting *two* ternary parameters to the ternary experimental data. In the work discussed here, no ternary parameters were used; only binary parameters are employed first, because sufficient ternary data are rarely available to fix two (or even one) unambiguous ternary parameters and second, because large uncertainties in the binary parameters make it essentially impossible to determine *meaningful* ternary parameters from data reduction.

In our experience, the numerical value of a ternary parameter varies appreciably with the experimental data used for data reduction: a ternary parameter obtained from one set of ternary data is likely to be different from that obtained from another set of data for the same ternary system. The severe need for better binary and ternary experimental data is evident.

Nevertheless, in some practical cases it may be empirically helpful to include a ternary term in the equation for the excess Gibbs energy which, through differentiation, gives the activity coefficients. In some cases a few ternary data may be available to the reader who wants to use the generalized method discussed here. In that event, Equation (8) must be augmented by

$$3 \sum_j \sum_k \mu_{ijk}\, m_j m_k \qquad (j, k \neq w)$$

and Equation (10) by

$$-2 M_w \sum_i \sum_j \sum_k \mu_{ijk}\, m_i m_j m_k \qquad (i, j, k \neq w)$$

where μ_{ijk} is a three-body parameter. To simplify matters, and to reduce the number of adjustable three-body parameters, it is probably best, as suggested by Beutier and Renon's results, to set all $\mu_{ijk} = 0$ except for the case where i, j and k are the important ionic species and then to use the mixing rules on page 224 of the article by Beutier and Renon. In this way, for a ternary system, there are only two adjustable ternary parameters.

Table 9. Sensitivity Analysis. Changes in Molality Required to Obtain Agreement Between Calculated and Observed Pressures

Temp., °C	Total molality in liquid		Total pressure, atm		Per cent change in molality of liquid phase for $P_{predict} \equiv P_{exp}$	
	NH_3	H_2S	Expt'l	Predicted	NH_3	H_2S
80	5.11	1.14	1.30	1.08	+30.0	—
	5.56	5.30	16.50	12.91	−3.0	—
	5.56	5.30	16.50	12.91	—	+2.6
	9.24	7.93	13.20	12.64	−0.7	—
	9.24	7.93	13.20	12.64	—	+0.5
	NH_3	CO_2			NH_3	CO_2
100	2.90	1.45	3.15	2.51	−17.6	—
	2.90	1.45	3.15	2.51	—	+19.5
	3.71	1.14	2.08	1.98	—	+15.4
	4.30	0.907	2.00	1.97	+5.7	—
	4.30	0.907	2.00	1.97	—	+20.3

In view of the present inadequate state of affairs pertaining to both theory and experiment, we prefer to refrain from using any three-body terms. We believe it is better at this time to restrict a correlational framework to two-body terms and then, using the best binary and ternary data available, to fix the two-body parameters with as much accuracy as the total data base permits.

NOTATION

a = activity
A_1, A_2, A_3, A_4 = parameters in Equation (7)
A_ϕ, A_γ = Debye-Huckel parameters
B_1, B_2, B_3, B_4 = parameters in Equation (13)
D = dielectric constant in evaluation of the Debye-Huckel parameter
E = parameter in Equation (14)
F = parameter in Equation (14)
H = Henry's constant, atm kg/mole
$\overline{H}^{(P)}$ = Henry's constant for molecular solute at pressure P
$H^{(P^s_w)}$ = Henry's constant evaluated at saturation pressure
I = ionic strength $= \frac{1}{2}\Sigma m_i z_i^2$
K = dissociation equilibrium constant, mole/kg
m = concentration, molality, mole/kg
M_w = molecular weight of water, 0.018 kg/mole
P = pressure, atm
P^s_w = saturation pressure of water at system temperature
R = gas constant, J/mole °K
$\overline{S}^\infty$ = partial molar entropy at infinite dilution
T = temperature, °K
$\overline{v}$ = partial molar volume, cm^3/mole
$\overline{v}_a^\infty$ = partial molar volume of molecular solute at infinite dilution
$\overline{v}_i^\infty$ = partial molar volume of individual ion at infinite dilution
y = vapor phase mole fraction
z_i = ionic charges on species i

Greek Letters

$\beta^{(0)}, \beta^{(1)}$ = interaction parameters
β_w = compressibility of water, atm^{-1}
β_{+-} = interaction parameter of a particular cation-anion pair
β_+, β_- = characteristic of specific ions
β_{molecule} = characteristic of a given molecule solute
γ = molal activity coefficient
ϕ = vapor phase fugacity coefficient
ν = stoichiometric coefficient
ρ = density

Superscripts

s = saturation
$*$ = unsymmetric convention
∞ = infinite dilution

Subscripts

A = stoichiometric
a = molecular
i, j = species or component
w = water
$+$ = cation
$-$ = anion

LITERATURE CITED

Akerlof, G. C., and H. I. Oshry, "The Dielectric Constant of Water at High Temperatures and in Equilibrium with its Vapor," *J. Am. Chem. Soc.*, 72, 2844 (1950).

Beuschlein, W. L., and L. O. Simenson, "Solubility of Sulfur Dioxide in Water," *ibid.*, 62, 610 (1940).

Brelvi, S. W., and J. P. O'Connell, "Corresponding States Correlations for Liquid Compressibility and Partial Molal Volumes of Gases at Infinite Dilution in Liquids," *AIChE J.*, 18, 1239 (1972).

Bromley, L. A., "Approximate Individual Ion Values of β (or B) in Extended Debye-Hückel Theory for Uni-univalent Aqueous Solutions at 298.15°K," *J. Chem. Thermo.*, **4**, 669 (1972).

Brönsted, J. N., "Studies on Solubility IV," *J. Am. Chem. Soc.*, 44, 877 (1922); "The Individual Thermodynamic Properties of Ions," *ibid.*, 45, 2898 (1923).

Charmichael, L., F. Selleck, and B. Sage, "Phase Behavior in the Hydrogen Sulfide-Water System," *Ind. Eng. Chem.*, **44**, 2219 (1952).

Clark, S. P., ed., *Handbook of Physical Constants*, Geological Society of America, New York (1966).

Clarke, E. C. W., and D. N. Glew, "Aqueous Nonelectrolyte Solutions. Part VIII," *Can. J. Chem.*, 49, 691 (1971).

Clifford, I. L., and E. Hunter, "The System Ammonia-Water at Temperatures up to 150°C and at Pressures up to Twenty Atmospheres," *J. Phys. Chem.*, 37, 101 (1933).

CRC Handbook of Chemistry and Physics, 51 ed., The Chemical Rubber Co., Cleveland, Ohio (1970-71).

"Hydrocyanic Acid," E. I. du Pont de Nemours & Co., Wilmington, Dela.; additional information was provided by F. C. Siegle of this company.

Edwards, T. J., J. Newman, and J. M. Prausnitz, "Thermodynamics of Aqueous Solutions Containing Volatile Weak Electrolytes," *AIChE J.*, 21, 248 (1975).

Faurholt, C., "Etudes sur les Solutions Aqueuses de Carbamates et de Carbonates," *J. Chim. Phys.*, 22, 1 (1925).

Harris, R., Personal communication, The Standard Oil Company, Ohio (1977).

Helgeson, H. C., and D. H. Kirkham, "Theoretical Prediction of the Thermodynamic Properties of Aqueous Electrolytes at High Pressures and Temperatures, Part I," *Am. J. Sci.*, 274, 1089 (1974); *ibid.*, 276, 98 (1976).

Houghton, G., A. M. McLean, and P. D. Ritchie, "Compressibility, Fugacity and Water Solubility of Carbon Dioxide in the Region 0-36 Atm. and 0-100°C," *Chem. Eng. Sci.*, **6**, 132 (1957).

———, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, McGraw-Hill, New York (1926).

Johnstone, H. F., and P. W. Leppla, "The Solubility of Sulfur Dioxide at Low Partial Pressures. The Ionization Constant and Heat of Ionization of Sulfurous Acid," *J. Am. Chem. Soc.*, 56, 2233 (1934).

Krichevsky, I. R., and J. S. Karsarnovsky, "Thermodynamic Calculation of Solubilities of Nitrogen and Hydrogen in Water at High Pressures," *ibid.*, 57, 2168 (1935).

———, Landolt-Börnstein, "Zahlenwerke und Funktionen," 2. Bd., 7 Teil, Springer Verlag Berlin, Göttingen, Heidelberg (1960).

Latimer, W. M., *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed., Prentice-Hall, Englewood Cliffs, N.J. (1952).

Lee, J. I., and A. E. Mather, "Solubility of Hydrogen Sulfide in Water," *Ber Bunsenges. Physik. Chem.*, 81, 1020 (1977); also private communication.

Lewis, G. N., M. Randall, K. S. Pitzer, and L. Brewer, *Thermodynamics*, Appendix 4, McGraw-Hill, New York (1961).

Malinin, S. D., "The System H$_2$O-CO$_2$ at High Temperatures and Pressures," *Geokhimiya*, 3, 235 (1959).

———, "Thermodynamics of the H$_2$O-CO$_2$ System," *Geochem. Int.*, 11, 1060 (1975).

Mason, D., Personal communication, Institute of Gas Technology, Chicago, Ill. (1977).

Morgan, O. M., and O. Maass, "An Investigation of the Equilibria existing in Gas-Water Systems forming Electrolytes," *Can. J. Research*, 5, 162 (1931).

Miles, D. H., and G. M. Wilson, "Vapor-Liquid Equilibrium Data for Design of Sour Water Strippers," 1974 Annual Report to American Petroleum Institute (1975).

Nakamura, R., G. J. F. Breedveld, and J. M. Prausnitz, "Thermodynamic Properties of Gas Mixtures Containing Common Polar and Nonpolar Components," *Ind. Eng. Chem. Proc. Design Develop.*, **15**, 557 (1976).

Newman, J. S., *Electrochemical Systems*, p. 92, Prentice-Hall, Englewood Cliffs, N.J. (1973).

Otsuka, E., S. Yoshimuri, M. Yakabe, and S. Inoue, "Equilibrium of the NH_3-CO_2-H_2O System," *Kogyo Kagaku Zasshi*, **62**, 1214 (1960).

Pitzer, K. S., "Thermodynamics of Electrolytes, I," *J. Phys. Chem.*, **77**, 268 (1973).

———, and J. J. Kim, "Thermodynamics of Electrolytes, IV," *J. Am. Chem. Soc.*, **96**, 5701 (1974).

Pitzer, K. S., and G. Mayorga, "Thermodynamics of Electrolytes, II," *J. Phys. Chem.*, **77**, 2300 (1973).

Rabe, A. E., and J. F. Harris, "Vapor Liquid Equilibrium Data for the Binary System, Sulfur Dioxide and Water," *J. Chem. Eng. Data*, **8**, 333 (1963).

Sherwood, T. K., "Solubilities of Sulfur Dioxide and Ammonia in Water," *Ind. Eng. Chem.*, **17**, 2300 (1973).

———, Smithsonian Physical Tables, Smithsonian Inst. Publ., Washington, D.C. (1954).

Stewart, P. B., and P. Munjal, "Solubility of Carbon Dioxide in Pure Water, Synthetic Sea Water, and Synthetic Sea Water Concentrates at −5° to 25°C and 10- to 45-Atm Pressure," *J. Chem. Eng. Data*, **115**, 67 (1970).

Tsonopoulos, C., D. M. Coulson, and L. B. Inman, "Ionization Constants of Water Pollutants," *J. Chem. Eng. Data*, **21**, 190 (1976).

Van Krevelen, D. W., P. J. Hoftijzer, and F. J. Huntjens, "Composition and Vapor Pressures of Aqueous Solutions of Ammonia, Carbon Dioxide, and Hydrogen Sulfide," *Rec. Trav. Chim. Pays-bas*, **68**, 191 (1949).

Wright, R. H., and O. Maass, "The Solubility of Hydrogen Sulfide in Water from the Vapor Pressures of the Solutions," *Can. J. Res.*, **6**, 94 (1932).

Wucherer, J., "Messung von Druck, Temperatur, und Zusammensetzung der flüssigen und dampfförmigen Phase von Ammoniak-Wassergemischen im Sättigungszustand," *Z. Gesamt. Kälte-Ind.*, **39**, 97-104, 136-140 (1932).

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On Dynamical Methods of Heat Integration Design

Perturbation theory is utilized in order to examine the change in stability characteristics due to heat integration between process units. Dynamical rules of design are obtained in order to select the unit integrations with the most desirable stability characteristics. The integration of nonisothermal CSTR's with endothermic and exothermic reactions is examined in detail. It is shown that heat integration can make the endothermic reactor more stable if it increases the slope of the heat removal line for this reactor. On the other hand, the stability of exothermic reactors tends to increase when heat integration moves the slope of the heat removal line for this reactor closer to a characteristic value. Approximate values are also calculated for the critical amount of heat integration which makes the system unstable.

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SCOPE

Owing to higher fuel costs, the interest on heat integration between different process units has increased in recent years (Mah, 1975; Rathore, Van Wormer, and Powers, 1974*a*, *b*). Such tighter unit integration results in changes in the dynamical characteristics of the process. Existing methodologies for the design of heat integration networks have focused only on the steady state characteristics, with an aim to obtain the heat integration design that will save the maximum amount of heat. In order to examine the dynamical characteristics of the resulting heat integrated processes, current methodologies require the separate examination of each heat integration design. This approach becomes quite cumbersome in view of the large number of possible designs that might need to be evaluated. Furthermore, extensive numerical calculations do not always provide important insights into the reasons of change of dynamical characteristics. In an important contribution, Gilliland, Gould, and Boyle (1964) have shown that material recycle in a chemical reactor-separator system results in a lesser stable process. Based on this analysis, it has been assumed that unit integration, either through material recycle or by heat integration, will always lead to less stable processes.

There appear to be three major questions that have not been addressed in the past with respect to the change in the dynamical characteristics of processes caused by unit integration. Does unit integration always lead to less stable processes, and if not, when does it not? How much integration can be allowed before the change in dynamical characteristics is significant? Particularly, how much integration is possible before the system becomes unstable? Can simple dynamical rules of design be developed to guide in the selection of those unit integrations that lead to processes with the most desirable dynamical characteristics? The present paper addresses the above three questions with respect to heat integration. In order to gain the maximum possible insight into the causes of dynamical change, a perturbation theory approach (Kato, 1963) is proposed, and the heat integration of endothermic and exothermic reactors is examined in detail.

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