m as having the largest activity coefficient rather than activity. But this alternative cannot be used with dilute solutes having high activity coefficients or vapor trial phases.

In the region of a plait point, the phase-splitting algorithm predicts two similar trial phases and four iterations of the minimization algorithm are often not sufficient to reduce Gibbs free energy. Occasionally 6 or 7 iterations are necessary.

Similar tests of the phase-splitting algorithm should be successful for phase diagrams with at least one partially miscible pair. For a design study, it is important to identify regions where the algorithm fails, and either modify or avoid using the algorithm in these regions. Systems must contain at least one partially miscible pair for the phase-splitting algorithm to apply.

The decision to accept the first trial phases that satisfy $\Delta G_{t_1t_2}^{(k+q)*} > 10^{-5}G^{(k)}$, rather than examine all combinations of source and trial phases, saves much computer time. But, it gives rise to the possibility that the same two trial phases are accepted repeatedly, with one rejected after q iterations of the minimization algorithm, preventing other trial phases from being considered. As an example, for a VL_1L_2 system at equilibrium, with initial guesses for two liquids L_1L_2, it might be possible for the sequence $L_1L_2 \rightarrow L_1L_2L_3 \rightarrow L_1L_2$ to be repeated, preventing examination of the trial phases L_2V. This is highly unlikely, as the composition of phases L_1L_2 would be closer to a constrained minimum in Gibbs free energy prior to the next split and the criteria, $\Delta G_{t_1t_2}^{(k+q)*} > 10^{-5}G^{(k)}$, would not likely be satisfied.

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NOTATION

a, b = coefficients in Equation (9)
a_j = activity of species j in a multicomponent phase
a^{b}_{js} = activity of species j in a binary mixture with species m; compositions in the binary mixture are proportional to those in phase s
A_{ij} = interaction coefficients for three-suffix Wohl equation—binary pair i-j
C = number of chemical species
f_{jl} = fugacity of pure species j in phase l at the temperature and pressure of the system
G = Gibbs free energy
$G^{(k)}$ = Gibbs free energy after iteration k prior to formation of trial phases
$G_{t_1t_2}^{(k)}$ = Gibbs free energy after formation of trial phases t_1 and t_2
k = number of most recent iteration of optimization algorithm
n_{jl} = moles of species j in phase l
P = number of phases, pressure
$P_{\max}$ = maximum number of phases
R = universal gas constant
s = weighted average slope of degree of convergence curve (see Equation 10)
T = absolute temperature
x_{jl} = mole fraction of species j in liquid phase l
y_{jl} = mole fraction of species j in vapor phase l

Greek Symbols

δ_i = $\Sigma\Delta_j'^2$ after iteration i
Δ_j' = $N_j' - n_j$
γ_{jl} = activity coefficient of species j in phase l
ϕ_{jl} = fugacity coefficient of species j in vapor phase l

Subscripts

m = species in source phase with highest activity
m' = species in source phase with highest a^{b}_{js}
s = source phase
t = trial phase

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Part III. Electrolytic Solutions

Methods for estimating the properties of electrolytic solutions are reviewed, with emphasis on molecule-molecule, molecule-ion, and ion-ion interactions. The algorithms of Parts I and II, to search for global minimum in Gibbs free energy, are extended to handle electrolytes and compared with an algorithm using k-values. Results are presented for SO_2-H_2O and H_2S-NH_3-H_2O systems and agree with experimental values.

SCOPE

In recent years, extensive work has been done to develop methods for estimating the properties of organic compounds that do not dissociate (Reid et al. 1977). But, many chemical processes involve aqueous solutions of inorganic compounds that dissociate into ionic species. These include salt crystallizers, acid gas scrubbers, and sour water strippers.

For compounds that completely dissociate, i.e., strong electrolytes, theoretical and empirical expressions estimate excess Gibbs free energy and activity coefficients. These involve terms for Coulombic (long-range) and van der Waals' (short-range) forces, with ion-ion interaction coefficients in the latter case. Recent developments have extended these expressions to apply for high ionic strengths in concentrated solutions.

Weak electrolytes do not completely dissociate and interact with ionic species and other molecules in solution. Hence, expressions to estimate excess Gibbs free energy involve terms that account for molecule-ion and molecule-molecule van der Waals' forces.

This paper extends the Rand method and phase-splitting algorithm, of Parts I and II, for analysis of electrolytic solutions in equilibrium. It compares this approach with traditional analysis using k-values in equations for phase and chemical equilibria. In addition, it reviews expressions for estimating the properties of electrolytes and discusses their applicability for solutions of varying ionic strength and miscibility.

CONCLUSIONS AND SIGNIFICANCE

Molecule-molecule interactions can be accounted for using the methods of Edwards et al. (1975) and Beutier and Renon (1978) at low molalities. These do not apply at high concentrations (multi-solvent systems), especially for partially miscible systems.

For ion-ion interactions at high ionic strengths, either the Bronsted-Guggenheim Equation (27), with interaction coefficients tabulated by Bromley (1973), or the Pitzer method as applied by Beutier and Renon, are applicable.

Molecule-ion interactions can be accounted for using the method of Edwards et al. or the Debye-McAuley theory, as applied by Beutier and Renon.

The algorithm to minimize Gibbs free energy in Parts I and II is easily extended for calculation of compositions at equilibrium in electrolytic systems. In principle, it can handle P mixed phases, P' without ions (e.g., vapor) and P-P' with ions. It is limited only by the assumptions in estimation of molecule-molecule and molecule-ion interactions. When phases are unknown at equilibrium, the algorithm adds or deletes phases, as necessary, during minimization calculations. The Gram-Schmidt orthogonalization procedure finds dependence, when it exists, among the atom balances and electroneutrality equation.

The advantages of our algorithm vis-a-vis the use of K-values (Zemaitis and Rafal 1975) are (1) independent dissociation reactions need not be specified, (2) the phases present at equilibrium need not be known prior to performing equilibrium calculations, and (3) it is not necessary to generate a FORTRAN subprogram to evaluate the residuals for each set of material balances and electroneutrality equation. Although it was not possible to perform timing comparisons, we expect our method to be faster for many systems.

For SO_2-H_2O and NH_3-H_2S-H_2O systems, calculated partial pressures and experimental data agree within 2%. These results depend on solution model, but confirm the ability of our algorithm to reach the global minimum in Gibbs free energy.

Let an electrolyte be described as $M_{\nu_+}X_{\nu_-}$ which dissociates in polar solvents according to

$$M_{\nu_+}X_{\nu_-} \rightleftharpoons \nu_+ M^{z_+} + \nu_- X^{z_-} \tag{1}$$

where M is the cation, X the anion, ν_+ and ν_- are the numbers of positive and negative ions, respectively, and z_+ and z_- are the charges on these ions. For neutral electrolytes the following charge balance holds

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{2}$$

This is not true where the dissociating species is itself an ion. For complex salts, such as $KCl \cdot MgCl_2$, containing more than two ionic species, Equations (1) and (2) are modified accordingly.

The dissociation of electrolytes in solution occurs rapidly; hence, most solutions closely approximate chemical equilibrium. Electrolytes are classified as strong or weak according to whether the degree of dissociation is large or small. When dissociation involves consumption of water, or hydrolysis, Equation (1) is modified. For example, the weak electrolyte Cl_2 is hydrolyzed to give

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO$$

When dissociation is according to Reaction (1), equilibrium is given by Equation (3, Part I)

$$-G_{aL} + \nu_+ G_{+L} + \nu_- G_{-L} = 0 \tag{3}$$

where G_{aL}, G_{+L} and G_{-L} are chemical potentials of the undissociated electrolyte, cation, and anion, in the liquid phase.

For species that are liquid at the temperature and pressure of the system, the activity coefficient is defined by

$$G_{aL} = G_a^* + RT \ln \gamma_a^* x_a \tag{4}$$

where G_a^* is the Gibbs free energy of formation of pure liquid at the temperature and pressure of the system and, at low pressures, $\gamma_a^* = p_a/x_a P_a^s$; p_a is partial pressure in the vapor phase and P_a^s is vapor pressure of a. Alternatively,

$$G_{aL} = G_a' + RT \ln \gamma_a^* x_a f_a \tag{5}$$

where G_a' is the Gibbs free energy of formation of pure vapor at the temperature of the system and 1.013 bar (1 atm). Equation (5) is convenient for equilibria involving vapor and liquid phases.

For species which are supercritical gases or solids, such as H_2S or sugar, at the temperature and pressure of the system

$$G_{aL} = G_a^{\square} + RT \ln \gamma_a^{\square} m_a \tag{6}$$

where $G_a^{\square}$ is the Gibbs free energy of formation of the species in a hypothetical ideal solution ($\overset{\square}{\gamma_a} = 1$) at unit molality, the temperature of the system and 1.013 bar (1 atm), and $\overset{\square}{\gamma_a} = p_a/x_a\overset{\square}{H_a}$; $\overset{\square}{H_a}$ is Henry's law constant on the molality scale. Ions are treated similarly

$$G_{+L} = \overset{\square}{G_+} + RT \ln \overset{\square}{\gamma_+} m_+$$
$$G_{-L} = \overset{\square}{G_-} + RT \ln \overset{\square}{\gamma_-} m_- \qquad (7)$$

$\overset{\square}{G_+}$ and $\overset{\square}{G_-}$ have been tabulated by the National Bureau of Standards (Rossini 1952) using the convention that the hydrogen ion has zero Gibbs free energy of formation. Other tabulations were prepared by Wagman et al. (1968, 1969), Parker et al. (1971), and Armstrong and Goldberg (1976).

Occasionally the mole fraction scale is used for supercritical species and solids

$$G_{aL} = \overset{\triangle}{G_a} + RT \ln \overset{\triangle}{\gamma_a} x_a \qquad (8)$$

where $\overset{\triangle}{G_a}$ is Gibbs free energy of formation of the species in a hypothetical state obtained by extrapolation along the Henry's law gradient from infinite dilution to pure a at the temperature of the system and $P = 1.013$ bar (1 atm), and $\overset{\triangle}{\gamma_a} = p_a/x_a\overset{\triangle}{H_a}$; $\overset{\triangle}{H_a}$ is Henry's law constant on the mole fraction scale. See Denbigh (1971) for a detailed discussion of standard states and mole fraction and molality scales.

When the aqueous phase is accompanied by vapor, other liquid, or solid solutions in equilibrium, Equation (3) is accompanied by

$$G_{j1} = G_{j2} = \cdots = G_{jP} \qquad (9)$$

where species j distribute among P phases. For example, water and 1-propanol can form a second liquid phase at high concentrations of LiCl (Rousseau and Boone 1978). Ionic species occur in the aqueous phase and other liquid phases containing appreciable amounts of water.

Fugacity coefficients for molecules in the vapor phase can be computed using equations of state such as Redlich-Kwong and fugacities for pure liquids using vapor pressures (e.g., Poynting Correction for subcritical species) and Henry's law or corresponding states (e.g., Chao-Seader method) for supercritical species.

ACTIVITY COEFFICIENTS IN ELECTROLYTIC SOLUTIONS

Numerous theoretical and empirical functions relate excess Gibbs free energy to temperature, pressure, and composition. These include terms that account for molecule-molecule, ion-ion, and molecule-ion interactions in the liquid phase. This section reviews these expressions and those for activity coefficient and shows their applicability for design purposes. Such interpretation is necessary to properly combine theoretical and empirical expressions in the analysis of a given system.

Molecule-Molecule Interactions

Consider molecular solute a in water. One of the simplest functions for excess Gibbs free energy is:

$$\frac{G^E}{(0.018)^2 n_w RT} = \beta_{aa} m_a^2 \qquad (10)$$

where G^E is proportional to the molality of a squared, β_{aa} is the proportionality constant, or molecule-molecule interaction parameter, and n_w is the moles of water. This expression models the interactions from short range (van der Waals' forces) using a Margules type term. The activity coefficient is given by

$$\ln \gamma_a = \frac{1}{RT} \frac{\partial G^E}{\partial n_a} \qquad (11)$$

and differentiating

$$\ln \gamma_a = 2\beta_{aa} m_a \qquad (12)$$

Edwards et al. (1975), fitted data for a few common species and tabulated β_{aa} values.

When more than one molecular species is present:

$$\frac{G^E}{(0.018)^2 n_w RT} = \sum_a \sum_{a'} \beta_{aa'} m_a m_{a'} \qquad (13)$$

and,

$$\ln \gamma_a = 2 \sum_{a'} \beta_{aa'} m_{a'} \qquad (14)$$

where Edwards et al., take $\beta_{aa'} = (\beta_{aa} + \beta_{a'a'})/2$.

Beutier and Renon (1978) neglect interactions between different molecules, but include ternary interactions between like molecules:

$$\frac{G^E}{(0.018)^2 n_w RT} = \beta_{aa} m_a^2 + \mu_{aaa} m_a^3 \qquad (15)$$

where μ_{aaa}, the ternary interaction parameter, equals $-\frac{1}{55.5}\left(\beta_{aa} + \frac{1}{166.5}\right)$. Hence,

$$\ln \gamma_a = 2\beta_{aa} m_a - \frac{3}{55.5}\left(\beta_{aa} + \frac{1}{166.5}\right) m_a^2 \qquad (16)$$

Ion-Ion Interactions

Equations (10)-(16) cannot model deviations from ideality of solutions with ionic species, where van der Waals' forces are accompanied by long range electrical (Coulombic) forces. The Debye-Hückel theory was the first to characterize these in terms of an interionic potential, assuming ions to be rigid spheres of equal diameter with negligible van der Waals' intermolecular, molecule-ion and ion-ion interactions (Harned and Owen 1958, Pitzer and Brewer 1961). But, these assumptions hold only at low concentrations (<0.001M).

Bronsted (1922) was the first to account for van der Waals' forces between ions of opposite charge. His expression for excess Gibbs free energy of electrolyte MX in aqueous solution is

$$\frac{G^E}{(0.018)^2 n_w RT} = f\{I\} + 2\beta_{MX} m_M m_X \qquad (17)$$

where the Coulombic force term given by Debye-Hückel theory is

$$f\{I\} = -\frac{4}{3}\alpha I^{3/2} \qquad (18)$$

I, the ionic strength, is

$$I = \frac{\sum_i m_i z_i^2}{2}$$

Differentiating Equation (17), the activity coefficient for each ion is obtained

$$\ln \gamma_M = -\alpha z_M^2 I^{1/2} + 2\beta_{MX} m_X$$
$$\ln \gamma_X = -\alpha z_X^2 I^{1/2} + 2\beta_{MX} m_M \qquad (19)$$

Guggenheim (1949) modified the Coulombic force term

$$f\{I\} = -4\alpha[\ln\{1 + I^{1/2}\} + I/2 - I^{1/2}] \qquad (20)$$

Substituting in Equation (17) and differentiating we have

$$\ln \gamma_M = -\alpha \frac{z_M{}^2 I^{1/2}}{1 + I^{1/2}} + 2\beta_{MX} m_X$$
$$\ln \gamma_X = -\alpha \frac{z_X{}^2 I^{1/2}}{1 + I^{1/2}} + 2\beta_{MX} m_M \quad (21)$$

It is convenient to define the mean-ion activity coefficient

$$\gamma_{MX} = [\gamma_M{}^{\nu_M} \gamma_X{}^{\nu_X}]^{1/\nu} \quad (22)$$

where $\nu = \nu_M + \nu_X$. Substituting (21) in (22)

$$\ln \gamma_{MX} = -\alpha \frac{|z_M z_X| I^{1/2}}{1 + I^{1/2}} + 2\bar{\nu}\beta_{MX} m_{MX} \quad (23)$$

where $m_{MX} = m_M/\nu_M = m_X/\nu_X$ and $\bar{\nu} = 2\nu_M\nu_X/\nu$. This equation was fitted to experimental data by Guggenheim and Turgeon (1955) and the interaction parameter β_{MX} tabulated. At 273.2K, freezing points were measured as a function of molality and at 298.2K E.M.F. was measured, as well as isopiestic measurements relative to NaCl. Equation (18) was demonstrated to extend the concentration range to 0.1M.

At higher molalities, Bromley (1973) presents a correlation, for ionic strengths up to six molal, which gives a good fit to most of the data on strongly ionized electrolytes:

$$\log \gamma_{MX} = \frac{-A_\gamma |z_M z_X| I^{1/2}}{1 + \rho I^{1/2}} + \frac{(0.06 + 0.6 B_{MX}) |z_M z_X| I}{\left(1 + \frac{1.5}{|z_M z_X|} I\right)^2} + B_{MX} I \quad (24)$$

where $A_\gamma = \alpha/\ln 10$. B_{MX} values at 298.2K with $\rho = 1.0$ are tabulated for many strong electrolytes. If a B_{MX} value is not available it can be approximated as the sum of values for individual ions plus a product term

$$B_{MX} = B_M + B_X + \delta_M \delta_X \quad (25)$$

Values for B_M, B_X, δ_M, δ_X are also tabulated. For electrolytes where values have not been tabulated, Bromley (1972, 1973) developed a correlation between B_M and B_X and the entropies of formation.

Equations for multi-electrolytic solutions are given by Meissner and Kusik (1972), but only for the case where all negative ions have the same charge and all positive ions have the same charge. To remove this restriction, formulas given by Guggenheim (1949) apply at low molalities; these incorporate Bronsted's principles of interaction between ions of opposite charge and extend Equations (21)

$$\ln \gamma_M = -\alpha \frac{z_M{}^2 I^{1/2}}{1 + I^{1/2}} + 2 \sum_X \beta_{MX} m_X$$
$$\ln \gamma_X = -\alpha \frac{z_X{}^2 I^{1/2}}{1 + I^{1/2}} + 2 \sum_M \beta_{MX} m_M \quad (26)$$

by summing terms that account for van der Waals' forces between ions of opposite charge. Substituting in Equation (22), we obtain the Bronsted-Guggenheim equation

$$\ln \gamma_{MX} = -\alpha \frac{|z_M z_X| I^{1/2}}{1 + I^{1/2}} + \frac{2\nu_M}{\nu_M + \nu_X} \sum_{X'} \beta_{MX'} m_{X'}$$
$$+ \frac{2\nu_X}{\nu_M + \nu_X} \sum_{M'} \beta_{M'X} m_{M'} \quad (27)$$

To extend this equation at higher molalities, Bromley (1973) relates β_{MX} for single electrolytes to tabulated values of B_{MX} by equating Equations (23) and (24)

$$\beta_{MX} = \frac{\ln 10}{2\bar{\nu} m_{MX}} \left[\frac{0.06 + 0.6\, B_{MX} |z_M z_X| I}{\left(1 + \frac{1.5}{|z_M z_X|} I\right)^2} + B_{MX} I \right] \quad (28)$$

Note that the ionic strength of the multi-electrolytic solution is used to compute the interaction coefficient for each electrolyte.

Pitzer (1973) extended Equation (17) for excess Gibbs free energy to apply for solutions of multiple electrolytes when $I > 6$,

$$\frac{G^E}{(0.018)^2 n_w RT} = f\{I\} + \sum_i \sum_j \beta_{ij} m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \quad (29)$$

where the counters i, j, and k, refer to the ions. The Coulombic force term

$$f\{I\} = -\frac{\alpha}{3}\left(\frac{4I}{b}\right) \ln\{1 + bI^{1/2}\} \quad (30)$$

was derived using relations between interionic potentials and the radial distribution function and statistical mechanics. He included terms for van der Waals' forces between ions of like charge and among ternary groups of ions. Pitzer also expressed β_{ij} as a function of I

$$\beta_{MX} = \beta^{(0)} + \beta^{(1)} \frac{2}{a^2 I} [1 - e^{-a\sqrt{I}}(1 + a\sqrt{I})] \quad (31)$$

and computed $\beta^{(0)}$ and $\beta^{(1)}$ using experimental data with $a = 2$ and $b = 1.2$ for many electrolytes.

Beutier and Renon (1978) differentiated Equations (29)-(31), assuming no van der Waals' forces between ions of like charge ($\beta_{MM} = \beta_{XX} = 0$) and no ternary interactions except those of type MXX, MMX, and MXY. They obtained, for single electrolytes:

$$\ln \gamma_{MX} = \frac{|z_M z_X|}{2} \frac{df}{dI} + \frac{2\nu_M \nu_X}{\nu} B'_{MX} m_{MX} + \frac{2(\nu_M \nu_X)^{3/2}}{\nu} C_{MX} m^2_{MX} \quad (32)$$

where

$$\frac{df}{dI} = -\frac{2\alpha}{3}\left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln\{1 + bI^{1/2}\}\right] \quad (33)$$

$$B'_{MX} = 2\beta_{MX} + I \frac{d\beta_{MX}}{dI} \quad (34)$$

$$\frac{d\beta_{MX}}{dI} = -\frac{2\beta^{(1)}}{a^2 I^2}\left[1 - e^{-a\sqrt{I}}\left(1 + a\sqrt{I} + \frac{a^2}{2} I\right)\right] \quad (35)$$

$$C_{MX} = \frac{9}{2(\nu_M \nu_X)^{1/2}} (\nu_M \mu_{MMX} + \nu_X \mu_{MXX}) \quad (36)$$

In addition to computing $\beta^{(0)}$, $\beta^{(1)}$, and C_{MX} for many electrolytes, Beutier and Renon (1978) relate $\beta^{(0)}$ +

$\beta^{(1)}$ to entropies of formation.

For multi-electrolytic solutions, differentiation of Equation (29) gives

$$\ln \gamma_i = \frac{z_i^2}{2}\frac{df}{dI} + 2\sum_j \beta_{ij}m_j + \frac{z_i^2}{2}\sum_j\sum_k \frac{d\beta_{jk}}{dI}m_jm_k + 3\sum_j\sum_k \mu_{ijk}m_jm_k \quad (37)$$

Renon and Beutier assume $\mu_{MMX} = \mu_{MXX}$ and $\mu_{MXY} = (\mu_{MXX} + \mu_{MYY})/2$.

Molecule-Ion Interactions

Edwards et al. (1975) expressed the excess Gibbs free energy for solutions of molecules and ions as

$$\frac{G^E}{(0.018)^2 n_w RT} = f\{I\} + \sum_i\sum_j \beta_{ij}m_im_j \quad (38)$$

where the Coulombic force term is given by Equation (20) and Margules-like terms account for molecule-ion, molecule-molecule, or ion-ion interactions. Differentiating, they obtained relations similar to Equation (26)

$$\ln \gamma_i = -\alpha\frac{z_i^2 I^{1/2}}{1 + I^{1/2}} + 2\sum_j \beta_{ij}m_j \quad (39)$$

where i represents a molecule or ion and j represents all other molecules or ions in solution, excluding water. Edwards et al. (1975) computed $\beta_{\text{mol-ion}}$ from experimental data for a few common weak electrolytes. Like Equation (26), this equation applies when $I < 0.1M$.

Beutier and Renon (1978) permit i, j and k in Equation (29) to represent molecular species as well as ions. For molecule-molecule and ion-ion interactions, terms were discussed in the preceding sections (Equations (15) and (29)). To estimate molecule-ion interaction coefficients, Beutier and Renon applied the Debye-McAulay electrostatic theory. It gives the electrical work to transfer ions between solutions with and without the molecules present and having different dielectric constants, D_f and D_i, both functions of molecule and ion concentrations. For molecule-ion pairs, this work is added to the Gibbs free energy, yielding expressions for β_{ja} (molecule-ion interaction coefficient) and $\overset{D}{\beta}_{jk}$, a contribution to the ion-ion interaction coefficient when molecules are present. β_{jk}, the ion-ion interaction coefficient is given by

$$\beta_{jk} = \overset{P}{\beta}_{jk} + \overset{D}{\beta}_{jk} \quad (40)$$

where $\overset{P}{\beta}_{jk}$ is computed using Pitzer's theory (31) without molecules present.

Other Solvents and Partially Miscible Systems

In solutions where non-aqueous molecular species are present in high concentrations, a three-suffix Margules equation can model molecule-molecule interactions when immiscibility does not occur. Although similar, the Beutier and Renon Equation (15) does not explicitly account for water composition and should be in error as water fraction decreases.

For partially miscible systems, a four-suffix Margules or "Uniquac" equation applies. Rousseau and Boone (1978) use the Uniquac equation and a "salting-out" parameter to correlate data for the 1-propanol-water-LiCl system. But, they do not explicitly account for molecule-ion and ion-ion interactions.

Electrolytes in polar solvents other than water could be handled using correlations similar to those developed for aqueous systems. To our knowledge, however, ion-ion and molecule-ion interactions have not been modeled for non-aqueous systems.

ACTIVITY OF WATER

Let $(a_w)_{MX}$ designate activity of water in a solution of electrolyte MX and $(a_w)_{\text{mix}}$ the activity in a solution of multiple electrolytes. $(a_w)_{\text{mix}}$ can be calculated from $(a_w)_{12}$, $(a_w)_{14}$, $(a_w)_{23}$, . . . (cations are numbered 1, 3, 5, . . . and anions 2, 4, 6, . . .), all at the ionic strength of the solution (Meissner and Kusik, 1973)

$$\begin{aligned}\log\{a_w\}_{\text{mix}} = X_1Y_2\log(\{a_w\}_{12} &+ X_1Y_4\log\{a_w\}_{14} + \cdots\\ &+ X_3Y_2\log\{a_w\}_{32} + X_3Y_4\log\{a_w\}_{34} + \cdots\\ &+ X_5Y_2\log\{a_w\}_{52} + X_5Y_4\log\{a_w\}_{54} + \cdots\end{aligned} \quad (41)$$

where X_j and Y_j are the cationic and anionic strength fractions,

$$X_j = \frac{m_jz_j^2}{\sum_l m_lz_l^2} \quad \begin{aligned} j &= 1, 3, 5, \ldots\\ l &= 1, 3, 5, \ldots\end{aligned} \quad (42)$$

$$Y_j = \frac{m_jz_j^2}{\sum_l m_lz_l^2} \quad \begin{aligned} j &= 2, 4, 6, \ldots\\ l &= 2, 4, 6, \ldots\end{aligned} \quad (43)$$

The activities of water in equilibrium with solutions of single strong electrolytes, $(a_w)_{MX}$, can be calculated using the Gibbs-Duhem equation and, for example, Equation (24). Integration (Zemaitis and Rafal 1975) gives

$$\begin{aligned}-55.51\ln\{a_w\}_{MX} = \frac{2I}{|z_Mz_X|} + \frac{2\ln\{10\}}{|z_Mz_X|}\Bigg[&-A_\gamma|z_Mz_X|\\ &\left\{(1 + I^{1/2}) - 2\ln(1 + I^{1/2}) - \frac{1}{1 + I^{1/2}}\right\}\\ &+ \frac{(0.06 + 0.6B_{MX})}{0.75}I|z_Mz_X|\cdot\left\{\frac{1 + 3I/(|z_Mz_X|)}{1 + 1.5I/(|z_Mz_X|)^2}\right.\\ &\left.- \frac{\ln(1 + 1.5I/|z_Mz_X|)}{1.5I/|z_Mz_X|}\right\}B_{MX}I^2/2\Bigg]\end{aligned} \quad (44)$$

TEMPERATURE DEPENDENCE IN ELECTROLYTIC SOLUTIONS

The temperature dependence of activity coefficients is given by the van't Hoff equation,

$$\frac{d\ln\gamma_{MX}}{dT} = \frac{\overset{\square}{H}_{MX} - H_{MX}}{RT^2} \quad (45)$$

where $\overset{\square}{H}_{MX}$ is the partial molal enthalpy of electrolyte MX in a hypothetical ideal solution at unit molality, temperature of the system, and 1.013 bar (1 atm), and H_{MX} is the partial molal enthalpy at the concentration and temperature of the system, and 1.013 bar (1 atm). Values of $\overset{\square}{H}_{MX}$ are tabulated for molecular species and ions by Wagman, et al. (1968) and Parker et al. (1971), who give $\Delta H_f^{\square}$, $\Delta G_f^{\square}$, $c_p^{\square}$ and $S^{\square}$, as well. For ions, the convention is that hydrogen ion has zero Gibbs free energy, enthalpy and entropy of formation in a hypothetical ideal solution at unit molality. Pitzer and Brewer (1961) calculate H_{MX} by differentiating their expression for $\ln\gamma_{MX}$ with respect to temperature. They tabulate dB'_{MX}/dT for many electrolytes.

COMPUTATION OF COMPOSITIONS AT EQUILIBRIUM

K-Value Approach

To determine compositions at equilibrium, Equations (3) and (9) are solved, subject to mass balance constraints. This approach has been implemented in the ECES (Equilibrium Computation of Electrolyte Systems) program by OLI Systems, Inc. (Zemaitis and Rafal 1975). Given the feed concentrations, the species present at equilibrium, dissociation reactions, and the phases in which species distribute at equilibrium, ECES prepares a file containing

1. Atom balance equations.
2. Electroneutrality equation.
3. Equations (3) for chemical equilibrium using K-values
4. Equations (9) for phase equilibrium using K-values.
5. Equations for activity coefficients (Guggenheim and Turgeon equation with Bromley extension for ion-ion interactions and Edwards, et al., method for molecule-ion interactions).

K-values are computed by ECES at the temperature and pressure of the system. The file is data for the ASAP program, which writes a FORTRAN function to evaluate the residuals of the algebraic equations. This function is compiled and linked with the ASAP routine to implement the Newton-Raphson method. With guesses for compositions at equilibrium, these routines compute a solution. ECES does not permit modeling of immiscible systems or non-aqueous systems involving polar solvents.

Minimization of Gibbs Free Energy

The approach in this work is to minimize the Gibbs free energy

$$G = \sum_{j=1}^{S} G_j^o n_j^c + \sum_{j=S+1}^{C'} \sum_{l=1}^{P'} G_{jl} n_{jl} + \sum_{j=S+1}^{C} \sum_{l=P'+1}^{P} G_{jl} n_{jl} \tag{46}$$

subject to mass balance constraints, Equation (1, Part I) has been modified to include ionic species and C' is the number of chemical species excluding ions, P' is the number of mixed phases (vapor, liquid, solid) that do not contain ions, and P is the number of mixed phases including those that contain ions. The last term in (46) gives the contribution of species in phases containing ions ($l = P' + 1, \ldots, P$).

When the number of independent ionization reactions equals $C - \rho$, where ρ is the rank of the atom matrix (m_{jk}), Gibbs free energy is minimized subject to atom balance and electroneutrality constraints

$$b_k = \sum_{j=1}^{S} m_{jk} n_j^c + \sum_{j=S+1}^{C'} \sum_{l=1}^{P'} m_{jk} n_{jl} + \sum_{j=S+1}^{C} \sum_{l=P'+1}^{P} m_{jk} n_{jl} \qquad k = 1, \ldots, E \tag{47}$$

$$\sum_{j=C'+1}^{C} \sum_{l=P'+1}^{P} z_j n_{jl} = 0 \tag{48}$$

Occasionally the atom balance and electroneutrality constraints are not independent. In this work, the Gram-Schmidt orthogonalization procedure identifies dependent equations and one of the equations is disregarded to avoid singularities in the Jacobian matrix.

In this section, we extend the Rand method to handle electrolytic systems. The quadratic Taylor Series to approximate the Gibbs free energy (Equation 9, Part I) has additional terms for electrolytic phases containing ionic species

$$\begin{aligned} Q\{N\} = {} & G\{n\} + \sum_{j=1}^{S} \frac{\partial G}{\partial n_j^c} (N_j^c - n_j^c) \\ & + \sum_{l=1}^{P'} \sum_{j=S+1}^{C'} \frac{\partial G}{\partial n_{jl}} (N_{jl} - n_{jl}) + \sum_{l=P'+1}^{P} \sum_{j=S+1}^{C} \\ & \frac{\partial G}{\partial n_{jl}} (N_{jl} - n_{jl}) + \frac{1}{2} \sum_{l=1}^{P'} \sum_{j=S+1}^{C'} \sum_{j'=S+1}^{C'} \\ & \frac{\partial^2 G}{\partial n_{jl} \partial n_{j'l}} (N_{jl} - n_{jl})(N_{j'l} - n_{j'l}) + \frac{1}{2} \\ & \sum_{l=P'+1}^{P} \sum_{j=S+1}^{C} \sum_{j'=S+1}^{C} \frac{\partial^2 G}{\partial n_{jl} \partial n_{j'l}} (N_{jl} - n_{jl})(N_{j'l} - n_{j'l}) \end{aligned} \tag{49}$$

The unconstrained objective function (Equation 10, Part I) includes the electroneutrality constraint when it is independent of the atom balances:

$$\begin{aligned} F\{N\} = {} & Q\{N\} + RT \sum_{k=1}^{E} \pi_k \Big(b_k - \sum_{j=1}^{S} m_{jk} N_j^c \\ & - \sum_{l=1}^{P'} \sum_{j=S+1}^{C'} m_{jk} N_{jl} - \sum_{l=P'+1}^{P} \sum_{j=S+1}^{C} m_{jk} n_{jl} \Big) \\ & - \pi_e \sum_{l=P'+1}^{P} \sum_{j=C'+1}^{C} z_j n_{jl} \end{aligned} \tag{50}$$

and is minimized using

$$\frac{\partial F\{N\}}{\partial N_j^c} = \frac{\partial F\{N\}}{\partial N_{jl}} = \frac{\partial F\{N\}}{\partial \pi_k} = \frac{\partial F\{N\}}{\partial \pi_e} = 0 \qquad \begin{aligned} j &= 1, 2, \ldots, C \\ l &= 1, 2, \ldots, P \\ k &= 1, 2, \ldots, E \end{aligned} \tag{51}$$

These linear equations are reduced to $S + P + E + 1$ linear equations in unknowns N_j^c, N_l, π_k, and π_e. The coefficient matrix, shown in Figure 1, is inverted and N_{jl} are computed using Equation (12, Part I) for $l = 1, \ldots, P'$ and

$$N_{jl} = -n_{jl} \left[\frac{G_{jl}\{n\}}{RT} + \frac{N_l}{n_l} + \sum_{k=1}^{E} \pi_k m_{jk} + \pi_e z_j \right] \qquad l = P' + 1, \ldots, P \tag{52}$$

A univariant search is conducted to give minimum G in the search direction, as described in Part I.

The phase-splitting algorithm of Part II applies with ionic species restricted from the vapor phase and certain liquid phases. In our work, only the aqueous phase is modelled, as activity coefficients for molecular and ionic species in partially-miscible, water-solvent systems have not been correlated as a function of composition. The aqueous phase is the source phase and activities of species in trial phases are relative to the species in a hypothetical ideal solution at unit molality.

The Rand method and phase-splitting algorithm were implemented as a FORTRAN module named GIBBS and will be installed in ASPEN (Advanced System for Process Engineering—Evans et al. 1977).

TABLE 1. EXPERIMENTAL AND CALCULATED RESULTS: SO_2-H_2O SYSTEM AT 283.2 K

Dissolved SO_2	0.1M Molality at equilibrium			0.001M Molality at equilibrium		
	Calc.*	Calc.	γ_{Calc}	Calc.*	Calc.	γ_{Calc}
SO_2	0.0588	0.06477	0.96708	4.56×10^{-5}	4.64667×10^{-5}	0.9901
H_2O		55.47478	1.0		55.509	1.000
H^+		0.035222	0.8525		9.5353×10^{-4}	0.8921
HSO_3^-		0.035222	1.0267		9.5353×10^{-4}	1.0011
OH^-		10^{-13}	0.8559		0.0	0.8729
$SO_3^=$		1.7088×10^{-7}	0.8353		4.2×10^{-10}	0.8638

	0.1M Partial pressure, bar		0.001M Partial pressure, bar	
	Expt.	Calc.	Expt.	Calc.
SO_2	2.563×10^{-2}	2.621×10^{-2}	1.925×10^{-5}	1.928×10^{-5}

* Edwards, et al. (1975).

For each species expected at equilibrium, the phase(s) in which it is expected to occur, and the methods for computing fugacities and activity coefficients, are specified. Details of this module are given elsewhere (GIBBS 1979 and Gautam 1978).

RESULTS

Solubility data for the system SO_2-H_2O at 283.2K are given by Edwards et al. (1975); the partial pressure of SO_2 is reported at several dissolved SO_2 concentrations. Calculations were performed at two concentrations: 0.1M and 0.001M, with liquid compositions and activity coefficients and the partial pressure of SO_2 shown in Table 1. Calculations were carried out using Equation (39) for activity coefficients of molecules and ions. Molecule-molecule interaction coefficients were computed using the unnumbered equation below Equation (14). Ion-ion interaction coefficients were obtained from Guggenheim and Turgeon (1955). Molecule-ion interaction coefficients are those given by Edwards et al. (1975). The partial pressures are within 2% of experimental values. Concentrations and activity coefficients differ by less than 10% with the calculated results of Edwards et al. For this system, the atom balances and electroneutrality equation are dependent. Hence, the latter is not used in minimization calculations. Approximately 7-8 iterations are necessary to achieve convergence, depending upon initial values. Each iteration consumes approximately 0.1 sec. on the Univac 90/70 computer.

Edwards et al. also present solubility data for the NH_3-H_2S-H_2O system at 293.2K; the partial pressure of H_2S is reported as a function of dissolved H_2S/dissolved NH_3 with dissolved NH_3 as a parameter. Figure 1 shows that calculated and experimental partial pressures agree within 2%. Table 2 gives calculated liquid compositions and activity coefficients. As for SO_2-H_2O, the atom balances and electroneutrality equation are dependent and the latter is not used in minimization calculations.

These results depend on solution model, but confirm the ability of our algorithm to reach the global minimum in Gibbs free energy. To match compositions reported by Edwards et al., total H_2S in the liquid phase (molecular and dissociated) was specified, and composition computed in the liquid phase prior to computing partial pressures: $p_j = x_j \overset{\triangle}{\gamma_j} \overset{\triangle}{H_j}$. When the total H_2S in the system is specified, the phase-splitting algorithm determines whether or not a vapor phase exists during calculations to minimize Gibbs free energy.

Unfortunately, we were unable to compare computation times using GIBBS with the use of K-values, as implemented in ECES. ECES uses the Newton-Raphson method to solve nonlinear algebraic equations, whereas

TABLE 2. CALCULATED RESULTS: NH_3-H_2S-H_2O SYSTEM AT 293.2 K

Dissolved NH_3 Dissolved H_2S	0.05M 0.10M		0.05M 0.20M		0.05M 0.40M	
	Moles	γ	Moles	γ	Moles	γ
NH_3	7.4677×10^{-5}	1.0023	2.5296×10^{-5}	1.0063	1.0407×10^{-5}	1.0144
H_2S	0.0501	1.0114	0.15002	1.0143	0.35000	1.0200
H_2O	55.51	0.8198	55.51	0.8333	55.51	0.8611
NH_4^+	0.04992	0.8220	0.04997	0.8370	0.04999	0.8680
H^+	2.3556×10^{-7}	0.8348	7.036×10^{-7}	0.8391	1.6335×10^{-6}	0.8479
OH^-	2.7974×10^{-8}	1.0080	9.4256×10^{-9}	1.0145	4.0402×10^{-9}	1.0275
HS^-	0.04992	0.4279	0.04997	0.42853	0.04999	0.4300
$S^=$	5.9292×10^{-8}	0.4215	1.2428×10^{-8}	0.42215	7.5410×10^{-9}	0.4236

	Partial pressure, bar		Partial pressure, bar		Partial pressure, bar	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
H_2S	0.434	0.422	1.276	1.279	2.968	2.975

N_1/n_1	…	$N_{P'}/n_{P'}$	…	N_P/n_P	N_1^c	…	N_S^c	π_1	…	π_E	π_e	Right hand side
$\sum_{j=S+1}^{C'} m_{j1}n_{j1}$	…	$\sum_{j=S+1}^{C'} m_{j1}n_{jP'}$	…	$\sum_{j=S+1}^{C} m_{j1}n_{jP}$	m_{11}	…	m_{S1}	B_{11}	…	B_{1E}	$\sum_{l=P'+1}^{P} \sum_{j=C'+1}^{C} m_{j1}z_jn_{jl}$	$b_1 + \frac{1}{RT} \sum_{l=1}^{P'} \sum_{j=S+1}^{C'} m_{j1}n_{jl}G_{jl}$ $+ \frac{1}{RT} \sum_{l=P'+1}^{P} \sum_{j=S+1}^{C} m_{j1}n_{jl}G_{jl}$
$\vdots$		$\vdots$		$\vdots$	$\vdots$		$\vdots$	$\vdots$		$\vdots$	$\vdots$	$\vdots$
$\sum_{j=S+1}^{C'} m_{jE}n_{j1}$	…	$\sum_{j=S+1}^{C'} m_{jE}n_{jP'}$	…	$\sum_{j=S+1}^{C} m_{jE}n_{jP}$	m_{1E}	…	m_{SE}	B_{E1}	…	B_{EE}	$\sum_{l=P'+1}^{P} \sum_{j=C'+1}^{C} m_{jE}z_jn_{jl}$	$b_E + \frac{1}{RT} \sum_{l=1}^{P'} \sum_{j=S+1}^{C'} m_{jE}n_{jl}G_{jl}$ $+ \frac{1}{RT} \sum_{l=P'+1}^{P} \sum_{j=S+1}^{C} m_{jE}n_{jl}G_{jl}$
								$\sum_{l=P'+1}^{P} \sum_{j=C'+1}^{C} m_{j1}z_jn_{jl}$	…	$\sum_{l=P'+1}^{P} \sum_{j=C'+1}^{C} m_{jE}z_jn_{jl}$	$\sum_{l=P'+1}^{P} \sum_{j=C'+1}^{C} z_j^2n_{jl}$	$\frac{1}{RT} \sum_{l=P'+1}^{P} \sum_{j=C'+1}^{C} z_jn_{jl}G_{jl}$
								$\sum_{j=S+1}^{C'} m_{j1}n_{j1}$	…	$\sum_{j=S+1}^{C'} m_{jE}n_{j1}$		$\frac{1}{RT} \sum_{j=S+1}^{C'} n_{j1}G_{j1}$
								$\vdots$		$\vdots$		$\vdots$
								$\sum_{j=S+1}^{C'} m_{j1}n_{jP'}$	…	$\sum_{j=S+1}^{C'} m_{jE}n_{jP'}$		$\frac{1}{RT} \sum_{j=S+1}^{C'} n_{jP'}G_{jP'}$
								$\vdots$		$\vdots$		$\vdots$
								$\sum_{j=S+1}^{C} m_{j1}n_{jP}$	…	$\sum_{j=S+1}^{C} m_{jE}n_{jP}$		$\frac{1}{RT} \sum_{j=S+1}^{C} n_{jP}G_{jP}$
								m_{11}	…	m_{1E}		G_1^0/RT
								$\vdots$		$\vdots$		$\vdots$
								m_{S1}	…	m_{SE}		G_S^0/RT

$$B_{kk'} = \sum_{j=S+1}^{C'} m_{jk}m_{jk'} \sum_{l=1}^{P'} n_{jl} + \sum_{j=S+1}^{C} m_{jk}m_{jk'} \sum_{l=P'+1}^{P} n_{jl}$$

Figure 1. Coefficient matrix.

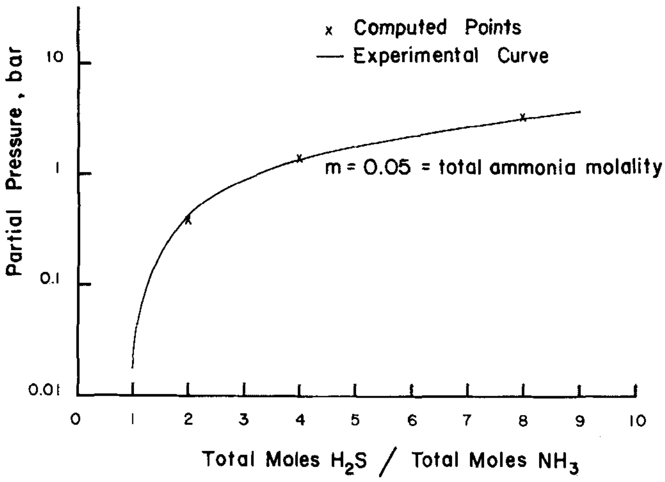

Figure 2. Partial pressure of H_2S in NH_3-H_2S-H_2O at 293.2 K.

our algorithm minimizes Gibbs free energy using Newton's method. Both require matrix inversion and computation times should depend on matrix size and numbers of iterations. We have observed 7-8 iterations on the average for both methods and note that matrix size varies with electrolytic system. For our algorithm, the order is $P + S + E + 1$, and for ECES it is given by the number of equations to be solved simultaneously. Consider the SO_2-H_2O system: $P + S + E + 1 = 1 + 0 + 3 + 1 = 5$ and the number of equations generated by ECES is 14. For many systems, our algorithm enjoys this advantage as well as the advantage of analytical rather than numerical derivatives. Hence, for many systems, we expect computation times to be considerably less using our algorithm. Note, however, that by substitution it is possible to reduce the number of simultaneous equations and the dimensionality of the Jacobian matrix. Such a procedure would be more competitive.

Other advantages of our algorithm are that 1) it does not require specification of an independent set of dissociation reactions, 2) the phase distribution need not be known prior to minimization calculations, and 3) a FORTRAN subprogram to evaluate the residuals for each set of material balances and electroneutrality equation is not generated. Program generation and compilation is time-consuming, although done once for each model.

The large spread in compositions amongst the species in electrolytic solutions requires the use of double precision for most problems.

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NOTATION

a = parameter in Pitzer Equation (31); activity
A_γ = Debye-Hückel constant/ln 10 = α/ln 10
b = parameter in Pitzer's Coulombic force term
b_k = number of gram-atoms of element k
B = Bromley's binary interaction coefficient
c_p = specific heat at constant pressure
C = number of chemical species
C' = number of chemical species excluding ions
E = number of elements
f_j = liquid fugacity of species j
$f\{I\}$ = Coulombic force term
G^E = excess Gibbs free energy
G_{jl} = chemical potential of species j in phase l
G^o = free energy of formation of species j
G = total Gibbs free energy
H_j = Henry's Law constant of species j
H_{MX} = partial molal enthalpy of electrolyte MX
I = ionic strength
m_j = molality of species j, moles per kg of water
m_{jk} = number of atoms of element k in species j
m_{MX} = $m_M/\nu_M = m_X/\nu_X$
M = cation
n = number of moles
n_{jl} = number of moles of species j in phase l
N = number of moles after iteration of Newton's method
p = partial pressure
P = number of mixed phases; pressure
P^s = vapor pressure
P' = number of mixed phases without ions
R = universal gas constant
S = entropy of formation; number of condensed species
T = absolute temperature
x = mole fraction in liquid
X = anion
X_j = cationic strength fraction (Equation 42)
Y_j = anionic strength fraction (Equation 43)
z = charge

Greek Symbols

α = Debye-Hückel constant = 1.177 kg$^{1/2}$ mol$^{-1/2}$ at 298.2K
β = binary interaction parameter
δ_j = parameter for ion j in Bromley Equation (25)
γ = activity coefficient
γ_{MX} = mean-ion activity coefficient
π = Lagrange multiplier
μ = ternary interaction parameter
ν = stoichiometric coefficient; number of ions
$\bar{\nu}$ = $2\nu_M\nu_X/\nu$

Subscripts

$+$ = cation
$-$ = anion
a = molecule
D = Debye-McAuley theory
f = denotes formation of species from elements
j = species counter
k = element counter
l = phase counter
L = liquid phase, usually aqueous phase
M = cation
P = Pitzer's theory
w = water
X = anion
Y = anion

Superscript

$*$ = denotes standard state as pure liquid at temperature and pressure of system
$'$ = denotes standard state as pure vapor at temperature of system and 1.013 bar (1 atm)
$\square$ = denotes standard state as hypothetical ideal solution of unit molality and at the temperature of the system and 1.013 bar (1 atm)
Δ = denotes standard state as hypothetical state corresponding to extrapolation from infinite dilution along Henry's Law gradient to pure a at the temperature of the system and 1.013 bar (1 atm)

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Diffusion of Gases Through Surfactant Films: Interfacial Resistance to Mass Transfer

A model is proposed for mass transfer of gases across surface-active films and into an aqueous phase. The interfacial region 1) obeys local equilibrium conditions, 2) has a capacity for the dissolved gases greater than the solubility in water, and 3) has a diffusion coefficient three orders of magnitude less than for that in water. The model is solved for and compared with three different experiments: the transient diffusion through monomolecular films into quiescent liquids studied by Plevan and Quinn (1966), the gas absorption through surfactant films into falling liquid films investigated by Emmert and Pigford (1954), and the frequency response of concentration pulses in surfactant films reported by Whitaker and Pigford (1966). The model consistently describes these experiments previously explained by three different models that either ignored the capacitance of the film or assumed local non-equilibrium.

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SCOPE

The presence of surfactants at a gas-liquid interface affects the rate of transfer of a solute from the gas to the liquid. The surfactant alters the interfacial region and provides additional resistance to diffusion even when the liquid is quiescent. Attempts to quantitatively describe this effect have been varied: models have been proposed with empirical overall mass transfer or permeability coefficients, with molecular accommodation coefficients, or with empirical rate constants for adsorption and desorption processes occurring in the interfacial region.

The objective here is to evaluate a quantitative model for this interfacial resistance, a model similar to those for

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