Computer Simulation of Chemical Processes with Electrolytes

by

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Chemical Processes with Electrolytes

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Submitted to the Department of Chemical Engineering in May, 1980 in partial fulfillment of the requirements for the Degree of Doctor of Science from the Massachusetts Institute of Technology

ABSTRACT

Two excess Gibbs energy models and one algorithm for single-stage phase and chemical equilibrium have been developed to facilitate the use of modern process simulators for the analysis and design of chemical processes with electrolytes. Various aspects in the design of a process simulator for simulating electrolyte systems were also considered.

Over the past few decades, process simulators have been developed in the petroleum and petrochemical industries to simulate many chemical processes. But the process engineer concerned with chemical processes with electrolytes, such as inorganic chemical manufacture and pollution control, cannot use the available simulators. Two fundamental problems are 1) representation of the thermodynamic properties of electrolyte solutions and 2) simultaneous chemical and phase equilibrium calculations for electrolyte systems.

The Pitzer equation for the excess Gibbs energy of aqueous electrolyte systems has been extended in a thermodynamically consistent manner to allow for molecular as well as ionic solutes. Under limiting conditions, the extended model reduces to the well-known Setschenow equation for the salting-out effect of molecular solutes. The validity of the model is supported by successful vapor-liquid equilibrium data correlations of aqueous electrolyte systems of industrial interest.

For mixed-solvent electrolyte systems, the Pitzer equation is not satisfactory because its parameters are unknown functions of solvent composition. The local composition model was therefore developed. It assumes that the excess Gibbs energy is the sum of two contributions, one resulting from long-range forces between ions and the other from short-range forces between all species. The long-range term is satisfactorily accounted for by the Debye-Hückel formula. The short-range contribution is modeled by the concept of local composition in a manner similar to the Nonrandom, Two-Liquid
(NRTL) equation but with additional assumptions appropriate for electrolyte systems. The model is applicable to a wide variety of systems without the need for ternary or higher order parameters. Systems can be composed of strong electrolytes, multiple solvents, molecular solutes, and weak electrolytes. In the absence of electrolytes, the model reduces to the NRTL equation for nonelectrolytes. Successful data correlations of numerous electrolyte systems have supported the validity of the model.

Both the extended Pitzer equation and the local composition model have been applied to correlate vapor-liquid equilibrium data of an industrially important electrolyte system: the NH₃-CO₂-H₂S-H₂O system of sour-water-strippers. With model parameters determined from subsystem data correlations, both models predict partial pressures satisfactorily close to the experimental data of the complete system over a wide range of conditions.

An inside-out algorithm was also developed for the rigorous solution of the multicomponent, single-stage flash with chemical equilibrium. The algorithm is a synergistic combination of the single-stage flash algorithm developed by Boston and Britt (1978) and the simultaneous chemical and phase equilibrium algorithm developed by Sanderson and Chien (1973). Because of the complexity of the problem due to strong interaction between chemical and phase equilibria, the advantages of the inside-out approach have been fully realized. The performance of the algorithm was demonstrated for a number of systems involving both electrolytes and nonelectrolytes.

Various aspects in the process simulation of electrolyte systems were considered, including components, streams, physical properties, unit models, flowsheet convergence, input language, and system concepts and structure. It was concluded that it is feasible and beneficial to develop a general-purpose process simulator for chemical processes with electrolytes.

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Dear Professor Newton:  

In accordance with the regulations of the Faculty, I herewith submit a thesis entitled "Computer Simulation of Chemical Processes with Electrolytes," in partial fulfillment of the requirements for the degree of Doctor of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Chau-Chyun Chen
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Summary

1. Introduction

Techniques for simulating industrial-scale chemical processes have evolved over the past few decades. Many process simulators have been developed in the petroleum and petrochemical industries to simulate chemical processes. Examples are CHESS, CONCEPT, FLOWTRAN, FLOWPACK, etc. (Evans, et al., 1976). However, these process simulators are not capable of handling electrolytes. The process engineer concerned with chemical processes with electrolytes, such as for inorganic chemical manufacture and pollution control, cannot not use the available simulators.

Electrolytes occur very widely in the chemical industry. Two well-known processes are acid-gas removal and sour-water stripping. Other examples are absorption of carbon dioxide and chlorine in aqueous solution of barium sulfide for the manufacture of barium carbonate and barium chloride, absorption of nitrogen dioxide in water for the production of nitric acid, distillation of salt-containing systems, crystallization of salts from solutions, and recovery of precious metals from ion exchangers.

Two fundamental problems in computer simulation of chemical
processes of electrolytes are 1) representation of the thermodynamic properties of electrolyte solutions in terms of excess Gibbs energy expressions; 2) simultaneous chemical and phase equilibrium calculations of electrolyte systems. The absence of general correlations for the excess Gibbs energy of electrolyte systems has been one of the most important causes for the lack of development in simulation of electrolyte systems. The complexity of simultaneous chemical and phase equilibrium calculation of electrolyte systems poses another major problem for unit operation modeling of electrolyte systems.

2. Objectives and Scope of Work

The first objective of this thesis was to study electrolyte thermodynamics and to develop appropriate thermodynamic models for the excess Gibbs energy. The models should be applicable to strong electrolytes, weak electrolytes, and molecular solutes in both aqueous and mixed-solvent electrolyte systems.

The second objective was to develop an algorithm to calculate rigorously single-stage phase and chemical equilibrium. Due to the complex nature of electrolyte systems, the algorithm should be reliable, robust and efficient.

The third objective of this thesis was to design a basic,
general framework for simulating chemical processes with electrolytes in a modern process simulator such as ASPEN (Evans et al., 1979). ASPEN (Advanced System for Process Engineering) is a public, state-of-the-art process simulator developed at M.I.T. and designed for a broad range of chemical processes. It was therefore chosen as the basic simulator for the development of process simulation techniques for chemical processes with electrolytes. Various aspects in the simulation of electrolyte systems were investigated.

3. The Extended Pitzer Equation

As in the nonelectrolyte case, the problem of representing the thermodynamic properties of electrolyte solutions is best regarded as that of finding a suitable expression for the non-ideal part of the chemical potential, or the excess Gibbs energy, as a function of composition, temperature, dielectric constant and any other relevant variables.

Recently, there have been a number of significant developments in the modeling of electrolyte systems. Bromley (1973), Meissner and Tester (1972), Meissner and Kusik (1972), Pitzer and co-workers (1973a, 1973b, 1974), and Cruz and Renon (1978), presented models for calculating the mean ionic activity coefficients of many types of aqueous electrolytes. Of these, the Pitzer equation is especially useful because it
is designed for convenient and accurate representation of aqueous strong electrolytes with any number of solutes.

In addition, Edwards, et al. (1975) proposed a thermodynamic framework to calculate equilibrium vapor-liquid compositions for aqueous solutions of one or more volatile weak electrolytes which involved activity coefficients of ionic species. Most recently, Beutier and Renon (1978) and Edwards, et al. (1980) used simplified forms of the Pitzer equation to represent ionic activity coefficients.

In this thesis, the Pitzer equation was extended in a thermodynamically consistent manner to allow for molecular as well as ionic solutes in the aqueous solutions. Under limiting conditions, the extended Pitzer equation reduces to the Pitzer equation for strong electrolytes, and is consistent with the well-known Setschenow equation for the salting-out effect of salt upon molecular solutes.

3.1. The Pitzer Equation

In a series of papers, Pitzer and his co-workers (1973a, 1973b, 1974) proposed a very useful semiempirical equation for the unsymmetric excess Gibbs free energy of aqueous electrolyte systems. The basic equation is

\[ \frac{(G^{ex})^*}{n_{RT}} = f(I) + \sum_{ij} \lambda_{ij}(I)m_{ij} + \sum_{ijk} \nu_{ijk}m_{ij}m_{jk} \]  

(1)
The function \( f(I) \) expresses the effect of long-range electrostatic forces between ions. It is a function of ionic strength, temperature and solvent properties. The empirical form chosen by Pitzer for \( f(I) \) is

\[
f(I) = -A_\Phi \frac{4I}{1.2} \ln(1+1.2\sqrt{I})
\]  

(2)

The parameters \( \lambda_{ij} \) are second virial coefficients giving the effect of short-range forces between solutes \( i \) and \( j \); the parameters \( \mu_{ijk} \) are corresponding third virial coefficients for the interaction of three solutes \( i, j, \) and \( k \). The second virial coefficients are a function of ionic strength. Dependence of the third virial coefficients on ionic strength is neglected. The \( \lambda \) and \( \mu \) matrices are taken to be symmetric.

To make the basic Pitzer equation more useful for data correlation of aqueous strong electrolyte systems, Pitzer modified it by defining a new set of more directly observable parameters representing certain combinations of the second and third virial coefficients. The modified Pitzer equation is

\[
\frac{G^\text{ex}}{n_w RT} = f(I) + \sum_{cc'} \frac{m_c m_{c'}}{(\theta_{cc'} + 2a_{cc'})} + \sum_{aa'} \frac{m_a m_{a'}}{(\theta_{aa'} + 2a_{aa'})} + \sum_{cc'} B_{cc'}(I) + \left( \sum_{ca} \frac{m_c m_a}{Z_{cc}^a} C_{ca} / \sqrt{Z_{cc}^a} \right)
\]

(3)

Essentially, the new parameters \( B \) and \( \theta \) are binary ion-ion parameters and \( C \) and \( \psi \) are ternary ion-ion parameters. The
ion-ion interaction parameters, \( B \) and \( C \), are characteristic of each aqueous single-electrolyte system. The ion-ion difference parameters, \( \Theta \) and \( \Psi \), are characteristic of each aqueous mixed-electrolyte system.

Recognizing the ionic strength dependence of the effect of short-range forces in binary interactions, Pitzer was able to develop an empirical relation for \( B_{ca}(I) \). The expression for systems containing strong electrolytes with one or both ions univalent is

\[
B_{ca}(I) = \beta^{(0)}_{ca} + \beta^{(1)}_{ca} (1 - (1 + 2\sqrt{I}) \exp(-2\sqrt{I})) / 2I
\]

(4)

Therefore, the adjustable parameters in the modified Pitzer equation are \( \beta's, C, \Theta, \) and \( \Psi \). The modified Pitzer equation has been successfully applied to the available data for many pure electrolytes (Pitzer and Mayorga, 1973) and mixed aqueous electrolytes (Pitzer and Kim, 1974). The fit to the experimental data is within the probable experimental error up to an ionic strength of six molality.

However, in most aqueous electrolyte systems of industrial interest, not only strong electrolytes but also weak electrolytes and molecular nonelectrolytes are present. While the modified Pitzer equation appears to be a useful tool for the representation of aqueous strong electrolytes including
mixed electrolytes, it cannot be used in the form just presented to represent the important case of systems containing molecular solutes. A unified thermodynamic model for both ionic solutes and molecular solutes is required to model these kinds of systems.

3.2. Extension of the Pitzer Equation

In this study the Pitzer equation was extended in a thermodynamically consistent manner. First, terms were added to the basic virial form of the Pitzer equation to account for molecule-ion and molecule-molecule interactions. Then, following Pitzer, a set of new, more observable parameters were defined as functions of the virial coefficients. Thus, the Pitzer equation was extended, to account for the presence of molecular solutes. The interpretation of the terms and parameters of the original Pitzer equation is unchanged. The resulting extended Pitzer equation is

\[
\frac{G_{\text{ex}}^{*}}{n_{w}RT} = f(I) + \sum_{c} m_{c} m_{c'} \left( \theta_{cc'} + \sum_{a} \psi_{cc'a} \right) + \sum_{a} m_{a} m_{a'} \left( \theta_{aa'} + \sum_{c} \psi_{aa'c} \right)
\]

\[
+ 2 \sum_{c} m_{c} m_{a} (B_{Ca} + (\sum_{c} z_{c} C_{Ca}) / \sqrt{z_{c} z_{a}})
\]

\[
+ \sum_{m} \sum_{m'} \lambda_{mm'} \delta_{mm'} \sum_{m} \sum_{m'} D_{Ca,m} m_{m} m_{m'} \psi_{cc'}
\]

(5)

The parameters \( D_{Ca,m} \) are binary parameters representing the interactions between salt \( Ca \) and molecular solute \( m \) in an aqueous single salt, single molecular solute system. Binary
parameters $\omega_{cc}', m$ and $\omega_{aa}', m$ represent the differences between the interactions of a specific molecular solute with two unlike salts sharing one common anion or cation. Ternary molecule-ion virial coefficients were neglected in this study to simplify the extension.

It is interesting to note that the molecule-ion interaction contribution in equation (5) is consistent with the well-known Setschenow equation. The Setschenow equation is used to represent the salting-out effect of salts on molecular nonelectrolyte solutes, when the solubilities of the latter are small (Gordon, 1975). The Setschenow equation is

$$
\ln \gamma^*_m = k_{s,m} m_s
$$

where $k_{s,m}$ is the Setschenow constant (a salt-molecule interaction parameter) and $m_s$ is the molality of the salt. The D's are equivalent to the Setschenow constants and the $\omega$'s are equivalent to differences between Setschenow constants.

The third virial coefficients for molecule-molecule interactions can be taken as zero for aqueous systems containing molecular solutes at low concentration. The remaining term for the molecule-molecule interaction contribution is equivalent to the unsymmetric two-suffix Margules model.
In short, an excess Gibbs energy model for both ionic and molecular solutes in aqueous electrolyte systems was obtained by extending the Pitzer equation to account for the presence of molecular solutes. Model parameters include binary ion-ion interaction and difference parameters, ternary ion-ion interaction and difference parameters, salt-molecule interaction parameters or Setschenow constants, salt-salt difference parameters for molecular solute salting, and unsymmetric Margules parameters for molecule-molecule interactions. Like the Pitzer equation, the model is designed for convenient and accurate representation of aqueous electrolyte systems, including mixtures with any number of molecular and ionic solutes.

3.3. Application of the Extended Pitzer Equation

The validity of the extended Pitzer equation was supported by successful correlations of vapor-liquid equilibrium data for three systems. Since the extended Pitzer equation reduces to the Pitzer equation for aqueous strong electrolyte systems, and is consistent with the Setschenow equation for molecular non-electrolytes in aqueous electrolyte systems, the main interest here is aqueous systems with weak electrolytes or partially dissociated electrolytes. The three systems considered were: the hydrochloric acid aqueous solution at 298.15 K and concentrations up to 18 molal; the NH₃-CO₂
aqueous solution at 293.15\textdegree K; and the K$_2$CO$_3$–CO$_2$ aqueous solution of the Hot Carbonate Process. In each case, the chemical equilibrium between all species was taken into account directly as liquid-phase constraints. Significant parameters in the model for each system were identified by a preliminary order of magnitude analysis and adjusted in the vapor-liquid equilibrium data correlation.

T-P-x-y data for hydrochloric acid concentration up to 18 molal were obtained from Vega and Vera (1976). The following reactions occur in the liquid phase.

\[
\begin{align*}
\text{HCl} & = \text{H}^+ + \text{Cl}^- \\
\text{H}_2\text{O} & = \text{H}^+ + \text{OH}^- 
\end{align*}
\]

The least squares data correlation was carried out on HCl vapor mole fraction and total pressure with $\beta^{(0)}_{\text{HCl}}$, $\beta^{(1)}_{\text{HCl}}$, $C_{\text{HCl}}$, $D_{\text{HCl}}$, $\lambda_{\text{HCl}}$, and the Henry's constant for hydrogen chloride as adjustable parameters. Figure 2-1 shows experimental data and correlation results. The average percentage deviation for total pressure is 0.46, and that for HCl vapor fraction is 0.28. The same data was previously correlated with the same objective function by Cruz and Renon (1976). Their results were 0.99 percent deviation for total pressure and 0.34 percent deviation for HCl vapor fraction.
The data reported by van Krevelen, et al. (1949) at 293.15°K were used for data correlation of the NH₃-CO₂ aqueous solution system. The following reactions occur in the liquid phase.

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} & = \text{NH}_4^+ + \text{OH}^- \\
\text{CO}_2 + \text{H}_2\text{O} & = \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & = \text{CO}_3^{2-} + \text{H}^+ \\
\text{NH}_3 + \text{HCO}_3^- & = \text{NH}_2\text{COO}^- + \text{H}_2\text{O} \\
\text{H}_2\text{O} & = \text{H}^+ + \text{OH}^-
\end{align*}
\]

The least squares data correlation was carried out on partial pressures of \text{NH}_3 and \text{CO}_2 with \( \beta^{(0)}_{\text{NH}_4\text{HCO}_3'} \), \( \beta^{(0)}_{(\text{NH}_4)_2\text{CO}_3'} \), \( \beta^{(0)}_{\text{NH}_4\text{NH}_2\text{COO}'} \), \( \beta^{(0)}_{\text{NH}_4\text{HCO}_3'\text{NH}_3'} \), \( \beta^{(0)}_{(\text{NH}_4)_2\text{CO}_3'\text{NH}_3'} \), \( \beta^{(0)}_{\text{NH}_4\text{NH}_2\text{COO', NH}_3'} \)

as adjustable parameters. Experimental data and calculated results are shown in Figure 2-2. The average percent deviation of calculated versus measured partial pressure is 11% for \text{CO}_2 and 3.9% for \text{NH}_3. The same system and the same least squares objective function have been studied by Beutier and Renon (1978). Their results, on the same basis, were 16% for \text{CO}_2 and 5% for \text{NH}_3. Edwards, et al. (1978) also studied vapor-liquid equilibrium of a NH₃-CO₂ aqueous system at 373.15°K. However, the accuracy of the fit was not reported quantitatively.

The equilibrium data obtained by Tosh and coworkers (1959)
were used for data correlation of the $K_2CO_3-CO_2$ aqueous solution system. The data have a temperature range from 343.15°C to 413.15°C and a range from 20 to 40 percent equivalent concentration of potassium carbonate. The following reactions occur in the liquid phase.

$$\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$$
$$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$$
$$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$$

The least squares data correlation was carried out on partial pressures of $\text{CO}_2$ and $\text{H}_2\text{O}$ with appropriate weight and with

$\beta^{(0)}_{\text{KHCO}_3}$, $\beta^{(0)}_{\text{K}_2\text{CO}_3}$, $\theta_{\text{HCO}_3^-}$, $\theta_{\text{CO}_3^{2-}}$, $\psi_{\text{K}^+}$, $\psi_{\text{HCO}_3^-}$, $\psi_{\text{CO}_3^{2-}}$, $C_{\text{KHCO}_3}$, and

$C_{\text{K}_2\text{CO}_3}$ as adjustable parameters. The temperature dependence of the parameters was assumed to be at the form $a + b/t$.

Experimental data and calculated results are shown in Figure 2-3.

3.4. **Limitations of the Pitzer Equation**

The Pitzer equation is subject to all of the limitations of a virial-expansion type equation. The equation parameters, denoting the short-range interactions between and among solute species, are arbitrary, highly temperature-dependent and are characteristic of the solvent. Binary parameters are expressed as empirical functions of ionic strength. Different empirical
functions are proposed for different types of electrolytes. Ternary parameters are required for electrolyte systems at higher ionic strength. Furthermore, for the industrially important class of mixed-solvent electrolyte systems, the Pitzer equation is not feasible because its parameters are unknown functions of solvent composition and because the empirical expressions required are available only for water. Therefore, although the Pitzer equation has been shown to be a convenient and accurate representation of aqueous electrolyte systems, another model known as the local composition model was developed to cover a wider variety of electrolyte systems.

4. The Local Composition Model

Nonelectrolyte systems, which are characterized by short-range forces between molecules, have frequently been studied using the local composition concept. Models such as Wilson (1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) have resulted. Such models have proved to be a great advancement over older models based on virial-type expansions of mole fraction, such as the Margules model. In this study the local composition concept was applied to the short-range interaction forces occurring in electrolyte systems with the hope that a similar advance over the Pitzer model would result. In particular, the local composition model was designed to apply to mixed-solvent, multi-electrolyte
systems over a wide range of electrolyte concentration without the need for ternary or higher order parameters.

A fundamental difference between electrolyte systems and nonelectrolyte systems is the presence of long-range ion-ion electrostatic forces in electrolyte systems. No attempt was made to develop a long-range contribution model based on the local composition concept. Instead, the Debye-Huckel formula as proposed by Fowler and Guggenheim (1949) was used without modification to represent the unsymmetric excess Gibbs energy contribution arising from the long-range ion-ion electrostatic forces. Nevertheless, the local composition concept and the Debye-Huckel formula are consistent in the sense that both are based on accounting for nonrandomness by introducing local compositions through Boltzmann-like factors. The Debye-Huckel formula is a function of solvent density, dielectric constant, and ionic strength. It is known to correctly account for the ion-ion electrostatic contribution in the limit of infinite dilution. When electrolyte concentration increases, short-range forces start to play a role and finally dominate in the region of high electrolyte concentration (Robinson and Stokes, 1970).

The general approach taken in the present study is as follows. The Debye-Huckel formula was used to represent long-range ion-ion interactions while the local composition
concept was used to represent short-range interactions of all kinds. The local composition model is based on two fundamental assumptions; 1) that the local composition of anions around anions is zero, and similarly for cations, which is equivalent to assuming that repulsive forces between ions of like charge are large, 2) that the distribution of anions and cations around solvent molecules is such that the net ionic charge is zero. The first assumption is referred to as like-ion repulsion and the second assumption as local electroneutrality.

The local composition model was developed as a symmetric model, based on pure solvent and hypothetical pure completely-dissociated liquid electrolyte. This model was then normalized by infinite dilution activity coefficients in order to obtain an unsymmetric local composition model. Finally the unsymmetric Debye-Hückel and local composition expressions were added to yield the excess Gibbs energy expression of electrolyte systems.

4.1. Development of the Local Composition Model

Among the various models incorporating the local composition concept for short-range interactions, the Nonrandom, Two-Liquid (NRTL) equation was adopted in this study. Electrolyte systems are characterized by extraordinarily large heats of mixing. Compared to the heat of mixing, the nonideal entropy of mixing is negligible, which is
consistent with the basic assumption behind the NRTL equation. In addition, the NRTL equation is algebraically simple while applicable to mixtures which exhibit phase splitting. Furthermore, no specific volume or area data are required. These data are not available for ions.

The same argument as presented for the NRTL equation by Renon and Prausnitz (1968) is followed. The local mole fractions \( x_{ji} \) and \( x_{ii} \) of species \( j \) and \( i \), respectively, in the immediate neighborhood of a central molecule of species \( i \) are related by

\[
x_{ji}/x_{ii} = (x_j/x_i)G_{ji}
\]  

(7)

where

\[
G_{ji} = \exp(-\alpha \tau_{ji}) 
\]  

(8)

\[
\tau_{ji} = (g_{ji} - g_{ii})/RT
\]  

(9)

The quantities \( g_{ji} \) and \( g_{ii} \) are, respectively, energies of interaction between \( j-i \) and \( i-i \) pairs of species, and are inherently symmetric (\( g_{ji} = g_{ij} \)). The nonrandomness factor was fixed at a value of 0.2 in this study.

For convenience in representing other local mole fraction ratios, we introduce additional notation as follows:
\[ \frac{x_{ji}}{x_{ki}} = (\frac{x_j}{x_k}) G_{ji,ki} \quad (10) \]

where

\[ G_{ji,ki} = \exp(-\alpha \tau_{ji,ki}) \quad (11) \]
\[ \tau_{ji,ki} = (g_{ji} - g_{ki}) / RT \quad (12) \]

While the derivation that follows may be generalized to handle all types of electrolyte systems, for simplicity, the derivation will be based on a binary system of single completely-dissociated electrolyte and single solvent. In such a system, it is assumed that there are three types of cells as shown in Figure 3-1. One type consists of a central solvent molecule with solvent molecules, anions and cations in the immediate neighborhood. The other two types have either an anion or cation as the central species, and an immediate neighborhood consisting of solvent molecules and oppositely-charged ions, but no ions of like charge (like-ion repulsion). The local mole fractions are related by:

\[ x_{cm} + x_{am} + x_{mm} = 1 \quad \text{(central solvent cells)} \quad (13-1) \]
\[ x_{mc} + x_{ac} = 1 \quad \text{(central cation cells)} \quad (13-2) \]
\[ x_{ma} + x_{ca} = 1 \quad \text{(central anion cells)} \quad (13-3) \]

Among the three types of cells there are four distinct local mole fraction ratios: \( x_{cm} / x_{mm}, x_{am} / x_{mm}, \)
\[ x_{mc}/x_{ac}, \text{ and } x_{ma}/x_{ca}. \] By combining equations (7), (10) and (13), the following expressions for the local mole fractions in terms of overall mole fractions may be derived:

\[ x_{im} = x_i G_{im}/(x_a G_{am} + x_c G_{cm} + x_m G_{mm}) \quad (i = c, a, m) \quad (14-1) \]
\[ x_{ac} = x_a/(x_a + x_m G_{mc,ac}) \quad (14-1) \]
\[ x_{ca} = x_c/(x_c + x_m G_{ma,ca}) \quad (14-2) \]

In order to obtain an expression for the excess Gibbs energy, we first define \( g^{(a)}, g^{(c)}, \) and \( g^{(m)} \) as the residual Gibbs energies per mole of cells of central anion, central cation and central solvent molecule, respectively. These Gibbs energies are related to the local mole fractions as follows:

\[ g^{(a)} = z_a(x_{ma} g_{ma} + x_{ca} g_{ca}) \quad (15-1) \]
\[ g^{(c)} = z_c(x_{mc} g_{mc} + x_{ac} g_{ac}) \quad (15-2) \]
\[ g^{(m)} = x_{am} g_{am} + x_{cm} g_{cm} + x_{mm} g_{mm} \quad (15-3) \]

We then adopt the pure solvent as the reference state for the solvent, and a hypothetical pure completely-dissociated liquid electrolyte as the reference state for the electrolyte. The reference Gibbs energies per mole are then:

\[ g^{(c)}_{\text{ref}} = z_c g_{ac} \quad (16-1) \]
\[ g^{(a)}_{\text{ref}} = z_a g_{ca} \quad (16-2) \]
\[ g^{(m)}_{\text{ref}} = g_{mm} \quad (16-3) \]
In both equations (15) and (16) the charge number $Z_c$ and $Z_a$ are introduced to account for the fact that the ratio of the coordination number of central anion cells to that of central cation cells must be equal to the corresponding ratio of charge numbers.

The molar excess Gibbs energy may now be derived by summing the changes in residual Gibbs energy resulting when $x_m$ moles of solvent are transferred from the solvent reference state to their cells in the mixture, and when $x_a$ moles of anions and $x_c$ moles of cations are transferred from the electrolyte reference state to their respective cells in the mixture. The expression is:

$$g_{ex,1c} = x_m (g(m) - g_{ref}) + x_c (g(c) - g_{ref}) + x_a (g(a) - g_{ref})$$

Substituting equations (15) and (16) into equation (17) we obtain

$$g_{ex,1c}/RT = x_m x_c m c + x_m x_a m a + x_c x_m c m c + a + x_a x_m a m a + c a$$

The assumption of local electroneutrality applied to the cells of central solvent molecules may be stated as
\[ x_{am}^a = x_{cm}^c \]  

(19)

Substituting equation (7) into this relationship leads to the following equality:

\[ g_{am} = g_{cm} \]  

(20)

Since the interaction energies are symmetric, it may be inferred from this result that:

\[ \tau_{am} = \tau_{cm} = \tau_{ca,m} \]  

(21-1)

\[ \tau_{mc,ac} = \tau_{ma,ca} = \tau_{m,ca} \]  

(21-2)

The binary parameters \( \tau_{ca,m} \) and \( \tau_{m,ca} \) then become the only two independent adjustable parameters for a binary system of single completely-dissociated electrolyte and single solvent.

4.2. General Multicomponent Electrolyte Equation

The equations for binary systems presented above can be generalized to multicomponent systems consisting of any combination of weak and strong electrolytes, molecular solvents, and molecular solutes.

Since only two-body, first-neighbor interactions are considered with the local composition concept, the assumptions
for multicomponent electrolyte systems are the same as those of binary systems. No additional assumptions are required. For multicomponent electrolyte systems, the short-range excess Gibbs energy expression is

\[
g_{\text{ex,lc}}^{\text{RT}} = \sum_{m} x_{m} \left( \sum_{jm} x_{jm} \tau_{jm} \right) + \sum_{c} x_{c} z_{c} \left( \sum_{a',c'} x_{ja',c'} \tau_{ja',c'} / \alpha_{a',c',a''} z_{a''} \right) + \sum_{a} x_{a} z_{a} \left( \sum_{c'} x_{ja',c'} \tau_{ja',c'} / \alpha_{c',c''} z_{c''} \right) \tag{22}
\]

In the absence of electrolytes, the local composition model is exactly the same as the NRTL equation, which has been used widely for nonelectrolyte systems. Therefore, binary parameters of nonelectrolyte pairs, i.e., molecule-molecule interaction parameters, can be obtained from studies of binary nonelectrolyte systems. The local composition model offers a unified model for electrolytes and nonelectrolytes.

In addition to molecule-molecule parameters, there are three types of interaction parameters in the derived short-range excess Gibbs energy expression, equation (22). They are ion-molecule parameters, molecule-ion parameters, and ion-ion parameters. A practical problem in the generalization of the local composition model is that binary interaction parameters determined from binary electrolyte systems of single solvent and single completely-dissociated electrolyte are salt-molecule binary parameters while the real interacting
species in electrolyte systems are ions and molecules. In binary electrolyte systems, the problem is resolved by the following consequence of the local electroneutrality assumption:

\[
\begin{align*}
\tau_{cm} &= \tau_{am} = \tau_{ca,m} \\
\tau_{mc,ac} &= \tau_{ma,ca} = \tau_{m,ca}
\end{align*}
\] (21-1) (21-2)

In other words, ion-molecule interaction parameters are equal to salt-molecule binary parameters. This is not in general true for multicomponent systems. However, ion-molecule interaction parameters and molecule-ion interaction parameters can always be derived from salt-molecule binary parameters as a result of the local electroneutrality assumption and the like-ion repulsion assumption. Therefore salt-molecule binary parameters are still considered to be the adjustable parameters of the local composition model for multicomponent electrolyte systems.

Ion-ion interaction parameters are directly related to salt-salt binary parameters. There are no binary parameters for salt-salt pairs without common ion. If two salts, \(c' a\) and \(c'' a\), are of the same type, such as uni-univalent electrolytes, ion-ion interaction parameters \(\tau_{c'a, c''a}\) and \(\tau_{c''a, c'a}\) can be related as
\[ \tau_{c',a,c''a} = \frac{(g_{c',a} - g_{c''a})}{RT} \]
\[ = -\frac{(g_{c''a} - g_{c',a})}{RT} \]
\[ = -\tau_{c''a,c',a} \]  

(23)

This is because both \( g_{c',a} \) and \( g_{c''a} \) are considered as pure electrolyte properties. Equation (23) may not be valid if the two mixing electrolytes have different coordination numbers or are not of the same type. In this case of "unsymmetric mixing", \( g_{c',a} \) and \( g_{c''a} \) of multicomponent systems may be different from those of pure components because of the change in lattice structure.

Since data are not available for salt-salt binary systems, the only way to obtain binary salt-salt parameters is through data fitting of solvent-salt-salt ternary systems. This is a special characteristic of electrolyte systems.

4.3. Application of the Local Composition Model

A wide variety of data for mean ionic activity coefficients, osmotic coefficients, vapor pressure depression, and vapor-liquid equilibrium of binary and ternary electrolyte systems have been correlated successfully by the local composition model.
In general, data are fit quite well with the model. For example, with only two binary parameters, the average standard deviation of calculated $\ln \gamma^*$ versus measured $\ln \gamma^*$ of the 50 uni-univalent aqueous single electrolyte systems listed in Table 3-1 is only 0.009. Although the fit is not as good as the Pitzer equation, which applies only to aqueous electrolyte systems and requires two binary parameters and one ternary parameter (Pitzer, 1973a), it is quite satisfactory and better than that of Bromley's equation (1973).

Data correlation results for single-salt, single-solvent binary systems are shown in Table 3-1 to Table 3-6 and Figure 3-2 to Figure 3-4. There is an obvious trend between $\tau_{m,ca}$ and standard deviation of calculated $\ln \gamma^*$ versus measured $\ln \gamma^*$. When the absolute value of $\tau_{m,ca}$ increases, standard deviation also increases. This is consistent with the physical meaning of $\tau_{m,ca}$. The larger the absolute value of $\tau_{m,ca}$, the stronger the interaction between cation and anion. In other words, the ions tend to associate and lack of fit on data correlation can be related to this ion association. When this occurs, chemical equilibrium of ion association should be taken into consideration. Larger standard deviations were found for several higher valent electrolytes. It also should be noted that the electrolyte concentration in these systems is very high and it seems reasonable that association should occur to some extent.
The temperature dependence of the binary parameters was found to be exceedingly weak as shown in Tables 3-7 to 3-9 and Figure 3-5. These tables and the figure show the results of isothermal fits for activity coefficient data of aqueous NaCl and KBr at various temperatures. The Pitzer equation parameters are, however, strongly dependent on temperature (Silvester and Pitzer, 1976).

There can be many different types of ternary electrolyte systems. The HCl-KCl-H₂O system is an example of a two-electrolyte, one-solvent ternary electrolyte system. Several data correlation results for the activity coefficients of salts in ternary electrolyte systems of this type are shown in Table 4-1 and Figure 4-1. Water-salt binary parameters were obtained from Table 3-1. Salt-salt binary parameters were adjusted and found to be relatively small compared with water-salt binary parameters.

A second type of ternary electrolyte system is a solvent-supercritical molecular solute-salt system. The concentration of supercritical molecular solutes in these systems is generally very low. Therefore, the salting out effects are essentially effects of the presence of salts on the unsymmetric activity coefficient of molecular solutes at infinite dilution. The interaction parameters for NaCl-CO₂ binary pair and KCl-CO₂ binary pair are shown in Table 4-4. Water-salt
binary parameters were obtained from Table 3-1. Water-carbon dioxide binary parameters were correlated assuming dissociation of carbon dioxide in water is negligible. It is interesting to note that the Setschenow equation was found to be unsatisfactory for these two systems (Yasunishi and Yoshida, 1979).

Another type of ternary electrolyte system consists of two solvents and one salt, such as methanol-water-NaBr. Vapor-liquid equilibrium of such mixed-solvent electrolyte systems has never been studied with a thermodynamic model that takes into account the presence of salts explicitly. However, it should be recognized that binary parameters of solvent-salt binary pairs are functions of mixed-solvent dielectric constant since ion-molecule interaction energies, $g_{ma}$ and $g_{mc}$, depend on the reciprocal of solvent dielectric constant (Robinson and Stokes, 1970). Results of data correlation on vapor-liquid equilibrium of methanol-water-NaBr and methanol-water-LiCl at 298.15°K are shown in Tables 4-2 and 4-3. The dielectric constant dependence parameters were used as correlation parameters.

Vapor-liquid equilibrium data correlations were also carried out for a weak electrolyte system: the Hot Carbonate Process system. To apply the local composition model to weak electrolyte systems, chemical equilibrium among various species
must be taken into account. Undissociated weak electrolytes exist as molecular solutes, and dissociated weak electrolytes exist as ionic solutes. Isothermal data of partial pressures of carbon dioxide and water at 343.15°K, 363.15°K, 383.15°K and 403.15°K were obtained from Tosh et al. (1949) and fit independently. In addition, the data from these four temperatures were lumped together and fit, assuming temperature dependence of the form \( a + b/T \) for each of the binary parameters. The resulting parameters are given in Table 4-5. The same set of data has been correlated successfully using the extended Pitzer equation. With the same number of parameters, the local composition model gives slightly better results than the extended Pitzer equation.

5. Correlation of Vapor-Liquid Equilibrium Data for the Sour-Water Stripper System

The advent of restrictive pollution abatement guidelines and regulations has spurred development of phase equilibrium calculation methods required for the design of a type of column designated as a sour-water stripper. Its purpose is to process foul water containing ammonia, hydrogen sulfide and carbon dioxide by means of stripping steam injected into the bottom of the tower, or by means of reboiler-generated steam (Newman, 1978).
The system is very complex because of the number of species present and the number of equilibrium reactions in the liquid phase. The following seven reactions establish the chemical equilibrium in the liquid phase.

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} &= \text{NH}_4^+ + \text{OH}^- \\
\text{CO}_2 + \text{H}_2\text{O} &= \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- &= \text{H}^+ + \text{CO}_3^2- \\
\text{NH}_3 + \text{HCO}_3^- &= \text{NH}_2\text{CO}_2^- + \text{H}_2\text{O} \\
\text{H}_2\text{S} &= \text{H}^+ + \text{HS}^- \\
\text{HS}^- &= \text{H}^+ + \text{S}^2- \\
\text{H}_2\text{O} &= \text{H}^+ + \text{OH}^- 
\end{align*}
\]

The pioneering effort in correlating the data for \text{NH}_3-\text{CO}_2-\text{H}_2\text{S}-\text{H}_2\text{O} system and subsystems was due to Van Krevelen (1949), whose work was popularized by Beychok (1967). Very recently, Wilson (1978) and Mason (1978) have independently developed modifications to the Van Krevelen approach. Simplified forms of the Pitzer activity coefficient expression were applied along with a rigorous thermodynamic framework by Edwards et al. (1978) and Beutier and Renon (1978).

In this study, the extended Pitzer equation model and the local composition model were applied to the phase equilibrium of this industrially important system. The objectives were two fold: 1) to demonstrate the validities of both the extended
Pitzer equation and the local composition model to this complicated electrolyte system, 2) to obtain correlation parameters for the system for the use of process design and analysis. Vapor phase fugacity coefficients were calculated by the Nakamura et al. (1976) correlation. The chemical equilibrium constants, Henry's constants and Debye-Huckel constant were obtained from Edwards et al. (1978) and Chapter 2. The temperature dependence expression for the interaction parameters was assumed to be $a + b/T$.

No high concentration data for the complete system have been reported other than the data of Cardon and Wilson (Newman, 1979), whose data are known to contain significant experimental error. Therefore, no high concentration data correlation was carried out for the complete system. Instead, subsystem data were correlated to determine subsystem interaction parameters and partial pressures of the complete system were predicted based on these subsystem parameters. This strategy was adopted for both models.

The high concentration data of Otsuka et al. (1960) for the NH$_3$-CO$_2$-H$_2$O subsystem were correlated. Otsuka's data cover a temperature range from 293.15$^\circ$K to 393.15$^\circ$K and NH$_3$ concentration range from 1 molal to 11 molal. The ratio of ammonia molality to carbon dioxide molality, $R$, is always larger than 1. In other words, ammonia is always in excess
relative to carbon dioxide. Data points with very large $R$ or very small $R$ were excluded because in these cases either carbon dioxide partial pressure or ammonia partial pressure is very small and subject to large experimental errors. Forty-one selected data points were used for data correlation of the $\text{NH}_3$-$\text{CO}_2$-$\text{H}_2\text{O}$ subsystem. The least squares data correlation was carried out on partial pressures of $\text{NH}_3$ and $\text{CO}_2$.

The high concentration data of Miles and Wilson (1975) were correlated for the $\text{NH}_3$-$\text{H}_2\text{S}$-$\text{H}_2\text{O}$ subsystem. The 17 experimental data points have been correlated and reported by the Institute of Gas Technology (1979). The temperatures of these data are $353^\circ\text{K}$ and $393^\circ\text{K}$. The $\text{NH}_3$ concentration ranges from 0.44 molal to 22 molal and the $\text{H}_2\text{S}$ concentration ranges from 0.11 molal to 7.9 molal. The ratio of $\text{NH}_3$ molality to that of $\text{H}_2\text{S}$ ranges from 0.73 to 4.8. In other words, $\text{NH}_3$ or $\text{H}_2\text{S}$ can be in excess. The least squares data correlation was carried out on partial pressures of $\text{NH}_3$ and $\text{H}_2\text{S}$.

5.1. The Extended Pitzer Equation

The extended Pitzer equation with parameters determined from the subsystems predicts partial pressures of the complete system fairly close to those obtained by Badger and Silver
(1938) and Mason and Kao. Their data cover temperature from 293\textdegree K to 393\textdegree K and ammonia concentration up to 30 molality. Comparisons are shown in Tables 5-10 and 5-12. The average percentages of deviation of partial pressures of NH\textsubscript{3}, CO\textsubscript{2} and H\textsubscript{2}S are 12.2, 10.4 and 43.8 respectively for data of Badger and Silver; and 10.4, 13.2 and 17.4 respectively for data of Mason and Kao. Prediction of the Cardon and Wilson data is also satisfactory. The average percentage deviations of partial pressures of NH\textsubscript{3}, CO\textsubscript{2}, and H\textsubscript{2}S are 40.7, 26.5, and 30.9 respectively. These results are satisfactory considering the facts that no data correlation was carried out for the complete system and that Cardon and Wilson's data contains significant experimental errors.

5.2. The Local Composition Model

Partial pressures of NH\textsubscript{3}, CO\textsubscript{2}, and H\textsubscript{2}S were calculated and compared with the experimental data of Badger and Silver, Mason and Kao, and Cardon and Wilson. The results are given in Tables 5-17 to 5-19. It was found that the model predicts partial pressures very close to the experimental results of Badger and Silver, and Mason and Kao. The average percentage deviations of partial pressures of NH\textsubscript{3}, CO\textsubscript{2}, and H\textsubscript{2}S are 12.4, 12.4 and 9.4 respectively for the data of Badger and Silver; and 10.2, 10.6 and 15.2 respectively for the data of Mason and Kao. This is better than the results
obtained with the extended Pitzer equation. The average percentage deviations of partial pressures of \( \text{NH}_3 \), \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) are 40.0, 30.9 and 27.6 respectively for the data of Cardon and Wilson.

6. **The Inside-Out Algorithm for Single-Stage Flash with Chemical Equilibrium**

Strong electrolytes dissociate completely into ionic species in the liquid phase. Weak electrolyte dissociate partially into ionic species. The dissociation of electrolytes in solution occurs rapidly; hence, most electrolyte solutions closely approximate chemical equilibrium. Therefore, a robust, efficient algorithm for solving phase and chemical equilibria is essential for computer simulation of electrolyte systems.

In the literature, there are two classes of methods for calculating the equilibrium composition of a chemical system. One solves the set of nonlinear equations of phase equilibrium, material balance, enthalpy balance and chemical equilibrium with known reaction stoichiometry algebraically; the other minimizes the free energy of the system using nonlinear programming techniques. The first is called the K-value approach; the second is called the free energy minimization approach.
Previous algorithms for solving the simultaneous chemical and phase equilibrium problem by the K-value approach can be divided into three categories. The first one solves the chemical equilibrium relationships as the outside loop of the phase equilibrium relationships. The second method adopts the pseudo-K approach, in which pseudo-phase-equilibrium-constants are calculated so that phase equilibrium calculations can be performed with the assumption that no chemical reaction occurs. The third method solves the set of chemical and phase equilibrium equations simultaneously using general nonlinear equation solving techniques. The most successful algorithm is due to Sanderson and Chien (1973) and is a member of the first category in which linear mass balance constraints formed by the reaction stoichiometry are removed by increasing the dimensionality of the problem.

6.1. Problem Description for Nonelectrolyte Systems

For a chemical system involving the following reactions:

$$\sum_{i=1}^{N} \mu_{ij} A_i = 0 \quad j=1,2,\ldots,M; \quad (24)$$

the criterion of chemical reaction equilibrium can be written as

$$\sum_{i=1}^{N} \mu_{ij} \bar{G}_i(T,P,x) = 0 \quad j=1,2,\ldots,M \quad (25)$$
For nonelectrolyte systems, we choose the standard state as ideal gas at a pressure of $1.01325 \times 10^5$ pascal (1 atm). Then, the chemical equilibrium relationship becomes

$$
\Pi_{i=1}^{N} \left( \phi_i \right) x_i P/P_{\text{ref}}^{\mu_{ij}} = \exp \left( - \sum_{i=1}^{N} \mu_{ij} G_i / RT \right) = K_j(T) \quad j=1,2,\ldots M \quad (26)
$$

In addition to the $M$ chemical equilibrium equations (26) given above the following phase equilibrium, and mass and energy balance equations apply to the system.

Reaction component mass balance:

$$
f_i = f_{i*} + \sum_{j=1}^{N} \mu_{ij} \xi_j \quad i=1,2,\ldots N \quad (27)
$$

Extensive constitutive:

$$
F = \sum_{i=1}^{N} f_i \quad (28)
$$

Phase equilibrium:

$$
y_i = K_i x_i \quad i=1,2,\ldots N \quad (29)
$$

Phase component mass balance:

$$
x_i L + y_i V = f_i \quad i=1,2,\ldots N \quad (30)
$$

Phase total mass balance:

$$
L + V = F \quad (31)
$$
Enthalpy balance:
\[ H_L + H_V = (H^*F^* + Q)F/F^* \]  
(32)

Intensive constitutive:
\[ \sum_{i=1}^{N} x_i = \sum_{i=1}^{N} y_i \]  
(33)

Heat of reaction does not appear in equation (32) because all enthalpy values are element-based. The enthalpy of formation of each component has been taken into account in these element-based enthalpies.

For an \( N \)-component, \( M \)-reaction system, there are \( 3N+M+4 \) equations. The system is completely described when the values of the variables listed below are known.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T )</td>
<td>1</td>
</tr>
<tr>
<td>( P )</td>
<td>1</td>
</tr>
<tr>
<td>( V )</td>
<td>1</td>
</tr>
<tr>
<td>( L )</td>
<td>1</td>
</tr>
<tr>
<td>( Q )</td>
<td>1</td>
</tr>
<tr>
<td>( F )</td>
<td>1</td>
</tr>
<tr>
<td>( \xi )</td>
<td>( N )</td>
</tr>
<tr>
<td>( Y )</td>
<td>( N )</td>
</tr>
<tr>
<td>( \xi^* )</td>
<td>( M )</td>
</tr>
</tbody>
</table>

\[ 3N+M+6 \]

If we adopt the premise that \( F, \xi, x, y, \xi^* \), and \( L \) are always to be calculated, then there remains four variables \( (T, P, V, Q) \) of which two may be fixed in order to completely specify the
system. The six types of flash calculations that represent all possible combinations of specified quantities are listed in Table 6-1.

6.2. The Sanderson-Chien Algorithm

The single phase chemical equilibrium problem may be formulated as an M dimensional system of nonlinear equations. The feasible region for a solution of these equations is formed by a set of N linear inequality constraints that prevent negative compositions. The reaction extents are the independent variables and equations (26) are the equations to be satisfied. The nonnegativity constraints are that

\[ f_i > 0 \quad \text{i=1,2,...N} \]  \hspace{1cm} (34)

or

\[ \sum_{j=1}^{M} \mu_{ij} \xi_j > f^* i \quad \text{i=1,2,...N} \]  \hspace{1cm} (35)

in the extent space. The two phase problem can be solved by imbedding a flash calculation within the problem formulation given above. However, generalized methods for solving multivariable nonlinear equations within a linearly constrained region have not been satisfactory for the two phase chemical equilibrium problem because of the very strong nonlinearity and interaction of the problem in the extent space (Sanderson and Chien, 1973). Sanderson and Chien proposed to overcome this
difficulty by reformulating the problem with both extents \( \xi \) and component molar flowrates \( f_i \) as independent variables and including equations (27) in the system of equations to be solved. Therefore, the problem becomes one of solving a system of \( M+N \) nonlinear equations with only simple nonnegativity bounds on the component molar flowrate independent variables.

The Sanderson-Chien algorithm proceeds as follows:

1. Begin with initial estimates of the \( \xi_j \)'s and \( f_i \)'s.
2. Perform a flash calculation on \( f_i \)'s to get \( x_i \)'s and \( y_i \)'s.
3. If equations (26) and (27) are satisfied, exit.
4. Else, use a nonlinear equation solver to estimate new values of \( \xi_j \)'s and \( f_i \)'s and return to step 2.

Therefore, there are two loops in the algorithm. The outside loop is the chemical equilibrium loop. The inside loop is the phase equilibrium loop.

6.3. The Inside-Out Algorithm

Recently, an inside-out algorithm has been developed for performing multicomponent, single-stage, vapor-liquid equilibrium flash calculations (Boston and Britt, 1978). The main iteration variables are parameters of approximate physical
property models, rather than temperature, phase rates, and compositions. The algorithm is capable of solving wide-boiling, narrow-boiling, and highly nonideal systems and greatly reduces the computational load associated with enthalpy and equilibrium ratio evaluations, especially for "difficult" problems.

In this thesis, an inside-out algorithm was developed for performing multicomponent, single-stage flash with chemical equilibrium calculations. The new algorithm is a synergistic combination of the Boston-Britt algorithm for single-stage flash and the Sanderson-Chien algorithm for simultaneous chemical and phase equilibrium calculations. Simple models were first developed for the necessary physical properties. Complex calculations of fugacities and enthalpies are only performed to generate parameters of these simple physical property models. These simple model parameters then become the outer loop iteration variables. The phase and chemical equilibrium equations, reformulated in terms of the simple physical property models, are solved using a modified Sanderson-Chien algorithm. The chemical equilibrium loop becomes the middle loop and the phase equilibrium loop is the innermost loop. Since these equilibrium equations are expressed in terms of the simple physical property models, no complex calculations of fugacities and enthalpies are required in the middle and inner loops. Furthermore, the equilibrium
equations of the middle and inner loops become much more well-behaved because the simple physical property model parameters are independent of system compositions. The inner phase equilibrium loop is solved by adopting the Boston-Britt inner loop in which reformulated flash describing equations are solved in terms of a single variable $R$. In other words, the rigorous multicomponent flash step of the Sanderson-Chien algorithm has been replaced by a very simple root finding problem in one equation and one unknown.

The new algorithm simplifies the strong interaction between the chemical and phase equilibrium equations in the middle and inner loops by isolating the effects of system nonideality, that is, by moving them to the outer loop. The complex chemical and phase equilibrium problem is therefore free of the influence of system nonideality. Hence, the Sanderson-Chien algorithm, an effective mathematical approach to the calculations of simultaneous chemical and phase equilibria, is further enhanced since it includes heuristics based on the assumption of ideality. The Boston-Britt inner loop is an ideal choice of phase equilibrium loop for the new algorithm since the computational load associated with its solution is almost trivial and since, as a doubly nested loop, it is executed so many times.

The outer loop variables of the new algorithm are the
simple physical property model parameters. Since chemical
equilibrium expressions involve fugacity coefficients, it is
necessary to introduce a set of outer loop variables based on
fugacity coefficients. Because vapor fugacity coefficients
($\phi_v^i$'s) are ordinarily not strongly dependent on
temperature, pressure, or vapor phase composition, the
$\phi_v^i$'s themselves should be well-behaved iteration
variables. However, liquid fugacity coefficients ($\phi_l^i$'s)
depend strongly on temperature and liquid composition, $x$. To
account for the temperature dependence of the liquid fugacity
coefficients, the $K_b$ model used by Boston and Britt is
retained. Therefore, the simple models used for vapor and
liquid fugacity coefficients are

\begin{align}
\ln \phi_v^i &= \text{constant} \quad (36) \\
\ln \phi_l^i/K_b &= \text{constant} \quad (37) \\
\ln K_b &= A + B(1/T - 1/T^*) \quad (38)
\end{align}

and the outside loop iteration variables associated with the
fugacity coefficients are $\ln \phi_v^i$'s, $\ln(\phi_l^i/K_b)$'s, $A,$
and $B$. In other words, the volatility parameters ($\ln K_i/K_b$)
of the original Boston-Britt algorithm are replaced by the
individual phase quantities $\ln \phi_v^i$'s and $\ln(\phi_l^i/K_b)$'s.
Given values of the outer loop parameters, $K_b$ can be
calculated from equation (38) and, $\phi_v^i$'s from equation
(36), $\phi_l^i$'s from equation (37) and phase equilibrium
constants from

\[ K_i = \phi_i^V / \phi_i^L. \]  

(39)

The simple enthalpy models used in this work for the vapor and liquid enthalpy departure functions are

\[ \Delta H_L / W_L = E + F (T - T^*) \]  

(40)

\[ \Delta H_V = C + D (T - T^*) \]  

(41)

where \( W_L \) is the liquid phase average molecular weight. Equation (40) is adopted by recognizing that, on a mass basis, vaporization enthalpies do not vary widely from component to component.

In summary, the simple physical property model parameters of the outer loop are \( \ln \phi_i^V \)'s, \( \ln (\phi_i^L / K_b) \)'s, A, B, C, D, E, and F.

The middle loop of the new algorithm is a modification of the Sanderson-Chien algorithm. The Sanderson-Chien residual functions are modified to eliminate scaling problems. The chemical equilibrium equations, equations (26), are redefined as

\[ S_j = 1 - \sum_{i=1}^{N} \mu_{ij} \ln (\phi_i x_i P / P_{ref}) / \ln K_j \quad j = 1, 2, \ldots, M \]  

(42)
The reaction component mass balance equations, equations (27), are redefined as

\[ S_{i+M} = (f_i - f^* - \sum_{j=1}^{M} \mu_{ij} \xi_j)/F \quad i=1,2,...,N \]  

(43)

The iteration variables of the middle loop are reaction extents \( \xi_j 's \) and logarithms of equilibrium component flow rates \( \ln f_i 's \). The system of \( M+N \) nonlinear equations is solved using Newton's method.

The original Sanderson-Chien algorithm used \( \xi_j 's \) and \( f_i 's \) as the iteration variables, which required strict inequality constraints on the \( f_i 's \) \( (f_i > 0) \). The change from \( f_i 's \) to \( \ln f_i 's \) is a transformation of variables to remove these constraints. This is particularly advantageous for problems with some \( f_i 's \) residing near the constraints, such as trace components. The logarithms also make equations (42) more linear and better-behaved.

Each iteration of the middle loop yields estimates of \( \xi_j 's \) and the \( \ln f_i 's \). With these values for \( \ln f_i \) the phase equilibrium equations are solved using the inner loop of the Boston-Britt algorithm. The only modification required here is the enthalpy balance which is written as

\[ (L/F)(\Delta H_v - \Delta H_l) - \sum_{i=1}^{N} v_i \hat{H}^{IG}_i /F - \Delta H_v + (H^* + Q)F/F^* = 0 \]  

(44)
in order to take into account the changing total number of moles.

The calculation of chemical equilibrium (middle) and phase equilibrium (inner) loops proceeds as follows:

1) Initialize $\xi_j = 0$ \hspace{1cm} j = 1, 2, \ldots, M
    
    $l_{nf_i} = l_{nf*_i}$ \hspace{1cm} i = 1, 2, \ldots, N
    
    (if $f*_i = 0$, set $f_i$ to $1 \times 10^{-5}$)

    If better estimates are available, they are used.

2) Calculate $S_k$, k = 1, 2, \ldots, M+N, solving the Boston-Britt reformulated phase equilibrium inner loop to obtain $T$, $P$, $V$, $x$ and $y$.

3) Calculate the partial derivative (Jacobian) matrix, $J$, numerically or analytically.

4) Obtain new values for $\xi_j$ and $l_{nf_i}$ using Newton's method.

    $$\Delta \left( \frac{\xi}{l_{nf}} \right) = -y^{-1}S$$

5) Return to step 2 and repeat until $S_k$'s are smaller than the convergence tolerance.

6.4. Considerations for Electrolyte Systems

To apply the new algorithm to electrolyte systems, two fundamental differences between electrolyte systems and
nonelectrolyte systems must be recognized. One is the choice of standard states of electrolyte systems. The other is the fact that ionic species of electrolyte systems are nonvolatile.

For single-solvent electrolyte systems, such as aqueous electrolyte systems, the most common standard state of the solvent species is the pure, condensed solvent at the system temperature and pressure. The standard state of the solutes species is the limiting state in which solute concentrations become infinitely dilute. Based on these standard states, the chemical equilibrium relationships can be written as follows:

$$
\prod_{i=1}^{N} \left( \gamma_i x_i \right)^{\mu_{ij}} = \exp \left( - \sum_{i=1}^{N} \mu_{ij} G_i^0 / RT \right) = K_j^0 (T) \quad j=1,2,...,M \quad (45)
$$

where $\gamma_i$'s are symmetric activity coefficients for solvents and infinite dilution activity coefficients for solutes. Also, the standard state free energies of solutes are the infinite dilution free energies, i.e., $G_i^0 = G_i^\infty$.

Although the standard states of electrolyte systems are different from those of nonelectrolyte systems, the inside-out algorithm is applicable to electrolyte systems. However, since ionic species are nonvolatile, liquid activity coefficients, instead of fugacity coefficients, are the essential physical property for chemical equilibrium relationships. Compared with
liquid fugacity coefficients, liquid activity coefficients are relatively independent of temperature and pressure. Hence, the $\ln \gamma_i$'s themselves should be suitable as outer loop iteration variables and are so used for the ionic species in electrolyte systems.

Actually, fugacity coefficients have not been defined for "nonvolatile" ionic species in the literature. However, in order to perform phase equilibrium calculations, phase equilibrium constants, vapor fugacity coefficients, and liquid fugacity coefficients of nonvolatile species are defined as follows:

$$K_i \equiv \frac{1}{\phi_i^{\text{V}}} \quad \phi_i^{\text{V}} = 1$$  
$$\phi_i = 0$$  

Therefore, the outer loop variables are $\ln \phi_i^{\text{V}}$'s, $\ln(\phi_i^{\text{1}}/K_B)$'s, A, B, C, D, E, and F with $\ln(\phi_i^{\text{1}}/K_B)$'s replaced by $\ln \gamma_i$'s if component i is nonvolatile.

The electroneutrality of electrolyte systems is automatically satisfied by the reaction component mass balance equations, equation (27), since $f^*$ is assumed to satisfy charge
balances. Two other noteworthy characteristics of electrolyte systems are 1) chemical reactions occur only in the liquid phase; 2) trace component concentrations may be critical for chemical equilibrium constraints because these constraints are very sensitive to trace component concentrations.

6.5. Electrolyte Examples

To test the performance of the inside-out algorithm on electrolyte systems, the Hot Carbonate Process system was used as the example electrolyte system. The three reactions occurring in the aqueous phase are

\[ \text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+ \]
\[ \text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \]
\[ \text{H}_2\text{O} = \text{OH}^- + \text{H}^+ \]

The liquid activity coefficients were calculated with the local composition model. The binary parameters and other physical property constants are shown in Table 6-6. Ideal vapor phase was assumed. Because no thermal data were available, only TP, TV and PV flashes were performed. With complete dissociation of potassium carbonate and potassium bicarbonate, the Hot Carbonate Process system contains initially
Species | Mole fraction
---|---
water | 0.81
carbon dioxide | 0.03
potassium ion | 0.10
hydrogen ion | 0.00
bicarbonate ion | 0.02
carbonate ion | 0.04
hydroxide ion | 0.00
molal flowrate | 100

Iteration history and results are shown in Table 6-7.

Recently, a free energy minimization algorithm was proposed for phase and chemical equilibrium of electrolyte systems (Gautam and Seider, 1979). Their algorithm is a nonstoichiometric algorithm and is based on the Rand method (White et al., 1958). As discussed by Smith (1980), nonstoichiometric algorithms can encounter numerical difficulties with the singularity of the coefficient matrix. Another inherent problem with their algorithm is that the free energy objective function is insensitive to trace components which can be very important for electrolyte systems. Examples are hydrogen ion and hydroxide ion concentrations. Furthermore, their algorithm is limited to the isothermal case. Therefore, it is believed that the new inside-out algorithm proposed here is superior to the free energy minimization algorithm.
7. Design of Electrolyte Simulation Capabilities Using ASPEN As the Basic Simulator

Two fundamental problems in the computer simulation of chemical processes with electrolytes have been 1) representation of the thermodynamic properties of electrolyte solutions and 2) simultaneous chemical and phase equilibrium calculations for electrolyte systems. These two problems have been the main obstacles in the use of modern process simulators for analysis and design of processes involving electrolytes. The development of the extended Pitzer equation, the local composition model, and the inside-out algorithm described in the previous chapters has made it feasible to use process simulators for chemical processes with electrolytes.

The most important characteristics of chemical processes with electrolytes can be attributed to the following points. First, electrolytes dissociate in solution and form ions. The presence of ions introduces ionic charges and the electroneutrality constraint. Second, weak electrolytes dissociate partially. Chemical equilibrium among various species should always be considered in addition to phase equilibrium. Third, strong electrolytes may precipitate as the solution becomes saturated. Solid handling capability is a necessity.
Although there has not been a general-purpose process simulator for electrolyte systems, there have been many significant developments in the technology of process simulation for nonelectrolyte systems. In the design of electrolyte process simulation techniques, it is the most desirable to build upon present technology of process simulation while taking into consideration the specific characteristics of chemical processes with electrolytes. ASPEN, a public, state-of-the-art process simulator designed for a broad range of chemical processes, was therefore chosen in this work as the basic simulator for the development of electrolyte simulation capabilities.

Various aspects in the simulation of electrolyte systems were considered. These include specification of components for electrolyte systems, structure of streams, physical property and data bank requirements, unit operation modeling strategy, consideration of flowsheet convergence, design of input language, and basic system concepts. Although the study was based on the ASPEN simulator, most of the simulation techniques should be equally applicable to other process simulators. The advanced features of ASPEN also make the development and incorporation of electrolyte simulation capabilities particularly amenable and attractive. It was concluded that it is both feasible and beneficial to incorporate electrolyte simulation capabilities into ASPEN as a process simulator for chemical processes with electrolytes.
8. Conclusions and Recommendations

8.1. General Conclusions

The extended Pitzer equation provides a consistent and unified model for the excess Gibbs energy of aqueous electrolyte systems with any number of ionic and molecular solutes. Under limiting conditions, the extended Pitzer equation reduces to the well-known Setschenow equation for the salting-out effect of molecular solutes.

The local composition model offers an excess Gibbs energy expression for the representation of thermodynamic properties of mixtures of strong electrolytes, weak electrolytes, molecular solutes, and multiple solvents. In the absence of electrolytes, the model reduces to the Nonrandom, Two-Liquid equation. It is particularly advantageous since only binary parameters are required for multicomponent systems. Thus, it facilitates estimation of properties of multicomponent systems from its constituent subsystems.

The inside-out algorithm for single-stage flash with chemical equilibrium demonstrates a general approach for modeling of various unit processes of electrolyte systems. The algorithm is very efficient computationally and exhibits robust and stable convergence behavior. It is especially suited for
use in process simulation systems in which the above characteristics are desirable.

As a result of these developments, the use of modern process simulators for analysis and design of processes involving electrolytes is now feasible. A study based on the ASPEN simulator concludes that electrolyte simulation capabilities can be incorporated into modern process simulators.

8.2. Recommendations

In spite of the numerous findings of this study, many challenging questions remain. The following topics are recommended for further research.

(1) A general expression for correlating mixed-solvent dielectric constants with solvent composition, or a mixing rule for estimating mixed-solvent dielectric constants would be extremely helpful for calculating both the short-range and long-range interaction contribution to the excess Gibbs energy of electrolyte systems.

(2) Many different Debye-Huckel expressions have been proposed in the literature. A study should be carried out to find the best form of Debye-Huckel expressions to be used in the local composition model.
(3) A new least squares formulation for phase equilibrium data correlation of weak electrolyte systems is needed to efficiently handle the liquid phase chemical equilibrium.

(4) A study of liquid-liquid equilibrium of electrolyte systems using the local composition model is important because salt concentration can affect phase splitting.

(5) The inside-out algorithm of Chapter 6 should be extended to predict salt precipitation, to perform single-stage liquid-liquid equilibrium calculations, and multi-stage separation calculations.

(6) The modeling of mass-transfer-limited processes with chemical reactions is particularly important for electrolyte systems and should be studied.

(7) Incorporation of electrolyte simulation capabilities into ASPEN is recommended.
Notation

\( A_\phi \): Debye-Huckel constant for the osmotic coefficient
\( A_i \): chemical species \( i \)
\( A, B \): \( K_b \) model coefficients
\( B_{ca} \): binary ion-ion interaction parameter
\( C_{ca} \): ternary ion-ion interaction parameter
\( D_{ca,m} \): binary salt-molecule interaction parameter or Setschenow constant
\( C, D \): vapor enthalpy model coefficients
\( E, F \): liquid enthalpy model coefficients
\( F \): total molal flowrates of the system (Kg-mole/sec)
\( F^* \): total molal flowrates of the feed (Kg-mole/sec)
\( G_{ex} \): excess Gibbs free energy
\( G_i \): Gibbs free energy of formation of component \( i \) (j/Kg-mole)
\( G^*_i \): chemical potential of component \( i \) (j/Kg-mole)
\( H^* \): feed enthalpy (j/Kg-mole)
\( H \): enthalpy (j/Kg-mole)
\( \Delta H \): enthalpy departure (j/Kg-mole)
\( H \): Henry's constant (atm Kg/g-mole)
\( I \): ionic strength (=1/2 \( \sum_i Z_i^2 \))
\( K_i \): phase equilibrium ratio for component \( i \)
\( K_j \): chemical equilibrium constant for reaction \( j \)
\( K_b \): \( K_b \) model of the inside-out algorithm
\( L \): total molal flowrates of liquid phase (kg-mole/sec)
\( M \): number of reactions
\( N \): number of components
\( P \): system pressure (N/m²)
\( P_{ref} \): reference pressure (1.01325*10^5 N/m²)
\( Q \): heat duty (j/sec)
\( R \): universal gas constant
\( S \): sum of squares of objective functions
\( T \): temperature (K)
\( V \): total molal flowrates of vapor phase (Kg-mole/sec)
\( W_l \): liquid phase molar average molecular weight
\( Z \): absolute value of ionic charge
\( f_{i} \): molal flowrates of component \( i \) in the system (Kg-mole/sec)
\( f^*_{i} \): molal flowrates of component \( i \) in the feed (Kg-mole/sec)
\( g_{ex} \): molar excess Gibbs energy
\( m \): molality (g-mole/Kg of solvent)
\( n_w \): number of Kg of the solvent, water
\( x_i \): mole fraction of component \( i \) in liquid phase
\( Y_i \): mole fraction of component \( i \) in vapor phase
Greek letters

$\beta$ : parameters of the empirical expression of $B(I)$
$\psi$ : ternary ion-ion difference parameter
$\phi$ : fugacity coefficient
$\lambda$ : second virial coefficient of the basic Pitzer equation
$\omega$ : binary salt-molecule difference parameter
$\mu$ : third virial coefficient of the basic Pitzer equation
$\gamma$ : stoichiometric coefficient of the reaction
$\tau$ : activity coefficient
$\sigma$ : standard deviation
$\xi$ : interaction parameter of the local composition model

Extent of reaction

Superscripts

IG : ideal gas standard state
l : liquid
lc : local composition model
v : vapor
$\infty$ : infinite dilution standard state
* : unsymmetric convention

Subscripts

$a,a'$ : anion
c,c' : cation
i,j,k : solute
i : component index
j : reaction index
m : molecular solute
ref : reference
w : water
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Chapter 1
Introduction

Techniques for simulating industrial-scale chemical processes have evolved over the past twenty years, and steady-state process simulators have been widely accepted as a basic design tool in the chemical industry. Most of the large chemical, petroleum, and construction companies have access to an in-house simulator or a simulator provided by a commercial organization. Many steady-state process simulators have therefore been developed to meet different needs. Examples are CHESS, CONCEPT, FLOWTRAN, SSI/100, etc. (Evans, et al., 1976). However, most of these process simulators were developed for processes in the petroleum-refining and petrochemical industries and are capable of simulating processes containing only organic hydrocarbons or nonelectrolytes. The tremendous advantages of using a process simulator for fast, rigorous, and optimal design of chemical processes with electrolytes has not been exploited.

Electrolytes occur very widely in the chemical industry. Two well-known processes are acid-gas removal and sour-water stripping. Some other examples are absorption of CO₂ and Cl₂ in an aqueous solution of barium sulfide for the manufacture of BaCO₃ and BaCl₂, absorption of NO₂ in water for the production of HNO₃, distillation of
salt-containing systems, crystallization of salts from electrolyte solutions, and recovery of precious metals with ion exchangers.

State-of-the-art of Computer Simulation of Chemical Processes with Electrolytes

Although there is no general process simulator capable of simulating electrolyte processes, the advantages of computer simulation have been recognized. There are computer programs developed to meet special needs, such as sour-water stripping simulation, crystallization, and leaching.

A recent paper by Melin, Niedzwiecki and Goldstein (1975) indicates that, for sour water strippers, a program was developed by EXXON that solves the liquid phase ionic equilibria for each stage and then calculates an activity correction to be used in vapor-liquid equilibrium calculation. A Newton-Raphson approach was used to solve the heat and material balances around each theoretical stage.

In a survey of software for chemical engineers, Peterson, Chen, and Evans (1978) identified several programs capable of handling electrolytes. Most of the crystallization and leaching programs are primitive and are of limited use. Of special interest are two programs developed by OLI Systems, Inc. FRACHEM is a fractionation program capable of simulating
different fractionator configurations. The imbedded thermodynamic framework for electrolyte systems, ECES program (Zemaitis, 1975), allows the complete description of electrolyte systems to be developed from simple mass law balances entered by the user describing the ionic reactions taking place in solution. The heat, material, and equilibrium relationships describing the fractionator are solved by the Newton-Raphson method. ECES is a computer program to predict the equilibrium concentrations of electrolyte systems. Facilities include a data bank of about 200 species and procedures to handle calculations of two or three phase equilibria. The user states the problem in terms of a list of species in solution and chemical equilibrium relations of interest.

A follow-up software survey (Chen and Evans, 1979) identified another program capable of handling an electrolyte process. Sour Water Stripper Program, developed by Elshout & Associates, performs a tray-by-tray heat and material-balance calculation. Input to the program includes the sour-water feed composition, stripping steam rate, condenser temperature and pressure, tray efficiency, and number of actual plates. Output from the program includes flow rates and compositions from each theoretical stages. Either the Van Krevelen or the API correlation of NH₃, CO₂, and H₂S volatility data from aqueous sour-water systems can be selected.
Another computer model was developed specifically for cooling tower water systems (Noblett, et al., 1979). The model is a multicomponent aqueous ionic equilibrium program. The classical Newton-Raphson procedure is used to solve aqueous phase equilibrium equations. The model is limited to cooling tower water systems with temperature less than 60°C and ionic strength less than 3 molality.

Compared with the state-of-the-art computer simulators being used in the petroleum and petrochemical industries, the programs available for electrolyte systems are under-developed. These programs are designed for specific units or systems. Most of them are unsophisticated and limited in scope. More sophisticated programs are proprietary and not available in the public domain. Development of a general-purpose, steady-state simulator for chemical processes with electrolytes is a definite need.

**Thesis Objectives**

Two fundamental considerations in computer simulation of electrolyte processes are electrolyte thermodynamics and unit operation modeling.

The key concern of electrolyte thermodynamics is to find an excess Gibbs energy expression which provides a good
approximation for the properties of electrolyte systems of interest. The absence of suitable correlations for the excess Gibbs energy of electrolyte systems has been one of the major reasons for the lack of development in computer simulation of electrolyte systems.

The main problem with unit operation modeling of electrolyte systems is the single-stage flash calculation, or simultaneous chemical and phase equilibrium calculations. Strong electrolytes dissociate completely into ionic species in the liquid phase with solubility product constraints. Weak electrolytes dissociate partially into ionic species. The dissociation of electrolytes in solution occurs rapidly; hence, most solutions closely approximate chemical equilibrium. Therefore, a robust, efficient algorithm for solving phase and chemical equilibria is essential for computer simulation of electrolyte systems. Multistage separation of electrolyte systems can be modeled with single-stage flash models.

The first objective of this research is to study electrolyte thermodynamics and to develop appropriate thermodynamic models for the excess Gibbs free energy. The excess Gibbs free energy models are required to carry out phase equilibrium calculations, such as vapor-liquid equilibrium, liquid-liquid equilibrium, or solid-liquid equilibrium of electrolyte systems. The models should be applicable to strong
electrolytes, weak electrolytes, and molecular solutes in both aqueous and mixed-solvent electrolyte systems. Important industrial electrolyte systems will be studied to illustrate the validity of the models.

The second objective is to develop an algorithm that can calculate rigorously single-stage flash with chemical equilibrium. Due to the complex nature of electrolyte systems, the algorithm should be reliable, robust and efficient. It is expected that the algorithm will serve as the basic tool when modeling various process units involving electrolytes. Therefore, the algorithm should also be capable of handling various specifications.

The third objective of this study is to design a basic, general framework compatible with the ASPEN simulator for simulating chemical processes with electrolytes. ASPEN is a next-generation steady-state process simulator developed for fossil-fuel conversion processes (Evans, et al., 1976). It will be in widespread use around the world in the 1980's. Potential benefits of being able to simulate electrolyte systems under ASPEN are tremendous. It is hoped that a general-purpose, steady-state process simulator for chemical processes with electrolytes will eventually result.
Thesis Overview

Chapter 2 presents the extension and application of the Pitzer equation for vapor-liquid equilibrium of aqueous electrolyte systems with molecular solutes. The Pitzer equation was designed for convenient and accurate representation of aqueous strong electrolytes (Pitzer, 1973). However, in most aqueous electrolyte systems of industrial interest, not only strong electrolytes but also weak ones and molecular nonelectrolytes are present. A unified thermodynamic model for both ionic solutes and molecular solutes is required to model these electrolyte systems. Therefore, the Pitzer equation was extended in a thermodynamically consistent manner to allow for molecular and well as ionic solutes. Under limiting conditions, the extended model reduces to the well-known Sestchenow equation for the salting out effect of molecular solutes.

The Pitzer equation is a virial-expansion type equation and subject to all of the limitations of a virial-expansion type equation. The equation parameters, denoting the short-range interactions between and among solute species, are arbitrary, temperature-dependent and are characteristic of the solvent. Therefore, although the Pitzer equation has been shown to be a successful model for aqueous electrolytes, a more versatile model is needed to cover a wider variety of electrolyte systems.
Chapters 3 and 4 describe a local composition model for the excess Gibbs energy of electrolyte systems. Nonelectrolyte systems, which are characterized by short-range forces between molecules, have frequently been studied using the local composition concept. Although the local composition concept is in no sense rigorous, the models employing the concept, such as Wilson (1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975), have been proven to be very successful and widely accepted. In this study, the local composition concept is adopted to account for the contribution from short-range interactions occurring in the electrolyte systems. The model is designed to apply to mixed-solvent, multi-electrolyte systems over a wide range of electrolyte concentration without the need for ternary or higher order parameters.

Chapter 5 reports the results on vapor-liquid equilibrium data correlation of the NH$_3$-CO$_2$-H$_2$S-H$_2$O system. Phase equilibrium calculation of the NH$_3$-CO$_2$-H$_2$S-H$_2$O system is required for the design of sour-water strippers. Both the extended Pitzer equation and the local composition model have been successfully applied to this industrially important system.

Chapter 6 proposes an algorithm for single-stage flash with chemical equilibrium. The algorithm is based on the inside-out approach used by Boston and Britt (1978) for single-stage flash
and the Sanderson-Chien algorithm (Sanderson and Chien, 1973) for simultaneous chemical and phase equilibrium calculations. Because of the complexity of the problem due to strong interaction between chemical and phase equilibria, the advantages of the inside-out approach are fully utilized.

Finally, Chapter 7 considers various aspects in the design of electrolyte simulation capabilities based on the extension of the ASPEN simulator. It involves specification of components for electrolyte systems, structure of streams, identification of pertinent physical property and unit operation models, consideration of flowsheet convergence, design of input language, and basic system concepts.

Literature Cited


Chapter 2
Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes

Abstract

The semi-empirical Pitzer equation for modeling equilibrium in aqueous electrolyte systems has been extended in a thermodynamically consistent manner to allow for molecular as well as ionic solutes. Under limiting conditions, the extended model reduces to the well-known Sellschenow equation for the salting out effect of molecular solutes. To test the validity of the model, correlations of vapor-liquid equilibrium data were carried out for three systems: the hydrochloric acid aqueous solution at 298.15°K and concentrations up to 18 molal; the NH₃-CO₂ aqueous solution studied by Van Krevelen et al. (1949) at 293.15°K; and the K₂CO₃-CO₂ aqueous solution of the Hot Carbonate Process with temperatures from 343.15°K to 413.15°K and concentrations up to 40 weight percent equivalent potassium carbonate. The success of the correlations suggests the validity of the model for aqueous electrolyte systems of industrial interest.
Scope

The use of modern process simulators for analysis and design of processes involving electrolytes has been greatly limited by the lack of adequate correlations for electrolyte thermodynamics. For most systems of industrial importance, empirical correlations are applicable only to one particular system, over a limited range of conditions. The empirical correlations do not provide a framework for treating new systems or for extending the range of existing data, because the nonidealities have not been accounted for in a general and consistent manner.

Aqueous electrolyte systems are common in the chemical industry. One example of interest is the potassium carbonate aqueous solution used in the Hot Carbonate Process as the acid gas removal agent in coal conversion plants. The Hot Carbonate Process was developed by the U.S. Bureau of Mines as part of a program on the synthesis of liquid fuel from coal. It provides an economical chemical absorption process for removing large quantities of CO₂ from synthesis gases (Riesenfeld and Kohl 1974).

Knowledge of the equilibrium solubility of carbon dioxide in the potassium carbonate aqueous solution is essential to the design of the Hot Carbonate Process. A large amount of
comprehensive physical data on the $\text{K}_2\text{CO}_3$-$\text{CO}_2$ aqueous solution system is available in the literature. However, due to inability to properly correlate electrolyte thermodynamics, empirical equations or nomographs of the vapor-liquid equilibrium data have been used as basic design tools (Bocard and Mayland 1962, Maddox and Burns 1967, Mapstone 1966, Wen 1971).

Recently, there have been a number of significant developments in the modeling of electrolyte behavior. Bromley (1973), Meissner and Tester (1972), Meissner and Kusik (1972), Pitzer and co-workers (1973a, 1973b, 1974, 1976), and Cruz and Renon (1978), presented models for calculating the mean ionic activity coefficients of many types of aqueous electrolytes. In addition, Edwards et al. (1975) proposed a thermodynamic framework to calculate equilibrium vapor-liquid compositions for aqueous solutions of one or more volatile weak electrolytes which involve activity coefficients of ionic species. Most recently, Beutier and Renon (1978) and Edwards et al. (1978) used simplified forms of the Pitzer equation to represent ionic activity coefficients.

The purposes of this study are to 1) reformulate the Pitzer equation in a more rigorous way, to obtain a thermodynamic model for aqueous electrolyte systems containing both ionic and molecular solutes, and 2) apply the model to various aqueous
electrolyte systems encountered in industry to demonstrate its validity.

**Conclusions and Significance**

Extending Pitzer equation, a thermodynamic model for both ionic and molecular solutes in aqueous electrolyte systems is obtained. Model parameters include binary ion-ion interaction and difference parameters, ternary ion-ion interaction and difference parameter, salt-molecule interaction parameters or Setschenow constants, salt-salt difference parameters for molecular solute salting, and unsymmetric Margules parameters for molecule-molecule interaction. Like the Pitzer equation, the model is designed for convenient and accurate representation and to predict aqueous electrolyte systems, including mixtures with any number of molecular and ionic solutes.

With this model, vapor-liquid equilibrium data for three systems are correlated. Significant parameters in the model for each system of interest are identified by a preliminary order of magnitude analysis and adjusted in the vapor-liquid equilibrium data correlation. The results show satisfactory agreement between experimental equilibrium vapor pressure data and the correlations, and, therefore, suggest the validity of the model for aqueous electrolyte systems of industrial
interest.

* * *

A molecular thermodynamic framework for vapor-liquid equilibrium of aqueous electrolyte systems containing both ionic and molecular solutes has been proposed by Edwards et al. (1975). Vapor pressures of ionic solutes are taken as negligible. The vapor-liquid equilibrium relationship for molecular solutes is

$$y_m \phi_m^{P=m} \gamma_m^{*H_m} (p_w^S) \exp \frac{\eta_m(p-p_w^S)}{RT}$$

(1)

Similarly, the vapor-liquid equilibrium expression for the solvent, water, is

$$y_w \phi_w^{P=a_w p_w^S} \phi_w^S \exp \frac{\eta_w(p-p_w^S)}{RT}$$

(2)

To correlate vapor-liquid equilibrium data using these expressions requires models for water activity and solute activity coefficients. From an expression for the excess Gibbs free energy of a system and its partial derivatives, all of the activities and activity coefficients of interest can be computed. The next several sections of this article are concerned with the excess Gibbs free energy of aqueous electrolyte systems.
The Pitzer Equation

In a continuing series of papers, Pitzer and his co-workers (1973a, 1973b, 1974) proposed a very useful semiempirical equation for the unsymmetric excess Gibbs free energy of aqueous electrolyte systems. The basic equation is

$$G^e_{ij} = f(I) + \sum I_{ij} \lambda_{ij} + \sum I_{ijk} \lambda_{ijk}$$

where $i, j$ and $k$ can be any solutes.

The function $f(I)$ expresses the effect of long-range electrostatic forces between ions. It takes into account the hard-core effects in Debye-Hückel theory, and is a function of ionic strength, temperature and solvent properties. The empirical form chosen by Pitzer for $f(I)$ is

$$f(I) = -A_{\phi} \frac{4I}{1.2} \ln(1+1.2\sqrt{I})$$

where $A_{\phi}$ is the usual Debye-Hückel constant for the osmotic coefficient. Values of the Debye-Hückel constant were tabulated as a function of temperature in Silvester and Pitzer's paper (1976) and these values have been correlated in this study as a cubic function of temperature. The correlation result is given in Table 1.
Table 1. Expressions for Debye-Hückel Coefficient, Henry's Constants and Equilibrium Constants

\[ A_\phi^a = -1.306568 + 0.1328238D - 1(T) - 0.3550803D - 4(T^2) + 0.3381968D - 7(T^3) \]

\[ \ln H_{\text{CO}_2}^a = -8477.711(1/T) - 21.95743\ln(T) + 0.005780748(T) + 155.1699 \]

\[ \ln H_{\text{NH}_3}^b = -157.552(1/T) + 28.1001 \ln(T) - 0.049227(T) - 149.006 \]

\[ pK_{\text{HCl}}^c = -3.8 \text{ (at } 298.15^\circ\text{K)} \]

\[ \ln K_{\text{NH}_3}^b = -3335.7(1/T) + 1.4971 \ln(T) - 0.0370566(T) + 2.76 \]

\[ \ln K_{\text{NH}_2\text{COO}^-}^b = -8.6 + 2900(1/T) \]

\[ \ln K_{\text{CO}_2}^b = -12092.1(1/T) - 36.78161\ln(T) + 235.482 \]

\[ \ln K_{\text{HCO}_3^-}^b = -12431.7(1/T) - 35.48191\ln(T) + 220.067 \]

\[ \ln K_{\text{H}_2\text{O}}^b = -13445.9(1/T) - 22.47731\ln(T) + 140.932 \]

\[ ^a \text{Correlated in this study.} \]

\[ ^b \text{Obtained from Edwards et al. (1978).} \]

\[ ^c \text{Obtained from Cruz and Renon (1978).} \]
The parameters \( \lambda_{ij} \) are second virial coefficients giving the effect of short-range forces between solutes \( i \) and \( j \); the parameters \( \mu_{ijk} \) are corresponding third virial coefficients for the interaction of three solutes \( i, j, \) and \( k \). The second virial coefficients for ion-ion interactions are a function of ionic strength. However, dependence of the third virial coefficients on ionic strength is neglected. The \( \lambda \) and \( \mu \) matrices are taken to be symmetric, i.e., \( \lambda_{ij} = \lambda_{ji} \) etc.

To make the basic Pitzer equation more useful for data correlation of aqueous strong electrolyte systems, Pitzer modified it by defining a new set of more directly observable parameters to represent certain combinations of the second and third virial coefficients. The modified Pitzer equation is

\[
\frac{G_{\text{ex}}}{n_{\text{w}RT}} = f(I) + \sum_{c'c} m_{c'} m_{c} \left( \frac{\theta_{c'c} + \frac{1}{2} \sum_{a} \psi_{c'c'a}}{a_{c}^{'}} \right) + \sum_{a'c} m_{a'} m_{c} \left( \frac{1}{2} \sum_{c} \psi_{a'a'c} \right) + 2 \sum_{c} m_{c} \left[ B_{c} (I) + \frac{\sum_{c'c} m_{c'} Z_{c'} c_{c'}}{\sqrt{Z_{c'} Z_{c}}} \right] c_{a} \tag{5}
\]

where \( c \) and \( c' \), \( a \) and \( a' \), and \( Z \) stand for cations, anions and absolute value of ionic charges respectively.

Essentially, the new parameters \( B \) and \( \theta \) are binary ion-ion parameters and \( C \) and \( \psi \) ternary ion-ion parameters. The ion-ion interaction parameters, \( B \) and \( C \), are characteristic of each
aqueous single-electrolyte system and are determined by the properties of pure electrolytes. The ion-ion difference parameters, \( \theta \) and \( \psi \), are characteristic of each aqueous mixed-electrolyte system. They represent differences between the virial coefficients for interaction of unlike ions of the same sign from the average of interactions of like ions of the same sign. In Pitzer's derivation, the third virial coefficients for ternary interactions with all ions of the same sign were eliminated, as they were certain to be exceedingly small. The defining relations for \( B, C, \theta, \) and \( \psi \) are

\[
B_{ca}(I) = \lambda_{ca}(I) + \left( \frac{\nu_c}{Z_a} \right) \lambda_{cc}(I) + \left( \frac{\nu_a}{Z_c} \right) \lambda_{aa}(I)
\] (6)

\[
C_{ca} = \frac{3}{2 \sqrt{\nu_C \nu_a}} \left( \nu_C \mu_{cca} + \nu_a \mu_{caa} \right)
\] (7)

\[
\theta_{cc'} = \lambda_{cc'}(I) - \left( \frac{Z_{c'}}{2Z_c} \right) \lambda_{cc}(I) - \left( \frac{Z_{c'}}{2Z_c} \right) \lambda_{c',c'}(I)
\] (8)

\[
\psi_{cc'a} = 6 \mu_{cc'a} - \left( \frac{3Z_{c'}}{Z_c} \right) \mu_{cca} - \left( \frac{3Z_{c'}}{Z_c} \right) \mu_{c',c'a}
\] (9)

The defining relations for \( \theta_{aa}, \) and \( \psi_{aa', c} \) are obtained from Equations (8) and (9) by replacing \( c \) with \( a \) and \( a \) with \( c \).

Recognizing the ionic strength dependence of the effect of short range forces in binary interactions, Pitzer was able to develop an empirical relation for \( B_{ca}(I) \). The expression for systems containing strong electrolytes with one or both ions
univalent is

\[ B_{\text{Ca}}(I) = \beta^{(0)}_{\text{Ca}} + \frac{\beta^{(1)}_{\text{Ca}}}{2I} \left[ 1 - (1 + 2\sqrt{I})\exp(-2\sqrt{I}) \right] \]

(10)

Therefore, the adjustable parameters in the modified Pitzer equation are \( \beta^{(0)} \), \( \beta^{(1)} \), \( C \), \( \theta \), and \( \psi \). The modified Pitzer equation has been successfully applied to the available data for many pure aqueous electrolytes (Pitzer and Mayorga 1973) and mixed aqueous electrolytes (Pitzer and Kim 1974). The fit to the experimental data is within the probable experimental error up to molalities of 6.

Thus, the modified Pitzer equation appears to be a useful tool for the representation of aqueous electrolytes including mixed electrolytes. However, it can not be used in the form just presented to represent systems containing molecular solutes.

Hereafter, Equation (3) is referred to as the basic Pitzer equation and Equation (5) is called the Pitzer equation.

Extension of The Pitzer Equation

In most aqueous electrolyte systems of industrial interest, not only strong electrolytes but also weak ones and molecular
nonelectrolytes are present. For example, in the Hot Carbonate 
Precess, potassium carbonate and potassium bicarbonate are 
strong electrolytes, carbon dioxide is a weak electrolyte, and 
methane, carbon monoxide and hydrogen are molecular 
onelectrolytes. Strong electrolytes dissociate completely to 
onic solutes, and weak electrolytes dissociate partially to 
onic solutes. A unified thermodynamic model for both ionic 
solutes and molecular solutes is required to model these kinds 
of systems. In the previous section, we discussed how Pitzer 
modified his basic equation for strong electrolyte solutes by 
introducing a set of new, observable parameters. In this study 
the same approach is adopted to include appropriate terms for 
molecular solutes.

To obtain an extended form of the Pitzer equation that 
applies to electrolyte systems with molecular solutes, the 
virial coefficients in the basic Pitzer equation for 
molecule-ion and molecule-molecule interaction must be 
considered. The contribution to the excess Gibbs free energy 
resulting from the presence of molecular solutes is

$$
\left( \frac{G_{\text{ex}}}{n_w RT} \right)_{\text{molecule}} = \sum_{m} \sum_{i \neq m} \left( 2\lambda_{mi} + 6\Sigma_{j} \mu_{mij} \right) \\
+ \sum_{m} \sum_{m', m''} \left( \lambda_{m m', m''} + \sum_{m'''} \mu_{m m', m'''} \right)
$$

(11)
where the subscripts \( m, m' \) and \( m'' \) represent molecular solutes and \( i, j \) represent all solutes.

The new observable parameters for binary molecule-ion interactions, \( D \) and \( \omega \), are defined as follows.

\[
D_{ca,m} = 2\left(\frac{\lambda_{cm}}{v_a} + \frac{\lambda_{am}}{\nu_c}\right)/\nu_c = D_{ac,m} \left(\frac{\nu_a}{\nu_c}\right)
\]

\[
\omega_{cc',m} = 2\left(\frac{\lambda_{cm}}{Z_c} - \frac{\lambda_{c'm}}{Z_{c'}}\right)/Z_{c'}
\]

\[
\omega_{aa',m} = 2\left(\frac{\lambda_{am}}{Z_a} - \frac{\lambda_{a'm}}{Z_{a'}}\right)/Z_{a'}
\]

The parameters \( D_{ca,m} \) are binary parameters representing the interactions between salt \( ca \) and molecular solute \( m \) in an aqueous single salt, single molecular solute system. Binary parameters \( \omega_{cc',m} \) and \( \omega_{aa',m} \) represent the differences between the interactions of a specific molecular solute with two unlike salts sharing one common anion or cation. Ternary molecule-ion virial coefficients are neglected in this study to simplify the extension.

It is interesting to note that the molecule-ion interaction contribution in Equation (11) is consistent with the well-known Setschenow equation. The Setschenow equation is used to represent the salting out effect of salts on molecular
nonelectrolyte solutes, when the solubilities of the latter are small (Gordon 1975). The Setschenow equation is

$$\ln \gamma^*_m = k_{s,m} m_s$$

(15)

where $k_{s,m}$ is the Setschenow constant (a salt-molecule interaction parameter) and $m_s$ is the molality of the salt. The D's are equivalent to the Setschenow constants and the $\omega$'s are equivalent to differences between Setschenow constants.

Approximate additivity of ionic contributions to the Setschenow constants is observed for inorganic salts (Gordon 1975). This suggests that third virial coefficients in Equation (11) for molecule-ion interactions can be neglected for inorganic salts. Salt mixtures involving organic ions, however, are non-additive in their salting out contributions. Therefore, neglecting ternary molecule-ion interactions can result in discrepancies for organic salt systems.

The third virial coefficients for molecule-molecule interactions can be taken as zero for aqueous systems containing molecular solutes at low concentration. The expression for molecule-molecule interaction contribution reduces to an unsymmetric two-suffix Margules model.

Summarizing the results of this section, the extended form
of the Pitzer equation proposed in this study is

\[
\frac{G_{\text{ex}}}{n_{w}RT} = f(I) + \sum_{cc'} \frac{m_{c}}{a_{c}} \omega_{cc'} + \frac{1}{2} \sum_{a} \frac{m_{a}}{a_{a}} \psi_{a} \omega_{cc'} + \sum_{aa'} \frac{m_{a}}{a_{a}} \theta_{aa'} + \frac{1}{2} \sum_{c} \frac{m_{c}}{c_{c}} \psi_{aa'} \omega_{cc'} + 2 \sum_{ca} \frac{m_{c}}{ca} \left[ B_{ca} (I) + \sum_{c} \frac{m_{c}}{c_{c}} \sum_{a} \frac{m_{a}}{a_{a}} C_{ca} \right] + \sum_{mm'} \omega_{mm'} + \sum \left( \sum_{ca} \frac{m_{c}}{m_{c}} \omega_{cc'} \omega_{cc'} \right)
\]

(16)

Previous Applications

Recently, the Pitzer equation has been applied to model vapor-liquid equilibrium behavior of weak electrolyte systems by Beutier and Renon (1978) and Edwards et al. (1978). Their works are briefly discussed here.

Beutier and Renon considered the excess Gibbs free energy \(G_{\text{ex}}\) of aqueous electrolyte systems as the sum of three terms, corresponding to ion-ion, ion-molecule, and molecule-molecule interactions.

\[
G_{\text{ex}} = G_{\text{ex-ion-ion}} + G_{\text{ex-ion-molecule}} + G_{\text{ex-molecule-molecule}}
\]

(17)
The Pitzer equation was used only for the ion-ion interaction contribution. The second virial coefficients for binary interactions between ions of the same sign were neglected. This eliminates \( \theta \) in Equation (5) and simplifies \( B_{ca}(I) \) to \( \lambda_{ca}(I) \). Beutier and Renon also neglected all third virial coefficients except \( \mu_{ca'a} \) and \( \mu_{cc'a} \), and they further assumed that

\[
\mu_{ca'a} = \frac{1}{2}(\mu_{ca'a} + \mu_{ca'a'}) \quad (18-a)
\]
\[
\mu_{cc'a} = \frac{1}{2}(\mu_{cca} + \mu_{c'c'a}) \quad (18-b)
\]

which eliminates the difference parameters \( \psi \) for ternary interactions among univalent ions. Other ternary difference parameters were also taken to be zero.

Ion-molecule interactions were estimated using Debye-McAulay's electrostatic theory (Harned and Owen 1958). For the molecule-molecule interactions, binary and ternary interactions between two different molecules were neglected, but both second and third virial terms were retained for each individual molecular solute. The form of the excess Gibbs free energy equation used by Beutier and Renon can be written as

\[
\frac{G^e}{n_wRT} = f(I) + 2\sum \sum \frac{m}{ca} \left[ \lambda_{ca}(I) \right] \frac{\sum m \frac{Z_c}{Z_a}}{c(c')c'} C \left[ \frac{C}{C} \right] C_c
\]

\[
+ \frac{W_{el}}{m} + \sum \frac{\left( \frac{C}{c} \right) m^2 \sum m^3}{\mu_{c'mm'n} m \mu_{c'mm'n} m}
\]

(19)
where

$$C_{ca} = \frac{3}{2\sqrt{\nu_c \nu_a}} (\nu_c \mu_{cca} + \nu_a \mu_{ca})$$  \hspace{1cm} (20)$$

with an additional assumption that

$$\mu_{cca} = \mu_{ca}$$  \hspace{1cm} (21)$$

$W_{el}$ in Equation (19) is the Debye-McAulay electrostatic work term used for the ion-molecule interaction contribution.

Beutier and Renon applied Bromley's idea (1973) on approximating interaction parameters as the sum of values for individual ions. A correlation with partial molar entropy of ions at infinite dilution was used to obtain \( \lim_{I \to 0} \lambda_{ca}(I) \) \( = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} \). Values of \( C_{ca}^{\phi} \) (which are twice the values of \( C_{ca} \)) were used as the only adjustable parameters to fit the vapor-liquid equilibrium data of the three weak electrolyte systems considered by them.

Unlike Beutier and Renon, Edwards et al. (1978) adopted Equation (10) for all ion-ion, ion-molecule, and molecule-molecule binary virial coefficients of the basic Pitzer equation. Ternary interactions of all types were totally neglected. Model parameters were further eliminated by excluding the second virial coefficients for binary
interactions between ions of the same sign and parameters $\beta^{(1)}$ for binary interactions with one or both solutes molecular. The parameters $\beta^{(0)}$ for binary interactions with both solutes molecular are the same as the unsymmetric Margules parameters used in this study for molecule-molecule interactions.

Edwards et al. also used the ideas of Bromley (1973) on additivity of interaction parameters of individual ions and correlation between individual ion and partial molar entropy of ions at infinite dilution. The idea of additivity of interaction parameters of specific ions was extended to molecule-ion interaction parameters. The form of the excess Gibbs free energy equation used by Edwards et al. is

$$\frac{G^{ex}}{n_{w}RT} = f(I)$$

$$+ \sum_{ca} \sum_{c} m_{a} \left\{ \beta^{(0)}_{ca} + \frac{\beta^{(1)}_{ca}}{2I} \right\} [1 - (1 + 2\sqrt{I})]$$

$$\exp(-2\sqrt{I})] + \sum_{mi} \sum_{m} \sum_{i} \beta^{(0)}{mi m i}$$

(22)

Both Beutier and Renon and Edwards et al. assumed the temperature dependence of the ion-ion interaction parameters to be negligible. Molecule-ion and molecule-molecule interaction parameters were treated as temperature dependent.
Discussion of Previous Applications

One new and two previous expressions for the excess Gibbs free energy of aqueous electrolyte systems have been presented. They all incorporate, in different ways, the Pitzer equation. In this section we point out some limitations of the previous approaches that do not apply to the new approach.

First, theoretical aspects of the physical chemistry of aqueous electrolyte solutions, including salting out effects on non-electrolytes, are still in a development stage. Although many theories have been proposed in the literature, none is quantitatively satisfactory. Adopting Debye-McAulay's electrostatic theory for molecular-ion interactions, Beutier and Renon (1978) note, for example, that their model does not seem reliable to represent solutions with high molalities of undissociated ammnonia.

Second, the Pitzer equation is a virial-expansion type equation and semi-empirical in nature. The exact meaning and interrelationships between the adjustable parameters are not fully understood. As shown in the results of Beutier and Renon (1978) and Edwards et al. (1978), estimating interaction parameters from ionic partial molar entropy at infinite dilution can only give acceptable results for aqueous electrolyte systems at low ionic strength. A more precise way
to estimate the parameters is required for the high ionic strength solutions often encountered in industrial processes.

Third, Bronsted's principle of specific ion interaction is the basis for assuming that interactions among ions of the same sign can be neglected. While both Beutier and Renon and Edwards et al. accept Bronsted's idea, the principle of specific ion interaction has been disproved, as stated in Pitzer's paper (1973). Thus, difference parameters should not be neglected for systems of high ionic strength.

Fourth, ternary ion-ion interaction and difference parameters in the Pitzer equation are significant for systems of high ionic strength. For example, the $\text{K}_2\text{CO}_3$-$\text{CO}_2$ aqueous solution system employed in the Hot Carbonate Process is a highly concentrated one. The ionic strength can be as high as 18 molal for solutions of 40% equivalent potassium carbonate at a conversion of 100%. Further, ternary parameters are kept as adjustable parameters in Pitzer's paper (1973a) for data fitting, unless ionic strength is less than 2 molality. Thus, ternary ion-ion interaction parameters should not be neglected without an analysis of the particular system of interest.

**Liquid Phase Equations**

For aqueous systems containing electrolytes with one or
both ions univalent, expressions for activity of water, activity coefficients of ionic solutes and activity coefficients of molecular solutes can be derived from the extended Pitzer equation as follows with the assumption that $\theta, \lambda_{mm}$, $D$ and $\psi$ are ionic strength independent.

\[
\ln a_w = \ln n_w + \ln \gamma_w \\
= \ln \left( \frac{55.55}{55.55 + \sum_{i} \epsilon_{mi}} \right) + \frac{(\partial G^e / \partial n_w)}{55.55RT} \\
= \ln \left( \frac{55.55}{55.55 + \sum_{i} \epsilon_{mi}} \right) - \frac{(\phi-1) \sum_{i} \epsilon_{mi}}{55.55} \\
(\phi-1) \sum_{i} \epsilon_{mi} = -A \phi \left( \frac{2I^{3/2}}{1+1.2\sqrt{I}} \right) \\
+ 2\Sigma \sum_{m} m_{a} [\beta_{ca}^{(0)} + \beta_{ca}^{(1)} \exp(-2\sqrt{I})] + \frac{2\sum_{c} Z_{c} Z_{a}}{\sqrt{Z_{c} Z_{a}}} \\
+ \Sigma \sum_{c} m_{a} m_{c}^{a} \theta_{cc}^{a} + \Sigma m_{a} m_{c}^{a} \psi_{cc}^{a} \\
+ \Sigma \sum_{m} m_{a} m_{a}^{'} \theta_{aa}^{a} + \Sigma m_{a} m_{a}^{'} \psi_{aa}^{a} \\
+ \Sigma \sum_{mm} m_{m} m_{m} \lambda_{mm} \\
+ \Sigma (\Sigma D_{m a} m_{m} m_{a}^{'} - \Sigma \omega_{cc}^{a}, m_{m} m_{c}^{a}) \\
(23)
\]
\[ \ln \gamma_a^* = \frac{1}{n_w RT} \left( \frac{\partial G^{ex}}{\partial m_a} \right) \]

\[ = -A_\phi Z_a^2 \left[ \frac{\sqrt{I}}{1 + 1.2\sqrt{I}} \right] \ln (1 + 1.2\sqrt{I}) \]

\[ + 2 \sum_c \left\{ \beta^{(0)}_{ac} + \frac{\beta^{(1)}_{ac}}{2I} [1 - (1 + 2\sqrt{I}) \exp(-2\sqrt{I})] \right\} \]

\[ + 2 \sum_a m_a, \theta_{aa'} \]

\[ \frac{Z_a^2}{\sqrt{I}} \sum_c m_{ca} \beta^{(1)}_{ca} [1 - (1 + 2\sqrt{I} + 2I) \exp(-2\sqrt{I})] \]

\[ + \sum_c \left\{ m_{ca} \psi_{aa'} + \sum_c m_{cc'} \psi_{cc'} + \sum_c m_{cc'} \sqrt{Z_{ca} Z_a} C_{ca} \right\} \]

\[ + Z_a \sum_{ca'} m_{ca'} C_{ca'} \sqrt{Z_{ca} Z_a} \]

\[ + \sum_{m} m_{ca} D_{ca}, \mu_{ca} \]

\[ \ln \gamma_m^* = \frac{1}{n_w RT} \left( \frac{\partial G^{ex}}{\partial m} \right) \]

\[ = 2 \sum_{m} m, \lambda_{mm}, \sum ca, m_{ca} m_{ca a} - \sum \omega_{cc'}, m_{cc'}, m_{cc'} \]
The equations for water activity and solute activity coefficients must be solved simultaneously with three other types of equations in order to calculate values for the activity and activity coefficients. They are: the equation of charge balance, equations of elemental mass balance and equations of chemical equilibrium. The equation of charge balance is

$$\sum_{c} m_{c} Z_{c} = \sum_{a} m_{a} Z_{a}$$  \hspace{1cm} (27)

The equations of elemental mass balance and chemical equilibrium depend upon the system under consideration. In general, equations of elemental mass balance are

$$\sum_{j} e_{i} m_{j} = b_{e}$$  \hspace{1cm} (28)

For a reaction \( m = i + j \), equations of chemical equilibrium are

$$K_{m}(T) = \frac{a_{i} \cdot a_{j} \cdot m_{i} \cdot \gamma_{i} \cdot m_{j} \cdot \gamma_{j}}{a_{m} \cdot m_{m} \cdot \gamma_{m}}$$  \hspace{1cm} (29)

Expressions for the equilibrium constants \( K(T) \) are required.

In this study, the equations for the liquid phase were solved with a general non-linear equation solver using a modified Gauss-Newton algorithm.
Vapor-Liquid Equilibrium Data Correlation

Data correlations were carried out for three systems with quite different characteristics to illustrate the range of application of the extended Pitzer equation. Since the extended Pitzer equation reduces to the Pitzer equation for aqueous strong electrolyte systems and is consistent with the Setschenow equation for molecular non-electrolytes in aqueous electrolyte systems, the main interest here is aqueous systems with weak electrolytes or partially dissociated "strong" electrolytes. The three systems considered are 1) hydrochloric acid aqueous solution at 298.15°C, 2) NH₃-CO₂ aqueous solution at 293.15°C, and 3) the K₂CO₃-CO₂ aqueous solution used in the Hot Carbonate Process. Although dilute hydrochloric acid is normally assumed to be a strong electrolyte in water, it is actually a partially dissociated electrolyte and is so treated here.

The parameters in the proposed model are numerous if several solutes are present. In practice, the characteristics of each system may be studied to determine which parameters should be included and which can be assumed negligible. As shown in Pitzer and Mayorga's results (1973), \( \beta^{(0)} \) and \( \beta^{(1)} \) are of the order of 0.1; \( C \) is of the order of 0.001. Also, \( D \) (Gordon 1975) and \( \lambda_{mm} \) (Edwards et al. 1978) are of the order of 0.1. Although only a few data are available for \( \theta \) and \( \psi \)
(Pitzer and Kim 1974) and no data are available for \( \omega \), it should be reasonable to expect that \( \alpha, \psi, \) and \( \omega \) are about of the same order of magnitude as \( \beta^{(0)} \), C and D, respectively. For systems of low concentrations, ternary parameters may be unnecessary. If concentrations of molecular solutes are exceedingly small, the ion-molecule interaction contribution to excess Gibbs free energy can be negligible. In addition, \( \beta^{(1)} \) can be estimated as functions of \( \beta^{(0)} \) as a convenient approximation as suggested by Pitzer and Mayorga (1973). The expressions adopted in this study are

\[
\begin{align*}
\beta_{1-1}^{(1)} &= 0.125 + 1.172 \beta_{1-1}^{(0)} \quad (30-a) \\
\beta_{1-2}^{(1)} &= 0.947 + 2.021 \beta_{1-2}^{(0)} \quad (30-b)
\end{align*}
\]

For each system, a suitable sum of squares objective function is chosen, depending on the form of the available data. This includes a choice of the variables to be fit and a choice of weighting. Adjustable parameters are varied, using a Gauss-Newton algorithm, to minimize the objective function. Each functional evaluation during data correlation requires a solution of the liquid phase equations discussed in the previous section. To save computer time, previous calculated results from the solution of the liquid phase equations are saved and used as initial guesses for the next solution of the liquid phase equations.
HCl Aqueous Solution System

Complete experimental data \((t,p,x,y)\) for hydrochloric acid concentration up to 18 molal were obtained from Vega and Vera (1976). The temperature of the experimental data, 298.15°K, is below the critical point of hydrogen chloride. In the gas phase, hydrogen chloride and water are present. In the liquid phase, there are hydrogen, hydroxide and chloride ions. The following reactions occur in the liquid phase.

\[
\begin{align*}
\text{HCl} & = \text{H}^+ + \text{Cl}^- \\
\text{H}_2\text{O} & = \text{H}^+ + \text{OH}^- 
\end{align*}
\]

The adjustable parameters of the extended Pitzer equation for this system are \(\beta^{(0)}_{\text{HCl}}, \beta^{(1)}_{\text{HCl}}, C_{\text{HCl}}, D_{\text{HCl, HCl}}\), and \(\lambda_{\text{HCl, HCl}}\). In addition, the Henry's constant for hydrogen chloride was treated as an adjustable parameter. Ideal gas behavior was assumed for the vapor phase, since the system pressures never exceed atmospheric pressure.

The sum of squares objective function used for data correlation was

\[
S = \sum_{i=1}^{n} (y_{\text{calc}} - y_{\text{exp}})^2 + \sum_{i=1}^{n} \frac{(p_{i,\text{calc}} - p_{i,\text{exp}})^2}{p_i} 
\]

Experimental data and correlation results are given in Figure 1.
Figure 1. Total Vapor Pressure and Vapor Phase Hydrogen Chloride Mole Fraction of the Hydrogen Chloride Aqueous Solution at 298.15°K

- O, A data from Vega and Vera (1976)
- Calculated
Table 2. Representation of Vapor-Liquid Equilibrium of HCl-H₂O System (Vega and Vera, HCl-H₂O Data at 298.15°K)

<table>
<thead>
<tr>
<th>(g mole/kg of solvent) m_{HCl}</th>
<th>exp Y_{HCl}</th>
<th>calc Y_{HCl}</th>
<th>(N/m²) x 10⁻³ p_{exp}</th>
<th>p_{calc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.045</td>
<td>0.0003</td>
<td>0.0002</td>
<td>2.666</td>
<td>2.671</td>
</tr>
<tr>
<td>4.462</td>
<td>0.0018</td>
<td>0.0013</td>
<td>2.400</td>
<td>2.388</td>
</tr>
<tr>
<td>6.017</td>
<td>0.0095</td>
<td>0.0079</td>
<td>2.080</td>
<td>2.072</td>
</tr>
<tr>
<td>6.854</td>
<td>0.022</td>
<td>0.019</td>
<td>1.920</td>
<td>1.917</td>
</tr>
<tr>
<td>7.735</td>
<td>0.051</td>
<td>0.047</td>
<td>1.773</td>
<td>1.784</td>
</tr>
<tr>
<td>8.656</td>
<td>0.116</td>
<td>0.110</td>
<td>1.720</td>
<td>1.709</td>
</tr>
<tr>
<td>9.635</td>
<td>0.243</td>
<td>0.238</td>
<td>1.760</td>
<td>1.764</td>
</tr>
<tr>
<td>10.67</td>
<td>0.446</td>
<td>0.443</td>
<td>2.106</td>
<td>2.103</td>
</tr>
<tr>
<td>11.75</td>
<td>0.668</td>
<td>0.666</td>
<td>3.013</td>
<td>3.030</td>
</tr>
<tr>
<td>12.90</td>
<td>0.836</td>
<td>0.834</td>
<td>5.186</td>
<td>5.192</td>
</tr>
<tr>
<td>14.13</td>
<td>0.928</td>
<td>0.926</td>
<td>9.852</td>
<td>9.894</td>
</tr>
<tr>
<td>15.42</td>
<td>0.970</td>
<td>0.968</td>
<td>19.52</td>
<td>19.34</td>
</tr>
<tr>
<td>16.81</td>
<td>0.987</td>
<td>0.987</td>
<td>37.41</td>
<td>37.61</td>
</tr>
<tr>
<td>18.28</td>
<td>0.994</td>
<td>0.994</td>
<td>69.05</td>
<td>68.98</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\beta_0^{(0)} & = 0.2380 & \beta_1^{(1)} & = 1.5702 & C_{HCl} & = -0.0022 & D_{HCl,HCl} & = 0.4012 & \lambda_{HCl,HCl} & = 0.0806 & H_{HCl} & = 0.2897D-3 & \delta P/P & = 0.46 & \delta Y_{HCl} & = 0.28 \\
& & & & & & & & & & & & \delta P/P & = 0.99 & \delta Y_{HCl} & = 0.34
\end{align*}
\]

\(a\) This work.

\(b\) Cruz and Renon (1978).
and Table 2.

The same data was previously correlated with the same objective function by Cruz and Renon (1978), using a model for solutions of a partially or completely dissociated electrolyte in an undissociated solvent. This model was not based on the Pitzer equation. It assumes a known dissociation constant and has six adjustable parameters. The Nothnagel et al. (1973) correlation is used to represent the vapor phase, and the fugacity coefficients differed from unity by less than 1%. Their results are compared with those of the present work in Table 2.

To use the extended Pitzer equation for the subcritical solute hydrogen chloride it was necessary to introduce a Henry's constant, defined as the saturated vapor pressure of a subcritical molecular solute, divided by 55.55, times the symmetric activity coefficient of that solute at infinite dilution in the binary system with water. This approach is suitable as long as the subcritical component concentration is not very high. When this is not the case, a more suitable way to handle subcritical molecular solutes would be to consider the molecular solutes and the water as a mixed solvent. In principle, the Pitzer equation can be modified for mixed solvent electrolyte systems. However, practical application of the Pitzer equation involves empirical expressions for
interactions among solutes in the solvent, water; required empirical expressions are not available for mixed solvent. The present approach should be satisfactory for systems containing subcritical molecular solutes at low concentrations.

**NH₃-CO₂ Aqueous Solution System**

The data reported by Van Krevelen et al. (1949) at 293.15°K are used for data correlation. Ammonia, carbon dioxide and water are present in the vapor phase. In the liquid phase, hydrogen, hydroxide, ammonium, carbonate, bicarbonate, and carbamate ions are present in addition to ammonia and carbon dioxide molecular solutes. The following reactions occur in the liquid phase

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} &= \text{NH}_4^+ + \text{OH}^- \\
\text{CO}_2 + \text{H}_2\text{O} &= \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- &= \text{CO}_3^- + \text{H}^+ \\
\text{NH}_3 + \text{HCO}_3^- &= \text{NH}_2\text{CO}_2^- + \text{H}_2\text{O} \\
\text{H}_2\text{O} &= \text{H}^+ + \text{OH}^- 
\end{align*}
\]

All ternary parameters are dropped from the proposed model, since the highest ammonia concentration is 2 normal. The three Setschenow constants of carbon dioxide are assumed negligible because ammonia is always in excess in Van Krevelen's data and carbon dioxide is almost completely dissociated. The ion-ion
interaction parameters for salts containing hydrogen ion or hydroxide ion are assumed negligible. The system is a buffer solution and both hydrogen ion concentration and hydroxide ion concentration are small, compared to those of other solutes. Also excluded are the three binary ion-ion difference parameters because they are significant only where the concentrations of bicarbonate, carbonate, and carbamate ions are large compared to the concentrations of ammonia and ammonium ion. The remaining adjustable parameters are the binary ion-ion interaction parameters and the Setschenow constants:

\[ \beta^{(0)}_{\text{NH}_4\text{HCO}_3}, \beta^{(0)}_{\text{(NH}_4\text{)}_2\text{CO}_3}, \beta^{(0)}_{\text{NH}_4\text{H}_2\text{COO}}, D^{(0)}_{\text{NH}_4\text{HCO}_3,\text{NH}_3}, D^{(0)}_{\text{(NH}_4\text{)}_2\text{CO}_3,\text{NH}_3}\text{, and } D^{(0)}_{\text{NH}_4\text{H}_2\text{COO, NH}_3}. \]

The equilibrium constants and Henry's constants used are given in Table 1. The Henry's constant for ammonia and the equilibrium constants are reported by Edwards et al. (1978) and Tsonopoulos (1976). Henry's constants for carbon dioxide were correlated from the work of Ellis and Golding (1963). They reported the solubility of CO₂ in water for temperatures up to 573.15 K. At the system pressures, vapor phase fugacity coefficients as predicted by the Nakamura et al. (1976) correlation are sufficiently close to unity to be neglected.

The sum of squares objective function used for data correlation was

\[ S = \sum_{i=1}^{n} \left( \frac{p^{\text{calc}}_{\text{NH}_3,i} - p^{\exp}_{\text{NH}_3,i}}{p^{\exp}_{\text{NH}_3,i}} \right)^2 + \sum_{i=1}^{n} \left( \frac{p^{\text{calc}}_{\text{CO}_2,i} - p^{\exp}_{\text{CO}_2,i}}{p^{\exp}_{\text{CO}_2,i}} \right)^2 \]

(32)
The correlation results and calculated adjustable parameters are shown in Figure 2 and Table 3, along with the correlated partial pressures given by Van Krevelen et al. (1949). In their model, activity coefficients were not taken into consideration and the correlation parameters were dependent on the ionic strength of solutions. The mean of the absolute values of the relative deviations of partial pressure of carbon dioxide is 11% and for ammonia is 3.9%.

Three Setschenow constants dominate in the ammonia-rich region and the three ion-ion interaction parameters dominate in the ammonia-lean region. When the three binary ion-ion difference parameters were included in the correlation, the minimum sum of squares dropped only slightly. This tends to support the conclusion that these parameters are not significant.

The same system and the same least squares objective function have been studied by Beutier and Renon (1978). The ion-molecule interaction parameters were estimated using Debye-McAulay's electrostatic theory. The binary ion-ion interaction parameters were estimated from correlations with partial molar entropy of ions at infinite dilution. Two ternary ion-ion interaction parameters, $C_{\text{NH}_4\text{HCO}_3}^\phi$ and $C_{\text{NH}_4\text{NH}_2\text{COO}}^\phi$ were adjusted. The mean of the absolute values of the relative deviations of partial pressure of carbon
Figure 2. Partial Pressures of Ammonia and Carbon Dioxide of the Ammonia-Carbon Dioxide Aqueous Solution at 293.15°C

Experimental data
- NH₃ (2N NH₃)
- NH₃ (1N NH₃)
- CO₂ (2N NH₃)
- CO₂ (1N NH₃)
  van Krevelen, et al. (1949)

Calculated

Partial Pressure of Weak Electrolytes, P kN/m²

R: Ratio of Total CO₂ Concentration vs. Total NH₃ Concentration
Table 3. Representation of Vapor-Liquid Equilibrium of NH₃-CO₂ Aqueous Solution System (Van Krevelen et al., NH₃-CO₂-H₂O at 293.15°K)

<table>
<thead>
<tr>
<th>Normal A</th>
<th>R</th>
<th>((N/m²) \times 10^{-3})</th>
<th>(\text{p}^{\text{exp}}_{\text{NH}_3})</th>
<th>(\text{p}^{\text{calc}}_{\text{NH}_3})</th>
<th>Van Krevelen</th>
<th>(\text{p}^{\text{exp}}_{\text{CO}_2})</th>
<th>(\text{p}^{\text{calc}}_{\text{CO}_2})</th>
<th>Van Krevelen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.96</td>
<td>0.347</td>
<td>1.25</td>
<td>1.20</td>
<td>1.16</td>
<td>0.111</td>
<td>0.116</td>
<td>0.133</td>
<td></td>
</tr>
<tr>
<td>1.99</td>
<td>0.246</td>
<td>1.73</td>
<td>1.70</td>
<td>1.61</td>
<td>0.033</td>
<td>0.038</td>
<td>0.044</td>
<td></td>
</tr>
<tr>
<td>2.01</td>
<td>0.271</td>
<td>1.67</td>
<td>1.59</td>
<td>1.49</td>
<td>0.051</td>
<td>0.051</td>
<td>0.057</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.298</td>
<td>0.757</td>
<td>0.714</td>
<td>0.720</td>
<td>0.160</td>
<td>0.065</td>
<td>0.068</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.48</td>
<td>0.393</td>
<td>0.389</td>
<td>0.387</td>
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<td>0.368</td>
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<td></td>
</tr>
<tr>
<td>1.00</td>
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<td>0.247</td>
<td>0.253</td>
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<td>0.97</td>
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<tr>
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</tr>
<tr>
<td>1.00</td>
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<td>0.041</td>
<td>0.040</td>
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<td>15.77</td>
<td>15.33</td>
<td></td>
</tr>
<tr>
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<td>0.929</td>
<td>0.907</td>
<td>0.307</td>
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</tr>
<tr>
<td>2.00</td>
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<td>0.452</td>
<td>0.467</td>
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<td>1.20</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
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<td>0.157</td>
<td>0.158</td>
<td>0.167</td>
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<td>7.50</td>
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</tr>
<tr>
<td>2.00</td>
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<td>0.023</td>
<td>0.024</td>
<td>0.023</td>
<td>89.17</td>
<td>85.57</td>
<td>99.99</td>
<td></td>
</tr>
</tbody>
</table>

\(p^{(0)}_{\text{NH}_4\text{HCO}_3}: -0.0275\)
\(p^{(0)}_{\text{(NH}_4\text{)}_2\text{CO}_3}: 0.8668\)
\(p^{(0)}_{\text{NH}_4\text{NH}_2\text{COO}}: 0.0155\)

\(D_{\text{NH}_4\text{HCO}_3,\text{NH}_3}: -0.0285\)
\(D_{\text{(NH}_4\text{)}_2\text{CO}_3,\text{NH}_3}: 0.1452\)
\(D_{\text{NH}_4\text{NH}_2\text{COO},\text{NH}_3}: 0.1704\)

\(S=0.4625\) (excluding \(\theta\)'s)
\(S=0.4033\) (including \(\theta\)'s)

A: total ammonia concentration
R: ratio of total carbon dioxide concentration vs. total ammonia concentration
dioxide was 16% and for ammonia was 5%. Edwards et al. (1978) also studied vapor-liquid equilibrium of a \( \text{NH}_3 - \text{CO}_2 \) aqueous system at \( 373.15^\circ\text{K} \), using experimental data from Otsuka, et al. (1960). However, the accuracy of the fit was not reported quantitatively.

\underline{\text{K}_2\text{CO}_3 - \text{CO}_2 \ \text{Aqueous Solution System}}

The equilibrium data obtained by Tosh and coworkers (1959) were used for data correlation. The data have a temperature range from \( 343.15^\circ\text{K} \) to \( 413.15^\circ\text{K} \), and a range from 20% to 40% equivalent concentration of potassium carbonate. "Equivalent concentration of potassium carbonate" refers to a solution in which only potassium carbonate and water are present. Thus, a 40% equivalent solution means a solution containing 40g of potassium carbonate and 60g of water, if all the carbonate in the system were converted back to carbonate. These equilibrium data cover the operating range of the Hot Carbonate scrubbing system for removing carbon dioxide from a gas mixture.

The stoichiometric equation for the carbon dioxide absorption by the potassium carbonate aqueous solution is

\[
\text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = 2\text{KHCO}_3
\]
In the gas phase, carbon dioxide and water molecules are present. In the liquid phase, there are two molecular solutes, water and carbon dioxide, and five ionic solutes: potassium ion, hydrogen ion, hydroxide ion, bicarbonate ion and carbonate ion. The three chemical equilibrium reactions occurring in the liquid phase are dissociation of carbonic acid, bicarbonate ion and water, respectively.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &= \text{HCO}_3^- + \text{H}^+ \\
\text{HCO}_3^- &= \text{CO}_3^{2-} + \text{H}^+ \\
\text{H}_2\text{O} &= \text{OH}^- + \text{H}^+
\end{align*}
\]

Vapor phase fugacity coefficients were calculated using the model of Nakamura et al. (1976). Since no suitable model is available for partial molar volume, \( \bar{V} \), it was approximated by the infinite dilute volume, \( \bar{V} \). The correlation of Brelvi and O'Connell (1972) was used to estimate the latter.

The sum of squares objective function used for data correlation was

\[
S = \sum_{i=1}^{n} \left( \frac{p_{\text{H}_2\text{O},i}^{\text{calc}} - p_{\text{H}_2\text{O},i}^{\text{exp}}}{0.1 p_{\text{H}_2\text{O},i}^{\text{exp}}} \right)^2 + \sum_{i=1}^{n} \left( \frac{p_{\text{CO}_2,i}^{\text{calc}} - p_{\text{CO}_2,i}^{\text{exp}}}{68.95 + 0.05 p_{\text{CO}_2,i}^{\text{exp}}} \right)^2
\]  

(33)
As shown in Table 4, there are many adjustable parameters in the proposed model for the K\(_2\)CO\(_3\)-CO\(_2\) aqueous solution system. However, the approximate ranges of molalities of solutes in the K\(_2\)CO\(_3\)-CO\(_2\) aqueous solution system for the Hot Carbonate Process are known to be

\[
\begin{align*}
  m_{\text{K}^+} & : 3-11 \text{m} \\
  m_{\text{H}^+} & < 10^{-9} \text{m} \\
  m_{\text{OH}^-} & < 10^{-2} \text{m} \\
  m_{\text{HCO}_3^-} & : 0-7 \text{m} \\
  m_{\text{CO}_3^-} & : 0-5 \text{m} \\
  m_{\text{K}_2\text{CO}_3} & : < 0.1 \text{m} \\
  m_{\text{CO}_2} & 
\end{align*}
\]

From Table 4 the parameters that should be considered in the vapor-liquid equilibrium data correlation of the system are \(\beta_{\text{KHCO}_3}^{(0)}, \beta_{\text{K}_2\text{CO}_3}^{(0)}, \theta_{\text{HCO}_3^-\text{CO}_3^-}, c_{\text{KHCO}_3}, c_{\text{K}_2\text{CO}_3}, \) and \(\psi_{\text{K}^+,\text{HCO}_3^-\text{CO}_3^-}\). Other parameters were assumed to be zero unless numerical values were available from other sources.

Before fitting the data obtained by Tosh, \(\beta_{\text{KHCO}_3}^{(0)}\), \(\beta_{\text{K}_2\text{CO}_3}^{(0)}\), and \(\theta_{\text{HCO}_3^-\text{CO}_3^-}\) were adjusted to fit experimental activity coefficient data for bicarbonate and carbonate ions at ionic strength less than 0.5 molal at 298.15°K (Walker 1927). The inclusion of \(\theta\) as adjustable parameters improves the data fitting significantly, as shown in Table 5. Also, \(\theta\) is of the same order of magnitude as \(\beta^{(0)}\). This implies that Bronsted's principle of specific ion interaction is not valid for the system.
Table 4. Order of Magnitude Analysis for the Adjustable Parameters of the K$_2$CO$_3$–CO$_2$ Aqueous Solution System

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Contribution from molality of the corresponding solutes in equation (16)</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{\text{KOH}}^{(0)}$</td>
<td>$&lt; 10^{-1}$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\beta_{\text{KHCO}_3}^{(0)}$</td>
<td>0–77 m$^2$</td>
<td>adjusted</td>
</tr>
<tr>
<td>$\beta_{\text{K}_2\text{CO}_3}^{(0)}$</td>
<td>0–55 m$^2$</td>
<td>adjusted</td>
</tr>
<tr>
<td>$\beta_{\text{HHCO}_3}^{(0)}$</td>
<td>$&lt; 10^{-8}$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\beta_{\text{H}_2\text{CO}_3}^{(0)}$</td>
<td>$&lt; 10^{-8}$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_{\text{K}^+,\text{H}^+}$</td>
<td>$&lt; 10^{-8}$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_{\text{OH}^-,\text{HCO}_3^-}$</td>
<td>$&lt; 10^{-1}$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_{\text{OH}^-,\text{CO}_3^-}$</td>
<td>$&lt; 10^{-1}$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_{\text{HCO}_3^-,\text{CO}_3^=}^{-}$</td>
<td>0–35 m$^2$</td>
<td>adjusted</td>
</tr>
<tr>
<td>$\psi_{\text{KOH}}$</td>
<td>$&lt; 1$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{KHCO}_3}$</td>
<td>0–800 m$^3$</td>
<td>adjusted</td>
</tr>
<tr>
<td>$\psi_{\text{K}_2\text{CO}_3}$</td>
<td>0–600 m$^3$</td>
<td>adjusted</td>
</tr>
<tr>
<td>$\psi_{\text{HHCO}_3}$</td>
<td>$&lt; 10^{-8}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{H}_2\text{CO}_3}$</td>
<td>$&lt; 10^{-8}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{K}^+,\text{H}^+,\text{CO}_3^=}$</td>
<td>$&lt; 10^{-7}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{K}^+,\text{H}^+,\text{OH}^-}$</td>
<td>$&lt; 10^{-10}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{K}^+,\text{HCO}_3^-,\text{OH}^-}$</td>
<td>$&lt; 10^{-7}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{K}^+,\text{OH}^-,\text{CO}_3^-}$</td>
<td>$&lt; 10^{-7}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{K}^+,\text{HCO}_3^-,\text{CO}_3^=}$</td>
<td>0–385 m$^3$</td>
<td>adjusted</td>
</tr>
<tr>
<td>$\psi_{\text{H}^+,\text{HCO}_3^-,\text{OH}^-}$</td>
<td>$&lt; 10^{-10}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{H}^+,\text{CO}_3^-,\text{OH}^-}$</td>
<td>$&lt; 10^{-7}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{H}^+,\text{OH}^-,\text{CO}_3^-}$</td>
<td>$&lt; 10^{-10}$ m$^3$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{KOH},\text{CO}_2}$</td>
<td>$&lt; 1$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{KHCO}_3,\text{CO}_2}$</td>
<td>$&lt; 1$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\psi_{\text{K}_2\text{CO}_3,\text{CO}_2}$</td>
<td>$&lt; 1$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\omega_{\text{K}^+,\text{H}^+,\text{CO}_2}$</td>
<td>$&lt; 10^{-10}$ m$^2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\omega_{\text{CO}_2,\text{CO}_2}$</td>
<td>$&lt; 10^{-2}$ m$^2$</td>
<td>$-0.4922 + 149.20$ (1/T)*</td>
</tr>
</tbody>
</table>

Table 5. Comparison between Representations of Data on $\ln\gamma_{\text{HCO}_3^-}$ and $\ln\gamma_{\text{CO}_3^=}$ (Walker et al., 1927),
a) without $\theta$, b) with $\theta$

<table>
<thead>
<tr>
<th></th>
<th>$\beta(0)_{\text{KHCO}_3}$</th>
<th>$\beta(0)_{\text{K}_2\text{CO}_3}$</th>
<th>$\theta_{\text{HCO}_3^-,\text{CO}_3^=}$</th>
<th>$\sigma\ln\gamma^*$</th>
<th># of data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>-0.4398</td>
<td>0.0125</td>
<td>---</td>
<td>0.0469</td>
<td>16</td>
</tr>
<tr>
<td>b)</td>
<td>0.1695</td>
<td>0.4530</td>
<td>-0.0724</td>
<td>0.0077</td>
<td>16</td>
</tr>
</tbody>
</table>

Data are interpolated or taken directly from Walker, et al. (1927). Sum of squares objective function is

$$S = \sum_{i=1}^{n} (\ln\gamma^*_{\text{HCO}_3^-} - \ln\gamma^*_{\text{HCO}_3^-})^2 + \sum_{i=1}^{n} (\ln\gamma^*_{\text{CO}_3^=} - \ln\gamma^*_{\text{CO}_3^=})^2$$
The inclusion of ternary ion-ion interaction parameters in the fitting of Tosh's data is justified by the comparison between representations of the data, as shown in Table 6. This table also shows that the six parameters selected from Table 4 are the significant ones. Adding less significant parameters does not give better representation of the data. As further justification for the inclusion of ternary ion-ion interaction parameters, an examination of the fitted parameter correlation matrix in Table 7 shows the ternary parameters to be substantially statistically independent of the binary parameters. It is also interesting that θ is substantially independent of the other parameters, consistent with the conclusion in the previous paragraph, that Bronsted's principle of specific ion interaction is not valid for the system.

The strong mutual correlation within the binary and ternary parameter subsets does not necessarily indicate that any single binary or ternary parameter should be dropped. Rather, it means that, locally, some linear combination of the correlated parameters is contributing to the goodness of fit. The correlation further implies that the parameters within a subset can not be individually well-determined. This could account for the lack of smoothness of the variation of the parameters with temperature.

All of the adjustable parameters in the extended Pitzer
Table 6. Comparison of Representations of Tosh's Data* with a) 3 Parameters, 
b) 6 Parameters, c) 9 Parameters

<table>
<thead>
<tr>
<th></th>
<th>$\beta_{KHCO_3}^{(0)}$</th>
<th>$\beta_{K_2CO_3}^{(0)}$</th>
<th>$\theta_{HCO_3^-CO_3}$</th>
<th>$C_{KHCO_3}$</th>
<th>$C_{K_2CO_3}$</th>
<th>$\psi_{K,HCO_3^-CO_3}$</th>
<th>$D_{KHCO_3,CO_2}$</th>
<th>$D_{K_2CO_3,CO_2}$</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>0.0369</td>
<td>0.1849</td>
<td>-0.0223</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.31</td>
</tr>
<tr>
<td>b)</td>
<td>0.0370</td>
<td>0.1590</td>
<td>-0.0215</td>
<td>0.0008</td>
<td>0.0072</td>
<td>-0.0010</td>
<td></td>
<td></td>
<td>8.56</td>
</tr>
<tr>
<td>c)</td>
<td>0.0359</td>
<td>0.1563</td>
<td>-0.0216</td>
<td>0.0008</td>
<td>0.0074</td>
<td>-0.0010</td>
<td>0.0004</td>
<td>-0.6600</td>
<td>8.56</td>
</tr>
</tbody>
</table>

*383.15°K, 40 data points.
Table 7. Parameter Correlation Matrix of Representation of Tosh's Data at 383.15°K

\[
\begin{array}{cccccc}
\beta_{\text{KHCO}_3}^{(0)} & \beta_{\text{K}_2\text{CO}_3}^{(0)} & \theta_{\text{HCO}_3^-\text{CO}_3}^- & C_{\text{KHCO}_3} & C_{\text{K}_2\text{CO}_3}^- & \psi_{\text{K}^+,\text{HCO}_3^-\text{CO}_3}^- \\
1.0000 & 0.9995 & -0.1648 & -0.1666 & 1.0000 & 0.9893 \\
0.9892 & 0.1820 & 0.9822 & -0.9845 & 0.1869 & 0.9740 \\
-0.9740 & -0.1174 & -0.9740 & 0.1869 & 0.9969 & -0.1269 \\
0.1011 & -0.1269 & -0.1174 & -0.1269 & 1.0000 & 0.1011 \\
0.9740 & 0.1869 & 0.9969 & 1.0000 & 0.1011 & -0.1269 \\
\end{array}
\]
equation may be temperature dependent. To study the significance of this dependence, data at 343.15, 363.15, 383.15, and 403.15°C were fit independently. In addition, the data from these four temperatures are lumped together and fit, assuming temperature dependence of $a+b/T$. The resulting parameters are shown in Table 8. The temperature dependency of $a+b/T$ appears to be adequate. Figures 3 and 4 show experimental data and correlation results for equilibrium partial pressure of carbon dioxide and water at 383.15°C for solutions of various concentrations. Figures 5 and 6 give the experimental data and the correlation results of equilibrium partial pressure of carbon dioxide and water at those temperatures for 30% equivalent potassium carbonate aqueous solution. Solid lines are the correlation results from the data at all four temperatures lumped together. Since the data are widely scattered and unreliable, less weight is given to the data for equilibrium water vapor pressure during correlation. Correlation results for water vapor pressure are, however, acceptable.
Table 8. Representation of Vapor-Liquid Equilibrium of $K_2CO_3-CO_2-H_2O$

System A) 343.15$^\circ$K, B) 363.15$^\circ$K, C) 383.15$^\circ$K, D) 403.15$^\circ$K,
E) All Temperatures (Data from Tosh et al.)

<table>
<thead>
<tr>
<th></th>
<th>$\beta_{KHCO_3}^{(0)}$</th>
<th>$\beta_{K_2CO_3}^{(0)}$</th>
<th>$\theta_{HCO_3^-CO_3}$</th>
<th>$C_{KHCO_3}$</th>
<th>$C_{K_2CO_3}$</th>
<th>$\Psi_{K^+,HCO_3^-CO_3}^{-}$</th>
<th># of data points</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>0.1208</td>
<td>0.3718</td>
<td>-0.0815</td>
<td>-0.0054</td>
<td>-0.0148</td>
<td>0.0163</td>
<td>18</td>
<td>3.99</td>
</tr>
<tr>
<td>b)</td>
<td>0.1037</td>
<td>0.3192</td>
<td>-0.0506</td>
<td>-0.0036</td>
<td>-0.0083</td>
<td>0.0068</td>
<td>17</td>
<td>5.88</td>
</tr>
<tr>
<td>c)</td>
<td>0.0370</td>
<td>0.1590</td>
<td>-0.0215</td>
<td>0.0008</td>
<td>0.0072</td>
<td>-0.0010</td>
<td>40</td>
<td>8.56</td>
</tr>
<tr>
<td>d)</td>
<td>-0.0835</td>
<td>-0.0792</td>
<td>-0.0628</td>
<td>0.0097</td>
<td>0.0304</td>
<td>0.0079</td>
<td>32</td>
<td>8.47</td>
</tr>
<tr>
<td>e)</td>
<td>-3.4960</td>
<td>-7.1312</td>
<td>-0.0397</td>
<td>0.2217</td>
<td>0.6445</td>
<td>0.0027</td>
<td>107</td>
<td>9.74</td>
</tr>
</tbody>
</table>

$+1330.9/T$   $+2753.2/T$   $-83.18/T$  $-240.97/T$
Figure 3. Equilibrium Pressure of Carbon Dioxide at $383.15^\circ$K over 20, 30 and 40 Percent Equivalent Potassium Carbonate Solution

Carbon Dioxide Vapor Pressure (newton/meter$^2$)

Percentage of $K_2CO_3$ Converted to $KHCO_3$

- $20\%$ data
- $30\%$ data
- $40\%$ data
- calculated
Figure 4. Equilibrium Pressure of Water at 383.15°K over 20, 30 and 40 Percent Equivalent Potassium Carbonate Solution

Water Vapor Pressure (10^3 newton/meter^2)

Percentage of K_2CO_3 Converted to KHCO_3

- 20% data
- 30% data
- 40% data
- calculated
Figure 5. Equilibrium Pressure of Carbon Dioxide of 30 Percent Equivalent Potassium Carbonate Solution at 343.15, 363.15, 383.15 and 403.15 °K
Figure 6. Equilibrium Pressure of Water of 30 Percent Equivalent Potassium Carbonate Solution at 343.15, 363.15, 383.15 and 403.15°K

Water Vapor Pressure (10^3 newtons/meter^2)

Percentage of K_2CO_3 Converted to KHCO_3
Notation

\( A_{ej} \) = stoichiometric number of element e in solute j
\( A_{\phi} \) = Debye-Huckel constant for the osmotic coefficient
\( B_{Ca} \) = binary ion-ion interaction parameter
\( C_{Ca} \) = ternary ion-ion interaction parameter
\( D_{Ca,m} \) = binary salt-molecule interaction parameter or
Setschenow constant
\( G^{ex} \) = excess Gibbs free energy
\( H \) = Henry's constant (atm Kg/q-mole)
\( I \) = ionic strength (=\( \frac{1}{2} \sum m_i z_i^2 \))
\( K \) = dissociation equilibrium constant
\( P \) = pressure N/m\(^2\)
\( PK \) = cologarithm of dissociation constant
\( R \) = gas constant
\( S \) = sum of squares of objective functions
\( T \) = temperature (\( ^0 \)K)
\( V \) = partial molar volume (cm\(^3\)/mole)
\( W_{el} \) = Debye-McAulay electrostatic work
\( Z \) = absolute value of ionic charge
\( a \) = activity
\( b_e \) = molality of element e (a constant)
\( m \) = molality (g-mole/Kg of solvent)
\( m_j \) = molality of any solute j
\( n_w \) = number of Kg of the solvent, water
\( x \) = liquid phase mole fraction
\( y \) = vapor phase mole fraction

Greek letters

\( \beta^{0}, \beta^{1} \) = parameters of the empirical expression of B(I)
\( \gamma \) = activity coefficient
\( \delta P/P \) = relative error of P, in percentage
\( \delta P_p = \frac{1}{P} \sum_{i=1}^{n} \left( \frac{p_i^{calc}}{p_i^{exp}} - 1 \right)^2 \right)^{1/2} \)
\( \delta y \) = absolute error of y, in percentage
\( \delta y_i = \frac{1}{y_i} \sum_{i=1}^{n} \left( y_i^{calc} - y_i^{exp} \right)^2 \right)^{1/2} \)
\( \theta \) = binary ion-ion difference parameter
\( \lambda \) = second virial coefficient of the basic Pitzer equation
\( \mu \) = third virial coefficient of the basic Pitzer equation
\( \nu \) = stoichiometric coefficient
\( \sigma \) = standard deviation
\( \phi \) = vapor phase fugacity coefficient
\( \phi \) = osmotic coefficient
\( \psi \) = ternary ion-ion difference parameter
\( \omega \) = binary salt-molecule difference parameter
Superscripts

s = saturation
* = unsymmetric convention
∞ = infinite dilution
calc = calculated
exp = experimental

Subscripts

a, a' = anion
c, c' = cation
i, j, k = solute
m = molecular solute
w = water
l-1 = univalent-univalent electrolyte
l-2 = univalent-divalent electrolyte

Literature cited


Chapter 3
A Local Composition Model for the Excess Gibbs Energy of
Electrolyte Systems - Binary Systems

Abstract

A local composition model is presented for the excess Gibbs energy of electrolyte systems. It assumes that the excess Gibbs energy is sum of two contributions, one resulting from long-range electrostatic forces between ions and the other from short-range forces between all the species. The long-range term has been satisfactorily described by the Debye-Hückel formula for dilute electrolyte systems, in which the long-range contribution dominates, and is retained. The short-range contribution is modeled by utilizing the concept of local composition in a manner similar to Renon and Prausnitz (1968) but with additional assumptions appropriate for electrolyte systems. The resulting expression has two binary parameters per binary pair of electrolyte systems. The equation reduces to the Nonrandom, Two-Liquid (NRTL) equation for systems without electrolytes. The validity of the model is supported by good fits to experimental data for a wide range of binary systems with only binary parameters.
Scope

As in the nonelectrolyte case, the problem of representing the thermodynamic properties of electrolyte systems is best regarded as that of finding suitable expressions for the non-ideal part of the chemical potential, or the excess Gibbs energy, as a function of composition, temperature, dielectric constant and any other relevant variables.

There have been many extensive investigations carried out both experimentally and theoretically on the thermodynamic properties of aqueous electrolytes over the past few decades. Recently, significant developments for calculation of the mean ionic activity coefficients of many types of aqueous electrolytes have been made by Meissner and co-workers (1972a, 1972b, 1979), Bromley (1973), Pitzer (1973), and Cruz and Renon (1978). Of these, the Pitzer equation is especially useful because it is designed for convenient and accurate representation of aqueous strong electrolytes with any number of solutes. It has been applied successfully to represent experimental data within experimental error from dilute solutions up to an ionic strength of six molality for both pure aqueous electrolytes (Pitzer and Mayorga, 1973) and aqueous mixed electrolytes (Pitzer and Kim, 1974).

In addition, Edwards et al. (1975) proposed a thermodynamic
framework to calculate vapor-liquid equilibrium compositions for aqueous solutions of one or more volatile weak electrolytes. Recently, simplified forms of the Pitzer equation have been incorporated by Beutier and Renon (1978) and Edwards et al. (1978) in modeling ionic activity coefficients of aqueous weak electrolyte systems. In this thesis, the Pitzer equation was extended (see Chapter 2) in a thermodynamically consistent manner to allow for molecular as well as ionic solutes in the aqueous systems. Under limiting conditions, the extended model reduces to the Pitzer equation for strong electrolytes, and is consistent with the well-known Setschenow equation for the salting out effect of salt upon molecular solutes.

However, the Pitzer's excess Gibbs energy equation is a virial-expansion type equation, and therefore, subject to all of the limitations of a virial-expansion type equation. The equation parameters, denoting the short-range interactions between and among solute species, are arbitrary, temperature-dependent and are characteristic of the solvent. Binary parameters are expressed as empirical functions of ionic strength. Different empirical functions are required for different types of electrolytes. Ternary parameters are necessary for electrolyte systems at high ionic strength. Furthermore, for the industrially important class of mixed solvent electrolyte systems, the Pitzer equation is not
feasible because its parameters are unknown functions of solvent composition and the empirical expressions required are available only for aqueous electrolytes. Therefore, although the Pitzer equation has been shown to be a convenient and accurate representation of aqueous electrolytes, a more versatile model is needed to cover a wider variety of electrolyte systems.

It is the objective considered in this chapter to develop a model for excess Gibbs energy of electrolyte systems that is not only applicable to aqueous electrolytes but also applicable to wide variety of electrolyte systems. The local composition concept was adopted in this study with the thought that representation of the properties of multi-solvent, multi-electrolyte systems over a wide range of electrolyte concentration would be possible without the need for ternary or higher order parameters and the interaction parameters would be relatively weak function of temperature.

Conclusions and Significance

A local composition model has been developed for the excess Gibbs energy of electrolyte systems. It is based on the local composition concept and is designed to represent the properties of multi-solvent, multi-electrolyte systems over a wide range of electrolyte concentration without the need for ternary or
higher order parameters. Weak temperature dependence was found for the model parameters. The validity of the local composition model is supported by good data correlation results on many binary electrolyte systems.

**Nature of Electrolyte Systems**

The thermodynamic properties of a mixture depend on the forces which operate between the species of the mixture. Electrolyte systems are characterized by the presence of both molecular species and ionic species, resulting in three different types of interaction. They are ion-ion interaction, molecule-molecule interaction, and ion-molecule interaction. The forces involved in each interaction are briefly discussed in the following paragraphs.

The ion-ion interaction is characterized by electrostatic forces between ions. These electrostatic forces are inversely proportional to the square of the separation distance and therefore have a much greater range than other intermolecular forces which depend on higher powers of the reciprocal distance. Except at short-range, other forces are relatively insignificant compared to the interionic electrostatic force.

Many different types of forces arise from molecule-molecule interaction. These forces may be electrostatic forces between
permanent dipoles, induction forces between a permanent dipole and induced dipoles, or dispersion forces between non-polar molecules, etc. (Prausnitz, 1969). Forces involved in molecule-molecule interaction are known to be short-range in nature.

The forces involved in ion-molecule interaction are also short-range in nature. The dominant forces are electrostatic forces between ions and permanent dipoles. As discussed by Robinson and Stokes (1970) regarding aqueous electrolyte systems, it seems likely that the ion-molecule interaction energies of the water molecules in the first layer about a monatomic ion would be large compared with the thermal energy (RT), and the second layer of water molecules will be much less strongly bound to the ion than the first. It is probably only with polyvalent monatomic ions of small size that the interaction energies of the water molecules in the second layer would be comparable to the thermal energy.

The excess Gibbs energy of electrolyte systems can be considered as sum of two terms, one related to long-range forces between ions and the other to short-range forces between all the species. As discussed by Robinson and Stokes (1970), long-range forces dominate in the region of dilute electrolyte concentration and short-range forces dominate in the region of high electrolyte concentration. It is the long-range nature of
the electrostatic forces between ions which yields effects that have no counterpart in nonelectrolyte systems.

The Local Composition Model

Nonelectrolyte systems, which are characterized by short-range forces between molecules, have frequently been studied using the local composition concept. Models such as Wilson (1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) have resulted. Such models have proven to be a great advancement over older models based on virial type expansions of mole fraction, such as the Margules model. In this study the local composition concept was applied to account for the contribution from short-range interactions occurring in electrolyte systems with the hope that a similar advance over the Pitzer equation would result. In particular, the local composition model is designed to apply to mixed-solvent, multi-electrolyte systems over a wide range of electrolyte concentration without the need for ternary or higher order parameters. However, it must be emphasized that the local composition concept is in no sense rigorous. It is used to develop correlating expressions, with adjustable parameters, for experimental data. The purpose in adopting a quasi-theoretical approach is to develop expressions with a small number of parameters, that apply over wide concentration ranges, may be expressed as simple function of temperature, and
may be used to predict the behavior of multicomponent systems. The validity of this approach may be determined only by its empirical success or failure. It is believed that the local composition model is quite successful by these criteria, as demonstrated by the work in this chapter and additional work with multicomponent systems involving weak electrolytes (see Chapters 4 and 5).

A fundamental difference between electrolyte systems and nonelectrolyte systems is the presence of long-range ion-ion electrostatic forces in electrolyte systems. No attempt was made to develop a long-range contribution model based on the local composition concept. Instead, the Debye-Huckel formula as proposed by Fowler and Guggenheim (1949) was used without modification to represent the unsymmetric excess Gibbs energy contribution arising from long-range ion-ion electrostatic forces. Nevertheless, the local composition concept and the Debye-Huckel formula are consistent in the sense that they are based on accounting for nonrandomness by introducing local compositions through Boltzmann-like factors. The Debye-Huckel formula is a function of solvent density, solvent dielectric constant, and ionic strength. It is known to correctly account for the ion-ion electrostatic contribution in the limit of infinite dilution. When electrolyte concentration increases, short-range forces start to play a role and finally dominate in the region of high electrolyte concentration (Robinson and

The local composition model is based on two fundamental assumptions: 1) that the local composition of cations around cations is zero, and similarly for anions, which is equivalent to assuming that repulsive forces between ions of like charge are extremely large, 2) that the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero. Hereafter, the first assumption is referred to as like-ion repulsion and the second assumption as local electroneutrality. For a pure, completely dissociated electrolyte, the like-ion repulsion assumption suggests that the liquid lattice structure should be similar to that of a solid salt crystal. When molecules are introduced into the liquid lattice structure, the local electroneutrality assumption suggests that they exist as interstitial species.

The general approach taken in the study is as follows. The Debye-Huckel formula is used to represent the contribution from long-range ion-ion interactions while the local composition concept is adopted to compute the contribution from short-range interactions of all kinds. The local composition model for the short-range interaction contribution is developed as a symmetric model, based on pure solvent and hypothetical pure completely-dissociated liquid electrolyte. This model is then normalized by infinite dilution activity coefficients in order
to obtain an unsymmetric local composition model. Finally the unsymmetric Debye-Huckel expression and the unsymmetric local composition expression are added to yield the excess Gibbs energy expression proposed in this study.

**Long-Range Interaction Contribution**

The long-range interaction contribution can be tested quantitatively only by comparison with experiment for very dilute solutions. In this region, only the long-range effects make any significant contribution to the nonideality of the solution and the short-range effects can be ignored. When electrolyte concentration increases, the latter starts to play a role.

Many Debye-Huckel type expressions have been proposed in the literature to represent the long-range contribution. In this study, the Debye-Huckel formula proposed by Fowler and Guggenheim (1949) was adopted. Known to be valid for the ion-ion interaction contribution in the limit of infinite dilution, the Debye-Huckel formula has been widely used to represent the nonideality of electrolyte solutions at very dilute concentration. Being a symmetric expression with respect to solvent and an unsymmetric expression with respect to electrolytes, the Debye-Huckel formula is an unsymmetric excess Gibbs energy expression.
Following Fowler and Guggenheim (1949), the Debye-Huckel formula can be written as

\[
\frac{G^{\text{ex}^*}}{kT} = -\sum_i N_i Z_i^2 e^{2K\zeta(Ka)} / 3DkT 
\]  

(1-1)

or adopting the molality scale,

\[
\frac{G^{\text{ex}^*}}{kT} = -(2/3)e^{2KN_o d_w I\zeta(Ka)} / 1000DkT
\]  

(1-2)

where

\[
\sum_i N_i Z_i^2 = 2N_o d_w I / 1000
\]  

(2)

\[
I = (1/2) \sum_i m_i Z_i^2
\]  

(3)

and \(N_i\) is the number of \(i\)-ions in the system of unit volume, and

\[
\zeta(Ka) = 3(\ln(1+Ka) - Ka + 0.5(Ka)^2) / (Ka)^3
\]  

(4)

\[
K^2 = 4\pi \sum_i N_i Z_i^2 e^2 / DkT
\]  

(5-1)

or

\[
K^2 = 8\pi e^2 N_o d_w I / 1000DkT
\]  

(5-2)

and a is the finite distance of closest approach of ions in electrolyte solutions.

From equation (1), one obtains by differentiating partially with respect to \(N_i\), the activity coefficient expression of
ionic species \( i \),

\[
\ln \gamma_i^* = \frac{\partial (G^{ex*}, e^1/kT)}{\partial N_i} = -Z_i^2 e^2 K_e/2DkT(l+Ka)
\]  

(6)

whence for a single electrolyte,

\[
\ln \gamma_{ca}^* = -Z_c Z_a e^2 K_e/2DkT(l+Ka)
\]  

(7)

Upon replacing \( K \) by its definition,

\[
\ln \gamma_i^* = -AZ_i^2 \sqrt{I} / (l+Ba/\bar{I})  
\]  

(8)

\[
\ln \gamma_{ca}^* = -AZ_c Z_a \sqrt{I} / (l+Ba/\bar{I})
\]  

(9)

where constants \( A \) and \( B \) involve temperature and the dielectric constant of the solvent, as follows:

\[
A^2 = (2\pi N_0 d_w/1000) (e^2/DkT)^3
\]  

(10)

\[
B^2 = 8\pi e^2 N_0 d_w/1000DkT
\]  

(11)

The osmotic coefficient expression is

\[
(\phi - 1) \sum m_i = -\partial (G^{ex*}, e^1/RT)/\partial n_w 
= 2IKE^2 \sigma (Ba/\bar{I})/DkT
\]  

(12)

where

\[
\sigma (x) = (\ln(1+x) - x + 0.5x^2 - x^3/2(1+x))/x^3
\]  

(13)
Up to ionic strength of about 0.1 molality, it is often possible to fit the data very accurately using values of the order of 4 Å for the distance of closest approach of ions (Robinson and Stokes, 1970). Although the distance of closest approach of ions is believed to be related to the ionic radii in solutions, it is not measurable and, therefore, was fixed to be 4 Å in this study.

Short-Range Interaction Contribution

The existence of long-range electrostatic forces between ions by no means excludes the simultaneous existence of short-range forces of the various sorts which operate between all the species. In this study, the short-range interaction contribution was accounted for using the local composition concept. Among the various models incorporating the local composition concept for short-range interactions, the Nonrandom, Two-Liquid (NRTL) approach of Renon and Prausnitz (1968) was adopted for the following reasons. Electrolyte systems are characterized by extraordinarily large heats of mixing. Compared with the heat of mixing, the nonideal entropy of mixing is negligible, which is consistent with the basic assumption behind the NRTL model. In addition, the resulting NRTL equation is algebraically simple while applicable to mixtures which exhibit liquid phase splitting. Furthermore, no specific volume or area data are required. These data are not
available for ionic species.

To introduce the local composition concept for electrolyte systems, the same argument as presented for the NRTL equation by Renon and Prausnitz (1968) is followed.

The local mole fractions $x_{ji}$ and $x_{ii}$ of species $j$ and $i$, respectively, in the immediate neighborhood of a central species $i$ are related by

$$\frac{x_{ji}}{x_{ii}} = (\frac{x_j}{x_i})^{G_{ji}}$$  \hspace{1cm} (14)

where

$$G_{ji} = \exp(-\alpha \tau_{ji})$$  \hspace{1cm} (15)

$$\tau_{ji} = (g_{ji} - g_{ii})/RT$$  \hspace{1cm} (16)

The quantities $g_{ji}$ and $g_{ii}$ are, respectively, energies of interaction between $j$-$i$ and $i$-$i$ pairs of species, and are inherently symmetric ($g_{ji} = g_{ij}$). The nonrandomness factor, $\alpha$, is fixed at a value of 0.2 in this study.

For convenience in representing other local mole fraction ratios, additional notation is introduced as follows:

$$\frac{x_{ji}}{x_{ki}} = (\frac{x_j}{x_k})^{G_{ji,ki}}$$  \hspace{1cm} (17)

where
G_{ji,k_i} = \exp(-\alpha_{ji,k_i}) \quad (18)

\alpha_{ji,k_i} = (g_{ji} - g_{k_i})/RT \quad (19)

While the derivation that follows may be generalized to handle all types of electrolyte systems, for the sake of simplicity, the derivation will be based on a binary system of single completely-dissociated electrolyte and single solvent. In this type of binary mixture, it is assumed that there are three types of cells. One type consists of a central solvent molecule with solvent molecules, anions and cations in the immediate neighborhood. The other two types have either an anion or cation as the central species, and an immediate neighborhood consisting of solvent molecules and oppositely-charged ions, but no ions of like charge (i.e., x_{cc} = x_{aa} = 0). The local mole fractions are related by:

\[ x_{cm} + x_{am} + x_{mm} = 1 \quad \text{(central solvent cells)} \quad (20-1) \]
\[ x_{mc} + x_{ac} = 1 \quad \text{(central cation cells)} \quad (20-2) \]
\[ x_{ma} + x_{ca} = 1 \quad \text{(central anion cells)} \quad (20-3) \]

Among the three types of cells there are four distinct local mole fraction ratios: \( x_{cm}/x_{mm}, x_{am}/x_{mm}, x_{mc}/x_{ac}, \) and \( x_{ma}/x_{ca}. \) It is notable that the assumption that \( x_{cc} = x_{aa} = 0 \) (like-ion repulsion) is equivalent to the assumption that \( g_{cc} \) and \( g_{aa} \) are much greater than the other interaction energies.
Figure 1. Three Types of Cells According to the Like-Ion Repulsion Assumption and the Local Electroneutrality Assumption

cation at center

anion at center

molecule at center
By combining equations (14), (17) and (20), the following expressions for the local mole fractions in terms of overall mole fractions may be derived:

\[ x_{im} = \frac{x_i G_{im}}{(x_a G_{am} + x_c G_{cm} + x_m G_{mm})} \quad (i = c, a, m) \quad (21-1) \]

\[ x_{ac} = \frac{x_a}{(x_a + x_m G_{mc,ac})} \quad (21-2) \]

\[ x_{ca} = \frac{x_c}{(x_c + x_m G_{ma,ca})} \quad (21-3) \]

In order to obtain an expression for the excess Gibbs energy, \( g^{(a)} \), \( g^{(c)} \), and \( g^{(m)} \) are defined as the residual Gibbs energies per mole of cells of central anion, central cation and central solvent molecule, respectively. These Gibbs energies are related to the local mole fractions as follows:

\[ g^{(a)} = \frac{g_{ma} x_m + g_{ca} x_c}{z_a} \quad (22-1) \]

\[ g^{(c)} = \frac{g_{mc} x_m + g_{ac} x_a}{z_c} \quad (22-2) \]

\[ g^{(m)} = \frac{g_{am} x_m + g_{cm} x_c + g_{mm} x_m}{z_m} \quad (22-3) \]

One then adopt the pure solvent as the reference state for the solvent, and a hypothetical pure completely-dissociated liquid electrolyte as the reference state for the electrolyte. The reference Gibbs energies per mole are then:

\[ g_{ref}^{(c)} = \frac{z_c g_{ac}}{z_c} \quad (23-1) \]

\[ g_{ref}^{(a)} = \frac{z_a g_{ca}}{z_a} \quad (23-2) \]

\[ g_{ref}^{(m)} = g_{mm} \quad (23-3) \]
In equations (22) and (23) the charge numbers, \( Z_c \) and \( Z_a \), are introduced to account for the fact that the ratio of the coordination number of central anion cells to that of central cation cells must be equal to the corresponding ratio of charge numbers. It is assumed that for central univalent ions the coordination number is five \((\alpha = 0.2)\) and the reference Gibbs energy is \( g_{ac} \). The coordination number of central multivalent ions is that of central univalent ions multiplied by the charge number. In order to account for the difference in the coordination numbers and to use the same nonrandomness factor for all ions, the reference Gibbs energy of central multivalent ions is that of central univalent ions multiplied by the charge number.

The molar excess Gibbs energy may now be derived by summing the changes in residual Gibbs energy resulting when \( x_m \) moles of solvent are transferred from the solvent reference state to their cells in the mixture, and when \( x_a \) moles of anions and \( x_c \) moles of cations are transferred from the electrolyte reference state to their respective cells in the mixture. The expression is:

\[
ge_{\text{ex},1c} = x_m (g^{(m)} - g_{\text{ref}}^{(m)}) + x_c (g^{(c)} - g_{\text{ref}}^{(c)}) + x_a (g^{(a)} - g_{\text{ref}}^{(a)})
\]  

(24)

Substituting equations (22) and (23) into equation (24) one
obtains

\[ g_{ex,lc}^{\text{ex}} = \frac{1}{RT} x_m x_c z_m z_c \tau_{mc,ac} + x_m x_a z_m \tau_{ma,ca} \]

\[ + x_c x_m z_c \tau_{mc,ac} + x_a x_m z_a \tau_{ma,ca} \quad (25) \]

The assumption of local electroneutrality applied to the cells of central solvent molecules may be stated as

\[ x_{am} z_a = x_c z_c \quad (26) \]

Substituting equation (14) into this relationship leads to the following equality:

\[ g_{am} = g_{cm} \quad (27) \]

Since the interaction energies are symmetric, it may be inferred from this result that:

\[ \tau_{am} = \tau_{cm} = \tau_{ca,m} \quad (28) \]

\[ \tau_{mc,ac} = \tau_{ma,ca} = \tau_{m,ca} \quad (29) \]

The binary parameters \( \tau_{ca,m} \) and \( \tau_{m,ca} \) then become the only two independent adjustable parameters for a binary pair of single completely-dissociated electrolyte and single solvent.

In order to combine equation (25) with the Debye-Hückel
formula, which accounts for the long-range contribution, it is necessary to normalize to the infinite dilution reference state for the ions:

$$g^{ex^*, l_c}/RT = g^{ex^* l_c}/RT - x_c \ln \gamma_c^\infty - x_a \ln \gamma_a^\infty$$  \hspace{1cm} (30)$$

After employing equation (25) to obtain $\ln \gamma_c^\infty$ and $\ln \gamma_a^\infty$ and substituting back into equation (30), the final result is:

$$g^{ex^*, l_c}/RT = x_m (x_{cm} + x_{am}) \tau_{ca,m} + x_c x_{mc} \tau_{m,ca} + x_a x_{ma} \tau_{m,ca} - x_c (Z_{cm,ca} + G_{cm,ca,m}) - x_a (Z_{am,ca} + G_{am,ca,m})$$  \hspace{1cm} (31)$$

The corresponding activity coefficient expressions for various species are

$$\ln \gamma_c^* = x_m^2 \tau_{cm} G_{cm} / (x_c G_{cm} + x_a G_{am} + x_m)^2$$

$$-Z_a x_{ma} x_m G_{ma} / (x_c + x_m G_{mc})^2 + Z_c x_{mc} G_{cm} / (x_a + x_m G_{mc})$$

$$-Z_c \tau_{mc} G_{cm,mc}$$  \hspace{1cm} (32)$$

$$\ln \gamma_a^* = x_m^2 \tau_{am} G_{am} / (x_c G_{cm} + x_a G_{am} + x_m)^2$$

$$-Z_c x_{mc} x_m G_{mc} / (x_a + x_m G_{mc})^2 + Z_a x_{ma} G_{ma} / (x_c + x_m G_{ma})$$

$$-Z_a \tau_{ma} G_{am,ma}$$  \hspace{1cm} (33)$$
\[ \ln \gamma_m = x_{cm}^\tau_{cm} + x_{am}^\tau_{am} \\
+ z_c x_c G_{mc}^\tau_{mc} x_a / (x_a + G_{mc} x_m)^2 \\
+ z_a x_a G_{ma}^\tau_{ma} x_c / (x_c + G_{ma} x_m)^2 \\
- x_c x_m G_{cm}^\tau_{cm} / (x_c G_{cm} + x_m G_{am} + x_m)^2 \\
- x_a x_m G_{am}^\tau_{am} / (x_c G_{cm} + x_m G_{am} + x_m)^2 \]  \hspace{1cm} (34)

The equations for binary systems just presented can be generalized to multicomponent systems consisting of any combination of weak and strong electrolytes, molecular solvents, and molecular solutes. This generalization is given in Chapter 4.

It is noteworthy that the short-range interaction contribution from the local composition model, equation (31), is expressed in terms of mole fractions while the long-range interaction contribution from the Debye-Hückel formula, equation (1), is expressed in terms of molalities. Molalities and mole fractions are related by equation (35).

\[ x_i = M_i m_i / (1000 + M_i \sum m_i) \]  \hspace{1cm} (35)

Discussion of the Assumptions

Two assumptions have been proposed in the study. Discussions of these assumptions are given in the following.
Repulsive forces between ions of the same charge are known to be very strong for neighboring species. Therefore, the like-ion repulsion assumption follows a simple physical reality. This reality is observed in the lattice of ionic salt crystals where the immediate neighbors of any central ion are ions of opposite charge. A similar phenomenon is observed in the coordination chemistry as ligands of any central ionic species are either ions of opposite charge or neutral molecules.

For any single solvent, single electrolyte binary system, the local electroneutrality assumption suggests that the interaction energy between cation and solvent molecule is the same as that between anion and solvent molecule. This is a reasonable assumption as the mutual potential energy of a point charge Ze and a dipole of moment μ̂, is known to be:

\[ Zε \mu \cos \theta / r^2 D \]

where θ is the angle between the axis of the dipole and the radius vector passing through the ion (Robinson and Stokes, 1970). Adjustment in the separation distance r or the angle θ can easily make the interaction energy between cation and solvent molecule equal that of anion and solvent molecule. Local electroneutrality is also observed for interstitial molecules in ionic salt crystals. An interesting result of the local electroneutrality assumption is that the pseudo cation activity coefficient and the pseudo anion activity coefficient are equal for any single solvent, single symmetric electrolyte
binary system.

Nonrandomness factor is known as the reciprocal of the lattice coordination number. Four to six are common coordination numbers for ionic salt crystals and complex compounds. Therefore, nonrandomness factor was chosen to be 0.2 for electrolyte solutions in this study. The data correlation results also show that 0.2 is satisfactory for practical purpose.

Data Fitting for Single-Electrolyte, Single-Solvent Systems

Many data on mean ionic activity coefficient, and vapor pressure depression of single electrolyte, single solvent binary systems have been correlated, with 4 \( \bar{A} \) being set for the closest approach distance of ions in the Debye-Huckel formula. Water dielectric constant at 293.15\(^\circ\)K is 78.30. Water density at 293.15\(^\circ\)K is 0.9971 gm/cm\(^3\). Results are shown in Tables 1 to 6 and Figures 2 to 4.

In general, data were fitted quite well using the local composition model. With only two adjustable binary parameters, the average standard deviation on data fitting of 50 uni-univalent aqueous single electrolyte systems listed in Table 1 is 0.009. Although it is not as good as the Pitzer equation, which requires two binary parameters and one additional ternary
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<th>Electrolyte</th>
<th>No. of data*</th>
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<th>$\gamma_{ca,m}$</th>
<th>$\phi_{1nY}^*$</th>
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<td>-3.776</td>
<td>0.003</td>
</tr>
<tr>
<td>NaH₂PO₄</td>
<td>23</td>
<td>0.1-6.0</td>
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<td>-3.711</td>
<td>0.002</td>
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<tr>
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<td>18</td>
<td>0.1-3.5</td>
<td>8.752</td>
<td>-4.535</td>
<td>0.009</td>
</tr>
<tr>
<td>Na malonate</td>
<td>21</td>
<td>0.1-5.0</td>
<td>7.527</td>
<td>-3.659</td>
<td>0.003</td>
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<tr>
<td>NaN₃</td>
<td>23</td>
<td>0.1-6.0</td>
<td>7.071</td>
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<td>0.003</td>
</tr>
<tr>
<td>NaOH</td>
<td>23</td>
<td>0.1-6.0</td>
<td>9.225</td>
<td>-4.647</td>
<td>0.026</td>
</tr>
<tr>
<td>Na propionate</td>
<td>17</td>
<td>0.1-3.0</td>
<td>8.277</td>
<td>-4.435</td>
<td>0.006</td>
</tr>
<tr>
<td>Na succinate</td>
<td>21</td>
<td>0.1-5.0</td>
<td>8.075</td>
<td>-3.968</td>
<td>0.002</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>23</td>
<td>0.1-6.0</td>
<td>7.614</td>
<td>-3.800</td>
<td>0.002</td>
</tr>
</tbody>
</table>
NH₄NO₃  23  0.1-6.0  7.170  -3.295  0.014
RbAc  18  0.1-3.5  8.602  -4.545  0.008
RbBr  21  0.1-5.0  7.920  -3.891  0.004
RbCl  21  0.1-5.0  8.086  -3.983  0.003
RbI  21  0.1-5.0  8.052  -3.949  0.004
RbNO₃  20  0.1-4.5  7.648  -3.287  0.013
TlAc  23  0.1-6.0  7.683  -3.618  0.014

*(Robinson and Stokes, 1970)

water dielectric constant: 78.30
water density: 0.9971 gm/cc

Table 2. Data and Results of Fit for Acids at 298.15°C
Assuming Complete Dissociation
- Mean Ionic Activity Coefficient Data

<table>
<thead>
<tr>
<th>Acid</th>
<th>No. of Data* Points</th>
<th>Highest Molality</th>
<th>τm,ca</th>
<th>τca,m</th>
<th>ClnY*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBr</td>
<td>17/3.0</td>
<td>9.742</td>
<td>-5.087</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>23/6.0</td>
<td>9.957</td>
<td>-5.106</td>
<td>0.031</td>
<td></td>
</tr>
<tr>
<td>HClO₄</td>
<td>23/6.0</td>
<td>10.488</td>
<td>-5.328</td>
<td>0.058</td>
<td></td>
</tr>
<tr>
<td>HI</td>
<td>17/3.0</td>
<td>9.483</td>
<td>-5.059</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>17/3.0</td>
<td>8.327</td>
<td>-4.341</td>
<td>0.008</td>
<td></td>
</tr>
</tbody>
</table>

*(Robinson and Stokes, 1970)
Table 3. Data and Results of Fit for Aqueous Solutions of Uni-bivalent Electrolytes at 298.15°K - Mean Ionic Activity Coefficient Data

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>No. of Data*</th>
<th>Molality</th>
<th>$\tau_{m,ca}$</th>
<th>$\tau_{ca,m}$</th>
<th>$\sigma_1\ln\gamma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$SO$_4$</td>
<td>14</td>
<td>0.1-1.8</td>
<td>8.037</td>
<td>-4.301</td>
<td>0.006</td>
</tr>
<tr>
<td>K$_2$CrO$_4$</td>
<td>18</td>
<td>0.1-3.5</td>
<td>8.348</td>
<td>-4.463</td>
<td>0.015</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>7</td>
<td>0.1-0.7</td>
<td>9.628</td>
<td>-5.017</td>
<td>0.008</td>
</tr>
<tr>
<td>Li$_2$SO$_4$</td>
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<td>0.1-3.0</td>
<td>8.616</td>
<td>-4.708</td>
<td>0.016</td>
</tr>
<tr>
<td>Na$_2$CrO$_4$</td>
<td>19</td>
<td>0.1-4.0</td>
<td>8.914</td>
<td>-4.793</td>
<td>0.048</td>
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<tr>
<td>Na$_2$ fumarate</td>
<td>15</td>
<td>0.1-2.0</td>
<td>9.082</td>
<td>-4.993</td>
<td>0.004</td>
</tr>
<tr>
<td>Na$_2$ maleate</td>
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<td>0.1-3.0</td>
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<tr>
<td>Na$_2$SO$_3$</td>
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<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>18</td>
<td>0.1-3.5</td>
<td>8.650</td>
<td>-4.612</td>
<td>0.022</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>19</td>
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<td>-4.485</td>
<td>0.023</td>
</tr>
<tr>
<td>Rb$_2$SO$_4$</td>
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<td>0.1-1.8</td>
<td>8.059</td>
<td>-4.263</td>
<td>0.005</td>
</tr>
</tbody>
</table>

*(Robinson and Stokes, 1970)
Table 4. Data and Results of Fit for Bi-univalent Electrolytes at 298.15°K
- Mean ionic Activity Coefficient Data

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>No. of Data Point</th>
<th>Highest Molality</th>
<th>$\tau_m,ca$</th>
<th>$\tau_{ca,m}$</th>
<th>$\sigma_{lnY^*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaBr₂</td>
<td>15</td>
<td>2.0</td>
<td>8.654</td>
<td>-5.031</td>
<td>0.022</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>14</td>
<td>1.8</td>
<td>7.561</td>
<td>-4.465</td>
<td>0.017</td>
</tr>
<tr>
<td>Ba(ClO₄)₂</td>
<td>21</td>
<td>5.0</td>
<td>9.629</td>
<td>-5.455</td>
<td>0.059</td>
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<tr>
<td>Ba₂</td>
<td>15</td>
<td>2.0</td>
<td>9.492</td>
<td>-5.515</td>
<td>0.031</td>
</tr>
<tr>
<td>CaBr₂</td>
<td>23</td>
<td>6.0</td>
<td>12.082</td>
<td>-6.451</td>
<td>0.331</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>23</td>
<td>6.0</td>
<td>11.296</td>
<td>-6.101</td>
<td>0.187</td>
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<tr>
<td>Ca(ClO₄)₂</td>
<td>23</td>
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<td>11.958</td>
<td>-6.476</td>
<td>0.252</td>
</tr>
<tr>
<td>Ca₂</td>
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<td>9.955</td>
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<tr>
<td>Ca(NO₃)₂</td>
<td>23</td>
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<tr>
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<td>11.339</td>
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</tr>
<tr>
<td>Co₂</td>
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<tr>
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<tr>
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<tr>
<td>FeCl₂</td>
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<tr>
<td>Mg(Al)₂</td>
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<tr>
<td>MgBr₂</td>
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<td>11.901</td>
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<tr>
<td>MgCl₂</td>
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<td>11.504</td>
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<td>Mg(ClO₄)₂</td>
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<tr>
<td>MnCl₂</td>
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<tr>
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<td>10.670</td>
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<tr>
<td>Pb(ClO₄)₂</td>
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<td>10.744</td>
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<tr>
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<tr>
<td>SrBr₂</td>
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<td>9.466</td>
<td>-5.426</td>
<td>0.033</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>19</td>
<td>4.0</td>
<td>10.252</td>
<td>-5.674</td>
<td>0.079</td>
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<tr>
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<td>11.307</td>
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<tr>
<td>Sr₂</td>
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<tr>
<td>Sr(NO₃)₂</td>
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<td>7.275</td>
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<td>0.019</td>
</tr>
<tr>
<td>UO₂Cl₂</td>
<td>17</td>
<td>3.0</td>
<td>9.014</td>
<td>-5.304</td>
<td>0.034</td>
</tr>
<tr>
<td>UO₂(ClO₄)₂</td>
<td>22</td>
<td>5.5</td>
<td>13.310</td>
<td>-7.105</td>
<td>0.426</td>
</tr>
<tr>
<td>UO₂(NO₃)₂</td>
<td>22</td>
<td>5.5</td>
<td>9.072</td>
<td>-5.381</td>
<td>0.046</td>
</tr>
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<td>ZnCl₂</td>
<td>23</td>
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<td>7.938</td>
<td>-4.471</td>
<td>0.105</td>
</tr>
<tr>
<td>Zn(ClO₄)₂</td>
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<td>12.064</td>
<td>-6.591</td>
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<tr>
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<td>6.0</td>
<td>10.639</td>
<td>-5.865</td>
<td>0.131</td>
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</tbody>
</table>

*(Robinson and Stokes, 1970)*
Table 5. Data and Results of Fit for Aqueous Solutions of Bi-valent Electrolytes at 298.15°K - Mean Ionic Activity Coefficient Data

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>No. of Data* Points</th>
<th>Molality</th>
<th>$\tau_{m,ca}$</th>
<th>$\tau_{ca,m}$</th>
<th>$\sigma_{\ln\gamma^*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeSO$_4$</td>
<td>18</td>
<td>0.2-4.0</td>
<td>11.728</td>
<td>-6.905</td>
<td>0.049</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>16</td>
<td>0.2-3.5</td>
<td>11.623</td>
<td>-6.827</td>
<td>0.047</td>
</tr>
<tr>
<td>MnSO$_4$</td>
<td>18</td>
<td>0.2-4.0</td>
<td>11.499</td>
<td>-6.732</td>
<td>0.046</td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>15</td>
<td>0.2-2.5</td>
<td>11.704</td>
<td>-6.826</td>
<td>0.042</td>
</tr>
<tr>
<td>CuSO$_4$</td>
<td>11</td>
<td>0.2-1.4</td>
<td>12.128</td>
<td>-7.043</td>
<td>0.043</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>17</td>
<td>0.2-3.5</td>
<td>11.693</td>
<td>-6.827</td>
<td>0.046</td>
</tr>
<tr>
<td>CdSO$_4$</td>
<td>17</td>
<td>0.2-3.5</td>
<td>11.481</td>
<td>-6.704</td>
<td>0.053</td>
</tr>
<tr>
<td>UO$_2$SO$_4$</td>
<td>22</td>
<td>0.2-6.0</td>
<td>11.316</td>
<td>-6.646</td>
<td>0.078</td>
</tr>
</tbody>
</table>

*(Robinson and Stokes, 1970)

Table 6. Data and Results of Fit for Uni-univalent Electrolyte Effect on the Vapor Pressure of Methanol at 298.05°K

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>No. of Data* Points</th>
<th>Highest Molality</th>
<th>$\tau_{m,ca}$</th>
<th>$\tau_{ca,m}$</th>
<th>$\sigma_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>9</td>
<td>5.3554</td>
<td>11.783</td>
<td>-5.562</td>
<td>0.034</td>
</tr>
<tr>
<td>NaBr</td>
<td>9</td>
<td>1.556</td>
<td>10.717</td>
<td>-5.176</td>
<td>0.002</td>
</tr>
<tr>
<td>NaOH</td>
<td>9</td>
<td>5.9413</td>
<td>10.372</td>
<td>-5.633</td>
<td>0.019</td>
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<tr>
<td>NaI</td>
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<td>4.5200</td>
<td>9.716</td>
<td>-5.186</td>
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<td>KI</td>
<td>9</td>
<td>1.1219</td>
<td>10.765</td>
<td>-5.138</td>
<td>0.002</td>
</tr>
</tbody>
</table>

*(Bixon et al., 1979)
methanol dielectric constant: 32.63
methanol density: 0.7868 gm/cc
methanol vapor pressure: 126.23 mmHg
Figure 2. Comparison of the Calculated and Experimental Mean Ionic Activity Coefficients of Three Uni-univalent Electrolytes at 298.15°C.

Data of Robinson and Stokes (1970)

Calculated

HCl

NaCl

CsCl

Mean Ionic Activity Coefficient

Electrolyte Concentration (Molality)
Figure 3. Comparison of the Calculated and Experimental Mean Ionic Activity Coefficients of Three Bi-bivalent Electrolytes at 298.15°K

+, o, o Data of Robinson and Stokes (1970)

- - - - Calculated

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration (Molality)</th>
<th>Mean Ionic Activity Coefficient $\gamma^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeSO$_4$</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.1</td>
</tr>
<tr>
<td>UO$_2$SO$_4$</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
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<td>1</td>
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<tr>
<td></td>
<td>4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Electrolyte Concentration (Molality)
Figure 4. Salt Effect on the Vapor Pressure of Methanol at 298.05 °K
parameter (Pitzer, 1973b), it is quite satisfactory and better than that of Bromley's equation (1973).

An interesting note is that $\tau_{m,ca}$ is always positive and $\tau_{ca,m}$ is always negative. This is because the two-body interaction between cation and anion is stronger than the interaction between solvent molecule and ionic species, and the latter again is stronger than the interaction between two molecules. It is known that there is a multi-root problem associated with the NRTL equation for nonelectrolyte systems. However, the multi-root problem of the NRTL equation is resolved for electrolyte systems with the knowledge that $\tau_{m,ca}$ should be positive and $\tau_{ca,m}$ should be negative.

There is a similar trend between $\tau_{m,ca}$ and the standard deviation. When the absolute value of $\tau_{m,ca}$ increases, the standard deviations also increases. This is consistent with the physical meaning of $\tau_{m,ca}$, which is the difference of interaction energies between the molecule-ion pair and the cation-anion pair. The larger the absolute value of $\tau_{m,ca}$, the stronger the interaction between cation and anion. In other words, the distance between neighboring cation and anion becomes smaller and the ions tend to associate and form ion-pairs or even molecular species. When this occurs, the assumption on complete dissociation of electrolytes becomes improper and the activity coefficient expressions, equations
(32) and (33), are no longer valid. These electrolyte systems should be considered as multicomponent and chemical equilibrium should be taken into account when correlating data.

The relation between $\tau_{m,ca}$ and ion association can be further supported by the acidic dissociation constants of three strong acids: HCl, HBr and HI. As shown in Table 7, $\tau_{m,ca}$ increases and ion association increases when acidic dissociation constants decreases ($pK_a$ increases). The weaker the acid is, the less complete the acid dissociates, and the larger the value of $\tau_{m,ca}$.

Also, it is noteworthy that $\tau_{m,ca}$'s have a similar trend as the lattice energies observed in salt crystals for lithium, sodium and potassium halides. It suggests that $\tau_{m,ca}$ is related to the salt crystal lattice energy. Table 8 shows $\tau_{m,ca}$'s and salt crystal lattice energies for several alkali halides. Slight increases in $\tau_{m,ca}$ for rubidium and cesium halides may be attributed to the increase of the coordination number in the crystal lattice structure of rubidium and cesium halides as the ionic radii of rubidium and cesium are larger than those of lithium, sodium and potassium.

Larger standard deviations were also found for several higher valent electrolytes. However, absolute values of $\ln^* Y$ of higher valent electrolytes are very large and the effect of
Table 7. Comparison of the Acidic Dissociation Constants with $\tau_{m,ca}$

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a*(\text{or }-\log K_a)$</th>
<th>$\tau_{m,ca}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>-6.1</td>
<td>9.957</td>
</tr>
<tr>
<td>HBr</td>
<td>-9</td>
<td>9.742</td>
</tr>
<tr>
<td>HI</td>
<td>-9.5</td>
<td>9.483</td>
</tr>
</tbody>
</table>

*(Lange's Handbook of Chemistry, 1973)*

Table 8. Comparison of Salt Crystal Lattice Energy with $\tau_{m,ca}$

<table>
<thead>
<tr>
<th>Salt</th>
<th>Lattice Energy* (Born-Habor Cycle)</th>
<th>$\tau_{m,ca}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>201.7</td>
<td>9.900</td>
</tr>
<tr>
<td>NaCl</td>
<td>183.9</td>
<td>8.715</td>
</tr>
<tr>
<td>KCl</td>
<td>168.3</td>
<td>7.917</td>
</tr>
<tr>
<td>RbCl</td>
<td>162.8</td>
<td>8.086</td>
</tr>
<tr>
<td>CsCl</td>
<td>157.2</td>
<td>8.368</td>
</tr>
<tr>
<td>LiBr</td>
<td>191.0</td>
<td>10.331</td>
</tr>
<tr>
<td>NaBr</td>
<td>175.5</td>
<td>8.672</td>
</tr>
<tr>
<td>KBr</td>
<td>160.7</td>
<td>7.901</td>
</tr>
<tr>
<td>RbBr</td>
<td>157.1</td>
<td>7.920</td>
</tr>
<tr>
<td>CsBr</td>
<td>151.2</td>
<td>8.381</td>
</tr>
<tr>
<td>LiF</td>
<td>178.4</td>
<td>9.157</td>
</tr>
<tr>
<td>NaI</td>
<td>164.8</td>
<td>8.752</td>
</tr>
<tr>
<td>KI</td>
<td>151.5</td>
<td>7.620</td>
</tr>
<tr>
<td>RbI</td>
<td>147.9</td>
<td>8.052</td>
</tr>
<tr>
<td>CsI</td>
<td>143.7</td>
<td>8.280</td>
</tr>
</tbody>
</table>

*(Day, Jr. M. C. and J. Selbin, 1969)*
electrolyte concentration upon solution ionic strength is much more pronounced. For example, molality of six for bi-bivalent electrolytes corresponds to an ionic strength of 24 molality. It is reasonable to expect that ion-pairing or ion association occurs at these high ionic strength conditions. In addition, complex ion formation of bivalent cations is a well known phenomenon for many bi-univalent electrolytes. This complex ion formation again makes the assumption of complete electrolyte dissociation invalid and chemical equilibrium of complex ions should have been considered when data correlations were carried out.

A few methanol electrolyte systems were studied. Absolute values of binary parameters were found to be larger for electrolytes in methanol solution than for those in aqueous solution. This can be explained by the fact that dielectric constant of methanol is smaller than that of water. Both the molecule-ion interaction energy and the ion-ion interaction energy are inversely proportional to solvent dielectric constant. Because dielectric constant of methanol is smaller, the interaction energies become larger and so are the absolute values of binary interaction parameters.

In all of the data fitting discussed above, the value of the distance of closest approach of ions was 4 Å. Better fit is expected if this distance is treated as an additional
adjustable parameter. With the distance of closest approach fixed at 4 Å, significant deviation on data fitting was found for several electrolytes at high dilution where long-range contribution dominates and the distance of closest approach of ions is critical in data fitting. However, this was not further pursued in this work.

Another interesting point is that magnitude of the difference of the two binary parameters (\(|\tau_{s,m} - \tau_{m,s}\)|) is around ten for electrolyte systems, while that of nonelectrolyte pairs is normally around one. This is expected as electrostatic interactions between ions are certainly much stronger than interactions between molecular species.

**Temperature Dependency of Binary Interaction Parameters**

The binary interaction parameters are weak function of temperature, as shown in Tables 9 to 11 and Figure 5. These tables and figure give the results of isothermal fits for mean ionic activity coefficient data for aqueous NaCl and KCl at various temperatures. The study of aqueous NaCl covered a 300°K temperature range. Values of the binary parameters of aqueous NaCl in Table 9 are slightly different from those in Table 11 because different water dielectric constant and water density correlations were used. The weak temperature dependence of binary parameters is a significant advantage of
Table 9. Temperature Effect on Data and Results of Fit for Aqueous NaCl Solutions - Mean Ionic Activity Coefficient Data

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>No. of Data* Points</th>
<th>Molality</th>
<th>$\mu_{m,ca}$</th>
<th>$\mu_{ca,m}$</th>
<th>$\sigma_{\ln \gamma}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.831</td>
<td>-4.406</td>
<td>0.018</td>
</tr>
<tr>
<td>298.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.744</td>
<td>-4.409</td>
<td>0.014</td>
</tr>
<tr>
<td>323.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.629</td>
<td>-4.380</td>
<td>0.011</td>
</tr>
<tr>
<td>348.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.510</td>
<td>-4.334</td>
<td>0.008</td>
</tr>
<tr>
<td>373.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.420</td>
<td>-4.288</td>
<td>0.005</td>
</tr>
</tbody>
</table>

*smoothed data (Silvester and Pitzer, 1976)
water dielectric constant = 224.09579 - 0.55576984*t + 0.75057678d-6*(t**2) + 0.75057678d-6*(t**3)
water density = 0.8772673 + 0.7249288d-3*t - 0.36577196d-8*(t**2) - 0.36577196d-8*(t**3)

Table 10. Temperature Effect on Data and Results of Fit for Aqueous KBr Solutions - Mean Ionic Activity Coefficient Data

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>No. of Data* Points</th>
<th>Molality</th>
<th>$\mu_{m,ca}$</th>
<th>$\mu_{ca,m}$</th>
<th>$\sigma_{\ln \gamma}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>333.15</td>
<td>14</td>
<td>0.1-4.0</td>
<td>7.860</td>
<td>-3.994</td>
<td>0.001</td>
</tr>
<tr>
<td>343.15</td>
<td>14</td>
<td>0.1-4.0</td>
<td>7.831</td>
<td>-3.989</td>
<td>0.001</td>
</tr>
<tr>
<td>353.15</td>
<td>14</td>
<td>0.1-4.0</td>
<td>7.773</td>
<td>-3.970</td>
<td>0.001</td>
</tr>
<tr>
<td>363.15</td>
<td>14</td>
<td>0.1-4.0</td>
<td>7.769</td>
<td>-3.971</td>
<td>0.002</td>
</tr>
<tr>
<td>373.15</td>
<td>14</td>
<td>0.1-4.0</td>
<td>7.760</td>
<td>-3.969</td>
<td>0.002</td>
</tr>
</tbody>
</table>

*(Robinson and Stokes, 1970)
water dielectric constant = 224.09579 - 0.55576984*t + 0.75057678d-6*(t**2) + 0.75057678d-6*(t**3)
water density = 0.8772673 + 0.7249288d-3*t - 0.36577196d-8*(t**2) - 0.36577196d-8*(t**3)
Table 11. Temperature Effect on Data and Results of Fit for Aqueous NaCl Solutions  
- Mean Ionic Activity Coefficient Data

<table>
<thead>
<tr>
<th>T°K</th>
<th>No. of Data Points</th>
<th>Molality</th>
<th>τ m,ca</th>
<th>τ ca,m</th>
<th>σ lnγ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.870</td>
<td>-4.418</td>
<td>0.017</td>
</tr>
<tr>
<td>298.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.756</td>
<td>-4.413</td>
<td>0.014</td>
</tr>
<tr>
<td>323.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.630</td>
<td>-4.380</td>
<td>0.011</td>
</tr>
<tr>
<td>348.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.504</td>
<td>-4.332</td>
<td>0.009</td>
</tr>
<tr>
<td>373.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.388</td>
<td>-4.278</td>
<td>0.006</td>
</tr>
<tr>
<td>398.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.281</td>
<td>-4.219</td>
<td>0.004</td>
</tr>
<tr>
<td>423.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.199</td>
<td>-4.162</td>
<td>0.003</td>
</tr>
<tr>
<td>448.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.143</td>
<td>-4.111</td>
<td>0.001</td>
</tr>
<tr>
<td>473.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.115</td>
<td>-4.063</td>
<td>0.002</td>
</tr>
<tr>
<td>498.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.126</td>
<td>-4.024</td>
<td>0.004</td>
</tr>
<tr>
<td>523.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.169</td>
<td>-3.988</td>
<td>0.008</td>
</tr>
<tr>
<td>548.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.245</td>
<td>-3.955</td>
<td>0.011</td>
</tr>
<tr>
<td>573.15</td>
<td>28</td>
<td>0.05-6.0</td>
<td>8.371</td>
<td>-3.924</td>
<td>0.017</td>
</tr>
</tbody>
</table>

* Smoothed data (Silvester and Pitzer, 1976)

1. Water density expression:
   \[
   \text{sum} = 0.015565 + 8.77583D-6(1.8T-459.67) \\
   - 5.30708D-8(1.8T-459.67)^2 \\
   + 2.63708D-10(1.8T-459.67)^3 \\
   - 4.92917D-13(1.8T-459.67)^4 \\
   + 3.70833D-16(1.8T-459.67)^5 \\
   \]
   density = 0.016018/sum

Figure 5. Dimensionless Interaction Parameters as Determined from Isothermal Fits at Various Temperatures
the local composition model. The Pitzer equation parameters are, however, a strong function of temperature (Silvester and Pitzer, 1976).

**Range of Applicability**

The local composition model is designed to be applicable to a wide variety of electrolyte systems. To test the applicability of the model on high electrolyte concentration systems, an electrolyte system extending in the liquid phase from a dilute solution in water to a pure fused salt was studied. The data are water vapor pressures of \([\text{Ag},\text{Tl}]\NO_3-\text{H}_2\text{O}\) system, measured by Trudelle, Abraham and Sangster (1977) at 98°C.

Table 12 shows the correlation results. The local composition model with the Debye-Huckel formula as the long-range interaction contribution model correlated the water activity data with standard deviations in water activity of 0.058. Much better results were obtained by replacing the Debye-Huckel formula with an extended form of the Debye-Huckel expression proposed by Pitzer (1979) for the long-range interaction contribution. The standard deviations in water activity dropped to 0.009 and 0.008, with \(\rho\) being set to 8.94 and 14.9, respectively. The Pitzer-Debye-Huckel expression is

\[
G^{ex,el}_{\text{el}}/RT = -\left(\sum_{k} n_k\right) (1000/M_s) \left(4A_\phi I_x/\rho\right) \ln(1+\rho I_x^{1/2})
\]  

(35)
<table>
<thead>
<tr>
<th></th>
<th>$\tau_{m,ca}$</th>
<th>$\tau_{ca,m}$</th>
<th>$\sigma_{a_w}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.097</td>
<td>-2.842</td>
<td>0.058</td>
</tr>
<tr>
<td>2</td>
<td>6.381</td>
<td>-2.755</td>
<td>0.008</td>
</tr>
<tr>
<td>3</td>
<td>6.382</td>
<td>-2.865</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Table 12. Data Correlation of Water Vapor Pressure of [Ag,Tl]NO$_3$-H$_2$O System at 98°C (Data from Trudelle et al., 1977) (1) Debye-Huckel formula (2) Pitzer-Debye-Huckel Formula, $\rho = 8.94$ (3) Pitzer-Debye-Huckel Formula, $\rho = 14.9$
where \( n_k \) is number of moles of any species. \( M_s \) is the molecular weight of the solvent. \( \rho \) is the "closest approach" parameter. \( I_x \) is the ionic strength on a mole fraction basis.

\[
I_x = (1/2) \sum_i Z_i^2 x_i
\]

(36)

\( A_\phi \) is the usual Debye-Huckel parameter for the osmotic coefficient

\[
A_\phi = (1/3) A
\]

(37)

More studies are necessary to fully understand which Debye-Huckel expression serves best for the local composition model. Nevertheless, this correlation result suggests that the local composition model is applicable for electrolyte systems with composition extending continuously from molecular liquids to fused salts.

Trudelle's data also have been studied successfully by Pitzer (1979). A new equation obtained by combining van Laar's equation with Pitzer-Debye-Huckel expression was adopted in his study.

**Discussion of the Local Composition Model**

The local composition model makes it possible to study
Figure 6. Comparison of the Short-Range Contribution and the Long-Range Contribution on Mean Ionic Activity Coefficients.
The local composition model is not consistent with the commonly accepted solvation theory. According to the solvation theory, ionic species are completely solvated by solvent molecules. In other words, the local mole fraction of solvent molecules around a central ion is unity. This becomes unrealistic when applied to high concentration electrolyte systems since the number of solvent molecules will be insufficient to completely solvate ions. With the local composition model, all ions are, effectively, completely surrounded by solvent molecules in very dilute electrolyte systems and only partially surrounded by solvent molecules in high concentration electrolyte systems. Therefore, the local composition model is believed to be a better physical model than the solvation theory.

Furthermore, the local composition model is consistent with the Debye-Hückel theory in the sense that Boltzmann distribution law is adopted in both models. Both models assume that there are more anions than cations in the immediate neighborhood of a central cation and there are more cations than anions in the immediate neighborhood of a central anion. In other words, there is a negative ionic atmosphere surrounding a central cation and there is a positive ionic atmosphere surrounding a central anion (Chu, 1967).

Incorporated with the Debye-Hückel formula, the Born
theory, and the solvation theory, the NRTL equation has been applied to single solvent, single electrolyte systems by Cruz and Renon (1978). The local composition of solvent molecules around ions is always assumed unity regardless if electrolytes dissociate completely or partially. Four adjustable parameters were proposed by Cruz and Renon to correlate data of isothermal, aqueous single electrolyte systems. Two parameters are involved in the dielectric constant expression of the Born theory and the remaining two are the NRTL parameters related to ion-solvent interaction. No physical meaning of these four parameters was given. It is believed that the local composition model presented in this chapter is superior to Cruz and Renon's model.
Notation

\( A_0 \) = Debye-Huckel constant for the osmotic coefficient
\( D \) = dielectric constant
\( G^e \) = excess Gibbs free energy
\( I \) = ionic strength
\( M_S \) = solvent molecular weight (kg/Kg-mole)
\( N_A \) = Avogadro's number
\( P \) = pressure (N/m\(^2\))
\( R \) = gas constant
\( T \) = temperature (\(^o\)K)
\( Z \) = absolute value of ionic charge
\( d \) = density
\( g^e \) = molar excess Gibbs free energy
\( k \) = Boltzmann constant
\( m \) = molality (g-mole/kg of solvent)
\( n_W \) = number of kg of the solvent, water
\( x \) = liquid phase mole fraction
\( y \) = vapor phase mole fraction

Greek Letters

\( \alpha \) = nonrandomness factor
\( \phi \) = osmotic coefficient
\( \gamma \) = activity coefficient
\( \nu \) = electrolyte stoichiometric coefficient
\( \sigma \) = standard deviation
\( \tau \) = binary interaction energy parameter

Superscripts

\( * \) = unsymmetric convention
\( \infty \) = infinite dilution
\( e_l \) = long-range electrostatic contribution
\( l_c \) = short-range local composition contribution

Subscripts

\( a, a' \) = anion
\( c, c' \) = cation
\( ca \) = salt ca
\( i, j, k \) = any species in the local composition model
\( m \) = any molecular species in the local composition model
\( \text{ref} \) = reference
\( s \) = salt
\( w \) = water
Literature Cited


Chapter 4
A Local Composition Model for the Excess Gibbs Energy of Electrolyte Systems – Multicomponent Systems

Abstract

The local composition model was generalized to multicomponent electrolyte systems. The model is capable of handling wide variety of electrolyte systems. Systems can be composed of strong electrolytes, multiple solvents, molecular solutes, and weak electrolytes. Binary parameters obtained from binary and ternary systems can be used in multicomponent systems. No ternary or higher order parameters are required for multicomponent systems. For the case of mixed-solvent electrolytes, a linear dependence of salt-solvent binary parameters upon the reciprocal of mixed-solvent dielectric constant is recognized. In the absence of electrolytes, the local composition model reduces to the non-random, two-liquid equation (Renon and Prausnitz, 1968) for multicomponent nonelectrolyte systems.

Successful data correlation of many multicomponent electrolyte systems has been carried out to demonstrate validity of the model. These systems include multisalt systems, such as HCl-NaCl-H₂O; mixed-solvent systems, such as CH₃OH-H₂O-NaBr; and weak electrolyte systems, such as Hot Carbonate Process system.
Scope

Because of the short-range of molecular interaction between nonelectrolytes, it is often permissible to consider only interactions between molecules that are first neighbors in calculating the thermodynamic properties of a mixture. The local composition concept, which accounts for the two-body, first neighbor interactions, has therefore been applied very successfully as a tool in molecular thermodynamics to obtain expressions for excess Gibbs energy in terms of adjustable interaction energy parameters. Examples are Wilson equation (1964), NRTL equation (Renon and Prausnitz, 1968), and UNIQUAC equation (Abrams and Prausnitz, 1975). These models consider only two-body intermolecular interactions. A useful consequence of this simplifying assumption is that extension to ternary (and higher) systems requires only binary, i.e., two-body, information; no ternary (or higher) parameters appear.

A fundamental difference between electrolyte systems and nonelectrolyte systems is the presence of long-range ion-ion interaction in electrolyte systems. In order to apply the local composition model to electrolyte systems, it was proposed (see Chapter 3) that the excess Gibbs energy of electrolyte systems be represented as the sum of two contributions, one resulting from long-range electrostatic forces between ions, and the other from short-range forces between all the species.
The long-range interaction contribution was modeled with the Debye-Huckel formula and the short-range contribution was modeled with the local composition concept. Because the Debye-Huckel formula is a function of solvent density, solvent dielectric constant and total electrolyte ionic strength, the long-range interaction contribution is universal for all types of electrolytes. It is the short-range interaction contribution that accounts for specific characteristics of interactions of various electrolytes.

The objective of the work described in this chapter is to generalize the local composition model to apply to multicomponent electrolyte systems. There are many different types of multicomponent electrolyte systems. Systems can be composed of any number of solvents, molecular solutes, weak electrolytes, and strong electrolytes. For instance, HCl-KCl-H$_2$O is a multi-electrolyte, one-solvent electrolyte system; H$_2$O-CO$_2$-NaCl is a solvent-molecular solute-salt system; methanol-water-LiBr is an mixed-solvent electrolyte system; and K$_2$CO$_3$-CO$_2$-H$_2$O is a weak electrolyte system.

**Conclusions and Significance**

The local composition model was generalized to make it applicable to all kinds of multicomponent electrolyte systems.
Components can be strong electrolytes, weak electrolytes, molecular solvent, and molecular solutes. Because only two-body short-range interactions are considered for the short-range interaction contribution, the model needs only binary parameters in the expression for excess Gibbs energy of multicomponent systems. Therefore, properties of a multicomponent system can be calculated using only binary parameters of the system's constituent binaries.

The linear dependence of salt-solvent binary parameters on reciprocal dielectric constant of the solvent is recognized for mixed-solvent electrolyte systems. The equation reduces to the Non-Random, Two-Liquid (NRTL) equation for systems without electrolytes. Validity of the model for multicomponent electrolyte systems has been demonstrated by successful data correlations of many multicomponent systems using only binary parameters.

General Multicomponent Electrolyte Equation

The basic approach of the local composition model is that the long-range interaction contribution be represented by a Debye-Hückel expression and the short-range interaction contribution be taken into account by applying the local composition concept.
For multicomponent systems, the excess Gibbs energy expression of the long-range interaction contribution calculated with the Debye-Huckel formula is essentially the same as that of binary systems (see Chapter 3). The Debye-Huckel formula is a function of solvent density, solvent dielectric constant, and total electrolyte ionic strength. Therefore, in the case of mixed-solvent electrolyte systems, mixed-solvent density and dielectric constant are required, and their dependence on solvent composition must be known. The details of the Debye-Huckel formula have been given in Chapter 3.

In developing the short-range interaction contribution of the excess Gibbs energy expression with the local composition concept, only two-body, first neighbor interactions are considered. Therefore the assumptions for multicomponent electrolyte systems are the same as those of binary systems. No additional assumptions are required for multicomponent systems.

Two fundamental assumptions proposed in developing the local composition model for binary electrolyte systems were:

1) The local composition of anions around a central anion is zero, and the local composition of cations around a central cation is zero;
2) The distribution of anions and cations around a central solvent molecule is such that the net ionic charge is zero.

The first assumption is referred to as the like-ion repulsion assumption and the second assumption as the local electroneutrality assumption.

The derivation of the excess Gibbs energy expression for the short-range interaction contribution of multicomponent electrolyte systems is given below.

The local mole fractions \( x_{ji} \) and \( x_{ij} \) of species \( j \) and \( i \), respectively, in the immediate neighborhood of a central species \( i \) are related by:

\[
x_{ji}/x_{ij} = (x_{j}/x_{i})G_{ji} \tag{1}
\]

where

\[
G_{ji} = \exp(-\alpha \tau_{ji}) \tag{2}
\]

\[
\tau_{ji} = (g_{ji} - g_{ii})/RT \tag{3}
\]

The local mole fractions \( x_{ji} \) and \( x_{ki} \) of species \( j \) and \( k \) in the immediate neighborhood of a central species \( i \) are related by:
\[ \frac{x_{ji}}{x_{ki}} = \frac{x_{j}}{x_{k}} G_{ji,k_i} \quad (4) \]

where
\[ G_{ji,k_i} = \exp(-\alpha_{ji,k_i}) \quad (5) \]
\[ \tau_{ji,k_i} = (g_{ji} - g_{ki}) / RT \quad (6) \]

In multicomponent electrolyte systems, there are three types of cells. One type consists of a central molecule with molecules, cations and anions in the immediate neighborhood. The other two types have either cation or anion as the central species, and an immediate neighborhood consisting of molecules and oppositely-charged ions, but no ions of like charge. The local mole fractions are related by:

\[ \sum_{c'} x_{c'm} + \sum_{a'} x_{a'm} + \sum_{m'} x_{m'm} = 1 \quad \text{(central molecule cells)} \quad (7-1) \]
\[ \sum_{a'} x_{a'c} + \sum_{m'} x_{m'c} = 1 \quad \text{(central cation cells)} \quad (7-2) \]
\[ \sum_{c'} x_{c'a} + \sum_{m'} x_{m'a} = 1 \quad \text{(central anion cells)} \quad (7-3) \]

By combining equations (1), (4) and (7) the following expressions for the local mole fractions in terms of overall mole fractions may be derived.

\[ x_{im} = x_{i} G_{im} / \left( \sum_{a'} x_{a'} G_{a'm} + \sum_{c'} x_{c'} G_{c'm} + \sum_{m'} x_{m'} G_{m'm} \right) \quad (8-1) \]
\[ x_{ac} = x_{a} / \left( \sum_{a'} x_{a'} G_{a'c} + \sum_{c'} x_{c'} G_{c'm} + \sum_{m'} x_{m'} G_{m'c} \right) \quad (8-2) \]
\[ x_{ca} = x_{c} / \left( \sum_{c'} x_{c'} G_{c'a} + \sum_{m'} x_{m'} G_{m'a} \right) \quad (8-3) \]
The residual Gibbs energies per mole of cells of central cation, central anion and central molecule are related to the local mole fractions as follows:

\[ g_c = \sum_{m'} g_{m'}^c + \sum_{a'} g_{a'}^c \]  \hspace{1cm} (9-1)
\[ g_a = \sum_{m'} g_{m'}^a + \sum_{c'} g_{c'}^a \]  \hspace{1cm} (9-2)
\[ g_m = \sum_{c'} g_{c'}^m + \sum_{a'} g_{a'}^m + \sum_{m'} g_{m'}^m \]  \hspace{1cm} (9-3)

One then adopts the pure component as the reference state for molecules, and the hypothetical, homogeneously-mixed, completely-dissociated liquid electrolytes as the reference state for electrolytes. The reference Gibbs energies per mole are then:

\[ g_{ref}^c = \sum_{a'} (x_{a'} g_{a'}^c) / \sum_{a''} (x_{a''}) \]  \hspace{1cm} (10-1)
\[ g_{ref}^a = \sum_{c'} (x_{c'} g_{c'}^a) / \sum_{c''} (x_{c''}) \]  \hspace{1cm} (10-2)
\[ g_{ref}^m = g_{ref}^m \]  \hspace{1cm} (10-3)

The molar excess Gibbs energy may now be derived by summing the changes in residual Gibbs energy resulting from transferring molecules and ions from their reference states to their respective cells in the mixture. The expression is:

\[ g_{ex, 1c} = \sum_m x_m (g_m - g_{ref}^m) \]
\[ + \sum_c x_c (g_c - g_{ref}^c) \]
\[ + \sum_a x_a (g_a - g_{ref}^a) \]  \hspace{1cm} (11)
Substituting equations (9) and (10) into equation (11), one obtains:

\[
g^\text{ex,lc}/RT = \sum_m \left( \sum_j x_{jm} \tau_{jm} \right) + \sum_c x_c Z_c \left( \sum_j x_j \tau_{jc}, a'c \right) / \sum_a x_a Z_a
\]

\[
+ \sum_a Z_a \left( \sum_j x_j \tau_{ja}, c'a \right) / \sum_c x_c Z_c
\]

(12)

The corresponding activity coefficient expressions for various species can be derived as follows.

\[
\ln \gamma_m = \sum_m G_{mk} x_{jm} \tau_{jm} / \sum_k G_{km} x_k
\]

\[
+ \sum_m G_m \left( \sum_{mm'} x_{km} G_{km} \right) / \sum_j G_{jm} x_j
\]

\[
+ \sum_j x_j \tau_{jc}, c'a \right) / \sum_c G_{jc} x_j
\]

(13)

\[
\ln \gamma_c = Z_c, a', \sum_j x_j, a'c \tau_{jc}, a'c / \sum_a x_a
\]

\[
+ \sum_j x_j \tau_{jm} \sum_k G_{km} \right) / \sum_j G_{jm} x_j
\]

\[
+ \sum_a Z_a, c', \left( x_a G_{ca}, c'a, c \right) / \sum_k G_{ka} x_k
\]

(14-1)

\[
\ln \gamma_a = Z_a, c, \sum_j x_j, c' \tau_{ja}, c' a / \sum_c x_c
\]

\[
+ \sum_j x_j \tau_{jm} \sum_k G_{km} \right) / \sum_j G_{jm} x_j
\]

\[
+ \sum_c Z_c, a', \left( x_c G_{ac}, a'c \right) / \sum_k G_{kc} x_k
\]

(14-2)
Unsymmetric excess Gibbs energy expression can be obtained from equation (12) and infinite dilution activity coefficient expressions. If water is the only solvent, infinite dilution activity coefficients of molecular solutes, cations and anions are:

\[ \ln \gamma_m^\infty = \tau_{wm} + G_{mw} \tau_{mw} \]  
\[ \ln \gamma_c^\infty = \sum_c x_c z_c \tau_{wc,c} + \sum_{a,a'} \frac{x_a z_a}{c_{a'} c} \]  
\[ + G_{cw} \tau_{cw} \]  
\[ \ln \gamma_a^\infty = \sum_c x_c z_c \tau_{wa,c} \frac{c}{c'} c \frac{c'}{c''} \]  
\[ + G_{aw} \tau_{aw} \]  

and unsymmetric excess Gibbs energy becomes:

\[ g_{ex^*,lc}^{\infty} = g_{ex,lc}^{\infty} - \sum_c x_c \ln \gamma_c^\infty - \sum_a x_a \ln \gamma_a^\infty - \sum_m x_m \ln \gamma_m^\infty \]  

In the absence of electrolytes, the local composition model is exactly the same as the NRTL equation, which has been used widely for nonelectrolyte systems. Therefore, binary parameters of nonelectrolyte pairs can be obtained from studies of nonelectrolyte systems. The local composition model offers a unified model for electrolytes and nonelectrolytes.

**Determination of Ion-Molecule Interaction Parameters**

There are three types of interaction parameters in the
derived short-range Gibbs energy expression, equation 12. They are ion-molecule parameters, molecule-ion parameters, and ion-ion parameters. A practical problem in the generalization of the local composition model is that binary interaction parameters determined from binary electrolyte systems of single solvent and single completely-dissociated electrolyte are salt-molecule binary parameters while real interacting species in electrolyte systems are ions and molecules. In binary electrolyte systems, the problem is resolved by the following consequence of the local electroneutrality assumption (see Chapter 3):

\[ ^\tau_{cm} = ^\tau_{am} = ^\tau_{ca,m} \quad (18-1) \]
\[ ^\tau_{mc} = ^\tau_{ma} = ^\tau_{m,ca} \quad (18-2) \]

In other words, ion-molecule interaction parameters are equal to salt-molecule binary parameters. This is not in general true for multicomponent systems. However, ion-molecule interaction parameters can always be derived from salt-molecule binary parameters as shown later in this section. Therefore salt-molecule binary parameters are still considered to be the adjustable parameters of the local composition model for multicomponent electrolyte systems.

Applying the local electroneutrality constraint to cells of central molecular species \( m \), the following expression can be
derived:

\[ \Sigma x_{cm}Z_{cm} = \Sigma x_{am}Z_{am} \]  \hspace{0.5cm} (19)

For a binary electrolyte system consisting of salt ca and solvent m, equation (19) reduces to

\[ x_{cm}Z_{cm} = x_{am}Z_{am} \]  \hspace{0.5cm} (20)

Since solution electroneutrality requires \( x_{cm}Z_{cm} = x_{am}Z_{am} \), it follows that:

\[ G_{cm} = G_{am} = G_{ca,m} \]  \hspace{0.5cm} (21)

or

\[ \tau_{cm} = \tau_{am} = \tau_{ca,m} \]  \hspace{0.5cm} (22)

Equation (22) is the same as equation (18-1).

However, the relationships between the parameters for a multicomponent system are more complicated. For a ternary electrolyte system consisting of salt ca', salt ca'', and solvent m, equation (19) becomes

\[ x_{cm}Z_{cm} = x_{am}Z_{am}G_{a,m} + x_{am}Z_{am}G_{a,m} \]  \hspace{0.5cm} (23)

Because the local composition concept considers only two
body interactions and like-ion repulsion is assumed, existence of anion a" should not affect the local composition around a' anion cells. This suggests that the local compositions around a' and a" anion cells in the ternary system ca'-ca"-m are the same as those in the binary systems ca'-m and ca"-m. Therefore,

\[
G_{a'm} = G_{ca'}, \quad (24-1) \\
G_{a"m} = G_{ca"}, \quad (24-2)
\]

Combining equations (23) and (24), one obtains

\[
G_{cm} = (x_{a'}Z_{a',}G_{ca'}, m + x_{a"}Z_{a"}G_{ca"}, m) / x_{c'}^Z_{c}
\]

or

\[
G_{cm} = (x_{a'}Z_{a',}G_{ca'}, m + x_{a"}Z_{a"}G_{ca"}, m) / (x_{a'}Z_{a'} + x_{a"}Z_{a"}) \quad (25)
\]

For an electrolyte system consisting of cations c', and c", anions a' and a", and solvent m, the local compositions around a' and a" anion cells of the system are the same as those in the ternary systems c'a'-c"a'-m and c'a"-c"a"-m. Similarly, the local compositions around c' and c" cation cells in the system are the same as those in the ternary systems c'a'-c'a"-m and c"a'-c"a"-m. Therefore,

\[
G_{c'm} = (x_{c'}Z_{c',}G_{c'a'}, m + x_{c"}Z_{c"}G_{c'a"}, m) / (x_{c'}Z_{c'} + x_{c"}Z_{c"}) \quad (26-1)
\]

\[
G_{c"m} = (x_{c'}Z_{c',}G_{c"a"}, m + x_{c"}Z_{c"}G_{c"a"}, m) / (x_{c'}Z_{c'} + x_{c"}Z_{c"}) \quad (26-2)
\]

\[
G_{a'm} = (x_{c'}Z_{c',}G_{c'a'}, m + x_{c"}Z_{c"}G_{c'a"}, m) / (x_{c'}Z_{c'} + x_{c"}Z_{c"}) \quad (26-3)
\]

\[
G_{a"m} = (x_{c'}Z_{c',}G_{c'a"}, m + x_{c"}Z_{c"}G_{c'a"}, m) / (x_{c'}Z_{c'} + x_{c"}Z_{c"}) \quad (26-4)
\]
Equations (26) can be generalized for any multicomponent system as follows:

\[
G_{cm} = \sum_a x_a Z_a G_{ac}, m/\sum_a x_a Z_a \quad (27-1)
\]

\[
G_{am} = \sum_c x_c Z_c G_{ac}, m/\sum_c x_c Z_c \quad (27-2)
\]

It should be noted that equations (27) satisfy equation (19).

Therefore, the values of \( G_{im} \)'s in multicomponent systems are different from those in binary systems. From \( G_{im} \)'s, \( \tau_{im} \)'s can be computed accordingly. Ion-molecule interaction parameters, \( \tau_{im} \)'s, are functions of salt-molecule binary parameters and system composition.

Molecule-ion interaction parameters are also functions of salt-molecule binary parameters and system composition. These interaction parameters can be calculated from \( \tau_{im} \)'s.

\[
\tau_{ma'}, c'a' = (g_{ma'} - g_{c'a'})/RT
\]

\[
= (g_{ma'} - g_{mm})/RT + (g_{mm} - g_{c'a'})/RT
\]

\[
= \tau_{a'm} - \tau_{c'a'}, m + \tau_{m}, c'a' \quad (28-1)
\]

and

\[
\tau_{mc'}, a'c' = \tau_{c'm} - \tau_{c'a'}, m + \tau_{m}, a'c' \quad (28-2)
\]

Ion-ion interaction parameters are directly related to salt-salt binary parameters. There are no binary parameters for salt-salt pairs without a common ion. If two salts, c'a
and $c''a$, are of the same type, such as uni-univalent electrolytes, ion-ion interaction parameters, $\tau_{c'a,c''a}$ and $\tau_{c''a,c'a}$ can be related by

$$
\tau_{c'a,c''a} = \frac{(g_{c'a} - g_{c''a})}{RT} \\
= -(g_{c''a} - g_{c'a}) / RT \\
= -\tau_{c''a,c'a}
$$

(29)

This is because both $g_{c'a}$ and $g_{c''a}$ are supposed to be pure electrolyte properties. This relationship may not be valid if the two mixing electrolytes have different coordination numbers or are not of the same type. In this case of "unsymmetric mixing", lattice structure is changed. Thus, $g_{c'a}$ and $g_{c''a}$ of multicomponent electrolyte systems may be different from those of pure components.

It should be emphasized that, except for cases of "unsymmetric mixing", interaction energies $g_{mm}$ and $g_{ca}$ are characteristics of pure component solvent $m$ and electrolyte $ca$, respectively. Therefore, they are pure component properties and do not change with system composition. However, interaction energies $g_{cm}$ and $g_{am}$ are functions of system composition and binary parameters.

**Study of Strong Electrolyte Systems**

In a system with more than two ions, electrolyte systems
can be complicated. For instance, two electrolytes, KCl and KBr, exist in an aqueous solution containing $K^+$, $Cl^-$ and $Br^-$ ions. Four electrolytes, KCl, KBr, NaCl and NaBr, exist in an aqueous solution containing $K^+$, $Na^+$, $Cl^-$ and $Br^-$ ions.

Binary parameters of the local composition model are developed to account for two-body molecule-molecule, molecule-salt, and salt-salt interactions. There are no binary parameters for salt-salt pairs without a common ion. In an aqueous electrolyte system with $H^+$, $K^+$ and $Cl^-$ ions, there are four binary parameters for the two water-salt pairs, i.e., $H_2O$-$HCl$ pair and $H_2O$-$KCl$ pair. There are another two binary parameters for the salt-salt pair with common ion, i.e., $HCl$-$KCl$ pair. Since these two salts are of same type, i.e., uni-univalent electrolytes, equation (29) can be applied. Therefore, there are five binary parameters in the three ion system. In an aqueous electrolyte system with $K^+$, $Na^+$, $Cl^-$, and $Br^-$ ions, there are eight binary parameters for the four water-salt binary pairs, i.e., $H_2O$-$KCl$ pair, $H_2O$-$KBr$ pair, $H_2O$-$NaCl$ pair, and $H_2O$-$NaBr$ pair. There are another eight parameters for the four salt-salt pairs with common ion, i.e., KCl-KBr pair, NaCl-NaBr pair, KCl-NaCl pair, and KBr-NaBr pair. Again, all four salts are uni-univalent electrolytes and equation (29) can be applied. For this four ion system, there are twelve binary parameters in total.
An advantage of models based on the local composition concept is that binary parameters of a multicomponent system and binary parameters of its constituent binary systems are the same and no higher order parameters are required. Therefore, binary parameters of solvent-salt pairs of a multicomponent system can be obtained from data correlations of binary solvent-salt systems. Since data are not available for salt-salt binary systems, the only way to estimate binary salt-salt parameters is through data fitting of solvent-salt-salt ternary systems. This is a special characteristic of electrolyte systems.

Mean ionic activity coefficient data of several ternary aqueous strong electrolyte systems have been correlated successfully using the local composition model. Results are given in Table 1. Binary parameters of all salt-water binary pairs were taken from Chapter 3. Only one salt-salt binary parameter was adjusted in each case. Compared with salt-water binary parameters, all salt-salt binary parameters reported in Table 1 are relatively small. It suggests that the interaction between two salts is relatively weak.

Study of Mixed-Solvent Electrolyte Systems

Another type of multicomponent electrolyte systems consists of salts and mixed-solvent, such as a methanol-water-salt
Table 1. Data and Results of Fit for the Mean Ionic Activity Coefficients of HCl and HBr in Halide Solutions at 298.15°K
Acid Concentration = 0.01M (approximated as 0.01m)

<table>
<thead>
<tr>
<th>Acid</th>
<th>Salt</th>
<th>No. of Data*</th>
<th>Highest Salt Molality</th>
<th>$\tau_{MX, HX} = -\tau_{HX, MX}$</th>
<th>$\sum \ln \gamma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>KCl</td>
<td>13</td>
<td>3.5</td>
<td>-1.633</td>
<td>0.020</td>
</tr>
<tr>
<td>HCl</td>
<td>NaCl</td>
<td>9</td>
<td>3.0</td>
<td>-1.129</td>
<td>0.008</td>
</tr>
<tr>
<td>HCl</td>
<td>LiCl</td>
<td>11</td>
<td>4.0</td>
<td>-0.106</td>
<td>0.022</td>
</tr>
<tr>
<td>HBr</td>
<td>KBr</td>
<td>12</td>
<td>3.0</td>
<td>-1.464</td>
<td>0.009</td>
</tr>
<tr>
<td>HBr</td>
<td>NaBr</td>
<td>11</td>
<td>3.0</td>
<td>-1.113</td>
<td>0.007</td>
</tr>
<tr>
<td>HBr</td>
<td>LiBr</td>
<td>15</td>
<td>3.0</td>
<td>-0.307</td>
<td>0.027</td>
</tr>
</tbody>
</table>

*(Harned and Owen, 1958)*
Figure 1. Comparison of the Calculated and Experimental Mean Ionic Activity Coefficients of HCl in the KCl Aqueous Solution at 298.15°K

\[ m_{\text{HCl}} = m_{\text{total}} \]
\[ m_{\text{HCl}} = 0.01 \]
\[ m_{\text{KCl}} = m_{\text{total}} - m_{\text{HCl}} \]
system. Vapor-liquid equilibrium of such mixed-solvent electrolye systems has never been studied with a thermodynamic model that takes into account the presence of salts explicitly. The local composition model provides a tool to study these electrolyte systems and does account for the presence of salts explicitly.

The addition of salt to a binary solution, such as a methanol-water system, has a notable effect on the vapor-liquid equilibrium of the system. For instance, it was observed that the presence of salt can either raise or lower the relative volatility between the components of the system and in extreme cases, causes the formation of two liquid phases.

In general, two approaches have been used to correlate the salt effects. Furter (1958) developed what appears to be the most popular approach by correlating the ratio of relative volatilities of the solvents as a function of salt concentration.

\[
\ln \frac{\alpha_s}{\alpha} = k_s x_s
\]  
(30)

In other words, the equation defines an improvement factor, which consists of the ratio of relative volatility with salt present (calculated using liquid composition on a salt-free basis) to relative volatility at the same liquid composition.
but without salt present. It relates the logarithm of this improvement factor in a direct proportionality with $x_s$, the actual mole fraction of salt present in the liquid on a ternary basis.

An alternative approach is to estimate the activity coefficients of the solvents from experimental data and correlate these activity coefficients using, for example, the Wilson equation. Essentially, the salt - solvent 1 - solvent 2 system is treated as a pseudobinary by expressing the solvent compositions on a salt-free basis. Then, the definition of the solvent reference state is modified. Instead of defining as the reference fugacity the saturated vapor pressure of the pure component, it is defined as that of the pure component as depressed individually by the presence of salt, at the salt concentration and temperature in question. Of course, the modified reference state is a function of salt concentration.

Recently, a procedure capable of correlating equilibrium data for various salt and solvent compositions was proposed by Boone, Rousseau, and Schoenborn (1976). In their model, the ternary mixture of salt - solvent 1 - solvent 2 was treated as a binary solution by defining the mixture of component 2 and salt as fixed ratio as a pseudocomponent. This pseudocomponent then forms a pseudobinary system with the other solvent. An obvious disadvantage is that each salt to solvent 2 ratio
results in a different pseudobinary system. The problem was resolved by a determination of the effect of salt molality on infinite dilution activity coefficients of the pseudobinary components. The technique of Shreiber and Eckert (1971) was then used to estimate the Wilson parameters from the infinite dilution activity coefficients. To correlate equilibrium data for various salt and solvent compositions, vapor pressure lowering data, salt free infinite dilution activity coefficients, and a single system dependent parameter (Sectchenow constant) are required. These values are used to estimate different Wilson parameters at different salt and solvent compositions.

The proposed local composition model is thermodynamically sound and generalized so that it can be used to correlate equilibrium data for systems of various salt and solvent compositions. To apply the local composition model to mixed-solvent electrolyte systems, mixed-solvent density and dielectric constant are necessary to calculate the long-range interaction contribution for the Debye-Huckel formula. The dependence of binary parameters on mixed-solvent dielectric constant is also required in calculating the short-range interaction contribution.

Binary parameters of solvent-salt binary pairs are function of mixed-solvent dielectric constant because ion-molecule
interaction energies, $g_{ma}$ and $g_{mc}$, are function of solvent dielectric constant. It is known that the mutual potential energy of a point charge $Z_e$ and a dipole of moment $\mu$, is known to be

$$Ze\mu \cos \theta/r^2$$

where $r$ is the separation distance. $\theta$ is the angle between the axis of the dipole and the radius vector passing through the ion (Robinson and Stokes, 1970). Therefore, ion-molecule interaction energies should be linear function of the reciprocal of solvent dielectric constant. However, pure component reference state interaction energies, such as $g_{mm}$ and $g_{ca}$, should be characteristics of each pure component and not dependent on solvent dielectric constant.

Therefore, the solvent dielectric constant dependence of binary parameters of solvent-salt binary pairs can be written as follows:

$$\tau_{m,ca}^{(D)} = \tau_{m,ca}^{(D')} + A(1/D-1/D') \quad (31-1)$$

$$\tau_{ca,m}^{(D)} = \tau_{ca,m}^{(D')} + A(1/D-1/D') \quad (31-2)$$

where $D'$ is a reference dielectric constant.

The linear function of ion-molecule interaction energies on the reciprocal of solvent dielectric constant can be approximated as negatively proportional to solvent dielectric
constant in the region of dielectric constants $D'$ and $D''$, equations (31) can be written as

\[ \tau_{m,ca}(D) = \tau_{m,ca}(D') + B(D' - D)/(D' - D'') \]  
\[ \tau_{ca,m}(D) = \tau_{m,ca}(D') + B(D' - D)/(D' - D'') \]

(32-1)  
(32-2)

Mixed-solvent ternary electrolyte system data are required to estimate the dielectric constant dependence parameters, A or B. However, the dielectric constant dependence parameters should be a characteristic of each salt-solvent binary pair and independent of solvent compositions. Ternary system data are used to obtain information about the dielectric constant dependence of binary parameters of binary salt-solvent binary pairs.

Vapor-liquid equilibrium data correlations of methanol-water-NaBr and methanol-water-LiCl at 298.15 K were carried out successfully. Results are given in Tables 2 and 3. Dielectric constant and density of the mixed-solvent, methanol-water, were expressed as polynorninal functions of solvent composition. Parameters B in equations (32) were adjusted during data correlation.

Study of Salting-Out Effect

The effect of strong electrolytes on the solubility of
Table 2. Vapor-Liquid Equilibrium Data Correlation for Methanol-Water-NaBr system at 298.15°K

<table>
<thead>
<tr>
<th>$x_1'$</th>
<th>$x_2'$</th>
<th>Salt Molality</th>
<th>Expt. Data*</th>
<th>Calc. Value</th>
<th>diff P</th>
<th>diff Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.148</td>
<td>0.852</td>
<td>1</td>
<td>49.8 0.603</td>
<td>50.4 0.622</td>
<td>+0.6</td>
<td>+0.019</td>
</tr>
<tr>
<td>0.148</td>
<td>0.852</td>
<td>2</td>
<td>50.1 0.627</td>
<td>52.7 0.655</td>
<td>+2.6</td>
<td>+0.028</td>
</tr>
<tr>
<td>0.148</td>
<td>0.852</td>
<td>4</td>
<td>51.1 0.675</td>
<td>53.2 0.686</td>
<td>+2.1</td>
<td>+0.011</td>
</tr>
<tr>
<td>0.148</td>
<td>0.852</td>
<td>7.1</td>
<td>50.4 0.756</td>
<td>47.7 0.693</td>
<td>-2.7</td>
<td>-0.063</td>
</tr>
<tr>
<td>0.292</td>
<td>0.708</td>
<td>1</td>
<td>68.0 0.742</td>
<td>68.7 0.766</td>
<td>+0.7</td>
<td>+0.024</td>
</tr>
<tr>
<td>0.292</td>
<td>0.708</td>
<td>2</td>
<td>68.9 0.762</td>
<td>70.9 0.783</td>
<td>+2.0</td>
<td>+0.021</td>
</tr>
<tr>
<td>0.292</td>
<td>0.708</td>
<td>4</td>
<td>68.6 0.798</td>
<td>69.3 0.792</td>
<td>+0.7</td>
<td>-0.006</td>
</tr>
<tr>
<td>0.292</td>
<td>0.708</td>
<td>5.7</td>
<td>65.2 0.820</td>
<td>64.2 0.788</td>
<td>-1.0</td>
<td>-0.032</td>
</tr>
<tr>
<td>0.500</td>
<td>0.500</td>
<td>1</td>
<td>85.1 0.850</td>
<td>86.9 0.859</td>
<td>+1.8</td>
<td>+0.009</td>
</tr>
<tr>
<td>0.500</td>
<td>0.500</td>
<td>2</td>
<td>84.4 0.860</td>
<td>86.7 0.862</td>
<td>+2.3</td>
<td>+0.002</td>
</tr>
<tr>
<td>0.500</td>
<td>0.500</td>
<td>4</td>
<td>80.4 0.884</td>
<td>79.9 0.853</td>
<td>-0.5</td>
<td>-0.031</td>
</tr>
<tr>
<td>0.700</td>
<td>0.300</td>
<td>1</td>
<td>99.5 0.920</td>
<td>100.4 0.916</td>
<td>+0.9</td>
<td>-0.004</td>
</tr>
<tr>
<td>0.700</td>
<td>0.300</td>
<td>2</td>
<td>95.7 0.926</td>
<td>97.2 0.911</td>
<td>+1.5</td>
<td>-0.015</td>
</tr>
<tr>
<td>0.700</td>
<td>0.300</td>
<td>2.8</td>
<td>91.4 0.932</td>
<td>92.7 0.906</td>
<td>+1.3</td>
<td>-0.026</td>
</tr>
<tr>
<td>0.900</td>
<td>0.100</td>
<td>1</td>
<td>114.2 0.977</td>
<td>113.6 0.969</td>
<td>-0.6</td>
<td>-0.008</td>
</tr>
<tr>
<td>0.900</td>
<td>0.100</td>
<td>1.9</td>
<td>107.3 0.979</td>
<td>107.1 0.966</td>
<td>-0.2</td>
<td>-0.013</td>
</tr>
</tbody>
</table>

Mean dev. 1.35 0.0195

$t_{H_2O,NaBr} = 8.672 + 0.244*(78.48-D)/(78.48-32.66)$

$t_{NaBr,H_2O} = -4.435 + 0.244*(78.48-D)/(78.48-32.66)$

$t_{CH_3OH,NaBr} = 10.717 - 3.493*(32.66-D)/(78.48-32.66)$

$t_{NaBr,CH_3OH} = -5.176 - 3.493*(32.66-D)/(78.48-32.66)$

$t_{H_2O,CH_3OH} = 0.2944$

$t_{CH_3OH,H_2O} = 0.1936$

(methanol-water binary data obtained from Gmehling, J. and U. Onken, 1977)

$d = 0.9971 + (-0.163939D - 2)*(x_1') + (0.170563D - 5)*(x_1')^2$ $- (0.6285073D - 7)*(x_1')^3$

$D = 78.48 - (0.4233608)*(x_1') - (0.3307047D - 3)*(x_1')^2$ $- (0.3434429D - 7)*(x_1')^3$

$x_1' = x_{CH_3OH}/(x_{CH_3OH} + x_{H_2O})$

$x_2' = x_{H_2O}/(x_{CH_3OH} + x_{H_2O})$

*(Ciparis, 1966)

**(unit: mmHg)
Table 3. Vapor-Liquid Equilibrium Data Correlation for Methanol-Water-LiCl system at 298.15K

<table>
<thead>
<tr>
<th>$x_1'$</th>
<th>$x_2'$</th>
<th>Salt Molality</th>
<th>Expt. Data*</th>
<th>Calc. Value</th>
<th>diff P</th>
<th>diff y</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P** Y1</td>
<td>P** Y1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.152</td>
<td>0.848</td>
<td>1</td>
<td>47.3 0.605</td>
<td>47.7 0.597</td>
<td>+0.4</td>
<td>-0.008</td>
</tr>
<tr>
<td>0.298</td>
<td>0.702</td>
<td>1</td>
<td>65.3 0.765</td>
<td>65.2 0.751</td>
<td>-0.1</td>
<td>-0.014</td>
</tr>
<tr>
<td>0.470</td>
<td>0.530</td>
<td>1</td>
<td>80.0 0.860</td>
<td>81.0 0.840</td>
<td>+1.0</td>
<td>-0.020</td>
</tr>
<tr>
<td>0.700</td>
<td>0.300</td>
<td>1</td>
<td>96.3 0.930</td>
<td>98.6 0.917</td>
<td>+2.3</td>
<td>-0.013</td>
</tr>
<tr>
<td>0.958</td>
<td>0.042</td>
<td>1</td>
<td>115.3 0.993</td>
<td>117.4 0.988</td>
<td>+2.1</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

| mean dev. | 1.2 | 0.012 |

\[
\begin{align*}
\tau_{H_2O,LiCl} &= 9.900 - 0.2239 \times (78.48 - D)/(78.48 - 32.66) \\
\tau_{LiCl,H_2O} &= -5.046 - 0.2239 \times (78.48 - D)/(78.48 - 32.66) \\
\tau_{CH_3OH,LiCl} &= 11.783 - 1.853 \times (32.66 - D)/(78.48 - 32.66) \\
\tau_{LiCl,CH_3OH} &= -5.562 - 1.853 \times (32.66 - D)/(78.48 - 32.66) \\
\tau_{CH_3OH,H_2O} &= 0.1936 \\
H_2O,CH_3OH &= 0.2944 \\
\end{align*}

(Methanol-water binary data obtained from Gmehling, J. and U. Onken, 1977)

\[
\begin{align*}
d &= 0.9971 + (-0.163939D - 2) \times (x_1') + (0.1701563D - 5) \times (x_1')^2 \\
&\quad - (0.6285073D - 7) \times (x_1')^3 \\
D &= 78.48 - (0.4233608) \times (x_1') - (0.3307047D - 3) \times (x_1')^2 \\
&\quad - (0.3434429D - 7) \times (x_1')^3 \\
\end{align*}
\]

\[
\begin{align*}
x_1' &= x_{CH_3OH}/(x_{CH_3OH} + x_{H_2O}) \\
x_2' &= x_{H_2O}/(x_{CH_3OH} + x_{H_2O}) \\
\end{align*}
\]

*(Cipariss, 1966)

**(unit: mmHg)
molecular solutes is often correlated using the Setschenow equation. The Setschenow equation is

$$\ln \gamma_m = k_{s,m} m_s$$

(33)

where $k_{s,m}$ is the Setschenow constant and $m_s$ is the molality of the salt. However, the Setschenow equation is not a good approximation unless solubility of molecular solutes is very small (Gordon, 1975). The relationship assumed by the Setschenow equation is often too simple to adequately describe a thermodynamic system with complex interactions.

The salting-out effect can be studied using the local composition model. One example is the NaCl-CO$_2$-H$_2$O system. In the absence of salt, the activity coefficient of CO$_2$ in H$_2$O is determined by the two-body short-range interaction between CO$_2$ and H$_2$O. Addition of NaCl introduces various interactions involving the NaCl-CO$_2$ and NaCl-H$_2$O pairs. Thus, activity coefficients of CO$_2$ and H$_2$O were changed. Since the Debye-Huckel formula is only a function of solvent properties and electrolyte ionic strength, there is no long-range interaction contribution for molecular solutes.

Effects of salting of NaCl and KCl on CO$_2$ in the aqueous solution were correlated successfully and reported in Table 4.
Table 4. Data and Results of Fit on Solubility of Carbon Dioxide in Aqueous Solutions at $298.15^\circ$K

<table>
<thead>
<tr>
<th>Salt</th>
<th>No. of Data+ Points</th>
<th>Highest Molality $\tau_{m,ca}$</th>
<th>$\tau_{ca,m}$</th>
<th>$\ln\gamma^*_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>9</td>
<td>5.732</td>
<td>5.697</td>
<td>-3.044</td>
</tr>
<tr>
<td>KCl</td>
<td>5</td>
<td>3.942</td>
<td>10.506</td>
<td>-5.016</td>
</tr>
</tbody>
</table>

$\tau_{CO_2,H_2O} = 10.0640 - 3268.135/t$

$H_2O,CO_2 = \tau_{CO_2,H_2O}$

(CO$_2$-H$_2$O binary data obtained from Houghton, G., A. M. McLean, and P. D. Ritchie, 1957)

+(Yasunishi, A. and F. Yoshida, 1979)

*original data were expressed in terms of molarity and the Ostwald coefficient*
These salting effects were represented successfully with the local composition model while the Setschenow equation was found to be inadequate for these two systems (Yasunishi and Yoshida, 1979).

**Study of Weak Electrolyte Systems**

To apply the local composition model to weak electrolyte systems, chemical equilibrium among various species must be taken into account. Undissociated weak electrolytes exist as molecular solutes, and dissociated weak electrolytes exist as ionic solutes.

To illustrate the applicability of the local composition model to weak electrolyte systems, the Hot Carbonate system was studied. In this system, carbon dioxide reacts with potassium carbonate to form potassium bicarbonate. The overall stoichiometric reaction is

$$\text{CO}_2 + \text{H}_2\text{O} + \text{K}_2\text{CO}_3 = 2\text{KHCO}_3$$

The three reactions involved are dissociations of water, carbon dioxide and bicarbonate:

$$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$$
$$\text{CO}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$$
$$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^=$$
There are seven species present in the system: two cations (K\(^+\) and H\(^+\)), three anions (HCO\(_3\)^-, CO\(_3\)^- and OH\(^-\)), and two molecular species (H\(_2\)O and CO\(_2\)). Four different salts can be formed from these cations and anions. They are KHCO\(_3\), K\(_2\)CO\(_3\), KOH, and H\(_2\)CO\(_3\). However, only KHCO\(_3\) and K\(_2\)CO\(_3\) are of significant concentration because the Hot Carbonate Process system is a buffer solution. Concentrations of hydrogen ion and hydroxide ion are negligible.

Compared with the concentration of water, the carbon dioxide concentration is also insignificant. Therefore, the three major interacting species are H\(_2\)O, KHCO\(_3\) and K\(_2\)CO\(_3\). The six local composition model binary parameters are the binary parameters of the H\(_2\)O-KHCO\(_3\), H\(_2\)O-K\(_2\)CO\(_3\) and KHCO\(_3\)-K\(_2\)CO\(_3\) pairs.

Vapor-liquid equilibrium data correlation was carried out for the Hot Carbonate Process system using data obtained from Tosh et al. (1949). Isothermal data of partial pressures of carbon dioxide and water at 343.15\(^\circ\)K, 363.15\(^\circ\)K, 383.15\(^\circ\)K and 403.15\(^\circ\)K were fit independently. In addition, the data from these four temperatures were lumped together and fit, assuming temperature dependence of the form a+b/T for each of the binary parameters. The resulting parameters are given in Table 5. The same set of data has been correlated successfully using the extended Pitzer equation (see Chapter 2). With the
Table 5. Representation of Vapor-Liquid Equilibrium of K$_2$CO$_3$-CO$_2$-H$_2$O System at a) 343.15$^\circ$K, b) 363.15$^\circ$K, c) 383.15$^\circ$K, d) 403.15$^\circ$K, e) All Temperatures (Data from Tosh et al.)

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{\text{KHC}}$, H$_2$O</td>
<td>-2.7406</td>
<td>-3.5198</td>
<td>-3.4341</td>
<td>-4.5737</td>
<td>-14.3683 $+4046.3/T$</td>
</tr>
<tr>
<td>$\tau_{\text{H}_2\text{O}, \text{KHC}}$</td>
<td>4.2522</td>
<td>5.4623</td>
<td>5.1720</td>
<td>7.5791</td>
<td>24.6411 $-7164.6/T$</td>
</tr>
<tr>
<td>$\tau_{\text{K}_2\text{CO}_3, \text{H}_2\text{O}}$</td>
<td>-2.5369</td>
<td>-3.3357</td>
<td>-3.1609</td>
<td>-3.9805</td>
<td>-6.7712 $+1232.3/T$</td>
</tr>
<tr>
<td>$\tau_{\text{H}_2\text{O}, \text{K}_2\text{CO}_3}$</td>
<td>-0.1029</td>
<td>1.8817</td>
<td>1.3912</td>
<td>2.5332</td>
<td>5.6969 $-1351.0/T$</td>
</tr>
<tr>
<td>$\tau_{\text{KHC}, \text{K}_2\text{CO}_3}$</td>
<td>-3.2929</td>
<td>-2.5343</td>
<td>-2.6714</td>
<td>-2.4090</td>
<td>-2.4015</td>
</tr>
<tr>
<td>$\tau_{\text{K}_2\text{CO}_3, \text{KHC}}$</td>
<td>3.7871</td>
<td>9.0184</td>
<td>10.5617</td>
<td>4.1897</td>
<td>8.5090</td>
</tr>
<tr>
<td>n</td>
<td>18</td>
<td>17</td>
<td>40</td>
<td>32</td>
<td>107</td>
</tr>
<tr>
<td>S/n</td>
<td>5.35</td>
<td>5.78</td>
<td>10.78</td>
<td>9.61</td>
<td>9.27</td>
</tr>
</tbody>
</table>

$$S = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{P_{\text{calc}, \text{H}_2\text{O}, i} - P_{\text{exp}, \text{H}_2\text{O}, i}}{0.1P_{\text{exp}, \text{H}_2\text{O}, i}} \right)^2 + \frac{1}{n} \sum_{i=1}^{n} \left( \frac{P_{\text{calc}, \text{CO}_2, i} - P_{\text{exp}, \text{CO}_2, i}}{68.95 + 0.05P_{\text{exp}, \text{CO}_2, i}} \right)^2$$
same number of parameters, the local composition model gives slightly better results than the extended Pitzer equation does.

**Notation**

\[
\begin{align*}
A &= \text{dielectric constant dependence parameter in eq. (31)} \\
B &= \text{dielectric constant dependence parameter in eq. (32)} \\
D &= \text{solvent dielectric constant} \\
G^\text{ex} &= \text{excess Gibbs free energy} \\
I &= \text{ionic strength (}=0.5 \ \text{m}^2) \\
P &= \text{pressure (N/m}^2) \\
R &= \text{gas constant} \\
S &= \text{sum of squares objective function} \\
T &= \text{temperature (}{^\circ}\text{K)} \\
Z &= \text{absolute value of ionic charge} \\
d &= \text{solvent density} \\
g^\text{ex} &= \text{molar excess Gibbs free energy} \\
m &= \text{molality (g-mole/kg of solvent)} \\
n &= \text{number of data points} \\
n_w &= \text{number of kg of the solvent, water} \\
x &= \text{liquid phase mole fraction} \\
y &= \text{vapor phase mole fraction}
\end{align*}
\]

**Greek Letters**

\[
\begin{align*}
\alpha &= \text{relative volatility} \\
\gamma &= \text{activity coefficient} \\
\nu &= \text{stoichiometric coefficient} \\
\sigma &= \text{standard deviation} \\
\tau &= \text{binary interaction energy parameter}
\end{align*}
\]

**Superscripts**

\[
\begin{align*}
\ast &= \text{unsymmetric convention} \\
\infty &= \text{infinite dilution} \\
lc &= \text{short-range local composition contribution}
\end{align*}
\]

**Subscripts**

\[
\begin{align*}
a, a', a'' &= \text{anion} \\
c, c', c'' &= \text{cation} \\
ca &= \text{salt ca} \\
i, j, k &= \text{any species} \\
m &= \text{molecular species} \\
\text{ref} &= \text{reference} \\
s &= \text{salt} \\
w &= \text{water}
\end{align*}
\]
Literature Cited


Chapter 5
Correlation of Vapor-Liquid Equilibrium Data for the
NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}S-H\textsubscript{2}O System

Abstract

The extended Pitzer equation and the local composition model have been successfully applied to correlate vapor-liquid equilibrium data for an industrially important electrolyte system: the NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}S-H\textsubscript{2}O system. An attempt was first made to correlate the low concentration data of van Krevelen et al. using the extended Pitzer equation. However, the correlation was found not able to be extrapolated to predict high concentration data. Due to lack of high concentration data for the system, data from subsystems, i.e., NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O and NH\textsubscript{3}-H\textsubscript{2}S-H\textsubscript{2}O, were correlated using both models. The two models, with parameters determined from high concentration subsystem data correlations, predict partial pressures fairly close to the experimental data compiled by Newman (1979) for the complete system. With the extended Pitzer equation, the overall average percentage deviations of partial pressures of NH\textsubscript{3}, CO\textsubscript{2} and H\textsubscript{2}S are 27.2, 19.6, and 33.5, respectively. With the local composition model, the overall average percentage deviations of partial pressures of NH\textsubscript{3}, CO\textsubscript{2} and H\textsubscript{2}S are 26.9, 19.3 and 20.7, respectively.
Scope

The advent of restrictive pollution abatement guidelines and regulations has spurred development of phase equilibrium calculation methods required for the design of a type of column designated as sour-water strippers. Its purpose is to process foul water containing ammonia, hydrogen sulfide and carbon dioxide by means of stripping steam injected into the bottom of the tower, or by means of reboiler-generated steam, these acid-gas contaminants are removed from the feed so that the bottoms water contains approximately 150 ppm (wt) ammonia and 10 ppm (wt) hydrogen sulfide. The carbon dioxide is easily removed and its concentration in the bottoms is usually nil (Newman, 1978).

The system is very complex because of the number of species present and the number of equilibrium reactions in the liquid phase. The following seven reactions establish the chemical equilibrium in the liquid phase.

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} & = \text{NH}_4^+ + \text{OH}^- \\
\text{CO}_2 + \text{H}_2\text{O} & = \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & = \text{H}^+ + \text{CO}_3^{2-} \\
\text{NH}_3 + \text{HCO}_3^- & = \text{NH}_2\text{CO}_2^- + \text{H}_2\text{O} \\
\text{H}_2\text{S} & = \text{H}^+ + \text{HS}^- \\
\text{HS}^- & = \text{H}^+ + \text{S}^{2-} \\
\text{H}_2\text{O} & = \text{H}^+ + \text{OH}^- 
\end{align*}
\]
The pioneering effort in correlating the data for \( \text{NH}_3-\text{CO}_2-\text{H}_2\text{S-H}_2\text{O} \) system and subsystems was due to Van Krevelen (1949), whose work was popularized by Beychok (1967). Very recently, Wilson (1978) and Mason (1978) have independently developed modifications to the Van Krevelen approach. Simplified forms of the Pitzer activity coefficient expression were applied along with a rigorous thermodynamic framework by Edwards et al. (1978) and Beutier and Renon (1978).

In this study, the extended Pitzer equation model (Chen et al., 1979a) and the local composition model (Chen et al., 1979) are applied to the phase equilibria of the industrially important \( \text{NH}_3-\text{CO}_2-\text{H}_2\text{S-H}_2\text{O} \) system. The objectives are two fold: 1) to demonstrate the validities of both the extended Pitzer equation and the local composition model to this complicated electrolyte system, 2) to obtain correlation parameters for the system for the use of process design and analysis. Vapor phase fugacity coefficients were calculated by the Nakamura et al. (1976) correlation. The chemical equilibrium constants, Henry's constants and Debye-Huckel constant were obtained from Edwards et al. (1978) and Chen et al. (1979, 1979a). The temperature dependency expression for the interaction parameters was assumed to be \( a+b/T \).
Conclusions and Significance

Vapor-liquid equilibrium data of the NH$_3$-CO$_2$-H$_2$S-H$_2$O electrolyte system of sour-water strippers has been successfully correlated using the extended Pitzer equation and the local composition model. The two models, with correlation parameters obtained from high concentration subsystem data correlations, predict partial pressures fairly close to the experimental data compiled by Newman (1979) for the complete system. These correlations cover temperature from 293$^\circ$K to 393$^\circ$K and ammonia concentration up to 30 molality. Therefore, the correlations provide useful tools for the process design and analysis of sour-water strippers.

Low Concentration Data Correlation Using the Extended Pitzer Equation

Van Krevelen's data were correlated first using the extended Pitzer equation. Van Krevelen et al. (1949) reported low concentration, low temperature experimental data for the vapor-liquid equilibrium of the NH$_3$-CO$_2$-H$_2$O subsystem, the NH$_3$-H$_2$S-H$_2$O subsystem, and the complete NH$_3$-CO$_2$-H$_2$S-H$_2$O system.

The scope of van Krevelen's data is that the highest concentration of ammonia is about 2 molality and ammonia is
always in excess relative to carbon dioxide and hydrogen sulfide. The data cover a temperature range from 293.15°K to 333.15°K. Because of low concentrations, all ternary parameters were dropped from the extended Pitzer equation. The Setschenow constants for carbon dioxide and hydrogen sulfide were assumed to be negligible because ammonia is always in excess and carbon dioxide and hydrogen sulfide are almost completely dissociated. The system is a buffer solution and both hydrogen ion concentration and hydroxide ion concentration are small compared to those of other solutes. Therefore, the ion-ion interaction parameters for salts containing hydrogen ion or hydroxide ion are also assumed negligible.

For the NH₃-CO₂-H₂O subsystem, ammonia, carbon dioxide and water are present in the vapor phase. In the liquid phase, hydrogen, hydroxide, ammonium, carbonate, bicarbonate, and carbamate ions are present in addition to ammonia and carbon dioxide molecular solutes. The following reactions occur in the liquid phase:

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + \text{OH}^- \\
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightarrow \text{H}^+ + \text{CO}_3^- \\
\text{NH}_3 + \text{HCO}_3^- & \rightarrow \text{NH}_2\text{CO}_2^- + \text{H}_2\text{O} \\
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- 
\end{align*}
\]
Besides those parameters excluded from previous analysis, also excluded are the binary ion-ion interaction parameter of salt \((\text{NH}_4)_2\text{CO}_3\), binary ion-ion difference parameters between carbonate and other anions, and the Setschenow constant between salt \((\text{NH}_4)_2\text{CO}_3\) and ammonia molecule. This is because the carbonate ion concentration is relatively low compared to bicarbonate and carbamate ion concentrations. Therefore, the adjusting parameters are: \(\beta^{(0)}_{\text{NH}_4\text{HCO}_3}\), \(\beta^{(0)}_{\text{NH}_4\text{NH}_2\text{CO}_2}\), \(D_{\text{NH}_4\text{HCO}_3,\text{NH}_3}\), \(D_{\text{NH}_4\text{NH}_2\text{CO}_2,\text{NH}_3}\) and \(\theta_{\text{HCO}_3^-}\), \(\text{NH}_2\text{CO}_2^-\).

The sum of squares objective function used for data correlation was

\[
S = \sum_{i=1}^{N} \left( \frac{p_{\text{NH}_3,i}^{\text{calc}} - p_{\text{NH}_3,i}^{\text{exp}}}{p_{\text{NH}_3,i}^{\text{exp}}} \right)^2 + \sum_{i=1}^{N} \left( \frac{p_{\text{CO}_2,i}^{\text{calc}} - p_{\text{CO}_2,i}^{\text{exp}}}{p_{\text{CO}_2,i}^{\text{exp}}} \right)^2
\]  

(1)

Van Krevelen et al. also reported data taken by Pexton and Badger (1938) for the subsystem. These data were correlated together with van Krevelen's data. The correlation results and calculated parameters are shown in Table 1. The results are better than those reported by the authors (Chen et al. 1979) before, because more pertinent parameters are used. Parameters not listed in Table 1 were set to zero. In addition, when \(\beta^{(0)}\)'s are treated as adjustable parameters, \(\beta^{(1)}\)'s are calculated as functions of \(\beta^{(0)}\)'s:
Table 1. Correlation Results for the NH$_3$-CO$_2$-H$_2$O System:
   a) 293.15 K, b) 313.15 K, c) 333.15 K, d) All Temperatures
   (Data from van Krevelen et al.)

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta^{(O)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>-0.0398</td>
<td>-0.0722</td>
<td>-0.0620</td>
<td>-0.1722+37.05/T</td>
</tr>
<tr>
<td>( \beta^{(O)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$NH$_2$COO</td>
<td>0.0406</td>
<td>-0.1424</td>
<td>-0.2655</td>
<td>-2.4870+753.96/T</td>
</tr>
<tr>
<td>( D_{NH_4HCO_3, NH_3} )</td>
<td>1.9760</td>
<td>-0.4705</td>
<td>-0.3552</td>
<td>-10.642+3408.4/T</td>
</tr>
<tr>
<td>( D_{NH_4NH_2COO, NH_3} )</td>
<td>0.4424</td>
<td>1.0439</td>
<td>0.8815</td>
<td>4.9497-1346.4/T</td>
</tr>
<tr>
<td>( \theta )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO$_3^-$,NH$_2$COO$^-$</td>
<td>0.0832</td>
<td>0.5314</td>
<td>0.5668</td>
<td>3.2884-960.71/T</td>
</tr>
<tr>
<td># of data points</td>
<td>43</td>
<td>26</td>
<td>19</td>
<td>88</td>
</tr>
<tr>
<td>Sum of squares (S)</td>
<td>0.9438</td>
<td>0.4934</td>
<td>0.2611</td>
<td>1.9377</td>
</tr>
</tbody>
</table>

Average % deviation of
NH$_3$ partial
pressure
4.0        6.8        4.1        5.5

Average % deviation of
CO$_2$ partial
pressure
8.1        8.2        8.3        8.1

Note:
\( \lambda_{NH_3, NH_3} = -0.0260 + 12.29/T \)
\( \lambda_{CO_2, CO_2} = -0.4922 + 149.20/T \)
These equations were also used in high concentration data correlation using the extended Pitzer equation.

For the NH₃-H₂S-H₂O subsystem, Hydrogen sulfide and water are present in the vapor phase. In the liquid phase, hydrogen, hydroxide, ammonium, bisulfide and sulfide ions are present in addition to ammonia and hydrogen sulfide molecular solutes. The following reactions occur in the liquid phase

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} & = \text{NH}_4^+ + \text{OH}^- \\
\text{H}_2\text{S} & = \text{H}^+ + \text{HS}^- \\
\text{HS}^- & = \text{H}^+ + \text{S}^= \\
\text{H}_2\text{O} & = \text{H}^+ + \text{OH}^- 
\end{align*}
\]

The dominant ions in the subsystem are ammonium cation and bisulfide anion. Therefore, only two adjusting parameters were used for data correlation. The two parameters are \( \beta^{(0)}_{\text{NH}_4\text{HS}} \) and \( d_{\text{NH}_4\text{HS},\text{NH}_3} \).

Only H₂S partial pressure data were reported by van Krevelen, therefore, the sum of squares objective function used for data correlation was
\[ S = \sum_{i=1}^{N} \left( \frac{p_{H_2S,i}^{\text{calc}} - p_{H_2S,i}^{\text{exp}}}{p_{H_2S,i}^{\text{exp}}} \right)^2 \]

(4)

Calculated results and calculated adjusting parameters are shown in Table 2. Parameters not listed in Table 2 were set to zero.

For the complete \( \text{NH}_3-\text{CO}_2-\text{H}_2\text{S}-\text{H}_2\text{O} \) System, the species present in the system are the constituents of the \( \text{NH}_3-\text{CO}_2-\text{H}_2\text{O} \), and the \( \text{NH}_3-\text{H}_2\text{S}-\text{H}_2\text{O} \) subsystems. The reactions occurring in the liquid phase of the system are those occurring in the subsystems. Interaction parameters of the subsystems are still applicable for the system with additional new ion-ion difference parameters between anions of the two subsystems.

Since only a limited amount of data are available for the system, the additional ion-ion difference parameters are assumed equal and treated as a lump sum adjusting parameter. Again, only \( H_2S \) partial pressure data were reported by van Krevelen, the sum of squares objective function used for data correlation was the same as equation (4).

Correlation results and calculated adjusting parameters are shown in Table 3.
Table 2. Correlation Results for the NH$_3$-H$_2$S-H$_2$O System:
   a) 293.15°K, b) 313.15°K, c) 333.15°K, d) All Temperatures
   (Data from van Krevelen et al.)

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{\text{NH}_4\text{HS}}$</td>
<td>0.0225</td>
<td>0.0642</td>
<td>0.0610</td>
<td>0.3566-96.47/T</td>
</tr>
<tr>
<td>$D_{\text{NH}_4\text{HS},\text{NH}_3}$</td>
<td>-0.0579</td>
<td>0.0088</td>
<td>0.1080</td>
<td>1.2891-395.30/T</td>
</tr>
<tr>
<td># of data points</td>
<td>28</td>
<td>25</td>
<td>27</td>
<td>80</td>
</tr>
<tr>
<td>Sum of squares (S)</td>
<td>1.6650</td>
<td>0.1578</td>
<td>0.2708</td>
<td>2.1915</td>
</tr>
<tr>
<td>Average &amp; deviation of $\text{H}_2\text{S}$ partial pressure</td>
<td>17.2</td>
<td>6.1</td>
<td>7.5</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Note:

$\lambda_{\text{NH}_3,\text{NH}_3} = -0.0260+12.29/T$

$\lambda_{\text{H}_2\text{S},\text{H}_2\text{S}} = -0.2106+61.56/T$
Table 3. Correlation Results for the NH$_3$–CO$_2$–H$_2$S–H$_2$O System:
(a) 293.15°K, b) 313.15°K, c) 333.15°K, d) All Temperatures
(Data from van Krevelen et al.)

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$ HS$^-$, $\cdot$ CO$_3^-$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\theta$ HS$^-$, CO$_3^{\pm}$</td>
<td>0.0476</td>
<td>0.0396</td>
<td>-0.0112</td>
<td>-0.4390+144.83/T</td>
</tr>
<tr>
<td>$\theta$ HS$^-$, NH$_2$COO$^-$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td># of data points</td>
<td>6</td>
<td>9</td>
<td>12</td>
<td>27</td>
</tr>
<tr>
<td>Sum of squares (S)</td>
<td>0.0355</td>
<td>0.2184</td>
<td>0.1466</td>
<td>0.4079</td>
</tr>
<tr>
<td>Average % deviation of H$_2$S partial pressure</td>
<td>6.9</td>
<td>14.4</td>
<td>8.9</td>
<td>10.8</td>
</tr>
</tbody>
</table>
With parameters determined from van Krevelen's data, the extended Pitzer equation is used to calculate partial pressures of \( \text{NH}_3 \), \( \text{CO}_2 \), and \( \text{H}_2\text{S} \) and results compared with the experimental data collected by Newman (1979). These experimental data were measured by Badger and Silver (1938), Mason and Kao, and Cardon and Wilson.

Comparison results are given in Tables 4 to 7. The extended Pitzer equation model predicts partial pressures fairly close to data obtained by Badger and Silver, and Mason and Kao. The average percentage deviations of partial pressures of \( \text{NH}_3 \), \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) are 5.3, 9.3 and 12.8 for data of Badger and Silver; and 20.7, 14.6 and 12.5 for data of Mason and Kao. This is expected because their data are within the temperature range of van Krevelen's data and the composition ranges also fall in the range of van Krevelen's data. This suggests that Badger and Silver's data and Mason and Kao's data are consistent with those of van Krevelen et al.

However, there is a very large discrepancy between predictive partial pressures from the model and the data obtained by Cardon and Wilson. Actually, it is not surprising because the data taken by Cardon and Wilson cover a wide range of solute concentrations while the binary parameters obtained from correlating Van Krevelen's low concentration, low temperature data are not sufficient to represent such a wide
Table 4. Comparison of Calculated Partial Pressures of NH₃, CO₂, and H₂S with the Experimental Results of Badger and Silver for NH₃–CO₂–H₂S–H₂O System at 20°C, using the Extend Pitzer Equation.

<table>
<thead>
<tr>
<th>Liquid Concentration Molality</th>
<th>NH₃ Partial Pressure, mmHg</th>
<th>CO₂ Partial Pressure, mmHg</th>
<th>H₂S Partial Pressure, mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.231</td>
<td>0.424</td>
<td>0.196</td>
<td>3.76</td>
</tr>
<tr>
<td>1.236</td>
<td>0.507</td>
<td>0.201</td>
<td>2.82</td>
</tr>
<tr>
<td>1.450</td>
<td>0.517</td>
<td>0.407</td>
<td>2.83</td>
</tr>
<tr>
<td>1.076</td>
<td>0.515</td>
<td>0.046</td>
<td>2.65</td>
</tr>
<tr>
<td>1.439</td>
<td>0.665</td>
<td>0.396</td>
<td>1.58</td>
</tr>
<tr>
<td>1.132</td>
<td>0.681</td>
<td>0.100</td>
<td>1.33</td>
</tr>
<tr>
<td>1.234</td>
<td>0.694</td>
<td>0.199</td>
<td>1.30</td>
</tr>
<tr>
<td>1.238</td>
<td>0.712</td>
<td>0.203</td>
<td>1.19</td>
</tr>
<tr>
<td>1.234</td>
<td>0.725</td>
<td>0.199</td>
<td>1.12</td>
</tr>
<tr>
<td>1.235</td>
<td>0.771</td>
<td>0.200</td>
<td>0.88</td>
</tr>
<tr>
<td>1.126</td>
<td>0.794</td>
<td>0.095</td>
<td>0.74</td>
</tr>
<tr>
<td>1.122</td>
<td>0.815</td>
<td>0.091</td>
<td>0.65</td>
</tr>
<tr>
<td>1.129</td>
<td>0.825</td>
<td>0.098</td>
<td>0.62</td>
</tr>
<tr>
<td>1.122</td>
<td>0.840</td>
<td>0.091</td>
<td>0.56</td>
</tr>
<tr>
<td>1.129</td>
<td>0.844</td>
<td>0.098</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Average % deviation 5.3 9.3 12.8
Table 5. Comparison of Calculated Partial Pressures of NH$_3$, CO$_2$, and H$_2$S with the IGT Data for NH$_3$-CO$_2$-H$_2$S-H$_2$O and NH$_3$-CO$_2$-H$_2$O systems at 60°C, using the Extended Pitzer Equation.

<table>
<thead>
<tr>
<th>Liquid Concentration</th>
<th>Molality</th>
<th>NH$_3$</th>
<th>CO$_2$</th>
<th>H$_2$S</th>
<th>Partial Pressure, mmHg</th>
<th>NH$_3$</th>
<th>CO$_2$</th>
<th>H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.076</td>
<td>1.516</td>
<td>0.064</td>
<td>10.27</td>
<td>14.73</td>
<td>606.9</td>
<td>751.5</td>
<td>32.44</td>
<td>31.64</td>
</tr>
<tr>
<td>2.098</td>
<td>1.601</td>
<td>0.052</td>
<td>8.82</td>
<td>13.59</td>
<td>769.6</td>
<td>738.1</td>
<td>31.14</td>
<td>23.29</td>
</tr>
<tr>
<td>1.954</td>
<td>1.471</td>
<td>0.040</td>
<td>9.22</td>
<td>11.44</td>
<td>659.0</td>
<td>691.9</td>
<td>21.85</td>
<td>22.80</td>
</tr>
<tr>
<td>2.160</td>
<td>1.581</td>
<td>0.050</td>
<td>10.74</td>
<td>13.70</td>
<td>601.3</td>
<td>705.3</td>
<td>24.60</td>
<td>22.43</td>
</tr>
<tr>
<td>1.795</td>
<td>1.022</td>
<td></td>
<td>22.84</td>
<td>22.00</td>
<td>129.5</td>
<td>181.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.043</td>
<td>1.510</td>
<td></td>
<td>11.09</td>
<td>12.86</td>
<td>538.0</td>
<td>638.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average &amp; deviation</td>
<td></td>
<td>20.7</td>
<td></td>
<td>14.6</td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6. Comparison of Calculated Partial Pressures of NH$_3$, CO$_2$, and H$_2$S with the Experimental Results of Cardon and Wilson for NH$_3$-CO$_2$-H$_2$S-H$_2$O System, using the Extended Pitzer Equation.

<table>
<thead>
<tr>
<th>Temp. OC</th>
<th>Liquid Concentration</th>
<th>Partial Pressure, mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH$_3$ Molality CO$_2$ H$_2$S</td>
<td>NH$_3$ Calc. Exp. CO$_2$ Calc. Exp. H$_2$S Calc. Exp.</td>
</tr>
<tr>
<td>50</td>
<td>7.355 2.305 3.633</td>
<td>9.05 30.5 468.6 239.9 2905.1 1132.2</td>
</tr>
<tr>
<td>50</td>
<td>17.385 4.568 6.362</td>
<td>203.3 263.2 37.5 54.3 1673.4 540.8</td>
</tr>
<tr>
<td>50</td>
<td>1.565 0.057 0.178</td>
<td>50.0 49.2 0.3 2.3 2.8 8.8</td>
</tr>
<tr>
<td>80</td>
<td>7.570 2.005 4.051</td>
<td>97.3 164.4 279.3 1613.0 7317.7 3960.2</td>
</tr>
<tr>
<td>80</td>
<td>2.063 0.029 0.173</td>
<td>203.9 153.4 0.4 7.6 10.1 20.4</td>
</tr>
<tr>
<td>80</td>
<td>5.965 2.769 2.330</td>
<td>24.2 95.1 4005.3 3453.6 5626.2 2585.0</td>
</tr>
<tr>
<td>80</td>
<td>5.212 2.541 1.889</td>
<td>- 127.7 - 3458.7 - 2517.8</td>
</tr>
<tr>
<td>80</td>
<td>1.081 0.210 0.085</td>
<td>70.4 102.4 25.7 65.5 14.5 18.4</td>
</tr>
<tr>
<td>80</td>
<td>0.561 0.476 0.096</td>
<td>3.6 - 3136.5 2436.6 328.1 246.1</td>
</tr>
<tr>
<td>80</td>
<td>0.780 0.142 0.518</td>
<td>15.2 7.8 240.0 346.9 658.8 589.4</td>
</tr>
<tr>
<td>80</td>
<td>0.599 0.396 0.051</td>
<td>11.0 29.5 718.0 453.4 59.2 47.6</td>
</tr>
<tr>
<td>80</td>
<td>3.088 1.141 1.281</td>
<td>36.4 102.4 795.6 987.5 1768.2 1354.5</td>
</tr>
<tr>
<td>80</td>
<td>30.589 5.550 7.635</td>
<td>19316. 2176.6 0.0 149.9 61.0 847.9</td>
</tr>
<tr>
<td>110</td>
<td>2.383 0.847 1.297</td>
<td>56.9 285.9 3586.0 5976.5 8573.0 4616.8</td>
</tr>
<tr>
<td>110</td>
<td>0.573 0.562 0.119</td>
<td>12.1 15.5 13198.7 9145.7 901.9 801.3</td>
</tr>
<tr>
<td>110</td>
<td>0.609 0.073 0.169</td>
<td>86.7 100.3 121.1 169.1 194.3 172.2</td>
</tr>
<tr>
<td>110</td>
<td>7.758 3.353 1.711</td>
<td>165.5 353.1 2070.2 10040.1 2584.9 4425.5</td>
</tr>
<tr>
<td>110</td>
<td>3.099 1.835 0.920</td>
<td>- 563.5 - 9988.4 - 7207.0</td>
</tr>
<tr>
<td>120</td>
<td>2.259 0.099 0.174</td>
<td>557.6 734.1 2.7 103.4 114.8 67.2</td>
</tr>
<tr>
<td>120</td>
<td>0.264 0.236 0.140</td>
<td>10.9 19.1 8362.3 6860.6 1366.0 1623.4</td>
</tr>
<tr>
<td>120</td>
<td>0.892 0.446 0.320</td>
<td>46.3 93.6 5663.0 5619.8 2012.7 1483.8</td>
</tr>
<tr>
<td>120</td>
<td>0.106 0.011 0.022</td>
<td>23.4 16.3 59.9 58.3 36.1 22.4</td>
</tr>
<tr>
<td>120</td>
<td>0.084 0.028 0.084</td>
<td>5.1 46.6 963.3 752.8 785.3 563.0</td>
</tr>
</tbody>
</table>

Average & deviation

85.1 49.9 60.8
Table 7. Summary of Results for the Extended Pitzer Equation
(Data from Van Krevelen et al.)

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Temp., C</th>
<th>No. of Data Points</th>
<th>Range of Liquid Conc., Molality</th>
<th>Range of Calc. Partial Pressure / Exp. Partial Pressure, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Badger &amp; Silver</td>
<td>20</td>
<td>15</td>
<td>1.08-1.45</td>
<td>0.42-0.84 0.05-0.41</td>
</tr>
<tr>
<td>Mason &amp; Kao</td>
<td>60</td>
<td>6</td>
<td>1.80-2.16</td>
<td>1.0-1.6 0.0-0.06</td>
</tr>
<tr>
<td>Cardon &amp; Wilson</td>
<td>50</td>
<td>3</td>
<td>1.56-17.4</td>
<td>0.06-4.6 0.18-6.4</td>
</tr>
<tr>
<td>Cardon &amp; Wilson</td>
<td>80</td>
<td>10</td>
<td>0.56-30.6</td>
<td>0.03-5.55 0.05-7.6</td>
</tr>
<tr>
<td>Cardon &amp; Wilson</td>
<td>110</td>
<td>5</td>
<td>0.57-7.58</td>
<td>0.07-3.35 0.12-1.71</td>
</tr>
<tr>
<td>Cardon &amp; Wilson</td>
<td>120</td>
<td>5</td>
<td>0.08-2.26</td>
<td>0.01-0.45 0.02-0.32</td>
</tr>
</tbody>
</table>
range of conditions. Also, the temperature dependency of the
Pitzer equation parameters is highly nonlinear. The
temperature dependency expression used in the study may not be
good enough to be extrapolated. On the other hand,
vapor-liquid equilibrium experiments of multicomponent aqueous
weak electrolyte systems are difficult to carry out and known
to be subject to significant errors.

Convergence problems were encountered when solving the
liquid phase equations for two data points of Cardon and
Wilson. Newton's method was used to solve liquid phase
equations simultaneously. When a convergence problem occurs,
it suggests that there is no feasible solution for given weak
electrolyte concentrations and given the Pitzer equation
parameters. This becomes possible because the Pitzer equation
is a virial expansion type equation. There is no physical or
numerical limitation as to what values the Pitzer equation
parameters should be. It is very likely that values of the
adjusting parameters are badly distorted during data
correlation and eventually cause convergence problems.

High Concentration Data Correlation Using Both the Extended
Pitzer Equation and the Local Composition Model

No high concentration data for the complete system are
known to the authors other than the data of Cardon and Wilson,
whose data are known to contain significant experimental error. Therefore, no high concentration data correlation was carried out for the complete system. Instead, subsystem data were correlated to determine subsystem interaction parameters and partial pressures of the complete system were predicted based on these subsystem parameters. This strategy was adopted for both models.

The high concentration data of Otsuka et al. (1960) for the \( \text{NH}_3 - \text{CO}_2 - \text{H}_2\text{O} \) subsystem were correlated. Otsuka's data cover a temperature range from 293.15\(^\circ\)K to 393.15\(^\circ\)K and \( \text{NH}_3 \) concentration range from 1 molal to 11 molal. The ratio of ammonia molality to carbon dioxide molality, \( R \), is always larger than 1. In other words, ammonia is always in excess relative to carbon dioxide. Data points with very large \( R \) or very small \( R \) were excluded because in these cases either carbon dioxide partial pressure or ammonia partial pressure is very small and subject to large experimental errors. Forty-one selected data points were used for data correlation of the \( \text{NH}_3 - \text{CO}_2 - \text{H}_2\text{O} \) subsystem. The sum of squares objective function used for data correlation was

\[
S = \sum_{i=1}^{N} \left( \frac{p_{\text{calc}}^{\text{NH}_3,i} - p_{\text{exp}}^{\text{NH}_3,i}}{p_{\text{exp}}^{\text{NH}_3,i}} \right)^2 + \sum_{i=1}^{N} \left( \frac{p_{\text{calc}}^{\text{CO}_2,i} - p_{\text{exp}}^{\text{CO}_2,i}}{p_{\text{exp}}^{\text{CO}_2,i}} \right)^2
\]

(5)

The high concentration data of Miles and Wilson (1975) were
correlated for the NH$_3$-H$_2$S-H$_2$O subsystem. The 17 experimental data points have been correlated and reported by the Institute of Gas Technology (1979). The temperatures of these data are 353$^\circ$K and 393$^\circ$K. The NH$_3$ concentration ranges from 0.44 molal to 22 molal and the H$_2$S concentration ranges from 0.11 molal to 7.9 molal. The ratio of NH$_3$ molality to that of H$_2$S ranges from 0.73 to 4.8. In other words, NH$_3$ or H$_2$S can be in excess. The sum of squares objective function used for data correlation was

$$ S = \sum_{i=1}^{N} \left( \frac{p_{\text{NH}_3,i}^{\text{calc}} - p_{\text{NH}_3,i}^{\text{exp}}}{p_{\text{NH}_3,i}^{\exp}} \right)^2 + \sum_{i=1}^{N} \left( \frac{p_{\text{H}_2\text{S},i}^{\text{calc}} - p_{\text{H}_2\text{S},i}^{\text{exp}}}{p_{\text{H}_2\text{S},i}^{\exp}} \right)^2 $$

(6)

**Application of the Extended Pitzer Equation**

In Otsuka's data, the highest ionic strength of the solution is about 5 molality and most data points have an ionic strength of less than 2 molality. Therefore, all ternary parameters from the extended Pitzer equation were set to zero. In addition, all of the interaction parameters are assumed to be independent of temperature. Correlation results and parameter values are given in Table 8. Parameters not listed in Table 8 were set to zero.

Both binary and ternary parameters of the extended Pitzer equation are used in the data correlation of the
Table 8. Correlation Results for the NH$_3$-CO$_2$-H$_2$O System using the Extended Pitzer Equation (Data from Otsuka et al.)

\[
\begin{align*}
\beta_{\text{NH}_4\text{HCO}_3}^{(0)} & \quad -0.00154 \\
\beta_{(\text{NH}_4)^2\text{CO}_3}^{(0)} & \quad 0.02695 \\
\beta_{\text{NH}_4\text{NH}_2\text{CO}_2}^{(1)} & \quad -0.01322 \\
\beta_{\text{NH}_4\text{HCO}_3}^{(1)} & \quad -0.16850 \\
\beta_{(\text{NH}_4)^2\text{CO}_3}^{(1)} & \quad -0.45565 \\
\beta_{\text{NH}_4\text{NH}_2\text{CO}_2} & \quad 0.74523 \\
D_{\text{NH}_4\text{HCO}_3,\text{NH}_3} & \quad -0.11493 \\
D_{(\text{NH}_4)^2\text{CO}_3,\text{NH}_3} & \quad 0.12654 \\
D_{\text{NH}_4\text{NH}_2\text{CO}_2,\text{NH}_3} & \quad 0.08331 \\
\theta_{\text{HCO}_3^-,\text{NH}_2\text{CO}_2^\text{w}} & \quad 0.01418
\end{align*}
\]

# of data points 41
Sum of squares (S) 3.668
Average % deviation of NH$_3$ partial pressure 18.7
Average % deviation of CO$_2$ partial pressure 16.1

Note:

\[
\begin{align*}
\lambda_{\text{NH}_3,\text{NH}_3} &= -0.0260+12.29/T \\
\lambda_{\text{CO}_2,\text{CO}_2} &= -0.4922+149.20/T
\end{align*}
\]
NH₃-H₂S-H₂O subsystem. Ammonium bisulfide is the dominant salt of the subsystem. Parameter values and correlation results are given in Table 9. The correlation using the extended Pitzer equation is significantly better than that of IGT. Parameters not listed in Table 9 were set to zero.

The extended Pitzer equation with parameters determined from the subsystems predicts partial pressures of the complete system fairly close to those obtained by Badger and Silver (1938) and Mason and Kao. Comparisons are shown in Tables 10 and 11. The average percentages of deviation of partial pressures of NH₃, CO₂ and H₂S are 12.2, 10.4 and 43.8 respectively for data of Badger and Silver; and 10.4, 13.2 and 17.4 respectively for data of Mason and Kao. Prediction of the Cardon and Wilson data is also satisfactory. The average percentage deviations of partial pressures of NH₃, CO₂, and H₂S are 40.7, 26.5, and 30.9 respectively. These results are satisfactory considering the facts that no data correlation was carried out for the complete system and that Cardon and Wilson's data contains significant experimental errors.

**Application of the Local Composition Model**

Binary parameters for the NH₃-H₂O pair, the CO₂-H₂O pair, and the H₂S-H₂O pair were determined in a priori from experimental data for these binary systems. Results are
Table 9. Correlation Results for the NH$_3$-H$_2$S-H$_2$O System using the Extended Pitzer Equation (Data from Miles and Wilson), (1) this study (2) IGT

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{NH_4HS}$</td>
<td>0.63298-218.69/T</td>
<td></td>
</tr>
<tr>
<td>$\beta_{NH_4HS}$</td>
<td>-2.13449+948.65/T</td>
<td></td>
</tr>
<tr>
<td>$C_{NH_4HS}$</td>
<td>0.001262</td>
<td></td>
</tr>
<tr>
<td>$D_{NH_4HS,NH_3}$</td>
<td>-0.00261</td>
<td></td>
</tr>
<tr>
<td>$D_{NH_4HS,H_2S}$</td>
<td>0.09691</td>
<td></td>
</tr>
<tr>
<td># of data points</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Sum of squares (S)</td>
<td>0.341</td>
<td></td>
</tr>
<tr>
<td>Average &amp; deviation of NH$_3$ partial pressure</td>
<td>10.6</td>
<td>14.5</td>
</tr>
<tr>
<td>Average &amp; deviation of H$_2$S partial pressure</td>
<td>5.3</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Note:

$\lambda_{NH_3,NH_3} = -0.0260 + 12.29/T$

$\lambda_{H_2S,H_2S} = -0.2106 + 61.56/T$
Table 10. Comparison of Calculated Partial Pressures of NH₃, CO₂, and H₂S with the Experimental Results of Badger and Silver for NH₃-CO₂-H₂S-H₂O System at 20°C, using the Extended Pitzer Equation

<table>
<thead>
<tr>
<th>Liquid Concentration (Molality)</th>
<th>NH₃</th>
<th>CO₂</th>
<th>H₂S</th>
<th>Partial Pressure, mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.231 0.424 0.196</td>
<td>3.55</td>
<td>4.11</td>
<td>1.62</td>
<td>1.45</td>
</tr>
<tr>
<td>1.236 0.507 0.201</td>
<td>2.59</td>
<td>2.92</td>
<td>3.40</td>
<td>3.50</td>
</tr>
<tr>
<td>1.450 0.517 0.407</td>
<td>2.56</td>
<td>2.42</td>
<td>4.06</td>
<td>3.70</td>
</tr>
<tr>
<td>1.076 0.515 0.046</td>
<td>2.44</td>
<td>2.72</td>
<td>3.24</td>
<td>3.65</td>
</tr>
<tr>
<td>1.439 0.665 0.396</td>
<td>1.35</td>
<td>1.54</td>
<td>13.90</td>
<td>13.10</td>
</tr>
<tr>
<td>1.132 0.681 0.100</td>
<td>1.18</td>
<td>1.35</td>
<td>14.49</td>
<td>12.15</td>
</tr>
<tr>
<td>1.234 0.694 0.199</td>
<td>1.13</td>
<td>1.31</td>
<td>16.84</td>
<td>13.10</td>
</tr>
<tr>
<td>1.238 0.712 0.203</td>
<td>1.04</td>
<td>1.30</td>
<td>19.60</td>
<td>19.00</td>
</tr>
<tr>
<td>1.234 0.725 0.199</td>
<td>0.97</td>
<td>0.89</td>
<td>21.79</td>
<td>20.45</td>
</tr>
<tr>
<td>1.235 0.771 0.200</td>
<td>0.77</td>
<td>0.90</td>
<td>31.98</td>
<td>29.2</td>
</tr>
<tr>
<td>1.126 0.794 0.095</td>
<td>0.65</td>
<td>0.71</td>
<td>38.02</td>
<td>35.15</td>
</tr>
<tr>
<td>1.122 0.815 0.091</td>
<td>0.58</td>
<td>-</td>
<td>45.62</td>
<td>42.45</td>
</tr>
<tr>
<td>1.129 0.825 0.098</td>
<td>0.54</td>
<td>-</td>
<td>50.00</td>
<td>45.1</td>
</tr>
<tr>
<td>1.122 0.840 0.091</td>
<td>0.49</td>
<td>0.55</td>
<td>57.10</td>
<td>-</td>
</tr>
<tr>
<td>1.129 0.844 0.098</td>
<td>0.48</td>
<td>0.57</td>
<td>59.37</td>
<td>-</td>
</tr>
</tbody>
</table>

Average % deviation: 12.2  10.4  43.8
Table 11. Comparison of Calculated Partial Pressures of NH₃, CO₂, and H₂S with the IGT Data for NH₃-CO₂-H₂S-H₂O and NH₃-CO₂-H₂O systems at 60°C, using the Extended Pitzer Equation

<table>
<thead>
<tr>
<th>Liquid Concentration Molality</th>
<th>NH₃</th>
<th>CO₂</th>
<th>H₂S</th>
<th>Partial Pressure, mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.076</td>
<td>1.516</td>
<td>0.064</td>
<td>12.19</td>
<td>14.73</td>
</tr>
<tr>
<td>2.098</td>
<td>1.601</td>
<td>0.052</td>
<td>10.59</td>
<td>13.59</td>
</tr>
<tr>
<td>1.954</td>
<td>1.471</td>
<td>0.040</td>
<td>10.97</td>
<td>11.44</td>
</tr>
<tr>
<td>2.160</td>
<td>1.581</td>
<td>0.050</td>
<td>12.75</td>
<td>13.70</td>
</tr>
<tr>
<td>1.795</td>
<td>1.022</td>
<td>-</td>
<td>24.25</td>
<td>22.00</td>
</tr>
<tr>
<td>2.043</td>
<td>1.510</td>
<td>-</td>
<td>13.09</td>
<td>12.86</td>
</tr>
<tr>
<td>Average % deviation</td>
<td>10.4</td>
<td>13.2</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>Temp. °C</td>
<td>Liquid Concentration</td>
<td>Partial Pressure, mmHg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>----------------------</td>
<td>-----------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>7.355</td>
<td>2.305</td>
<td>3.633</td>
<td>17.9</td>
</tr>
<tr>
<td>50</td>
<td>17.385</td>
<td>4.568</td>
<td>6.362</td>
<td>140.8</td>
</tr>
<tr>
<td>50</td>
<td>1.565</td>
<td>0.057</td>
<td>0.178</td>
<td>48.8</td>
</tr>
<tr>
<td>80</td>
<td>7.570</td>
<td>2.005</td>
<td>4.051</td>
<td>111.1</td>
</tr>
<tr>
<td>80</td>
<td>2.063</td>
<td>0.029</td>
<td>0.173</td>
<td>201.6</td>
</tr>
<tr>
<td>80</td>
<td>5.965</td>
<td>2.769</td>
<td>2.330</td>
<td>55.3</td>
</tr>
<tr>
<td>80</td>
<td>5.212</td>
<td>2.541</td>
<td>1.889</td>
<td>50.5</td>
</tr>
<tr>
<td>80</td>
<td>1.081</td>
<td>0.210</td>
<td>0.085</td>
<td>76.7</td>
</tr>
<tr>
<td>80</td>
<td>0.561</td>
<td>0.476</td>
<td>0.096</td>
<td>4.3</td>
</tr>
<tr>
<td>80</td>
<td>0.780</td>
<td>0.142</td>
<td>0.518</td>
<td>15.8</td>
</tr>
<tr>
<td>80</td>
<td>0.599</td>
<td>0.396</td>
<td>0.051</td>
<td>14.0</td>
</tr>
<tr>
<td>80</td>
<td>3.088</td>
<td>1.141</td>
<td>1.281</td>
<td>53.4</td>
</tr>
<tr>
<td>80</td>
<td>30.589</td>
<td>5.550</td>
<td>7.635</td>
<td>1639.5</td>
</tr>
<tr>
<td>110</td>
<td>2.383</td>
<td>0.847</td>
<td>1.297</td>
<td>113.4</td>
</tr>
<tr>
<td>110</td>
<td>0.573</td>
<td>0.562</td>
<td>0.119</td>
<td>16.5</td>
</tr>
<tr>
<td>110</td>
<td>0.609</td>
<td>0.073</td>
<td>0.169</td>
<td>91.7</td>
</tr>
<tr>
<td>110</td>
<td>7.578</td>
<td>3.353</td>
<td>1.711</td>
<td>456.2</td>
</tr>
<tr>
<td>110</td>
<td>3.099</td>
<td>1.835</td>
<td>0.920</td>
<td>123.1</td>
</tr>
<tr>
<td>120</td>
<td>2.259</td>
<td>0.099</td>
<td>0.174</td>
<td>633.2</td>
</tr>
<tr>
<td>120</td>
<td>0.264</td>
<td>0.236</td>
<td>0.140</td>
<td>12.2</td>
</tr>
<tr>
<td>120</td>
<td>0.892</td>
<td>0.446</td>
<td>0.320</td>
<td>75.1</td>
</tr>
<tr>
<td>120</td>
<td>0.106</td>
<td>0.011</td>
<td>0.022</td>
<td>23.7</td>
</tr>
<tr>
<td>120</td>
<td>0.084</td>
<td>0.028</td>
<td>0.084</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Average % deviation 40.7 26.5 30.9
Table 13. Summary of Results for the Extended Pitzer Equation

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Temp., °C</th>
<th>No. of Data Points</th>
<th>Range of Liquid Conc., Molality</th>
<th>Range of Calc. Partial Pressure / Exp. Partial Pressure, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NH₃</td>
<td>CO₂</td>
</tr>
<tr>
<td>Badger &amp; Silver</td>
<td>20</td>
<td>15</td>
<td>1.08-1.45</td>
<td>0.42-0.84</td>
</tr>
<tr>
<td>Mason &amp; Kao</td>
<td>60</td>
<td>6</td>
<td>1.80-2.16</td>
<td>1.0-1.6</td>
</tr>
<tr>
<td>Cardon &amp; Wilson</td>
<td>50</td>
<td>3</td>
<td>1.56-17.4</td>
<td>0.06-4.6</td>
</tr>
<tr>
<td>Cardon &amp; Wilson</td>
<td>80</td>
<td>10</td>
<td>0.56-30.6</td>
<td>0.03-5.55</td>
</tr>
<tr>
<td>Cardon &amp; Wilson</td>
<td>110</td>
<td>5</td>
<td>0.57-7.58</td>
<td>0.07-3.35</td>
</tr>
<tr>
<td>Cardon &amp; Wilson</td>
<td>120</td>
<td>5</td>
<td>0.08-2.26</td>
<td>0.01-0.45</td>
</tr>
<tr>
<td>Overall average</td>
<td></td>
<td>41</td>
<td>27.2</td>
<td></td>
</tr>
<tr>
<td>% deviation</td>
<td></td>
<td>42</td>
<td>19.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
summarized in Table 14.

Except for the interaction parameters listed in Tables 14, 15 and 16, all other parameters were set to $-4.063$ for $\tau_{l-1,m}$, $8.187$ for $\tau_{m,l-1}$, $-4.641$ for $\tau_{l-2,m}$, and $8.731$ for $\tau_{m,l-2}$. These values are average values of binary parameters determined for 50 aqueous uni-univalent electrolytes and 11 aqueous uni-bivalent electrolytes. Binary parameters of salt-salt pairs were set to zero. In addition, the following two relationships were adopted for $\tau_{ca,m}$ and $\tau_{m,ca}$:

\[ \tau_{l-1,m} = -2.015 \tau_{m,l-1} \]  
\[ \tau_{l-2,m} = -1.881 \tau_{m,l-2} \]  

Correlation results and parameter values for the two subsystems are given in Tables 15 and 16. With the same number of adjustable parameters as the extended Pitzer equation study, the local composition model gives slightly better results.

Partial pressures of NH$_3$, CO$_2$, and H$_2$S were calculated and compared with the experimental data of Badger and Silver, Mason and Kao, and Cardon and Wilson. The results are given in Tables 17 to 20. It was found that the model predicts partial pressures very close to the experimental results of Badger and Silver, and Mason and Kao. The average percentage deviations of partial pressures of NH$_3$, CO$_2$, and
Table 14. Binary Interaction Parameters of NH$_3$-H$_2$O pair$^1$, CO$_2$-H$_2$O pair$^2$ and H$_2$S-H$_2$O pair$^3$

\[
\tau_{\text{NH}_3, \text{H}_2\text{O}} = 0.7449 - 453.80/T
\]
\[
\tau_{\text{H}_2\text{O}, \text{NH}_3} = 1.6707 - 932.82/T
\]
\[
\tau_{\text{CO}_2, \text{H}_2\text{O}} = 10.0640 - 3268.135/T
\]
\[
\tau_{\text{H}_2\text{O}, \text{CO}_2} = \tau_{\text{CO}_2, \text{H}_2\text{O}}
\]
\[
\tau_{\text{H}_2\text{S}, \text{H}_2\text{O}} = -3.6740 + 1155.90/T
\]
\[
\tau_{\text{H}_2\text{O}, \text{H}_2\text{S}} = \tau_{\text{H}_2\text{S}, \text{H}_2\text{O}}
\]

1) data from Macriss et al. (1964)
2) data from Houghton et al. (1957)
3) data from Clarke and Glew (1971); Miles and Wilson (1975)
Table 15. Correlation Results for the NH$_3$-CO$_2$-H$_2$O System using the Local Composition Model (Data from Otsuka et al.)

\[
\begin{array}{lcc}
\tau & \text{NH}_4\text{HCO}_3, \text{H}_2\text{O} & -3.5061 \\
& \text{H}_2\text{O}, \text{NH}_4\text{HCO}_3 & 7.7888 \\
& (\text{NH}_4)_2\text{CO}_3, \text{H}_2\text{O} & -4.5394 \\
& \text{H}_2\text{O}, (\text{NH}_4)_2\text{CO}_3 & 8.8226 \\
& \text{NH}_4\text{NH}_2\text{COO}, \text{H}_2\text{O} & -2.1657 \\
& \text{H}_2\text{O}, \text{NH}_4\text{NH}_2\text{COO} & 2.4122 \\
& \text{NH}_4\text{HCO}_3, \text{NH}_3 & -6.3717 \\
& (\text{NH}_4)_2\text{CO}_3, \text{NH}_3 & -5.1450 \\
& \text{NH}_4\text{NH}_2\text{COO}, \text{NH}_3 & -0.3678 \\
& \text{NH}_4\text{HCO}_3, \text{NH}_4\text{NH}_2\text{CO}_2 & -2.1439 \\
\end{array}
\]

# of data points
Sum of squares (S)
Average % deviation of NH$_3$
partial pressure
Average % deviation of CO$_2$
partial pressure

41
3.544
16.1
17.4
Table 16. Correlation Results for the NH₃-H₂S-H₂O System, using the Local Composition Model (Data from Miles and Wilson), (1) this study, (2) IGT

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau ) NH₄HS-H₂O</td>
<td>-5.9459 + 773.68/T</td>
<td></td>
</tr>
<tr>
<td>( \tau ) H₂O,NH₄HS</td>
<td>10.0356 - 910.23/T</td>
<td></td>
</tr>
<tr>
<td>( \tau ) NH₄HS,NH₃</td>
<td>-5.2261</td>
<td></td>
</tr>
<tr>
<td>( \tau ) NH₃,NH₄HS</td>
<td>7.7517</td>
<td></td>
</tr>
<tr>
<td>( \tau ) NH₄HS,H₂S</td>
<td>-2.0967</td>
<td></td>
</tr>
</tbody>
</table>

# of data points 17

Sum of squares (S) 0.338

Average % deviation of NH₃ partial pressure 8.75 14.5

Average % deviation of H₂S partial pressure 7.74 11.2
Table 17. Comparison of Calculated Partial Pressures of NH₃, CO₂, and H₂S with the Experimental Results of Badger and Silver for NH₃-CO₂-H₂S-H₂O System at 20°C, using the Local Composition Model

<table>
<thead>
<tr>
<th>Molality NH₃</th>
<th>CO₂</th>
<th>H₂S</th>
<th>NH₃ Partial Pressure, mmHg</th>
<th>CO₂ Partial Pressure, mmHg</th>
<th>H₂S Partial Pressure, mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.231</td>
<td>0.424</td>
<td>0.196</td>
<td>3.67 (Calc.)</td>
<td>4.11 (Exp.)</td>
<td>1.57 (Calc.)</td>
</tr>
<tr>
<td>1.236</td>
<td>0.507</td>
<td>0.201</td>
<td>2.65 (Calc.)</td>
<td>2.92 (Exp.)</td>
<td>3.36 (Calc.)</td>
</tr>
<tr>
<td>1.450</td>
<td>0.517</td>
<td>0.407</td>
<td>2.64 (Calc.)</td>
<td>2.42 (Exp.)</td>
<td>4.01 (Calc.)</td>
</tr>
<tr>
<td>1.076</td>
<td>0.515</td>
<td>0.046</td>
<td>2.48 (Calc.)</td>
<td>2.72 (Exp.)</td>
<td>3.26 (Calc.)</td>
</tr>
<tr>
<td>1.439</td>
<td>0.665</td>
<td>0.396</td>
<td>1.37 (Calc.)</td>
<td>1.54 (Exp.)</td>
<td>14.16 (Calc.)</td>
</tr>
<tr>
<td>1.132</td>
<td>0.681</td>
<td>0.100</td>
<td>1.18 (Calc.)</td>
<td>1.35 (Exp.)</td>
<td>14.83 (Calc.)</td>
</tr>
<tr>
<td>1.234</td>
<td>0.694</td>
<td>0.199</td>
<td>1.13 (Calc.)</td>
<td>1.31 (Exp.)</td>
<td>17.21 (Calc.)</td>
</tr>
<tr>
<td>1.238</td>
<td>0.712</td>
<td>0.203</td>
<td>1.03 (Calc.)</td>
<td>1.30 (Exp.)</td>
<td>20.08 (Calc.)</td>
</tr>
<tr>
<td>1.234</td>
<td>0.725</td>
<td>0.199</td>
<td>0.97 (Calc.)</td>
<td>0.89 (Exp.)</td>
<td>22.37 (Calc.)</td>
</tr>
<tr>
<td>1.235</td>
<td>0.771</td>
<td>0.200</td>
<td>0.76 (Calc.)</td>
<td>0.90 (Exp.)</td>
<td>33.0 (Calc.)</td>
</tr>
<tr>
<td>1.126</td>
<td>0.794</td>
<td>0.095</td>
<td>0.64 (Calc.)</td>
<td>0.71 (Exp.)</td>
<td>39.45 (Calc.)</td>
</tr>
<tr>
<td>1.122</td>
<td>0.815</td>
<td>0.091</td>
<td>0.57 (Calc.)</td>
<td>- (Exp.)</td>
<td>47.47 (Calc.)</td>
</tr>
<tr>
<td>1.129</td>
<td>0.825</td>
<td>0.098</td>
<td>0.53 (Calc.)</td>
<td>- (Exp.)</td>
<td>52.1 (Calc.)</td>
</tr>
<tr>
<td>1.122</td>
<td>0.840</td>
<td>0.091</td>
<td>0.48 (Calc.)</td>
<td>0.55 (Exp.)</td>
<td>59.62 (Calc.)</td>
</tr>
<tr>
<td>1.129</td>
<td>0.844</td>
<td>0.098</td>
<td>0.47 (Calc.)</td>
<td>0.57 (Exp.)</td>
<td>62.03 (Calc.)</td>
</tr>
</tbody>
</table>

Average % deviation: NH₃ = 12.4, CO₂ = 12.4, H₂S = 9.4
Table 18. Comparison of Calculated Partial Pressures of NH₃, CO₂, and H₂S with the IGT Data for NH₃-CO₂-H₂S-H₂O and NH₃-CO₂-H₂O systems at 60°C, using the Local Composition Model

<table>
<thead>
<tr>
<th>Liquid Concentration Molality</th>
<th>Partial Pressure, mmHg</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>CO₂</td>
<td>H₂S</td>
<td>NH₃</td>
<td>CO₂</td>
<td>H₂S</td>
</tr>
<tr>
<td>2.076</td>
<td>1.516</td>
<td>0.064</td>
<td>12.11</td>
<td>14.73</td>
<td>631.0</td>
</tr>
<tr>
<td>2.098</td>
<td>1.601</td>
<td>0.052</td>
<td>10.56</td>
<td>13.59</td>
<td>788.7</td>
</tr>
<tr>
<td>1.954</td>
<td>1.471</td>
<td>0.040</td>
<td>10.91</td>
<td>11.44</td>
<td>675.8</td>
</tr>
<tr>
<td>2.160</td>
<td>1.581</td>
<td>0.050</td>
<td>12.67</td>
<td>13.70</td>
<td>628.6</td>
</tr>
<tr>
<td>1.795</td>
<td>1.022</td>
<td>-</td>
<td>23.80</td>
<td>22.00</td>
<td>154.7</td>
</tr>
<tr>
<td>2.043</td>
<td>1.510</td>
<td>-</td>
<td>13.00</td>
<td>12.86</td>
<td>560.1</td>
</tr>
</tbody>
</table>

Average % deviation | 10.2 | 10.6 | 15.2
Table 19. Comparison of Calculated Partial Pressures of NH\textsubscript{3}, CO\textsubscript{2}, and H\textsubscript{2}S with the Experimental Results of Cardon and Wilson for NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}S-H\textsubscript{2}O System, using the Local Composition Model

<table>
<thead>
<tr>
<th>Temp. (^\circ\text{C})</th>
<th>Liquid Concentration</th>
<th>Partial Pressure, mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH\textsubscript{3}</td>
<td>CO\textsubscript{2}</td>
</tr>
<tr>
<td>50</td>
<td>7.355</td>
<td>2.305</td>
</tr>
<tr>
<td>50</td>
<td>17.385</td>
<td>4.568</td>
</tr>
<tr>
<td>50</td>
<td>1.565</td>
<td>0.057</td>
</tr>
<tr>
<td>80</td>
<td>7.570</td>
<td>2.005</td>
</tr>
<tr>
<td>80</td>
<td>2.063</td>
<td>0.029</td>
</tr>
<tr>
<td>80</td>
<td>5.965</td>
<td>2.769</td>
</tr>
<tr>
<td>80</td>
<td>5.212</td>
<td>2.541</td>
</tr>
<tr>
<td>80</td>
<td>1.081</td>
<td>0.210</td>
</tr>
<tr>
<td>80</td>
<td>0.561</td>
<td>0.476</td>
</tr>
<tr>
<td>80</td>
<td>0.780</td>
<td>0.142</td>
</tr>
<tr>
<td>80</td>
<td>0.599</td>
<td>0.396</td>
</tr>
<tr>
<td>80</td>
<td>3.088</td>
<td>1.141</td>
</tr>
<tr>
<td>80</td>
<td>30.589</td>
<td>5.550</td>
</tr>
<tr>
<td>110</td>
<td>2.383</td>
<td>0.847</td>
</tr>
<tr>
<td>110</td>
<td>0.573</td>
<td>0.562</td>
</tr>
<tr>
<td>110</td>
<td>0.609</td>
<td>0.073</td>
</tr>
<tr>
<td>110</td>
<td>7.578</td>
<td>3.353</td>
</tr>
<tr>
<td>110</td>
<td>3.099</td>
<td>1.835</td>
</tr>
<tr>
<td>120</td>
<td>2.259</td>
<td>0.099</td>
</tr>
<tr>
<td>120</td>
<td>0.264</td>
<td>0.236</td>
</tr>
<tr>
<td>120</td>
<td>0.892</td>
<td>0.446</td>
</tr>
<tr>
<td>120</td>
<td>0.106</td>
<td>0.011</td>
</tr>
<tr>
<td>120</td>
<td>0.084</td>
<td>0.028</td>
</tr>
</tbody>
</table>
$H_2S$ are 12.4, 12.4 and 9.4 respectively for the data of Badger and Silver; and 10.2, 10.6 and 15.2 respectively for the data of Mason and Kao. This is better than the results obtained with the extended Pitzer equation. The average percentage deviations of partial pressures of $NH_3$, $CO_2$ and $H_2S$ are 40.0, 30.9 and 27.6 respectively for the data of Cardon and Wilson.

**Notation**

- $D$ = Setschenow constant of the Extended Pitzer Equation
- $N$ = number of data points
- $P$ = pressure, N/m²
- $S$ = sum of squares objective function

**Greek letters**

- $\beta^{(0)}, \beta^{(1)}$ = binary interaction parameters of the Extended Pitzer Equation
- $\Theta$ = binary difference parameter of the Extended Pitzer Equation
- $\tau$ = binary interaction parameter of the Local Composition Model

**Superscripts**

- calc = calculated
- exp = experimental
- i = data index

**Subscripts**

- a = anion
- c = cation
- m = molecular species
- 1-1 = uni-univalent electrolyte
- 1-2 = uni-bivalent electrolyte
Literature Cited


Newman, S. A., Personal communication.


Wilson, G. M., "A New Correlation of NH₃, CO₂, and H₂S Volatility Data from Aqueous Sour Water Systems," Final report to API Committee on Refinery Environmental Control under EPA Grant No. R804364010, Thermochemical Institute, BYU University, Provo, Utah (1978).
Chapter 6
An Inside-out Algorithm for Single-Stage Flash with
Chemical Equilibrium

Abstract

An algorithm is presented for the rigorous solution of the multicomponent, single-stage flash with chemical equilibrium. The algorithm is based on the inside-out approach used by Boston and Britt (1979) for single-stage flash and the Sanderson-Chien algorithm (Sanderson and Chien, 1973) for simultaneous chemical and phase equilibrium calculations. Because of the complexity of the problem due to strong interaction between chemical and phase equilibria, the advantages of the inside-out approach can be fully realized. The algorithm involves treating reaction extents and component concentrations as inside loop variables and the parameters of simple physical property models as outside loop variables. All phase and chemical equilibrium computations are carried out in the inside loop, thereby greatly reducing the computational load associated with enthalpy and fugacity evaluations. The algorithm generally requires no more property evaluations for complete solution than a single iteration of the original Sanderson-Chien algorithm. A particularly important feature of the algorithm is that good initial guesses of reaction extent are not required. The new algorithm was developed in order to
efficiently perform flash calculations involving electrolytes. The performance of the algorithm is demonstrated for a number of systems involving both electrolytes and non-electrolytes.

Scope

The multicomponent, single-stage, vapor-liquid equilibrium flash with chemical equilibrium can be used to represent many unit operations in the chemical process industry. Two examples are the esterification reaction with phase equilibrium and the Hot Carbonate process used to remove CO$_2$ from synthesis gases.

In the literature, there are two classes of methods for calculating the equilibrium composition of a chemical system. One solves the set of nonlinear equations of phase equilibrium, material balance, enthalpy balance and chemical equilibrium with known reaction stoichiometry algebraically; the other minimizes the free energy of the system using nonlinear programming techniques. The first is called the K-value approach and is more direct for data correlation and for process simulation. The second is called the free energy minimization approach and is more suitable for large systems and for estimation (Sanderson and Chien, 1973).

Previous algorithms for solving the simultaneous chemical and phase equilibria problem by the K-value approach can be
divided into three categories. The first one solves the chemical equilibrium relationships as the outside loop of the phase equilibrium relationships. The second method adopts the pseudo-K approach, in which pseudo-phase-equilibrium-constants are calculated so that flash calculations can be performed with the assumption that no chemical reaction occurs. The third method solves the set of chemical and phase equilibrium equations simultaneously using general nonlinear equation solving techniques. The most successful algorithm is due to Sanderson and Chien (1973) and is a member of the first category in which linear mass balance constraints formed by the reaction stoichiometry are removed by increasing the dimensionality of the problem.

Recently, an inside-out algorithm has been developed for performing multicomponent, single-stage, vapor-liquid equilibrium flash calculations (Boston and Britt, 1978). The main iteration variables are parameters of approximate physical property models, rather than temperatures, phase rates, and compositions. The algorithm is capable of solving wide-boiling, narrow-boiling, and highly nonideal systems and greatly reduces the computational load associated with enthalpy and equilibrium ratio evaluations, especially for "difficult" problems.

The objective of this study is to apply the inside-out
approach to the problem of simultaneous chemical and phase equilibrium calculations. Because of the complexity of the problem, due to the strong interaction between chemical and phase equilibria, the advantages of the inside-out algorithm can be fully exploited and utilized. Example problems are solved to demonstrate the reliability and efficiency of the algorithm.

**Conclusions and Significance**

An inside-out algorithm has been developed for performing multicomponent, single-stage flash with chemical equilibrium calculations. The algorithm has the following desirable performance characteristics: (1) The algorithm exhibits robust and stable convergence behavior. (2) The algorithm is more efficient than conventional algorithms. Efficiency is measured by the number of enthalpy and phase equilibrium ratio evaluations. (3) The user is not required to furnish initial estimates of vapor and liquid composition and the algorithm is relatively insensitive to initial estimates of temperature, pressure or reaction extents. This is especially important for phase and chemical equilibrium calculations because initial estimates are difficult to obtain. (4) Convergence is achieved very rapidly when the flash calculation is restarted from a previously converged solution at different conditions. The algorithm is especially suited for use in a process simulation
system in which case all of the characteristics listed above are desirable.

**Problem Description for Nonelectrolyte Systems**

Figure 1 schematically depicts a multicomponent, single-stage flash with chemical equilibrium. In the most common situation, the composition and condition of the feed and reaction stoichiometry are known, and it is desired to determine the compositions, conditions and flow rates of the vapor and liquid effluent streams. When the heat duty is not specified, it is usually desired to calculate it from an enthalpy balance. It is assumed that reactions specified in the system are linearly independent. This assumption is not restrictive since any chemical equilibrium problem can always be formulated this way.

For a reaction system involving the following reactions:

\[ \sum_{i=1}^{N} \mu_{ij} A_i = 0 \quad j=1,2,\ldots,M; \quad (1) \]

the criterion of chemical reaction equilibrium can be written as

\[ \sum_{i=1}^{N} \mu_{ij} G_i(T,P,X) = 0 \quad j=1,2,\ldots,M \quad (2) \]

For nonelectrolyte systems, we choose the standard state as
Figure 1. Schematic Diagram of Single-Stage Flash with Chemical Equilibrium
ideal gas at a pressure of 1.01325*10^5 pascal (1 atm). Then, the chemical equilibrium relationship becomes

\[
\prod_{i=1}^{N} (\phi_i x_i P/P_{\text{ref}}^{\mu_{ij}}) = \exp\left(-\sum_{i=1}^{N} \mu_{ij} G_i^{IG}/RT\right) = K_j(T) \quad j=1,2,...,M \quad (3)
\]

In addition to the M chemical equilibrium equations (3) given above the following phase equilibrium, and mass and energy balance equations apply to the system.

Reaction component mass balance:

\[
f_i = f_i^* + \sum_{j=1}^{N} \mu_{ij} \text{ext}_j \quad i=1,2,...,N \quad (4)
\]

Extensive constitutive:

\[
F = \sum_{i=1}^{N} f_i \quad (5)
\]

Phase equilibrium:

\[
y_i = K_i x_i \quad i=1,2,...,N \quad (6)
\]

Phase component mass balance:

\[
x_i L + y_i V = f_i \quad i=1,2,...,N \quad (7)
\]

Phase total mass balance:

\[
L + V = F \quad (8)
\]

Enthalpy balance:

\[
H_L^1 L + H_V V = (H^* F^* + Q) F/F^* \quad (9)
\]
Intensive constitutive:
\[ \sum_{i=1}^{N} x_i = \sum_{i=1}^{N} Y_i \]  

Heat of reaction does not appear in equation (10) because all enthalpy values are element-based. The enthalpy of formation of each component has been taken into account in these element-based enthalpies.

For an \( N \)-component, \( M \)-reaction system, there are \( 3N+M+4 \) equations. The system is completely described when the values of the variables listed below are known.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T )</td>
<td>1</td>
</tr>
<tr>
<td>( P )</td>
<td>1</td>
</tr>
<tr>
<td>( V )</td>
<td>1</td>
</tr>
<tr>
<td>( L )</td>
<td>1</td>
</tr>
<tr>
<td>( Q )</td>
<td>1</td>
</tr>
<tr>
<td>( F )</td>
<td>1</td>
</tr>
<tr>
<td>( f )</td>
<td>( N )</td>
</tr>
<tr>
<td>( X )</td>
<td>( N )</td>
</tr>
<tr>
<td>( Y )</td>
<td>( N )</td>
</tr>
<tr>
<td>( \xi )</td>
<td>( M )</td>
</tr>
</tbody>
</table>

\[ 3N+M+6 \]

If we adopt the premise that \( F, f, X, Y, \xi, \) and \( L \) are always to be calculated, then there remains four variables \( (T, P, V, Q) \) of which two may be fixed in order to completely specify the system. The six types of flash calculations that represent all possible combinations of specified quantities are listed in Table 1.
Table 1. Types of Single-Stage Flash with Chemical Equilibrium

<table>
<thead>
<tr>
<th>Flash type</th>
<th>Specified quantities</th>
<th>Calculated quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Q,P</td>
<td>T,V</td>
</tr>
<tr>
<td>II</td>
<td>Q,T</td>
<td>V,P</td>
</tr>
<tr>
<td>III</td>
<td>Q,V</td>
<td>T,P</td>
</tr>
<tr>
<td>IV</td>
<td>V,T</td>
<td>P,Q</td>
</tr>
<tr>
<td>V</td>
<td>V,P</td>
<td>T,Q</td>
</tr>
<tr>
<td>VI</td>
<td>T,P</td>
<td>V,Q</td>
</tr>
</tbody>
</table>

All cases:
- $F^*$, $f^*$, $H^*$ specified
- $F$, $f$, $X$, $Y$, $\xi$, $L$ calculated
The Inside-Out Algorithm

The inside-out approach used in this study was first presented by Boston and Sullivan (1974), who demonstrated the exceptional capability and efficiency of the resulting algorithm for multi-component distillation problems. An excellent discussion of the basic inside-out concepts was later given by Boston and Britt (1978), who applied them to the single-stage two-phase flash problem. The approach has also been successfully applied to the three-phase flash problem (Boston and Fournier, 1978) and the three-phase distillation problem (Boston and Shah, 1979). Recently, Boston (1979) reviewed the development of the inside-out approach.

The concepts may be summarized as follows:

(1) Complex phase equilibrium and enthalpy models, such as equation of state, are used only to generate parameters for simple models of phase equilibrium K-value and enthalpy departure.

(2) These simple model parameters become the main (or "outer loop") iteration variables, the role played by temperature, pressure, and vapor and liquid composition in conventional methods.
(3) The new outer loop iteration variables are relatively free of interaction with each other, and are relatively independent of temperature, pressure, and the compositions, thereby promising rapid and robust convergence. Another consequence is that precise initialization is not critical to good algorithm performance.

(4) The phase equilibrium and material and energy balance equations describing the system are solved in an inner loop in which they are expressed in terms of the simple physical property models. Therefore, no evaluations of phase equilibrium ratios and enthalpies are required in the inner loop.

(5) Each inner loop iteration variable is a unique combination of temperature and phase ratio which eliminates the need to make a distinction between wide- and narrow-boiling systems and also reduces the number of equations to be solved simultaneously.

(6) The temperature, pressure and compositions resulting from the solution of the inner loop for a given set of values of the outer loop variables are used to calculate a new set of the latter based on new physical property evaluations. The problem is solved when these calculated values match the corresponding assumed values.
In the Boston-Britt single-stage, two phase flash algorithm, the main outer loop iteration variables are the "volatility parameters", and are defined as

\[ u_i = \ln \left( \frac{K_i}{K_b} \right) \quad i=1,2,...,N \]  \hspace{1cm} (11)

where \( K_b \) is a reference equilibrium ratio defined as a weighted average of the form:

\[ \ln K_b = \frac{1}{N} \sum_{i=1}^{N} w_i \ln K_i \]  \hspace{1cm} (12)

The \( w \)'s are weighting factors, expressions for which are given by Boston and Britt (1978).

The following model is used for \( K_b \) for those cases in which temperature is a variable:

\[ \ln K_b = A + B(1/T - 1/T^*) \]  \hspace{1cm} (13)

where \( T^* \) is a reference temperature. The coefficients \( A \) and \( B \) are determined by

\[ B = \frac{\partial \ln K_b}{\partial (1/T)} \] \hspace{1cm} (14)
\[ A = \ln K_b - B(1/T - 1/T^*) \] \hspace{1cm} (15)

A model of similar nature is used for \( K_b \) for those cases
in which pressure is a variable. The $K_D$ model along with the
$u_i$'s account for most of the change in $K$ values with
temperature and pressure, but do not take into account changes
with composition.

Simple enthalpy models are used for the two enthalpy
departure functions, $\Delta H_v$ and $\Delta H_1$. They are

$$\Delta H_v = C + D(T - T^*) \quad (16)$$
$$\Delta H_1 = E + F(T - T^*) \quad (17)$$

Equation (23) is different from the model presented in
Boston and Britt (1978) but has since been adopted by the
authors. Equations (16) and (17) along with ideal gas enthalpy
evaluations account for most of the change in enthalpy with
temperature or pressure but not composition.

The simple physical property model parameters, $\ln u_i$'s, $A$, $B$, $C$, $D$, $E$, and $F$ are the outer loop iteration variables.
Given values of these parameters, the flash describing
equations, expressed in terms of the simple models, may be
solved for $T$, $P$, $V$, $x$, and $y$.

The flash describing equations solved in the inner loop are
reformulated in terms of a single inside loop iteration
variable, $R$, defined as
\[
R = \frac{K_b V}{(K_b V + K^0_b)} \tag{18}
\]

where \( K^0_b \) is a reference value of \( K_b \). Thus the inner loop involves only one equation and one unknown. Note that \( R \) reflects changes in both \( V \) and \( T \) (through \( K_b \)) and is therefore a suitable iteration variable for both narrow- and wide-boiling systems.

**The Sanderson-Chien Algorithm**

The single phase chemical equilibrium problem may be formulated as an \( M \) dimensional system of nonlinear equations. The feasible region for a solution of these equations is formed by a set of \( N \) linear inequality constraints that prevent negative compositions. The reaction extents are the independent variables and equations (3) are the equations to be satisfied. The nonnegativity constraints are that

\[
f_i > 0 \quad i = 1, 2, \ldots, N \tag{19}
\]

or

\[
\sum_{j=1}^{M} \mu_{ij} \text{ext}_j > -f^*_i \quad i = 1, 2, \ldots, N \tag{20}
\]

in the extent space. The two phase problem can be solved by imbedding a flash calculation within the problem formulation given above. However, generalized methods for solving multivariable nonlinear equations within a linearly constrained
region have not been satisfactory for the two phase chemical equilibriums problem because of the very strong nonlinearity and interaction of the problem in the extent space (Sanderson and Chien, 1973). Sanderson and Chien proposed to overcome this difficulty by reformulating the problem with both extents ($\xi$) and component molar flowrates ($f$) as independent variables and including equations (4) in the system of equations to be solved. Therefore, the problem becomes one of solving a system of M+N nonlinear equations with only simple nonnegativity bounds on the component molar flowrate independent variables.

The Sanderson-Chien algorithm proceeds as follows:

1. Begin with initial estimates of the $\xi_j$'s and $f_i$'s.
2. Perform a flash calculation on $f_i$'s to get $x_i$'s and $y_i$'s.
3. If equations (3) and (4) are satisfied, exit.
4. Else, use a nonlinear equation solver to estimate new values of $\xi_j$'s and $f_i$'s and return to step 2.

Therefore, there are two loops in the algorithm. The outside loop is the chemical equilibrium loop. The inside loop is the phase equilibrium loop. The original Sanderson-Chien algorithm was proposed for isothermal (TP) flash with chemical equilibrium. The inside phase equilibrium loop has been extended by White (1979) to allow for other types of flash
calculations, such as adiabatic (PQ) flash with chemical equilibrium.

New Algorithm for Flash with Chemical Equilibrium

The new inside-out algorithm for flash with chemical equilibrium is a synergistic combination of the Boston-Britt inside-out algorithm for single-stage flash and the Sanderson-Chien algorithm for simultaneous chemical and phase equilibrium calculations. Simple models are first developed for the necessary physical properties. Complex calculations of fugacities and enthalpies are only performed to generate parameters of these simple physical property models. These simple model parameters then become the outer loop iteration variables. The phase and chemical equilibrium equations, reformulated in terms of the simple physical property models, are solved using a modified Sanderson-Chien algorithm. The chemical equilibrium loop becomes the middle loop and the phase equilibrium loop is the innermost loop. Since these equilibrium equations are expressed in terms of the simple physical property models, no complex calculations of fugacities and enthalpies are required in the middle and inner loops. Furthermore, the equilibrium equations of the middle and inner loops become much more well-behaved because the simple physical property model parameters are independent of system compositions. The inner phase equilibrium loop is solved by
adopting the Boston-Britt inner loop in which reformulated flash describing equations are solved in terms of a single variable R. In other words, the rigorous multicomponent flash solution step of the Sanderson-Chien algorithm has been replaced by a very simple root finding problem in one equation and one unknown.

The new algorithm simplifies the strong interaction between the chemical and phase equilibrium equations in the middle and inner loops by isolating the effects of system nonideality, that is, by moving them to the outer loop. The complex chemical and phase equilibrium problem is therefore free of the influence of system nonideality. Hence, the Sanderson-Chien algorithm, an effective mathematical approach to the calculation of simultaneous chemical and phase equilibria, is further enhanced since it includes search direction heuristics based on the assumption of ideality. The Boston-Britt inner loop provides an ideal phase equilibrium loop for the new algorithm since the computational load associated with its solution is almost trivial and since, as a doubly nested loop, it is executed so many times.

The outer loop variables of the new algorithm are the simple physical property model parameters. Since chemical equilibrium expressions involve fugacity coefficients, rather than phase equilibrium constants, it is necessary to introduce a
set of outer loop variables based on fugacity coefficients. Because vapor fugacity coefficients \( \phi_v^i \)'s are ordinarily not strongly dependent on temperature, pressure, or vapor phase composition, the \( \phi_v^i \)'s themselves should be well-behaved iteration variables. However, liquid fugacity coefficients \( \phi_l^i \)'s depend strongly on temperature and liquid composition, \( x \). To account for the temperature dependence of the liquid fugacity coefficients, the \( K_b \) model used by Boston and Britt is retained. Therefore, the simple models used for vapor and liquid fugacity coefficients are

\[
\begin{align*}
\ln \phi_v^i &= \text{constant}, \\
\ln \phi_l^i / K_b &= \text{constant}, \\
\ln K_b &= A + B \left( 1/T - 1/T^* \right)
\end{align*}
\] (21) (22) (23)

and the outside loop iteration variables associated with the fugacity coefficients are \( \ln \phi_v^i \)'s, \( \ln (\phi_l^i / K_b) \)'s, \( A \), and \( B \). In other words, the \( \ln u_i \)'s (volatility parameters) of the original Boston-Britt algorithm are replaced by the individual phase quantities \( \ln \phi_v^i \)'s and \( \ln (\phi_l^i / K_b) \)'s.

Given values of the outer loop parameters, \( K_b \) can be calculated from equation (23) and, \( \phi_v^i \)'s from equation (21), \( \phi_l^i \)'s from equation (22) and phase equilibrium constants from
are redefined as

\[ S_{i+M} = \frac{\sum_{j=1}^{M} (f_i - f_i^*) \xi_j f_j}{F} \quad i=1,2,\ldots,N \]  

(28)

The iteration variables of the middle loop are reaction extents \( \xi_j \)'s and logarithms of equilibrium component flow rates \( \ln f_i \)'s). The system of \( M+N \) nonlinear equations is solved using Newton's method.

The original Sanderson-Chien algorithm used \( \xi_j \)'s and \( f_i \)'s as the iteration variables, which required strict inequality constraints on the \( f_i \)'s (\( f_i > 0 \)). The change from \( f_i \)'s to \( \ln f_i \)'s is a transformation of variables to remove these constraints. This is particularly advantageous for problems with some \( f_i \)'s residing near the constraints, such as trace components. The logarithms also make equations (27) more linear and better-behaved.

Each iteration of the middle loop yields estimates of \( \xi_j \)'s and the \( \ln f_i \)'s. With these values for \( \ln f_i \) the phase equilibrium equations are solved using the inner loop of the Boston-Britt algorithm. The only modification required here is the enthalpy balance which is written as

\[(L/F)(\Delta H_v - \Delta H_1) - \sum_{i=1}^{N} \frac{f_i H_{vi}}{F} - \Delta H_v + (H*F^*+Q)/F^* \]  

(29)
in order to take into account the changing total number of moles.

The calculation of chemical equilibrium (middle) and phase equilibrium (inner) loops proceeds as follows:

1) Initialize $\xi_j = 0$ \hspace{2cm} $j=1,2,\ldots M$

   $\ln f_i = \ln f^*_i$ \hspace{2cm} $i=1,2,\ldots N$

   (if $f^*_i = 0$, set $f_i$ to $1 \times 10^{-5}$)

   If better estimates are available, they are used.

2) Calculate $S_k$, $k=1,2,\ldots M+N$, solving the Boston-Britt reformulated phase equilibrium inner loop to obtain $T$, $P$, $V$, $x$ and $y$.

3) Calculate the partial derivative (Jacobian) matrix, $J$, numerically or analytically.

4) Obtain new values for $\xi_j$ and $\ln f_i$ using Newton's method.

   $$\Delta \left( \begin{array}{c} \xi_j \\ \ln f_i \end{array} \right) = -J^{-1} S$$

5) Return to step 2 and repeat until $S_k$'s are smaller than the convergence tolerance.

An approximate Jacobian matrix is calculated analytically. The matrix has elements as follows:
\[
\begin{align*}
t & = 1, 2, \ldots, M \\
\frac{\partial s_s}{\partial \xi_t} & = 0 \\
\frac{\partial s_s}{\partial n_{t-M}} = \sum_{k=1}^{N} \frac{\partial y_k}{\partial x_k} \frac{\partial x_k}{\partial n_{t-M}} \\
& \quad \left[ \frac{\partial \ln x_k}{\partial n_{t-M}} \right] \\
& \quad \left[ \frac{\partial \ln y_k}{\partial n_{t-M}} \right] \\
& \quad \left[ \frac{\partial f_{t-M}}{\partial n_{t-M}} \right] \\
\frac{\partial f_{t-M}}{\partial x_k} & = \delta _{ki} \frac{f_k}{F} - \frac{f_k}{[1-(V/F)+K_k(V/F)]F^2} \\
\frac{\partial f_{t-M}}{\partial n_{t-M}} & = f_{t-M} \\
s & = M + 1, M + 2, \ldots, M + N \\
\frac{\partial s_s}{\partial \xi_t} & = \mu _{s-M,t} \\
\frac{\partial s_s}{\partial n_{t-M}} = \delta _{st} f_{t-M} \\
\text{where} \\
\frac{\partial s_s}{\partial \ln x_k} & = \frac{\mu _{ks}}{\ln K_s} \\
\frac{\partial \ln x_k}{\partial x_k} & = 1 \\
\frac{\partial \ln y_k}{\partial y_k} & = 1 \\
\frac{\partial f_{t-M}}{\partial x_k} & = \delta _{ki} \frac{f_k}{F} - \frac{f_k}{[1-(V/F)+K_k(V/F)]F^2} \\
\frac{\partial f_{t-M}}{\partial n_{t-M}} & = f_{t-M}
\end{align*}
\]
The elements of $\partial S_k / \partial t$ and $\partial S_k (k=M+1, M+2, \ldots M+N) / \partial \ln f_i$ are known and exact. The elements of $\partial S_k (k=1, 2, \ldots M) / \partial \ln f_i$ involve phase equilibrium relationships and are good approximations.

In general, phase equilibrium constants are functions of temperature, pressure and composition. However, the phase equilibrium constants in equations (30) to (34) are independent of composition since they are expressed in terms of the simple physical property model parameters. Therefore, the analytical derivatives of equation (34) are better approximations than those of the Sanderson-Chien algorithm.

Since the analytical derivatives are independent of system nonideality, it does not matter if the analytical derivative calculation is carried out based on vapor or liquid compositions. In fact, liquid composition is preferred because chemical reactions may occur only in the liquid phase.

The iteration scheme of the inside-out algorithm for the type I adiabatic flash with chemical equilibrium is shown in Table 2.

The outer loop variables are converged by a modification of the Broyden quasi-Newton method as in the original Boston-Britt
Table 2. Type I Adiabatic Flash with Chemical Equilibrium, the Inside-Out Algorithm

0. Initialize $\xi$ and $f'$ ($f_i' = \ln f_i$)
1. Assume $u', u'', A, B, C, D, E, F$
   ($u_i' = \ln \phi Y_i; u_i'' = \ln \phi Y_i''/K_D$)
2. Assume $\xi$ and $f'$
3. Assume $\bar{r}$
4. Calculate $K_B, T, x, y, L$
5. Calculate $\Delta H_v, \Delta H_1, H_{IV}$
6. Check enthalpy balance equation
7. Assume new $R$ and return to (3) until enthalpy balance equation is satisfied.
8. Calculate $K_j$ (chemical equilibrium constants), and check chemical equilibrium and reaction component mass balance residual functions ($S$)
9. Calculate the Jacobian matrix, $J$.
10. Assume new $\xi$ and $f''$, and return to (2) until all residual functions are converged
11. Calculate $V$
12. Calculate $\phi V, \phi^1, H_v, H_1$ using actual models
13. Calculate $u', u'', A, C, E$
    (and $B, D, F$ first iteration only)
14. Assume new values of $u', u'', A, C, E$
    (and $B, D, F$ first iteration only) and return to (2) until calculated values match assumed values
algorithm. It should be noted that no attempt was made to eliminate the composition dependence of the outer loop parameters. While this may seem to be a violation of the principle of iteration variable independence, especially for highly nonideal systems, it actually represents an efficient tradeoff between the effects that the simple models ought to account for and the effects that the Broyden convergence procedure ought to account for. As is explained in the Boston-Britt paper, the Broyden method used is particularly well-suited to account for composition dependence of the outer loop parameters.

Nonelectrolyte Examples

To illustrate the performance of the new algorithm for nonelectrolyte systems, several cases were solved based on one system. Involving phase equilibrium and an esterification reaction, the system contains ethanol, acetic acid, ethyl acetate, and water. The esterification reaction is

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \]

Data required for the phase and chemical equilibria include vapor pressures, liquid activities, enthalpy data and ideal gas Gibbs free energy. The vapor phase is assumed to be ideal. The vapor pressure, enthalpy, and ideal gas Gibbs free energy
are calculated by ASPEN (ASPN user's manual, 1979). The physical property option set is SYSOP0 with the liquid activity coefficient model replaced by the Wilson equation. The Watson equation is used to calculate enthalpies of vaporization. Liquid activity coefficients are calculated using the Wilson equation with binary parameters obtained from Sanderson and Chien (1973).

The specific problem was to flash a stream containing initially:

<table>
<thead>
<tr>
<th>component</th>
<th>mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>0.5</td>
</tr>
<tr>
<td>acetic acid</td>
<td>0.5</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>0.0</td>
</tr>
<tr>
<td>water</td>
<td>0.0</td>
</tr>
<tr>
<td>molal flowrate</td>
<td>100</td>
</tr>
<tr>
<td>temperature</td>
<td>350°K</td>
</tr>
<tr>
<td>pressure</td>
<td>1.013d5 pascal</td>
</tr>
</tbody>
</table>

Five cases were studied. These five cases are PQ, TQ, TV, PV and TP flashes. Results are shown in Table 3.

The TP case of this example has been studied by various investigators (Sanderson and Chien, 1973; George et al., 1976; Gautam and Seider, 1979). Of these, Sanderson and Chien's algorithm is the only one adopting the K-value approach. To show the advantages of the new algorithm, the state-of-the-art Sanderson-Chien algorithm (White, 1979) is used to solve all five cases. In White's version, the phase equilibrium loop of
Table 3. Iteration History of the Esterification Reaction Example Using the Inside-Out Algorithm.

Case a) Specified $P=1.013d5$ N/m$^2$, $Q=0.0$, initial $T=350^\circ K$, $V/F=0.5$, $\xi=0.2$

<table>
<thead>
<tr>
<th>iteration number</th>
<th>$\xi$</th>
<th>$T$</th>
<th>$V/F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3626</td>
<td>349.10</td>
<td>0.1876</td>
</tr>
<tr>
<td>2</td>
<td>0.3715</td>
<td>349.11</td>
<td>0.2403</td>
</tr>
<tr>
<td>3</td>
<td>0.3732</td>
<td>349.00</td>
<td>0.2517</td>
</tr>
<tr>
<td>4</td>
<td>0.3739</td>
<td>348.95</td>
<td>0.2571</td>
</tr>
<tr>
<td>5</td>
<td>0.3739</td>
<td>348.94</td>
<td>0.2579</td>
</tr>
</tbody>
</table>

Case b) Specified $T=350^\circ K$, $Q=0.0$, initial $P=1.013d5$ N/m$^2$, $V/F=0.5$, $\xi=0.2$

<table>
<thead>
<tr>
<th>iteration number</th>
<th>$\xi$</th>
<th>$P$</th>
<th>$V/F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3617</td>
<td>1.0494d5</td>
<td>0.1843</td>
</tr>
<tr>
<td>2</td>
<td>0.3708</td>
<td>1.0471d5</td>
<td>0.2373</td>
</tr>
<tr>
<td>3</td>
<td>0.3725</td>
<td>1.0511d5</td>
<td>0.2480</td>
</tr>
<tr>
<td>4</td>
<td>0.3730</td>
<td>1.0529d5</td>
<td>0.2530</td>
</tr>
<tr>
<td>5</td>
<td>0.3731</td>
<td>1.0532d5</td>
<td>0.2537</td>
</tr>
</tbody>
</table>

Case c) Specified $T=350^\circ K$, $V/F=0.0$, initial $P=1.013d5$ N/m$^2$, $\xi=0.2$

<table>
<thead>
<tr>
<th>iteration number</th>
<th>$\xi$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3494</td>
<td>1.0833d5</td>
</tr>
<tr>
<td>2</td>
<td>0.3562</td>
<td>1.0833d5</td>
</tr>
<tr>
<td>3</td>
<td>0.3567</td>
<td>1.0841d5</td>
</tr>
<tr>
<td>4</td>
<td>0.3567</td>
<td>1.0841d5</td>
</tr>
</tbody>
</table>

Case d) Specified $P=1.013d5$ N/m$^2$, $V/F=1.0$, initial $T=350^\circ K$, $\xi=0.2$

<table>
<thead>
<tr>
<th>iteration number</th>
<th>$\xi$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4263</td>
<td>354.46</td>
</tr>
<tr>
<td>2</td>
<td>0.4256</td>
<td>356.13</td>
</tr>
<tr>
<td>3</td>
<td>0.4254</td>
<td>356.53</td>
</tr>
<tr>
<td>4</td>
<td>0.4253</td>
<td>356.78</td>
</tr>
<tr>
<td>5</td>
<td>0.4253</td>
<td>356.79</td>
</tr>
<tr>
<td>6</td>
<td>0.4253</td>
<td>356.73</td>
</tr>
<tr>
<td>7</td>
<td>0.4253</td>
<td>356.73</td>
</tr>
</tbody>
</table>

Case e) Specified $T=350^\circ K$, $P=1.013d5$ N/m$^2$, initial $V/F=0.5$, $\xi=0.2$

<table>
<thead>
<tr>
<th>iteration number</th>
<th>$\xi$</th>
<th>$V/F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3750</td>
<td>0.3721</td>
</tr>
<tr>
<td>2</td>
<td>0.3823</td>
<td>0.4010</td>
</tr>
<tr>
<td>3</td>
<td>0.3851</td>
<td>0.4264</td>
</tr>
<tr>
<td>4</td>
<td>0.3872</td>
<td>0.4463</td>
</tr>
<tr>
<td>5</td>
<td>0.3880</td>
<td>0.4553</td>
</tr>
<tr>
<td>6</td>
<td>0.3882</td>
<td>0.4573</td>
</tr>
</tbody>
</table>
the Sanderson-Chien algorithm is improved by adopting the Boston-Britt flash algorithm. In addition, the phase equilibrium flash calculation is always restarted from a previously converged solution. The iteration history of TP flash is shown in Table 4. The number of iterations for all five cases are compared with those of the new algorithm, and the summary is given in Table 5. The new algorithm proves to be a better algorithm for single-stage flash with chemical equilibrium.

Considerations for Electrolyte Systems

To apply the new algorithm to electrolyte systems, two fundamental differences between electrolyte systems and nonelectrolyte systems must be recognized. One is the choice of standard states of electrolyte systems. The other is the fact that ionic species of electrolyte systems are nonvolatile.

For single-solvent electrolyte systems, such as aqueous electrolyte systems, the most common standard state of the solvent species is the pure, condensed solvent at the system temperature and pressure. The standard state of the solutes species is the limiting state in which solute concentrations become infinitely dilute. Based on these standard states, the chemical equilibrium relationships can be written as follows:
Table 4. Isothermal Flash Iteration History of the Esterification Reaction Example Using the Sanderson-Chien Algorithm.

Specified $T=350^\circ$K, $P=1.013$ d5, 
initial $V/F=0.5$, $\xi=0.2$

<table>
<thead>
<tr>
<th>Chem. equil.</th>
<th>Phase equil.</th>
</tr>
</thead>
<tbody>
<tr>
<td>iteration #</td>
<td>iteration #</td>
</tr>
<tr>
<td></td>
<td>$\xi$</td>
</tr>
<tr>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>1</td>
<td>0.3221</td>
</tr>
<tr>
<td>2</td>
<td>0.3596</td>
</tr>
<tr>
<td>3</td>
<td>0.3765</td>
</tr>
<tr>
<td>4</td>
<td>0.3836</td>
</tr>
<tr>
<td>5</td>
<td>0.3864</td>
</tr>
<tr>
<td>6</td>
<td>0.3875</td>
</tr>
<tr>
<td>7</td>
<td>0.3880</td>
</tr>
<tr>
<td>8</td>
<td>0.3881</td>
</tr>
<tr>
<td>9</td>
<td>0.3882</td>
</tr>
<tr>
<td>10</td>
<td>0.3882</td>
</tr>
<tr>
<td>11</td>
<td>0.3882</td>
</tr>
</tbody>
</table>
Table 5. Comparison of Iteration Numbers of the Esterification Reaction Example

<table>
<thead>
<tr>
<th>Case</th>
<th>Inside-Out Algorithm</th>
<th>Sanderson-Chien Algorithm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>iteration #</td>
<td>chem. equil. iteration #</td>
</tr>
<tr>
<td>a) PQ</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>b) TQ</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>c) TV</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>d) PV</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>e) TP</td>
<td>6</td>
<td>11</td>
</tr>
</tbody>
</table>
\[ \Pi_{i=1}^{N} (\gamma_i x_i)_{ij}^\mu \exp \left( \sum_{i=1}^{N} \mu_{ij} G_i^O / RT \right) = K_j'(T) \quad j=1,2,\ldots,M \ (35) \]

where \( \gamma_i \)'s are symmetric activity coefficients for solvents and infinite dilution activity coefficients for solutes. Also, the standard state free energies of solutes are the infinite dilution free energies, i.e., \( G_i^O = G_i^\infty \).

For solvent species, \( G_i^O \) can be calculated from \( G_i^{IG} \) and saturated vapor pressure.

\[ G_i^O = G_i^{IG} + RT \ln p_i^{Sat} / p_{ref} \quad (36) \]

For molecular solutes, \( G_i^\infty \) can be calculated from \( G_i^{IG} \) and Henry's constant.

\[ G_i^\infty = G_i^{IG} + RT \ln H_i / p_{ref} \quad (37) \]

For ionic solutes, \( G_i^\infty \) can be calculated from \( G_i^{IG} \) and standard real potential.

\[ G_i^\infty = G_i^{IG} + \alpha_i^S \quad (38) \]

The standard real potential, \( \alpha_i^S \), is the standard free energy change per mole on transferring ions of species \( i \) from the ideal vapor phase to the ideal solution phase when there is no net charge on the solution phase (Parsons, 1959).
Therefore, chemical equilibrium relationships of electrolyte systems can be rewritten as follows:

\[ \prod_{i=1}^{N} \left( \gamma_i x_i c_i \right)^{\mu_{ij}} = \exp \left( -\sum_{i=1}^{N} \mu_{ij} G_i^{\text{IG}} / RT \right) = K_j(T) \quad j=1,2,\ldots M \]  \hspace{1cm} (39)

where

\[ c_i = \frac{p_i^{\text{sat}}}{P_{\text{ref}}} \quad \text{(if component i is a solvent species)} \]

\[ c_i = \frac{H_i}{P_{\text{ref}}} \quad \text{(if component i is a molecular solute)} \]

\[ c_i = \exp (\alpha_i^{\text{S}} / RT) \quad \text{(if component i is a ionic solute)} \]

For mixed solvent electrolyte systems, equations (39) are still valid with \( H_i \) and \( \alpha_i^{\text{S}} \) being mixed solvent quantities.

Although the standard states of electrolyte systems are different from those of nonelectrolyte systems, the inside-out algorithm is applicable to electrolyte systems. However, since ionic species are nonvolatile, liquid activity coefficients, instead of fugacity coefficients, are the essential physical property for chemical equilibrium relationships. Compared with liquid fugacity coefficients, liquid activity coefficients are relatively independent of temperature and pressure. Hence, the \( \ln \gamma_i \)'s themselves should be suitable as outer loop iteration
variables and are so used for the ionic species in electrolyte systems.

Actually, fugacity coefficients have not been defined for nonvolatile ionic species in the literature. However, in order to perform phase equilibrium calculations, phase equilibrium constants, vapor fugacity coefficients, and liquid fugacity coefficients of nonvolatile species are defined as follows:

\[ K_i \equiv \frac{\phi_i^L}{\phi_i^V} = 0 \]  \hspace{1cm} (40)
\[ \phi_i^L = 0 \]  \hspace{1cm} (41)
\[ \phi_i^V = 1 \]  \hspace{1cm} (42)

Therefore, the outer loop variables are \( \ln \phi_i^V \)'s, \( \ln (\phi_i^L/K_B) \)'s, A, B, C, D, E, and F with \( \ln (\phi_i^L/K_B) \)'s replaced by \( \ln \gamma_i \)'s if component i is nonvolatile.

Quite often, electrolyte system liquid compositions are expressed in terms of molalities. Molalities and mole fractions can be related by equation (43).

\[ x_i = \frac{m_i}{(1000 + \sum m_i)} \]  \hspace{1cm} (43)

The electroneutrality of electrolyte systems is automatically satisfied by the reaction component mass balance
equations, equation (4), since \( f^* \) is assumed to satisfy charge balances. Two other noteworthy characteristics of electrolyte systems are 1) chemical reactions occur only in the liquid phase; 2) trace component concentrations may be critical for chemical equilibrium constraints because these constraints are very sensitive to trace component concentrations.

**Electrolyte Examples**

To test the performance of the inside-out algorithm on electrolyte systems, the Hot Carbonate Process system was used as the example electrolyte system. The three reactions occurring in the aqueous phase are

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & = \text{HCO}_3^- + \text{H}^+ \\
\text{HCO}_3^- & = \text{CO}_3^{2-} + \text{H}^+ \\
\text{H}_2\text{O} & = \text{OH}^- + \text{H}^+
\end{align*}
\]

The liquid activity coefficients were calculated with the local composition model and the binary parameters were taken from Chapter 4. The binary parameters and other physical property constants are shown in Table 6. Ideal vapor phase was assumed. Because no thermal data were available, only TP, TV and PV flashes were performed. With complete dissociation of potassium carbonate and potassium bicarbonate, the Hot Carbonate Process system contains initially
Table 6. Physical Property Expressions for the Hot Carbonate Process System (Data from Chen et al., 1979).

**CO₂ Henry's Constant (atm.kg/g-mole):**
\[ \ln H_{CO₂} = -8477.711 \frac{1}{T} - 21.95743 \ln(T) + 0.005780748(T) + 155.1699 \]

**Chemical Equilibrium Constants:**
(solute concentrations in terms of molalities)
\[ \ln K_{CO₂} = -12092.1 \frac{1}{T} - 36.7816 \ln(T) + 235.482 \]
\[ \ln K_{HCO₃}^- = -12431.7 \frac{1}{T} - 35.4819 \ln(T) + 220.067 \]
\[ \ln K_{H₂O}^- = -13445.9 \frac{1}{T} - 22.4773 \ln(T) + 140.932 \]

**Vapor Phase: Ideal Gas**

**Liquid Activity Coefficient Model:**

<table>
<thead>
<tr>
<th>System</th>
<th>Local Composition Model</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂-H₂O</td>
<td>10.064 - 3268.135/T</td>
<td>ditto</td>
</tr>
<tr>
<td>K₂CO₃-H₂O</td>
<td>-3.5198</td>
<td>5.4623</td>
</tr>
<tr>
<td>K₂CO₃-H₂O</td>
<td>-3.3357</td>
<td>1.0817</td>
</tr>
<tr>
<td>KHCO₃-K₂CO₃</td>
<td>-2.5343</td>
<td>9.0184</td>
</tr>
<tr>
<td>1-1 salt - molecule</td>
<td>-4.063</td>
<td>8.187</td>
</tr>
<tr>
<td>1-2 salt - molecule</td>
<td>-4.641</td>
<td>8.731</td>
</tr>
<tr>
<td>molecule - molecule</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>salt - salt</td>
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<td>0.0</td>
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<td>Species</td>
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</tr>
<tr>
<td>-------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>potassium ion</td>
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</tr>
<tr>
<td>hydrogen ion</td>
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</tr>
<tr>
<td>bicarbonate ion</td>
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</tr>
<tr>
<td>carbonate ion</td>
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</tr>
<tr>
<td>hydroxide ion</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>molal flowrate</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Iteration history and results are shown in Table 7.

Recently, a free energy minimization algorithm was proposed for phase and chemical equilibrium of electrolyte systems (Gautam and Seider, 1979). Their algorithm is a nonstoichiometric algorithm and is based on the Rand method (White et al., 1958). As discussed by Smith (1980), nonstoichiometric algorithms can encounter numerical difficulties with the singularity of the coefficient matrix. Another inherent problem with their algorithm is that the free energy objective function is insensitive to trace components which can be very important for electrolyte systems. Examples are hydrogen ion and hydroxide ion concentrations. Furthermore, their algorithm is limited to the isothermal case. Therefore, it is believed that the new inside-out algorithm proposed here is superior to the free energy minimization algorithm.
Table 7. Iteration History and Results of the Hot Carbonate Process Example Using the Inside-Out Algorithm

Case a) Specified T=363.15°K, P=1d5 N/m²,
initial V/F=0.5, $\xi(1)=0.028$, $\xi(2)=-0.027$,
$\xi(3)=0.0001$

<table>
<thead>
<tr>
<th>iteration history:</th>
<th>$\xi(1)$</th>
<th>$\xi(2)$</th>
<th>$\xi(3)$</th>
<th>V/F</th>
</tr>
</thead>
<tbody>
<tr>
<td>iteration #</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.1984d-1</td>
<td>-0.1985d-1</td>
<td>0.1568d-4</td>
<td>0.0202</td>
</tr>
<tr>
<td>2</td>
<td>0.2124d-1</td>
<td>-0.2125d-1</td>
<td>0.1492d-4</td>
<td>0.0172</td>
</tr>
<tr>
<td>3</td>
<td>0.2106d-1</td>
<td>-0.2108d-1</td>
<td>0.1514d-4</td>
<td>0.0176</td>
</tr>
<tr>
<td>4</td>
<td>0.2108d-1</td>
<td>-0.2110d-1</td>
<td>0.1512d-4</td>
<td>0.0175</td>
</tr>
</tbody>
</table>

Case b) Specified T=363.15°K, V/F=0d0,
initial P=1d5 N/m², $\xi(1)=0.028$, $\xi(2)=-0.027$,
$\xi(3)=0.0001$

<table>
<thead>
<tr>
<th>iteration history:</th>
<th>$\xi(1)$</th>
<th>$\xi(2)$</th>
<th>$\xi(3)$</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>iteration #</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.2885d-1</td>
<td>-0.2886d-1</td>
<td>0.6626d-5</td>
<td>0.2006d6</td>
</tr>
<tr>
<td>2</td>
<td>0.2888d-1</td>
<td>-0.2889d-1</td>
<td>0.6955d-5</td>
<td>0.1980d6</td>
</tr>
<tr>
<td>3</td>
<td>0.2888d-1</td>
<td>-0.2889d-1</td>
<td>0.6954d-5</td>
<td>0.1980d6</td>
</tr>
</tbody>
</table>

Case c) Specified P=1d5 N/m², V/F=0d0,
initial T=200.°K, $\xi(1)=0.028$, $\xi(2)=-0.027$,
$\xi(3)=0.0001$

<table>
<thead>
<tr>
<th>iteration history:</th>
<th>$\xi(1)$</th>
<th>$\xi(2)$</th>
<th>$\xi(3)$</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>iteration #</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.2992d-1</td>
<td>-0.2992d-1</td>
<td>0.6360d-11</td>
<td>221.90</td>
</tr>
<tr>
<td>2</td>
<td>0.2984d-1</td>
<td>-0.2984d-1</td>
<td>0.2959d-9</td>
<td>246.71</td>
</tr>
<tr>
<td>3</td>
<td>0.2978d-1</td>
<td>-0.2978d-1</td>
<td>0.5355d-8</td>
<td>270.14</td>
</tr>
<tr>
<td>4</td>
<td>0.2973d-1</td>
<td>-0.2973d-1</td>
<td>0.3950d-7</td>
<td>289.32</td>
</tr>
<tr>
<td>5</td>
<td>0.2964d-1</td>
<td>-0.2964d-1</td>
<td>0.1369d-6</td>
<td>302.76</td>
</tr>
<tr>
<td>6</td>
<td>0.2964d-1</td>
<td>-0.2964d-1</td>
<td>0.5881d-6</td>
<td>319.95</td>
</tr>
<tr>
<td>7</td>
<td>0.2960d-1</td>
<td>-0.2960d-1</td>
<td>0.1875d-5</td>
<td>333.97</td>
</tr>
<tr>
<td>8</td>
<td>0.2958d-1</td>
<td>-0.2958d-1</td>
<td>0.1881d-5</td>
<td>334.00</td>
</tr>
<tr>
<td>9</td>
<td>0.2958d-1</td>
<td>-0.2958d-1</td>
<td>0.1812d-5</td>
<td>333.57</td>
</tr>
<tr>
<td>10</td>
<td>0.2958d-1</td>
<td>-0.2958d-1</td>
<td>0.1772d-5</td>
<td>333.32</td>
</tr>
<tr>
<td>11</td>
<td>0.2958d-1</td>
<td>-0.2958d-1</td>
<td>0.1765d-5</td>
<td>333.27</td>
</tr>
</tbody>
</table>
Notation

\( A_i \): chemical species \( i \)
\( A, B \): \( K_B \) model coefficients
\( C, D \): vapor enthalpy model coefficients
\( E, F \): liquid enthalpy model coefficients
\( F \): total molar flowrates of the system (Kg-mole/sec)
\( F^* \): total molar flowrates of the feed (Kg-mole/sec)
\( f_i \): molar flowrates of component \( i \) in the system (Kg-mole/sec)
\( f^*_i \): molar flowrates of component \( i \) in the feed (Kg-mole/sec)
\( G_i \): Gibbs free energy of formation of component \( i \) (J/Kg-mole)
\( \Delta G_j \): Gibbs free energy of reaction \( j \) (J/Kg-mole)
\( G^*_i \): chemical potential of component \( i \) (J/Kg-mole)
\( H^* \): feed enthalpy (J/Kg-mole)
\( H \): enthalpy (J/Kg-mole)
\( \Delta H \): enthalpy departure (J/Kg-mole)
\( K_i \): phase equilibrium ratio for component \( i \)
\( K_j \): chemical equilibrium constant for reaction \( j \)
\( K_B \): \( K_B \) model of the inside-out algorithm
\( L \): total molar flowrates of liquid phase (kg-mole/sec)
\( M \): number of reactions
\( M_S \): solvent molecular weight (Kg/Kg-mole)
\( m \): molality
\( N \): number of components
\( P_i \): partial pressure of species \( i \) (N/m\(^2\))
\( P^\text{sat}_i \): saturation vapor pressure of component \( i \) (N/m\(^2\))
\( P \): system pressure (N/m\(^2\))
\( P_{ref} \): reference pressure (1.01325*10\(^5\) N/m\(^2\))
\( Q \): heat duty (J/sec)
\( R \): universal gas constant
\( T \): temperature (K)
\( u_i \): volatility parameter for component \( i \)
\( V \): total molar flowrates of vapor phase (Kg-mole/sec)
\( W_l \): liquid phase molar average molecular weight
\( w_i \): weighting factor of component \( i \) for \( K_B \) model
\( x_i \): mole fraction of component \( i \) in liquid phase
\( y_i \): mole fraction of component \( i \) in vapor phase

Greek letters

\( \phi \): fugacity coefficient
\( \mu \): stoichiometric coefficient
\( \gamma \): activity coefficient
\( \xi \): extent of reaction
Subscripts

a: anion
c: cation
i: component index
j: reaction index

Superscripts

l: liquid
v: vapor
IG: ideal gas standard state
∞: infinite dilution standard state

Other symbols

*: unsymmetric convention

Literature Cited


Chapter 7
Design of Electrolyte Simulation Capabilities Using ASPEN as the Basic Simulator

Abstract

The development of the extended Pitzer equation, the local composition model and the inside-out algorithm has made it feasible to use modern process simulators for analysis and design of processes involving electrolytes. ASPEN, a next-generation process simulator designed for a broad range of chemical processes, was therefore used in this work as a basic framework for the design of process simulation techniques for chemical processes with electrolytes. Various aspects in the simulation of electrolyte systems were considered. These include components, streams, physical properties, unit models, flowsheet convergence, input language, and system concepts and structure. The advanced features of ASPEN make it particularly amenable and attractive for incorporation of electrolyte process simulation capabilities. It was concluded that it is feasible and beneficial to develop a general-purpose process simulator for chemical processes with electrolytes.
Scope

Over the past few decades, steady-state process simulators have been developed for use in the petroleum and petrochemical industries to simulate many steady-state, liquid-vapor processes. But the process engineer concerned with chemical processes with electrolytes, such as inorganic chemical manufacture and pollution control, cannot use the available simulators.

Two fundamental problems in the computer simulation of chemical processes with electrolytes have been 1) representation of the thermodynamic properties of electrolyte solutions and 2) simultaneous chemical and phase equilibrium calculations for electrolyte systems. These two problems have been the main obstacles in the use of modern process simulators for analysis and design of processes involving electrolytes. The development of the extended Pitzer equation, the local composition model, and the inside-out algorithm described in the previous chapters has made it feasible to use process simulators for chemical processes with electrolytes.

There is a definite need of process simulators for chemical processes with electrolytes. Electrolyte systems occur widely in the chemical industry. Specifically, to meet the current needs of simulating new fossil-fuel conversion processes,
capability to simulate electrolyte systems is indispensable. It is known that the major, distinct feature of the new fossil-fuel conversion processes is the nature of coal. In addition to heterogeneity and complex chemistry, coal is characterized as sulfur and nitrogen rich, and containing inorganics. Conventional process simulators cannot handle coal mainly because the scope of components considered has been limited to hydrocarbons. The shift of raw materials from petroleum to coal emphasizes the fact that electrolytes as well as solids are becoming more and more significant in the chemical industry.

Sulfur and nitrogen-rich coal makes pollution control a major task in fossil-fuel conversion processes. Acid gas removal in many coal gasification processes under development is a major part of the pollution control scheme. Typical acid gas removal units use aqueous electrolyte systems. The Benfield process, one of the most popular acid gas removal processes, utilizes an aqueous potassium carbonate solution as the acid gas removing media. Many important acid gas removal processes utilize amine-water solutions as the gas removing media. These amine solutions are also electrolyte systems. The stringent limits on allowable emissions of pollutants and the nature of coal make acid gas removal a major feature of the new processes. The importance of being able to simulate acid gas removal, a typical electrolyte process, cannot be
It was the objective of this chapter to develop process simulation techniques for chemical processes with electrolytes. ASPEN, a public, next-generation process simulator designed for a broad range of chemical processes, was used as the basic framework. Various aspects in the simulation of electrolyte systems were considered. Potential problems and general approaches were studied. In addition, system concepts and the structure of ASPEN were pursued for incorporation of electrolyte process simulation capabilities.

**Conclusions and Significance**

Process simulation techniques were designed for the computer simulation of chemical processes with electrolytes. ASPEN, a public, state-of-the-art process simulator, was used as the basic framework. Thus, the state-of-the-art technology in process simulation is fully utilized. The advanced features of ASPEN also make the development and incorporation of electrolyte simulation capabilities particularly amenable and attractive. It is both feasible and beneficial to extend ASPEN as a process simulator for chemical processes with electrolytes.
Basic Considerations

The most important characteristics of chemical processes with electrolytes can be attributed to the following points. First, electrolytes dissociate in solution and form ions. The presence of ions introduces ionic charges and the electroneutrality constraint. Second, weak electrolytes dissociate partially. Chemical equilibrium among various species should always be considered in addition to phase equilibrium. Third, strong electrolytes may precipitate as the solution becomes saturated. Solid handling capability is a necessity.

Although there has not been a general-purpose process simulator for electrolyte systems, there have been many significant developments in the technology of process simulation for nonelectrolyte systems. In the design of electrolyte process simulation techniques, it is the most desirable to build upon present technology of process simulation while taking into consideration the specific characteristics of chemical processes with electrolytes. ASPEN, a public, state-of-the-art process simulator designed for a broad range of chemical processes, was therefore chosen in this work as the basic simulator for the development of electrolyte simulation capabilities.
The advantages of using ASPEN as the basic simulator are evident as one realizes the advanced features of ASPEN and its flexibility. The following discussion is therefore based on the extension of ASPEN for electrolyte systems. However, most of this design study should be equally applicable to other process simulators.

The ASPEN Simulator

Despite the considerable effort expended by the chemical and petroleum companies on steady-state process simulators, it was evident that the tools available for computer-aided industrial process modeling would not be adequate to meet the needs for development of new processes and for redesign of conventional industrial processes for greater energy efficiency in the 1980's. The difficulties have been traced to four characteristics of existing programs: 1) they are not publicly available; 2) they handle a limited class of processes; 3) they do not fully utilize current computing technology; and 4) they are not well-integrated (Evans and Seider, 1974).

The concept of the ASPEN Project was to develop a next-generation process simulator that would extend the technology of process simulation to cover a much broader range of processes (Evans, et al., 1979). Although developed primarily for fossil-fuel conversion processes, the system has
been designed to be very flexible so that it can be expanded to meet future simulation requirements. For processes such as coal gasification or coal liquefaction, it can be used to perform steady-state material and energy balances, calculate equipment sizes, and carry out economic evaluation. The main features of the ASPEN simulator can be summarized as follows:

1) Advanced computing technology is utilized in the system. It is a file-oriented system. A plex data structure is adopted in ASPEN to gain flexibility and modularity. Therefore, the system is flexible. It is easy to add new types of process units, new types of streams, and new types of chemical compounds.

2) It is capable of modeling diverse types of streams (such as vapor-liquid, liquid-solid, and vapor-solid) characterized by different sets of variables (particle size distributions, particle shape parameters, porosities, etc.).

3) State-of-the-art physical property models are built in the system. It allows specifications of different physical property models in different parts of a flowsheet. It is capable of calculating physical properties under widely different conditions.

4) State-of-the-art algorithms for single-stage flash and
multistage separation are incorporated in the system. It allows for simulation of many different types of process equipment. Models are also provided for important process units that involve solids.

5) The system has a good preliminary cost estimation capability that permits the comparison of alternative processes on an economically consistent basis at an early stage of process analysis and development.

6) The system input language is oriented towards process engineers familiar with chemical engineering calculations, but without extensive knowledge of computer programming. It is completely free format. The default principle is fully exercised.

7) It is a public and integrated system. ASPEN will be publicly available and many different process development teams will have access to the same simulator; it will be easy to share models.

**Components**

Chemical components are the most fundamental entities in a process simulation. In ASPEN, there are two types of components: conventional and nonconventional.
Conventional components are pure compounds or pseudo-compounds that may be characterized in terms of standard pure properties such as molecular weight, critical pressure, vapor pressure coefficients, heat of formation, and heat capacity coefficients.

The term "nonconventional components" has been adopted to refer to components that are not pure compounds (or pseudo-compounds) and that are characterized by "component attributes" rather than the standard pure compound properties. Examples of nonconventional components include coal, ash, char, and slag. The component attributes are "state" information required by nonconventional property models to calculate physical properties of the components. It should be noted that component attributes are allowed for conventional components.

Electrolyte systems should be treated as conventional components because electrolyte systems are characterized in terms of standard pure properties.

There are many kinds of electrolytes. Strong electrolytes dissociate completely into ionic species when dissolved into the liquid phase, and exist as solid precipitates if not dissolved. Weak electrolytes dissociate partially into ionic species. Undissociated weak electrolytes exist as molecular species. Therefore, in electrolyte systems, there can be solid
electrolyte precipitates, molecular weak electrolytes, and ionic species dissociated from either strong electrolytes or weak electrolytes.

There are several possible ways of representing electrolytes as ASPEN components. The first way is to assume electrolytes but not ions as components. This means that all ions are counted as part of electrolytes. The second way is to assume both ions and electrolytes as components. Chemical reactions between ions and electrolytes may occur. The third way is to assume electrolytes as components and "ions" as a pseudo-component with component attributes describing the distribution of ions.

If only electrolytes are treated as components, the system electroneutrality will always be satisfied. However, there is a problem of nonuniqueness in specifying system compositions due to various possible combinations of forming electrolytes from ions, which are the true fundamental entities of electrolyte systems. Furthermore, the system composition will not reflect the true composition of the electrolyte system.

If component attributes are used to represent the distribution of ions for the pseudo-component "ions", the problem of nonuniqueness can be solved. In addition, the system electroneutrality and solid electrolyte precipitates can
be taken care of. However, there is a problem of interfacing with the physical property system of ASPEN because the physical property system requires complete information of system composition. Component attributes cannot transfer system composition information, since they are currently not utilized for standard physical property calculations of conventional components.

Therefore, it is suggested that all electrolytes and ions be treated as conventional components in the ASPEN simulator. Electrolytes can represent solid electrolyte precipitates, undissociated weak electrolytes, feed electrolytes, or if desirable, combinations of ions. Ions can represent dissociated ionic species to reflect real system composition.

**Streams**

As in other process simulators, an ASPEN stream represents the flow of material from one process unit to another. In ASPEN, a stream may simultaneously represent two distinctly different kinds of material. The first kind of material, may be a vapor, liquid, or solid, or a number of phases in equilibrium. In any case, equilibrium assumptions may be applied to determine the phase condition of the material. The second type of material, is a solid not in equilibrium with the remainder of the stream.
In order to adequately model these complex streams ASPEN has adopted the concept of substreams. Streams are subdivided into any number of substreams. There are three types of substreams: mixed substreams, conventional inert solid substreams, and nonconventional inert solid substreams. Conventional inert solid substreams are composed of conventional components and nonconventional inert solid substreams are composed of nonconventional components.

Electrolytes are always in equilibrium, physically and chemically, among different phases of a stream. For example, salt NaCl can be present as a solid precipitate while in chemical equilibrium with Na\(^+\) ion and Cl\(^-\) ion in aqueous solution for a system containing water and NaCl. Therefore, electrolytes should be modeled as part of the mixed substream.

**Physical Properties**

Many physical property calculations are required to support a process simulator. Those important for electrolyte systems are enthalpy, heat capacity, molar volume, excess Gibbs energy, activity coefficient and osmotic coefficient. All these quantities can be derived from appropriate derivatives of the Gibbs energy.

For electrolyte systems, the usual standard state for the
solvents is the pure, condensed phase at the temperature and pressure of the electrolyte system. The standard state for the solutes is the limiting state in which solute concentrations become infinitely dilute again at system temperature and pressure.

Various thermodynamic functions of electrolyte solutions can be calculated from a knowledge of the standard state thermodynamic functions and the excess Gibbs energy. The standard state thermodynamic functions can be calculated from pure solvent data, pure electrolyte data, and the standard thermodynamic functions of solution.

The extended Pitzer equation (see Chapter 2) and the local composition model (see Chapter 3) provide good excess Gibbs energy expressions for the thermodynamic properties of electrolyte systems. Since the trend of recent developments has been to represent multicomponent systems without ternary or higher order parameters, it has been decided that no liquid excess Gibbs energy models in ASPEN should require them. The local composition model meets this ASPEN policy. However, the extended Pitzer equation requires ternary parameters and, therefore, special arrangement is needed to incorporate the extended Pitzer equation into ASPEN. One possible way is to treat the extended Pitzer equation as a user's model.
Standard free energy ($\Delta G_i^0$), enthalpy ($\Delta H_i^0$), entropy ($S_i^0$), and heat capacity ($C_p^0$) have been defined for ions in aqueous solution at 25°C relative to the hydrogen ion. The standard real potential ($\alpha_i^S$) is the standard free energy change per mole on transferring ions of species $i$ from the ideal vapor phase to the ideal solution phase where there is no net charge on the solution phase. These thermodynamic functions are convenient and can be used to estimate thermodynamic functions of many electrolytes (Parsons, 1959).

ASPEX contains a Data Bank covering about 400 conventional, nonelectrolyte components. Pure compound properties and certain universally applicable binary parameters are included in the Data Bank. To simulate electrolyte systems, it is necessary to extend the Data Bank to include dielectric constant data of nonelectrolyte solvent components, pure electrolyte properties, standard thermodynamic functions of solution, and standard state thermodynamic functions. Due to the importance of aqueous electrolyte systems, a special data bank is suggested to store data for aqueous electrolytes and ions. In addition, specific routes and models for both major physical properties (properties required for unit operation model calculations) and subordinate physical properties (combinations of properties required for calculating major properties) should be established for aqueous and mixed-solvent
electrolyte systems. System built-in property option sets should have access to these electrolyte property routes and models.

**Unit Operation Models**

An ASPEN block refers to the process flowsheet element representing a process unit. Each block has one or more inlet streams and one or more outlet streams. An ASPEN model refers to the collection of subroutines used to model the unit operation and, in effect, defines the transformation that takes place in converting inlet streams into outlet streams.

The most commonly-encountered unit operations for electrolyte processes are absorption, stripping, azeotropic distillation, extraction, ion exchange, salt crystallization, etc.

Absorption, distillation and extraction can be grouped as multistage separations. Due to the nonvolatility and chemical equilibrium nature of electrolytes, conventional algorithms for multistage separations are not valid for electrolyte systems. To model multistage separations for electrolyte systems, the ZFLASH model can be used by constructing a flowsheet with multiple single-stage flash units. Incorporating the inside-out algorithm presented in Chapter 6, ZFLASH is an
efficient and robust subroutine developed for single-stage flash of electrolyte systems and should be included in ASPEN. Of course, it is desirable to have models that are developed specifically for multistage separations of electrolyte systems. Furthermore, ZFLASH cannot handle liquid-liquid equilibrium. Solvent extraction modeling of electrolyte systems will not be possible without an algorithm that can calculate liquid-liquid equilibrium with chemical equilibrium. It is believed that the inside-out algorithm of ZFLASH can be extended to perform multicomponent liquid-liquid equilibrium, vapor-liquid-liquid equilibrium, and multistage separations with chemical equilibrium.

Ion exchange and crystallization are normally operated in semi-batch fashion. Both can be represented as simple component splitter in ASPEN. Ion exchange is a separation process with chemical equilibrium between a fluid phase and a solid resin phase. Crystallization is a separation process involving liquid-solid phase equilibrium. Decent unit models based on the inside-out approach of Chapter 6 can also be developed to simulate ion exchange and crystallization.

**Flowsheet Convergence**

ASPN uses a sequential modular approach to flowsheet calculations. In this approach, individual unit operation
models compute outlet streams and block results, given inlet streams and block parameters. Recycle streams are torn and the tear-stream variables are used as iteration variables. Design specifications are imposed by freeing certain block parameters or feed stream variables and adjusting their values to meet specifications on stream variables or block results.

The proposed ASPEN electrolyte stream structure contains ionic species, neutral electrolytes and molecular nonelectrolytes. Due to the presence of ionic species in streams, the electroneutrality of stream will have to be satisfied when flowsheet convergence is being carried out. Therefore, the electroneutrality imposes a linear constraint to flowsheet convergence, i.e.,

\[ \sum Z_i f_i = 0 \]  \hspace{1cm} (1)

There are many flowsheet convergence acceleration methods proposed in the literature for flowsheet convergence of nonelectrolyte systems. For these systems, there are no constraints for flowsheet convergence. However, there is an electroneutrality constraint for electrolyte systems. If the direct substitution method is used in flowsheet convergence, the electroneutrality can always be satisfied because unit operation models always impose this constraint upon streams. When convergence acceleration methods such as Wegstein or
Broyden are used, problems may arise because these convergence acceleration methods as currently implemented do not impose constraints and may violate the constraint. To solve this problem, one easy way is to adopt a mixed convergence acceleration scheme. For example, direct substitution is used for ionic species while other acceleration methods are applied for other stream components. ASPEN is capable of adopting mixed convergence acceleration scheme. Thus, flowsheet convergence of chemical processes with electrolytes can be taken care of in ASPEN.

**System Concepts**

In previous sections, various aspects in the simulation of electrolyte processes have been discussed. These include component entities, streams, physical properties, unit models, and flowsheet convergence. In this section, system concepts and the structure of the electrolyte process simulator are to addressed on to ensure the previous general considerations are feasible and compatible with ASPEN.

Typical information flow of an ASPEN simulation run is given in Figure 1. The simulation main program, which is generated by the ASPEN input translator, calls unit models and flowsheet convergence routines. These unit models then call various process routines for feed stream initialization,
Figure 1. Typical Information Flow of ASPEN Simulation Runs

- MAIN PROGRAM
  - CONVERGENCE
  - SIMULATION ROUTINES
    - RECYCLE
    - STREAM I
      - UNIT MODEL I
    - STREAM II
      - UNIT MODEL II
    - STREAM III
      - UNIT MODEL III
  - PROCESS ROUTINES
    - XFLASH
    - YFLASH
    - ZFLASH
  - PHYSICAL PROPERTY MONITORS
    - SMTHRM
    - LMTHRM
    - VMTHRM
  - PHYSICAL PROPERTY MODELS
    - GM001
    - GM002
    - GM003
recycle stream initialization, and/or energy balances. Essentially, these process routines compute stream variables, i.e., temperature, pressure, vapor and liquid fractions, enthalpy, entropy, density, and average molecular weight, under user-specified conditions. These conditions include stream specifications, unit block parameters, physical property option set, and system equilibrium specifications. Process routines also call appropriate physical property monitors, which are the interface routines between the process routines and the physical property models.

The ASPEN design concept has been that the system is open-ended, easy to modify and easy to implement new features. Indeed, this is the case. To extend to electrolyte processes, no major revisions are required.

New physical property models for electrolytes are necessary. These include models for activity coefficients, excess Gibbs energy, molar volume, enthalpy, dielectric constant, etc. Similar to supercritical components, it is necessary to differentiate solutes and solvents of electrolyte systems because excess Gibbs energy models of electrolyte systems are unsymmetric models.

If a flowsheet consists of both electrolyte systems and nonelectrolyte systems, it is desirable to be able to use
different models for different systems. For example, one may want to use the Wilson Equation for computing activity coefficients of nonelectrolyte systems and the local composition model for activity coefficients of electrolyte systems. In this case, the problem can be resolved by having users define two physical property option sets, and assign one option set to each unit operation block.

Currently, ASPEN physical property monitors return values of fugacity coefficients, enthalpies, free energies, entropies, and molar volumes. Since activity coefficients are required for flash calculations of electrolytes (see Chapter 6), it is necessary to assign a monitor that returns values of activity coefficients from physical property models.

Three process routines for flash calculations are being used in ASPEN at present. They are WFLASH, XFLASH, AND YFLASH, and were developed for single phase, vapor-liquid, and vapor-liquid-liquid flash calculations, respectively. For electrolyte systems, these three process routines are applicable if there are no chemical reactions involved. The phase and chemical equilibrium algorithm developed in Chapter 6 will provide another process routine, ZFLASH, to handle weak electrolytes and chemical equilibrium. It is up to the unit models and the users to decide what process routine should be used for particular systems. This has a significant impact
upon ASPEN unit operation models since chemical equilibrium calculations may be performed without the need of calling reactor models.

It is the most desirable to have all current ASPEN unit models, except multistage separations and solid handling models, capable of simulating electrolyte systems. This means that these models should have access to ZFLASH and electrolyte equilibrium system specifications. This can be made possible by designing a new kind of "bead" which stores chemical equilibrium relationships for interested systems. A bead is a unit of storage space in computer systems and one bead is created for one equilibrium system. When a unit model is called, this bead is accessed by the unit model and ZFLASH to perform model calculations. Several equilibrium systems can be defined in a simulation run. Each equilibrium system is identified by an equilibrium system ID. These equilibrium system ID's are similar to the property option sets. They may be global to a flowsheet, to a subsection, or specific to a unit block. For stream initialization, a feed stream can refer to its destination block and a recycle stream can refer to its source block for these equilibrium system specifications.

**Input language**

The ASPEN input language is oriented towards process
engineers familiar with chemical engineering calculations, but without extensive knowledge of computer programming. The input can be considered to be made up of paragraphs, sentences, and words. A paragraph begins with a primary keyword and may consist of one or more sentences. Each sentence begins with a secondary keyword that indicates the category of data appearing in the sentence. Tertiary keywords are used to enter data and their values are the data items.

Except for minor modifications, the current ASPEN input language is applicable to electrolyte systems.

Minor changes are required for unit models to invoke ZFLASH process routine. This is done by assigning -2 to the KPHASE tertiary keyword of the PARAMETER secondary keyword of all unit models. Minus sign is used to specify electrolyte systems and number "2" is used to specify two phase vapor-liquid equilibrium.

Ionic charge number is treated as a pure component property data. The property name is CHARGE.

Similar to the SC-COMP primary keyword, a new primary keyword SOLVENTS is proposed to specify solvent components of electrolyte systems. The recommended form of input for SOLVENTS is as follows:
SOLVENTS  cidlist

where **cidlist** is a list of component ID's.

the SYSTEM primary keyword, as proposed in the previous section as EQUILIBRIUM SYSTEM, is used to specify phase and chemical equilibrium conditions of electrolyte systems, although it can also be used for nonelectrolyte systems. There are three secondary keywords which are used to enter data for the SYSTEM primary keyword: SALT, STOICHIOMETRY, and EQUIL-CONST. The recommended form of input for these keywords are as follows:

```
SYSTEM  sysid
SALT  seid  cid  nc  aid  na/...
STOICHIOMETRY  rxid  compid  coef/  rxid  compid  coef/...
EQUIL-CONST  rxid  A  B  C  D/...
```

where **sysid** is the equilibrium system ID. **seid** is a strong electrolyte component ID. **cid** is a cation component ID. **aid** is an anion component ID. **nc** and **na** are stoichiometric coefficients of cation and anion of a strong electrolyte. **rxid** is a reaction ID. **compid** is a component ID. **coef** is a stoichiometric coefficient of a component in a reaction. A, B, C, and D are parameters of the empirical equilibrium constant equation:
\[ \ln K = A/T + B \ln T + C + D \]

Since equilibrium constants can be calculated from Gibbs energies, the EQUIL-CONST secondary keyword is optional. Also, equilibrium constants can be expressed in terms of molalities or mole fractions. Therefore, several types of the EQUIL-CONST secondary keyword may be necessary.

A simple flowsheet for absorption of carbon dioxide using the Hot Carbonate system is shown in Figure 2 and used as an example to illustrate major features of the ASPEN input language in simulating chemical processes with electrolytes. The ASPEN input language statements are given in Figure 3.

Literature Cited


Figure 2. A Flowsheet of Absorption of Carbon Dioxide Using the Hot Carbonate Process
Figure 3. Statements in ASPEN Input Language for Simulation of Absorption of Carbon Dioxide Using the Hot Carbonate System

NEW
TITLE "HOT CARBONATE PROCESS"
DESCRIPTION "THIS IS A SAMPLE PROBLEM TO SHOW THE MAJOR FEATURES OF ASPEN INPUT LANGUAGE IN SIMULATING CHEMICAL PROCESSES WITH ELECTROLYTES"

FLOWSHEET
M1 IN=S1 S2 OUT=S3
F1 IN=S3 S4 OUT=S5 S6

COMPONENTS
CO2 CARBON-DIOXIDE/ H2O WATER/ K2CO3 POTASSIUM-CARBONATE/
KHC03 POTASSIUM-BICARBONATE/ K POTASSIUM/ CO3 CARBONATE/
HCO3 BICARBONATE/ H HYDROGEN/ OH HYDROXIDE

PROP-DATA
COMP-LIST K CO3 HCO3 H OH
CVAL CHARGE 1 1 1 -2 -1 1 -1

SOLVENTS
H2O

PROPERTIES SYSOP10 GLOBAL SOLVENT=H2O

SYSTEM SOLUB
SALT K2CO3 K 2 CO3 1
SALT KHC03 K 1 HCO3 1

SYSTEM HTCARB
STOICHIOMETRY 1 CO2 -1/ H2O -1/ HCO3 1/ H 1
STOICHIOMETRY 2 HCO3 -1/ CO3 1/ H 1
STOICHIOMETRY 3 H2O -1/ OH 1/ H 1
EQUIL-CONST 1 -12092 -36.78 0 235.48
EQUIL-CONST 2 -12432 -35.48 0 220.07
EQUIL-CONST 3 -13446 -22.48 0 140.93

STREAM S1
TEMP=100 PRES=15
MOLE-FLOW H2O 2000

STREAM S2
TEMP=100 PRES=50
MOLE-FLOW K2CO3 500 KHC03 100

STREAM S4
TEMP=140 PRES=70
MOLE-FLOW CO2 500

BLOCK M1 MIXER
PARAM KPH=-2; TWO-PHASE ELECTROLYTE SYSTEM
SYSTEM SOLUB

BLOCK F1 FLASH2
PARAM TEMP=150 PRES=30 KPH=-2
SYSTEM HTCARB
Chapter 8
Recommendations for Future Work

During the course of this study, many interesting and important topics of research were recognized. However, some of them could not be pursued due to limitations of manpower and time. These topics are briefly discussed here.

1) Dielectric constant of solvent is required in calculating the long-range interaction contribution upon the excess Gibbs energy of electrolyte systems. It is also required in calculating the short-range interaction contribution of the local composition model when solvent composition changes, because salt-solvent binary parameters are functions of solvent dielectric constant. In this study, polynomial expressions were used in representing solvent dielectric constant as functions of solvent composition. A good, general expression for correlating solvent dielectric constant with solvent composition will be very helpful. In the literature, significant progress has been made for mixtures of nonpolar compounds. However, much remains to be done for mixtures of polar compounds. In particular, a good mixing rule for estimating dielectric constant of mixed solvents from dielectric constant of pure solvents is most desirable, because dielectric constant of mixed solvent is seldom available.
2) In chapters 3, 4, and 5, it was shown that the idea of applying the local composition concept to account for the short-range interaction contribution on the excess Gibbs energy of electrolyte solutions is a valid and successful approach. After all, the traditional Debye-Hückel formulation for the long-range interaction contribution of electrolyte solutions is a local composition model. However, many different Debye-Hückel formulations have been proposed in the literature. It will be a very important study to identify a Debye-Hückel formulation that goes best with the local composition model.

3) When phase equilibrium data correlations of weak electrolyte systems were carried out in this study, it was necessary to solve for every data point a set of nonlinear equations composed of the relationships of mass balances, electroneutrality, and chemical equilibrium in liquid phase. Therefore, it is computationally very expensive and inefficient in carrying out data regression of weak electrolyte systems. A new least squares formulation of this regression problem should be possible to properly treat the liquid phase relationships as nonlinear, equality constraints.

4) In this study, phase equilibrium data correlations have been limited to vapor-liquid equilibrium. However, the addition of electrolytes can cause miscible solvents to form
immiscible mixtures. For example, when potassium carbonate is added to ethanol-water mixtures, the liquid can separate into two phases (Rousseau and Boone, 1978). The local composition model is believed to be capable of modeling liquid phase splitting of electrolyte systems. Study of liquid-liquid equilibrium of electrolyte systems using the local composition model should be a challenging topic.

5) Salt precipitation is an important aspect of electrolyte systems. Solubility of a salt in a solution can be calculated from the standard Gibbs energy of solution or the solubility constant. Unlike phase and chemical equilibrium constraints, salt precipitation is an inequality constraint. The algorithm developed in Chapter 6 for calculations of phase and chemical equilibrium can be extended to check solubility limits and predict salt precipitation. This extension is required for the modeling of salt crystallization units.

6) An algorithm is needed to carry out calculations of two-liquid phase, single-stage flash with chemical equilibrium. This algorithm can be used not only in vapor-liquid-liquid equilibrium calculations but also in liquid-liquid equilibrium calculations. Liquid-liquid equilibrium is of special interest to electrolyte systems because solvent extraction is one of the most commonly employed operations for chemical processes with electrolytes.
7) Although multistage operations can be simulated as a series of single-stage flash units as discussed in chapter 7, it is desirable to have an algorithm, designed specifically to meet the characteristics of multistage operations of chemical processes with electrolytes. This algorithm should compute rigorously heat and material balances along with chemical equilibrium for every stage. It should be robust and reliable.

8) Although the equilibrium stage approach is often employed in simulation of both plate and packed columns, the continuous column approach is also very important for electrolyte operations. This is because the overall plate efficiencies for columns of electrolyte systems are generally very small, in the magnitude of 5 to 10 percent. Therefore, the continuous column approach may be more desirable in calculating performance of columns for many electrolyte processes. A rigorous formulation and solution of heat and material balances of continuous columns is very important in this regard. The continuous column approach should take into account mass transfer rates of various species in the system.

9) Flowsheet convergence calculation with constraints in simulating chemical processes with electrolytes (see Chapter 7) is a new, interesting problem. Exact significance and impacts of constraints upon flowsheet convergence should be exploited.
In particular, mathematical formulation as well as the most efficient numerical solving procedure of the problem should be examined.

10) It is the most rewarding if the proposed ASPEN electrolyte capability can be implemented in the ASPEN simulator and a general purpose flowsheet simulator for electrolyte systems can result. Many more problems are expected for the implementation. It is hoped that this research has made contribution in making computer simulation of chemical processes with electrolytes a day-to-day practice.

Literature Cited