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Phase equilibrium simulation and its application in crystallization processes

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Phase equilibrium simulation and its application in crystallization processes

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TABLE OF CONTENTS

GENERAL INTRODUCTION 1

Review Of the Thermodynamic Model for Gibbs Free Energy and Activity Coefficient Of Concentrated Electrolyte Solutions 2

Pitzer's Model 4

NRTL (Non-Random Two Liquid) Model 6

UNIQUAC (Universal Quasi Chemical Theory) Model 8

Equation of State for Electrolyte Solutions 9

Review Of the Phase Equilibrium Computation 10

Explanation of Dissertation Format 17

PART I. ACTIVITY COEFFICIENT MODEL OF CONCENTRATED ELECTROLYTE SOLUTIONS 19

1. INTRODUCTION 20

2. MODIFIED LIU, HARVEY AND PRAUSNITZ NRTL MODEL 22

2.1 Long-range interaction contribution 22

2.2 Short-range interaction contribution 23

3. BINARY SOLUTIONS 27

4. MULTICOMPONENT SOLUTIONS 30

5. CONCLUSION 36

6. NOMENCLATURE 37

7. LITERATURE CITED 39

PART II. PHASE EQUILIBRIUM CALCULATION BY USING LARGE-SCALE OPTIMIZATION TECHNIQUE 41

1. ABSTRACT 42

2. INTRODUCTION 43

3. SOME TERMINOLOGY OF LINEAR PROGRAMMING (LP) 46

3.1 Basic Solution 46

3.2 Basic Feasible Solution of Linear Programming (LP) 46

3.3 Simplex Method 47

3.4 Revised Simplex Method 47

3.5 Duality of LP 48

3.6 Optimality Conditions 49

4. OPTIMIZATION CONDITIONS FOR PHASE EQUILIBRIUM PROBLEM 50

4.1 First-Order Necessary Conditions (Kuhn-Tucker Conditions) 51

4.2 Second-Order Conditions 52

5. UNIQUENESS OF CHEMICAL AND PHASE EQUILIBRIUM PROBLEM 53

6. PHASE EQUILIBRIUM ALGORITHM USING LARGE-SCALE OPTIMIZATION TECHNIQUES 54

7. NUMERICAL EXAMPLES 61

7.1 $NaCl - KCl - MgCl_2 - H_2O$ system at 298.15 K and 273.15 K . . 62

7.2 $NaCl - KCl - CaCl_2 - H_2O$ system at 298.15 K 64

7.3 $NaCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K 64

7.4 $KCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K 69

7.5 $NaCl - KCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K 69

8. CONCLUSIONS 74

9. NOMENCLATURE 75

10. LITERATURE CITED 77

APPENDIX A. STABILITY AND OPTIMUM CRITERIA 81

APPENDIX B. PITZER'S EQUATIONS 83

PART III. PHASE EQUILIBRIUM OF THE Na-K-Mg-Cl-NO_3-H_2O SYSTEM AT THE TEMPERATURES BELOW 25°C 84

1. ABSTRACT 85

2. INTRODUCTION 86

3. GENERAL EQUATIONS FOR ACTIVITY AND OSMOTIC COEFFICIENTS (PITZER MODEL) 89

4. EQUATIONS OF STATE FOR THE STANDARD STATE CHEMICAL POTENTIAL OF AQUEOUS IONS 92

5. RESULTS 94

5.1 The Single Salt (Binary) Systems 95

5.2 Common-ion Ternary Systems 97

5.2.1 NaCl-KCl-H_2O System 98

5.2.2 NaCl-$NaNO_3$-H_2O System 99

5.2.3 KCl-KNO_3-H_2O System 99

5.2.4 $NaNO_3$-KNO_3-H_2O System 99

5.2.5 $MgCl_2$-KCl-H_2O System 99

5.2.6 $MgCl_2$-$Mg(NO_3)_2$-H_2O System 100

5.2.7 $Mg(NO_3)_2 - KNO_3 - H_2O$ System 100

5.3 The Quaternary Systems 100

6. CONCLUSIONS 112

7. NOMENCLATURE 114

8. LITERATURE CITED 116

SUMMARY AND DISCUSSION **119**

ADDITIONAL REFERENCES CITED **121**

APPENDIX A. DEBYE-HUCKEL THEORY **127**

APPENDIX B. SOURCE PROGRAM **130**

ACKNOWLEDGEMENTS 147

GENERAL INTRODUCTION

Freeze concentration of aqueous solutions has become an alternative energy saving technique for concentration in a variety of chemical processes. Three applications seem to get the most attention:

1. Treating hazardous wastes (environmental concern);
2. Concentrating fruit juices (food industry);
3. Purifying organic chemicals (pharmaceutical industry).

Basic techniques used are as follows: a solution is cooled to below its freezing point and pure ice is formed, concentrating the solution. Depending on the degree of concentration the process may result in precipitation of dissolved salts.

The advantage of the freezing concentration technique is that it is an energy-saving process. The energy involved in freezing one pound of water is of the order of 150 BTU, for boiling is of the order of 1,000 BTU. Furthermore, corrosion problems are minimized since it operates at low temperatures. As an example, CBI Freeze Technologies, Inc., Plainfield, Ill., developed the first FC unit for treating hazardous wastewater in early April, 1988. The process is capable of treating aqueous wastes containing reactive ions, metals, and organics with 1 - 10 wt% solids. The wastewater is precooled to the freezing point. The ice in the concentrated slurry is separated

and melted to produce pure water. The remaining liquor is either recycled for more ice formation or removed as a concentrated stream. If concentration is such that it becomes supersaturated in its solutes, provision is made to cause crystallization to take place separately from the ice formation.

The thermodynamic basis of those crystallization processes is the phase equilibrium. Since the phase diagrams of multicomponent systems are usually not available and experimental determination is extremely tedious, a computer simulation scheme is employed. It is based on the thermodynamic theory that states that the Gibbs free energy of the system at equilibrium is at its minimum value.

From the above discussion, it is clear that an accurate thermodynamic model for predicting the Gibbs free energy of the system and an effective mathematical procedure for finding the minimum of the Gibbs free energy is necessary so that the computer simulation of the system phase equilibrium can be carried out. The literature review of the thermodynamic models and the phase equilibrium computation algorithms is given below.

Review Of the Thermodynamic Model for Gibbs Free Energy and Activity Coefficient Of Concentrated Electrolyte Solutions

The peculiarities of strong electrolyte solutions were a major puzzle to physical chemists in the first two decades of this century. In 1923 Debye and Huckel proposed their solution theory and obtained the simple limiting law that resolved the primary puzzle (see Appendix A.). The complete Debye-Huckel model is useful up to ionic strength of 0.1 m with one adjustable parameter. An empirical linear form in ionic strength can be added and the modified model can obtain good representation up to

2 m with two adjustable parameters.

It was not until the last two decades, owing to the development of molecular thermodynamics, that the prediction of thermodynamic properties of mixed electrolyte solutions at high concentrations became possible. Among those, the following four models have gained success in different applications:

- The extended Pitzer's model (Virial form) (Pitzer, 1973);
- The NRTL model of Cruz and Renon (Cruz and Renon, 1978);
- The NRTL model of Chen (Chen et al., 1982);
- The UNIQUAC model of Sander (Sander et al., 1986a,b).

Generally speaking, all solution models assume certain forms of excess Gibbs free energy. The thermodynamic properties of the solution can then be obtained from derivatives of the excess Gibbs free energy. The excess Gibbs free energy of the electrolyte solutions is usually assumed to be the summation of the excess Gibbs free energy of different contributions:

1. Long-range interactions;
2. Short-range interactions;
3. The concentration dependence of dielectric constants.

The four models mentioned above also can be called primitive models because they all use an extended Debye-Huckel model to express long-range interactions. The different contributions of these four models are compared in Table 1. The equation of state model (a nonprimitive model), will be discussed later.

Table 1: Comparison of different models

Model	Long-range	Short-range	Dielectric constant
Pitzer	Extended DH (Pitzer, 1973)	Virial	No
Renon	Extended DH (Fowler and Guggenheim, 1956)	NRTL	Debye-McAulay (Harned and Owen,1958)
Chen	Extended DH as Pitzer	NRTL	No
Sander	Extended DH (Sander et al., 1986a)	UNIQUAC	No

Pitzer's Model

Since Pitzer and his coworkers proposed the extended virial model in 1973, it has been applied to predict various thermodynamic properties of electrolyte systems. The simple analytical form of the equation gives a quantitative representation of all reliable and available activity and osmotic coefficient data of strong electrolytes. The accuracy is usually good up to 6 molality. The model can be readily extended to complex electrolyte mixtures using binary and common-ion ternary parameters. Pitzer (1979) compiled an extensive database for the 25^oC binary and ternary model parameters. The first-order temperature derivatives of the binary parameters were also listed for many systems. However, the model assumes complete dissociation of the solute, water as the major solvent. Two extensions of the Pitzer's model have been made by Beutier and Renon (1978) and Chen et al. (1979) for the calculation of vapor-liquid equilibrium involving molecular solutes.

Some problems have been discovered in determining density with this model. Fitting density data of the $CaCl_2$, NaCl and their mixture, Kumar et al. (1983)

found that fit for $CaCl_2$ was distinctly inferior. This problem has also been observed in fitting the activity coefficients of $CaCl_2$ above 5 molal (Phutela and Pitzer, 1983). This is due to the fact that the hydration sphere of the Ca^{2+} ion is changing in the concentration range above 1 m. There is no simple way this can be accommodated in the theory. Actually, Pitzer did not distinguish the hard-core effect and the hydration effect that made the model very empirical.

Despite some limitations, Pitzer's model remains the most widely used. Harvie and Weare (1980) applied Pitzer's model to the prediction of mineral solubilities in natural waters at 25^oC with great success. Following their work, a series of articles have been published that predict mineral solubilities within temperature ranges of - 54 to 250^oC and at pressures up to 1 kbar (Harvie, Moller and Weare, 1984; Felmy and Weare, 1986; Pabalan and Pitzer, 1987; Moller, 1988; Greenberg and Moller, 1989; Spencer, Moller and Weare, 1990; Monnin, 1990). Monnin (1989) applied Pitzer's model to calculate density and partial molal volumes of natural waters. The author concluded that the Pitzer model gave good accuracy at moderate concentration using only the binary parameters. The accuracy decreased at higher concentration because ternary parameters could not be obtained with reasonable confidence and therefore were not used.

The Pitzer model has also been used to calculate the activity coefficients of the supersaturated solutions (Sohnel, Garside and Jancic, 1977; Sohnel and Garside, 1979) with the assumption that there is no discontinuity in water activity between the saturation and the supersaturation region.

These applications demonstrated the capability of the Pitzer model. It is probably the most suitable model for engineers dealing with aqueous electrolyte solutions.

NRTL (Non-Random Two Liquid) Model

All parameters in the Pitzer's model are empirical. Binary parameters are empirical functions of ionic strength and ternary parameters are necessary at high concentration and for mixtures. Since Pitzer's model is based on a virial expansion, it is subject to all the limitations of a virial model. Pitzer's equation cannot be used for a mixed solvent system because its parameters are unknown functions of solvent composition.

To apply the thermodynamic model to a mixed solvent and a system involving molecular species, another approach was proposed based on the NRTL model of nonelectrolyte solutions (Cruz and Renon, 1979; Chen et al., 1982).

Although both models use the NRTL approach for short-range interactions, the difference between the work of the two is that different assumptions were used. Cruz and Renon assumed the complete solvation of all solutes; Chen et al. adopted Bronsted's principle of specific interaction, which states that there would be specific interactions only between ions of the opposite sign (like-ion repulsion), and the distribution of anions and cations around a neutral molecule is such that the net charge is zero.

As for long-range interactions, Chen used the same extended Debye-Huckel model as Pitzer did. Cruz and Renon followed the extension of Debye-Huckel model made by Fowler and Guggenheim (1956), and considered the concentration dependence of the dielectric constant. The concentration dependence of the dielectric constant is expressed as Born or Debye and McAulay theory (Harned and Owen, 1958).

The comparison of Pitzer equation to Chen's NRTL and modified Cruz and Renon's NRTL was given by Ball and Renon (1985). In both single electrolyte and mixture cases (single solvent water), best fit was achieved with Pitzer's model (truncated with only binary parameters used). Both NRTL models gave similar accuracy. The advantage of NRTL models, however, is that they are more flexible and easy to handle mixed solvents and systems including molecules as well as ions. Chen and coworkers have applied Chen's NRTL model to calculate the phase equilibrium of amino acids (Chen et al., 1989) and antibiotics (Zhu et al., 1990) with success.

In 1989, Liu et al. (1989a,b) proposed an activity coefficient model for electrolyte solutions, which goes beyond previous models because it is based on a theoretically improved combination of the Debye-Huckel theory and the local-composition (NRTL) concept. Recall that all the models consider the long-range and short-range interactions independent of each other. The new model gives appropriate attention to the effect of the short-range interaction on long-range interaction and vice versa. The parameters are ion-specific, not electrolyte-specific. The unique feature of the Liu et al.'s model is their modification of the Debye-Huckel expression. The Debye-Huckel expression used in previous models gives the interactions between each central ion and *all* the other ions in the solution. The Debye-Huckel expression of Liu et al. gives *only* the interactions between each central ion and ions outside the first coordination shell. The interactions of ions inside the first coordinate shell are considered in the NRTL expression (see Figure 1). The dielectric constant, D, of the solution is assumed to be a function of the water mole fraction x_w:

$$D = 31.65 + 46.65x_w$$

The disadvantage of NRTL model is that the parameters are not in linear form.

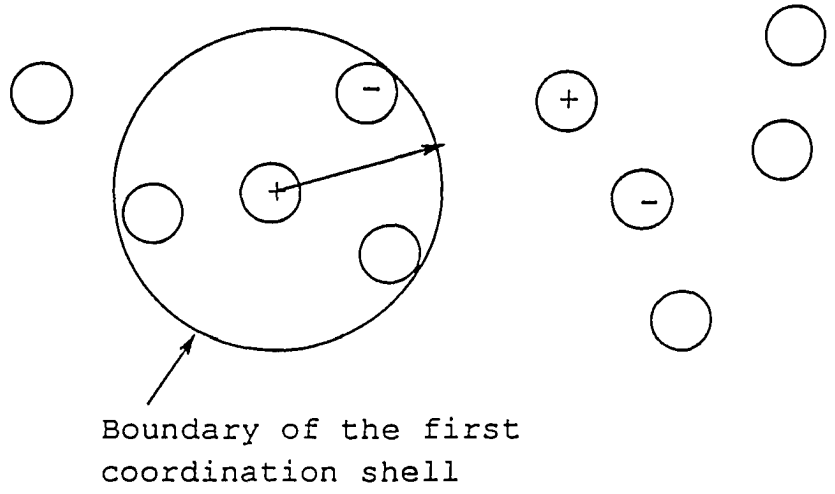

Figure 1: Long-range and short-range interaction in Liu et al. model

This leads to some difficulties in data treatment. The parameters are generally strongly correlated; the initial values may influence the final correlation; and multiple roots exist. Therefore there is some uncertainty about the best values of the parameters.

UNIQUAC (Universal Quasi Chemical Theory) Model

An interesting fact drawn from the above discussion of the different kind of models is that the major distinction between them is the way short-range interactions are handled, which is related to the interactions within the non-electrolyte system. The basis of the virial or NRTL idea is really taken from non-electrolyte VLE (Vapor-

Liquid Equilibrium) predictions. All the successful VLE models can be incorporated into the electrolyte system in a suitable way.

In 1986, Sander et al. (1986a) proposed the UNIQUAC model. The excess Gibbs function is assumed to be the sum of two contributions, the Debye-Huckel type for long-range and modified UNIQUAC for short-range interactions. The Debye-Huckel equation was generalized to handle mixed solvents. The application to the VLE and SLE ($K^+ - Mg^{2+} - Ca^{2+} - NO_3 - H_2O$ phase equilibrium) yields good results (Sander et al., 1986b). The extension of the UNIQUAC model has been made by Rennotte et al. (1988, 1989). The Debye-McAulay theory was added and a new correlation of the concentration dependence of dielectric constant is proposed:

$$D = D_w \frac{A + D_{ab}Y}{A + D_w Y}$$

with $A = 2/3(D_w - D_{ab})$, D_{ab} is a constant and D_w is dielectric constant of pure water.

Equation of State for Electrolyte Solutions

The most recently published thermodynamic model for aqueous electrolyte solutions containing multiple salts is an equation of state model by Jin and Donohue (1991). Unlike the previous models, this equation of state model uses only one adjustable parameter for each ion that must be determined from all available binary activity coefficient data concerning each ion.

One unique feature of this equation of state model is that it is based on the perturbation theory, a nonprimitive model. All the above models are extensions of the Debye-Huckel model, a primitive model. The distinction between the primitive and nonprimitive models is that the primitive model treats the solvent as a continuous

medium with a certain dielectric constant; the nonprimitive model treats the solvent as a discrete medium, and no dielectric constant is used. This is further illustrated in Figure 2.

Jin and Donohue claimed in their paper that their model gave better results than Pitzer's model for the prediction of solubilities. One example was the comparison of the calculated phase diagram of NaCl-$CaSO_4 - H_2O$ system at 25°C using the equation of state model and Pitzer model. However, the calculated phase diagram given by Jin and Donohue using Pitzer's model was quite different from that given by Harvie and Weare (1980). Harvie and Weare reported excellent agreement between experimental data and the Pitzer model prediction. This leads to another problem in the phase equilibrium simulation, i.e., the accuracy of the numerical solutions. The following review addresses this problem.

Review Of the Phase Equilibrium Computation

The phase equilibria problem includes vapor-liquid, liquid-liquid, solid-liquid, vapor-liquid-liquid, etc. equilibria. Since the primary interest of this study is the crystallization process, only solid-liquid equilibria will be considered. The condensed phases are assumed to be pure solid phases. All computation methods reviewed below will be discussed with respect to those aspects.

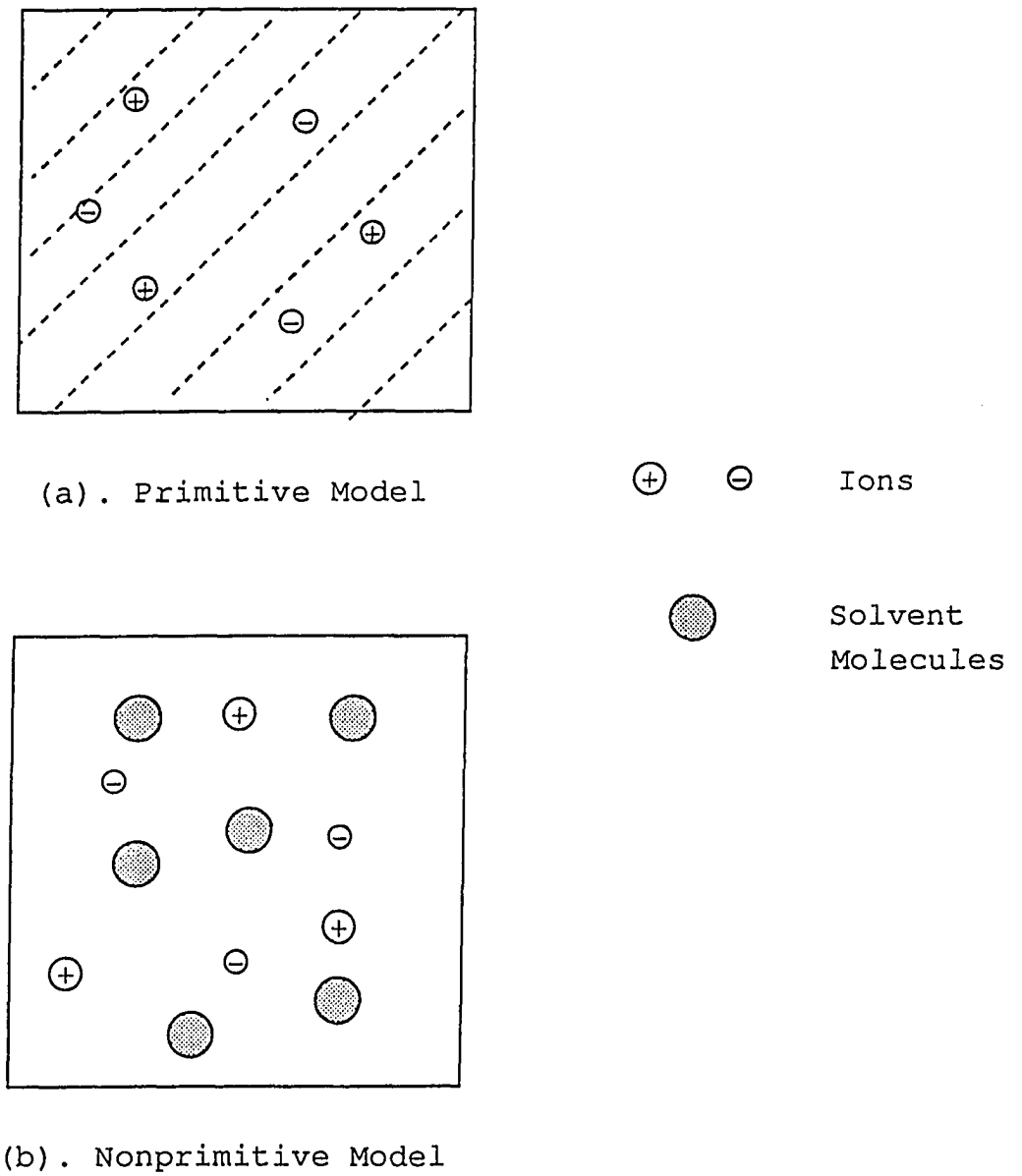

Figure 2: Comparison between primitive and nonprimitive models

The mathematical equivalent form of the phase equilibrium problem is:

$$\begin{aligned} Min \quad & G = \sum_i n_i \mu_i \\ s.t. \quad & A\mathbf{n} = \mathbf{b} \\ & \mathbf{n} \geq \mathbf{0} \end{aligned}$$

where G is Gibbs free energy, n_i and μ_i are mole number and chemical potential of species i, respectively. The linear constraints are the mass and charge balance.

As mentioned before, the difficulty with the phase equilibrium problem is that the phases precipitated at equilibrium are not known *a priori.* Although the maximum number of phases precipitated at equilibrium is restricted by the Gibbs phase rule, there may still be many possibilities that must satisfy the phase rule. Suppose that a maximum of 2 solid phases can exist out of 4 possible ones and there are 10 possible combinations as shown in Figure 3.

In general, there are two different approaches to solve this problem. One is solving for all the combinations and choosing the one with the lowest free energy value. The other is solving the minimization problem with all four possible solid phases. It is expected that the concentrations of non-existing phases are zero at the minimum point. The first approach is usually called *phase-splitting* approach and the second one *phase-eliminating.*

The *phase-splitting* approach was first proposed by Gautam and Seider (1979). To reduce the number of combinations that actually need to be solved, the thermodynamic stability criteria were used. Although the original applications of this method were the solving of vapor-liquid, liquid-liquid equilibria problems, the solid-liquid equilibrium problem is discussed below. The most recent applications of this

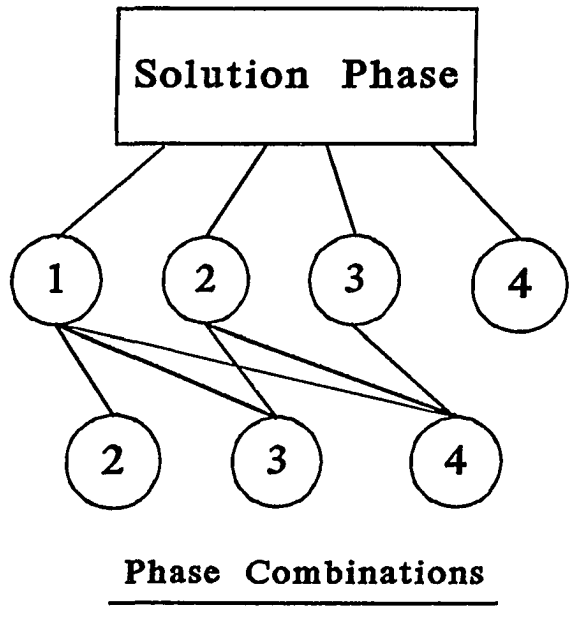

Figure 3: Possible combinations of phase assemblage

approach have been done by Sander et al. (1986b) for solving the solid-liquid equilibrium problem and Walraven and Rompay (1988) for suggesting an improved *phase-splitting* method.

First, locate a source phase, for instance a solution phase. The thermodynamic stability criteria are then used to identify unstable components within the source phase. *Split* the unstable component from the source phase to form a trial phase followed by the minimization procedure for obtaining the compositions in both source and trial phases. If the quantity of the trial phase is large (larger than the pre-

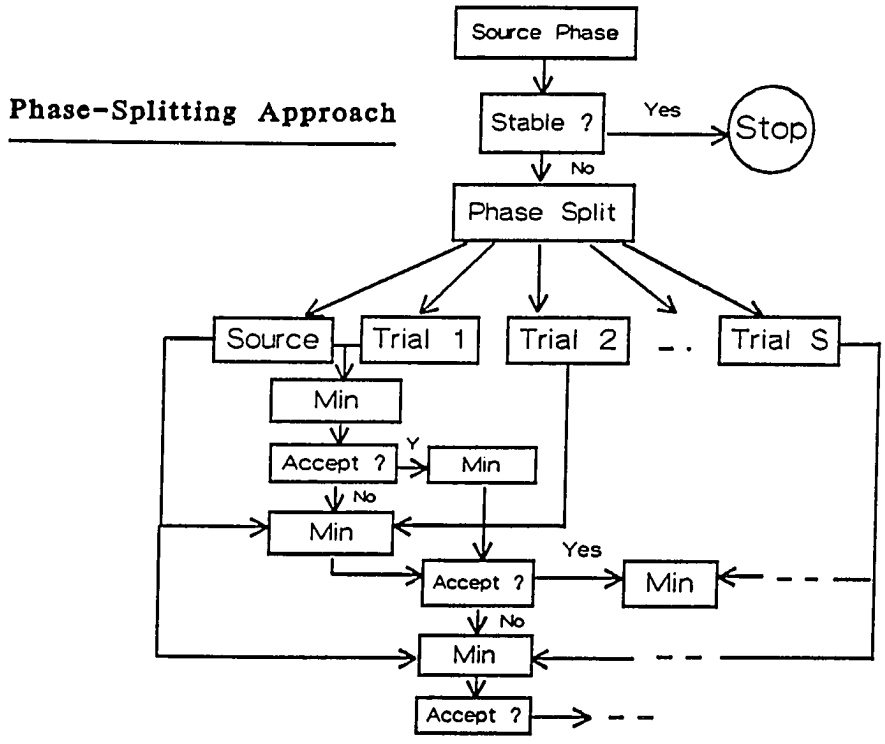

Figure 4: Phase-splitting approach

specified trace amount), the trial phase is accepted. The similar procedure is carried out for other unstable components. The procedure is illustrated in Figure 4. Clearly several minimization procedures should be carried out.

For a complex multicomponent system, the *phase-splitting* procedure might have to deal with many possible subsystems. Castillo and Grossmann (1981) proposed an alternative approach based on a *phase-eliminating* procedure. The phase equilibrium problem was solved with nonlinear programming techniques. All possible phases were

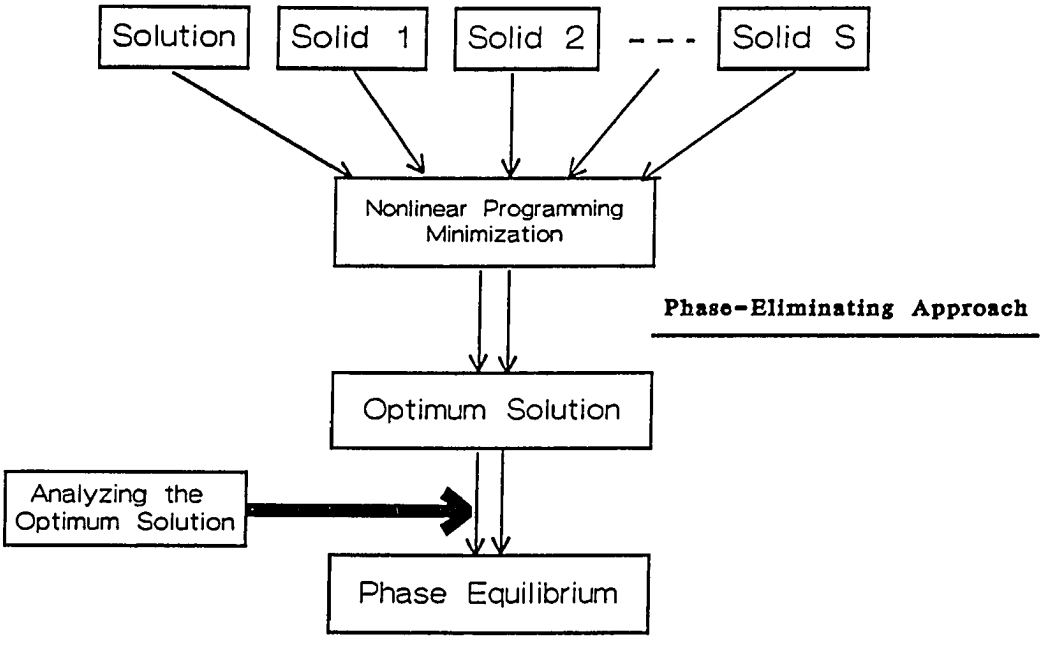

Figure 5: Phase-eliminating approach

assumed. No thermodynamic criterion was used. The equilibrium phase assemblage was obtained simply by analyzing the optimum solution. The zero mole number corresponded to non-existing component. Since the chemical potential was undefined at zero concentration, precautions were used. An arbitrary small positive value was used for variable constraints instead of zero. The *phase-eliminating* procedure is illustrated in Figure 5. Neither the *phase-splitting* nor the *phase-eliminating* procedure so used can guarantee that the Gibbs phase rule is satisfied at the optimum solution.

Since the phase equilibrium problem is a constrained minimization problem, modern optimization techniques are applicable. The phase selection criteria can be incorporated in the minimization algorithm by carefully analyzing the optimization theorem (Kuhn-Tucker conditions).

The constrained minimization algorithms can be categorized as primal methods, penalty methods and dual methods. Various attempts have been made by several authors to solve the equilibrium problem by using different methods. The detailed nonlinear programming techniques were described by Luenberger (1984).

Harvie and Weare (1980) solved the phase equilibrium problem for the $Na - K - Mg - Ca - Cl - SO_4 - H_2O$ system by using the dual and cutting plane method. The derivation of the dual problem was given in detail by Greenberg (1986). The minimization problem was transformed into a maximization problem (dual problem) with nonlinear constraints. The phase selection procedure was easy to implement. The Gibbs phase rule was guaranteed. The disadvantage was that this method was initial value sensitive and suitable initial point was not easily found.

Primal methods also can be employed because the phase equilibrium problem is linearly constrained. The whole class of linearly constrained nonlinear minimization methods was discussed by Gill et al. (1981). The algorithm most often used is SQP (Sequential Quadratic Programming). Harvie, Greenberg and Weare (1987) described the application of the SQP method for solving highly non-ideal multiphase equilibrium problems. But the phase selection procedure was very complicated and it was hard to guarantee that the Gibbs phase rule would be satisfied. A similar algorithm was used by Castier, Rasmussen and Fredenslund (1989). A stability test was also used to identify unstable phases.

As an alternative to the primal and dual methods, the penalty method was suggested by Lantague, Marcos and Cayrol (1988). The phase-eliminating approach was used. The original constrained minimization problem was transformed into unconstrained minimization problem by using penalty functions. Again, the Gibbs phase rule could not be guaranteed. The efficiency of the method depended drastically upon the choice of the penalty parameters.

Of all the existing methods for the chemical and phase equilibrium computation discussed above, the phase stability test and mathematical programming are considered separately. By carefully analyzing the optimization algorithm it will be shown that there is a more unified approach toward this problem. The mathematical condition for optimization is identical with the thermodynamic stability criterion. The phase selection procedure based on thermodynamic criteria is the same as the mathematical considerations toward finding the optimum solution. The optimum solution will always satisfy Gibbs phase rule. The algorithm is based on the large-scale optimization technique developed by Murtagh and Saunders (1978). The reason for using this method is not because problem is large, but because it offers the desired properties. Clearly, this algorithm has advantages over other algorithms for very large problems. The source program is provided in Appendix B. It was written in FORTRAN 77 and run on the NAS/9180 mainframe at the Iowa State University Computation Center.

Explanation of Dissertation Format

This dissertation consists of three parts, each written in a form suitable for publication in a scientific journal. A general introduction has been included to give a

general review of the relevant work done by various scientists. References cited in the general introduction are given at the end of the dissertation. The research presented in each part represents the author's original work.

PART I.

ACTIVITY COEFFICIENT MODEL OF CONCENTRATED ELECTROLYTE SOLUTIONS

1. INTRODUCTION

Since Debye and Huckel proposed their simple limiting law predicting the activity coefficients of dilute electrolyte solutions, there have been many attempts to extend their theory to solutions of high concentration. Little success had been achieved until the last two decades during which a number of models utilizing methods of statistical mechanics were developed. The most successful of these are the virial model of Pitzer (1973), the NRTL (Non-Random Two Liquid) model of Cruz and Renon (1978), the NRTL model of Chen et al. (1982) and the UNIQUAC model of Sander et al. (1986).

Generally speaking, the development of these models is based on the summation of the excess Gibbs free energy of the electrolyte solution coming from the following contributions:

a) Long-range interactions or electrostatic interactions,

b) Short-range interactions (Virial, NRTL, or UNIQUAC model),

c) Concentration dependence of dielectric constants.

In all of the four above mentioned models the long range and short range interactions are taken as independent, i.e., they assume that long range interactions have little effect on short range interactions and short range interactions have little effect on long range interactions.

Liu et al. (1989a) proposed a different approach. Their model was based on the assumption that long range and short range interactions would interact. The local composition, NRTL model was used to accommodate these effects. The NRTL model they used abandoned the "local electroneutrality" assumption that was made by Chen and coworkers. In addition all the model parameters used were ion specific.

The main limitation of the Liu et al.'s model is lack of extensive model parameter database. Using the "ion-specific" parameter has the advantage that no additional parameter is needed to extend the activity coefficient model for multicomponent prediction. But from a practical point of view, the disadvantage of ion-specific parameters is that they are difficult to correlate from experimental data since the ion-solvent energy parameters would tend to have different values when correlated with different salts with common ions. Even if it were possible to correlate the experimental activity coefficient data from a large number of salts with the same ion at the same temperature so that universal ion- solvent interaction parameters could be obtained, it would not be practical at temperatures other than 25°C due to lack of extensive experimental data. From a theoretical point of view, the same ion- solvent interaction might have different values in different environments since all ions are not acting independently.

A new method of correlating data using the Liu et al.'s NRTL model (Liu et al., 1989a) was used in this analysis. The parameters of this analysis are electrolyte-specific rather than ion-specific, making the model more practical to use. The relationship between the proposed electrolyte-specific parameter and the ion-specific parameter is given. The salt-salt interaction parameters in the multicomponent prediction can be obtained from the corresponding binary parameters.

2. MODIFIED LIU, HARVEY AND PRAUSNITZ NRTL MODEL

The modification of Liu et al.'s NRTL model is in the formulation of the energy parameter in the original model. The structure of Liu, Harvey and Prausnitz NRTL model is left unchanged. Four new parameters $\tau_{w,ca}, \tau_{ca,w}, \tau'_{w,ca}$ and $\tau'_{ca,w}$ are defined, which are electrolyte-specific instead of ion-specific. The new parameters and the equations for calculating activity coefficients are defined as follows.

2.1 Long-range interaction contribution

The Long-range interaction contribution is obtained by modifying the original Debye-Huckel model. It is the combination of classical Poisson-Boltzmann theory and the local-composition concept.

The activity coefficients of cation c_i and anion a_i due to long-range interaction are given as (Liu et al., 1989b):

$$ln\gamma_{c_i,LR} = \frac{e^2}{2DkT}\left(\frac{z_{c_i}}{r_{c_i}}\left[(z_{c_i} + C_{c_i}\sum_{a_j} x_{a_j c_i} z_{a_j})\frac{exp[\kappa(r^r_{c_i} - r_{c_i})]}{(1+\kappa r^r_{c_i})} - z_{c_i}\right]\right) \quad (2.1)$$

$$ln\gamma_{a_i,LR} = \frac{e^2}{2DkT}\left(\frac{z_{a_i}}{r_{a_i}}\left[(z_{a_i} + C_{a_i}\sum_{c_j} x_{c_j a_i} z_{c_j})\frac{exp[\kappa(r^r_{a_i} - r_{a_i})]}{(1+\kappa r^r_{a_i})} - z_{a_i}\right]\right) \quad (2.2)$$

where

$$x_{a_j c_i} = \frac{x_{a_j}}{x_w G_{wc_i,a_j c_i} + \sum_{a_k} G_{a_k c_i,a_j c_i}}$$

$$x_{c_j a_i} = \frac{x_{c_j}}{x_w G_{wa_i,c_j a_i} + \sum_{c_k} G_{c_k a_i,c_j a_i}}$$

$$r^r_{a_i} = r_{a_i} + \frac{\sum_{c_j} \lambda_{c_j} r_{c_j} x_{c_j}}{\sum_{c_j} x_{c_j}}$$

$$r^r_{c_i} = r_{c_i} + \frac{\sum_{a_j} \lambda_{a_j} r_{a_j} x_{a_j}}{\sum_{a_j} x_{a_j}}$$

$$\kappa^2 = \frac{4\pi e^2}{DkT} n_T (\sum_{c_j} x_{c_j} z^2_{c_j} + \sum_{a_j} x_{a_j} z^2_{a_j})$$

2.2 Short-range interaction contribution

The short-range interaction contribution is based on the local- composition concept. It is similar to Chen's NRTL model except "local electroneutrality" is not assumed.

The activity coefficients of cation c_i and anion a_i due to short-range interaction are given as (Liu et al., 1989b):

$$ln \ \gamma_{c_i,SR} = -\frac{C_w}{2}\left(\frac{x_w G_{c_i w,ww}}{x_w + \sum_{c_j} x_{c_j} G_{c_j w,ww} + \sum_{a_j} x_{a_j} G_{a_j w,ww}} - x_w - G_{c_i w,ww} + 1\right) - \frac{C_{c_i}}{2\sum_{a_j} x_{a_j}} \sum_{a_k} x_{a_k} ln \frac{x_w G_{wc_i,a_k c_i} + \sum_{a_j} x_{a_j} G_{a_j c_i,a_k c_i}}{(1 - \sum_{c_j} x_{c_j}) G_{wc_i,a_k c_i}}$$

$$+ \frac{1}{2(\sum_{c_j} x_{c_j})^2} \sum_{a_k} C_{a_k} x_{a_k} \left[\sum_{c_k} x_{c_k} ln \frac{x_w G_{wa_k,c_k a_k} + \sum_{c_j} x_{c_j} G_{c_j a_k,c_k a_k}}{(1 - \sum_{a_j} x_{a_j}) G_{wa_k,c_k a_k}} \right]$$

$$- \frac{1}{2\sum_{c_j} x_{c_j}} \sum_{a_k} C_{a_k} x_{a_k} \left[ln \frac{x_w G_{wa_k,c_i a_k} + \sum_{c_j} x_{c_j} G_{c_j a_k,c_i a_k}}{(1 - \sum_{a_j} x_{a_j}) G_{wa_k,c_i a_k}} \right.$$

$$\left. + \sum_{c_k} x_{c_k} \left(\frac{G_{c_i a_k,c_k a_k}}{x_w G_{wa_k,c_k a_k} + \sum_{c_j} x_{c_j} G_{c_j a_k,c_k a_k}} - \frac{1}{1 - \sum_{a_j} x_{a_j}} \right) \right] \tag{2.3}$$

$$ln \ \gamma_{a_i,SR} = -\frac{C_w}{2} \left(\frac{x_w G_{a_i w,ww}}{x_w + \sum_{c_j} x_{c_j} G_{c_j w,ww} + \sum_{a_j} x_{a_j} G_{a_j w,ww}} - x_w \right.$$

$$\left. - G_{a_i w,ww} + 1 \right) - \frac{C_{a_i}}{2\sum_{c_j} x_{c_j}} \sum_{c_k} x_{c_k} ln \frac{x_w G_{wa_i,c_k a_i} + \sum_{c_j} x_{c_j} G_{c_j a_i,c_k a_i}}{(1 - \sum_{a_j} x_{a_j}) G_{wa_i,c_k a_i}}$$

$$+ \frac{1}{2(\sum_{a_j} x_{a_j})^2} \sum_{c_k} C_{c_k} x_{c_k} \left[\Sigma_{a_k} x_{a_k} ln \frac{x_w G_{wc_k,a_k c_k} + \sum_{a_j} x_{a_j} G_{a_j c_k,a_k c_k}}{(1 - \sum_{c_j} x_{c_j}) G_{wc_k,a_k c_k}} \right]$$

$$- \frac{1}{2\sum_{a_j} x_{a_j}} \Sigma_{c_k} C_{c_k} x_{c_k} \left[ln \frac{x_w G_{wc_k,a_i c_k} + \sum_{a_j} x_{a_j} G_{a_j c_k,a_i c_k}}{(1 - \sum_{c_j} x_{c_j}) G_{wc_k,a_i c_k}} \right.$$

$$\left. + \sum_{a_k} x_{a_k} \left(\frac{G_{a_i c_k,a_k c_k}}{x_w G_{wc_k,a_k c_k} + \sum_{a_j} x_{a_j} G_{a_j c_k,a_k c_k}} - \frac{1}{1 - \sum_{c_j} x_{c_j}} \right) \right] \tag{2.4}$$

Then the activity coefficient for salt $c_i a_i$ is obtained as:

$$ln\gamma_{c_i a_i} = \frac{1}{(\nu_{c_i} + \nu_{a_i})} [\nu_{c_i}(ln\gamma_{c_i,LR} + ln\gamma_{c_i,SR}) + \nu_{a_i}(ln\gamma_{c_i,SR} + ln\gamma_{a_i,SR})]$$

The model parameter $G_{ji,ki}$ is defined as:

$$G_{ji,ki} = \exp[-(g_{ji} - g_{ki})/RT]$$

where the energy parameter g_{ji} accounts for the interaction between two species i and j.

Here we define the following relations:

$$(g_{wc} - g_{ac})/RT = \tau_{w,ca} \tag{2.5}$$

$$(g_{wa} - g_{ca})/RT = \tau'_{w,ca} \tag{2.6}$$

$$(g_{cw} - g_{ww})/RT = \tau_{ca,w} \tag{2.7}$$

$$(g_{aw} - g_{ww})/RT = \tau'_{ca,w} \tag{2.8}$$

where τ and τ' are the new parameters, which are electrolyte-specific. And the following relation holds:

$$\tau'_{w,ca} - \tau_{w,ca} = \tau'_{ca,w} - \tau_{ca,w} \tag{2.9}$$

Those relations differ from Chen's NRTL in the sense that the following relations do not necessarily hold:

$$g_{wc} = g_{wa} = g_{ca}$$

and

$$g_{cw} = g_{aw} = g_{ww}$$

which are the results of the local electroneutrality assumption. This is reflected by the fact that τ does not have the same values as τ'.

If we assume $g_{ww} = 0$, we have the following equations:

$$g_{cw}/RT = \tau_{ca,w} \tag{2.10}$$

$$g_{aw}/RT = \tau'_{ca,w} \tag{2.11}$$

$$g_{ac}/RT = \tau_{ca,w} - \tau_{w,ca} \tag{2.12}$$

which relates the proposed electrolyte-specific parameters to the ion-specific parameters.

3. BINARY SOLUTIONS

The parameters of the modified Liu, Harvey and Prausnitz NRTL model $\tau_{w,ca}$, $\tau_{ca,w}$, $\tau'_{w,ca}$ and $\tau'_{ca,w}$ are obtained by least-square analysis on deviations between calculated and experimental values:

$$S_r = \sum_i (ln\gamma_{\pm,ca}^{cal.} - ln\gamma_{\pm,ca}^{exptl.})^2$$

where the experimental activity coefficient data are taken from Robinson and Stokes (1970).

The conversion of the values of the activity coefficients between true-mole-fraction scale, which is the scale of the current model, and the molality scale, which is the scale of the experimental data, is given as follows:

$$ln\gamma_{\pm,m} = ln\gamma_{\pm,x} - ln(1 + M_w(\nu_c + \nu_a)m/1000)$$

where M_w is the molecular weight of water.

The concentration dependence of the dielectric constant is:

$$D = 31.65 + 46.65x_w$$

following the suggestion by Liu et al. (1989b).

The densities of the electrolyte solutions used in this analysis were the density of pure water instead of the real densities of the solutions that are usually not available. The density of pure water at 25^oC is 0.9970449 g/cm^3 (Kell, 1975).

It has been customary to use crystal ionic radii as the actual ionic radii in the solution since the latter are not known. Several sets of ionic radii are available. The set used in this study is based on Marcus (1983). The radius of H^+ ($r_{H^+} = 0.7$ Å) is obtained from the fit of the activity coefficient data since its radius is not available. All coordination numbers are fixed as 6.

The correlation results are given in Table 3.1 and Table 3.2. The size constants, λ, used were: 1.5 for cation, except for K^+ and NH_4^+ that were 1.1; 1.1 for anion except for Cl^- that was 1.5. It seemed that the λ tended to have small values for large ions. The parameters corresponding to the cation-water interaction, $\tau_{ca,w}$, had negative values, while parameters corresponding to the anion-water interaction, $\tau'_{ca,w}$, had positive values. This trend was also observed from the correlation of the $H^+ - K^+ - Li^+ - Br^- - Cl^- - H_2O$ binary parameters by Liu et al. (1989b).

Table 3.1: Parameters for 1-1 type electrolyte at 25°C. (Experimental data from Robinson and Stokes, 1970)

Salt	$\tau_{w,ca}$	$\tau_{ca,w}$	$\tau'_{w,ca}$	$\tau'_{ca,w}$	Max m	$\sigma_{ln\gamma}$
HBr	-1.7797	-1.0630	0.2715	0.9881	3.0	0.010
HCl	-0.7649	-1.4127	1.6674	1.0196	6.0	0.002
HI	-0.9262	-1.0722	0.5215	0.3755	3.0	0.011
HNO_3	-0.8164	-0.7205	0.6033	0.6992	3.0	0.007
KBr	-1.0952	-1.1504	1.5313	1.4761	5.5	0.011
KCl	-1.2436	-1.5801	1.9821	1.6457	6.0	0.000
KI	-1.5565	-1.3583	1.6087	1.8060	4.5	0.002
KNO_3	-0.0840	-1.7639	2.5079	0.8280	3.5	0.010
LiBr	-2.1481	-0.8308	0.2660	1.5833	6.0	0.009
LiCl	-0.8052	-0.9061	1.1960	1.0951	6.0	0.002
$LiNO_3$	-0.8982	-0.7323	0.5998	0.7657	6.0	0.008
NaBr	-0.8455	-1.4758	1.9201	1.2899	4.0	0.000
NaCl	-1.0511	-1.4521	1.8366	1.4356	6.0	0.002
NaI	-2.7038	-1.0488	1.1556	2.8107	3.5	0.006
$NaNO_3$	-0.9565	-1.4924	2.0043	1.4684	6.0	0.005
NH_4Cl	-3.8275	-0.8782	1.1434	4.0927	6.0	0.023
NH_4NO_3	-12.0185	-1.8198	2.4882	12.6869	6.0	0.007

Table 3.2: Parameters for high valence electrolyte at 25°C. (Experimental data from Robinson and Stokes, 1970)

Salt	$\tau_{w,ca}$	$\tau_{ca,w}$	$\tau'_{w,ca}$	$\tau'_{ca,w}$	Max m	$\sigma_{ln\gamma}$
$MgBr_2$	-0.1564	-1.0089	1.6597	0.8072	5.0	0.019
$MgCl_2$	0.3886	-1.5094	2.6870	0.7891	5.0	0.183
MgI_2	0.1246	-0.4527	2.0752	1.4979	5.0	0.036
$Mg(NO_3)_2$	0.1361	-1.7172	2.3617	0.5084	5.0	0.070
$CaBr_2$	-0.8806	-0.7248	1.2933	1.4492	6.0	0.040
$CaCl_2$	0.0066	-1.9034	2.4935	0.5767	6.0	0.026
CaI_2	-0.4501	-0.1280	1.6972	2.0193	2.0	0.009
$Ca(NO_3)_2$	-0.3779	-0.7421	1.9126	1.5484	6.0	0.020
K_2SO_4	-0.9120	-1.1784	2.5549	2.2885	0.7	0.008
Li_2SO_4	-0.2089	-0.6220	2.4055	1.9922	3.0	0.063
Na_2SO_4	-0.4884	-0.5596	2.4056	2.3315	4.0	0.047
$MgSO_4$	0.7006	-0.9831	3.6784	1.9948	3.0	0.317

4. MULTICOMPONENT SOLUTIONS

The parameters for calculating multicomponent solutions activity coefficients are further defined as:

$$G_{c_i w,ww} = \sum_{a_j} x_{a_j} exp(-\tau_{c_i a_j,w}) / \sum_{a_j} x_{a_j} \tag{4.1}$$

$$G_{a_j w,ww} = \sum_{c_i} x_{c_i} exp(-\tau_{c_i a_j,w}) / \sum_{c_i} x_{c_i} \tag{4.2}$$

To characterize the mixture activity coefficients, the salt-salt interaction parameters are necessary. The salt-salt interaction parameters are $G_{c_i a_j,c_k a_j}$ and $G_{c_i a_j,c_i a_k}$, which can be directly calculated from the binary parameters.

If we assume $g_{ww} = 0$, then:

$$\begin{aligned} G_{c_i a_j,c_k a_j} &= exp[-(g_{c_i a_j} - g_{c_k a_j})/RT] \\ &= exp[(\tau_{c_k a_j,w} - \tau_{w,c_k a_j}) - (\tau_{c_i a_j,w} - \tau_{w,c_i a_j})] \end{aligned} \tag{4.3}$$

$$\begin{aligned} G_{c_i a_j,c_i a_k} &= exp[-(g_{c_i a_j} - g_{c_i a_k})/RT] \\ &= exp[(\tau_{c_i a_k,w} - \tau_{w,c_i a_k}) - (\tau_{c_i a_j,w} - \tau_{w,c_i a_j})] \end{aligned} \tag{4.4}$$

The activity coefficients of HCl and HBr in halide solutions at 25^oC were then calculated. The results were shown in Figure 4.1 to Figure 4.5. The experimental data were taken from Harned and Owen (1958).

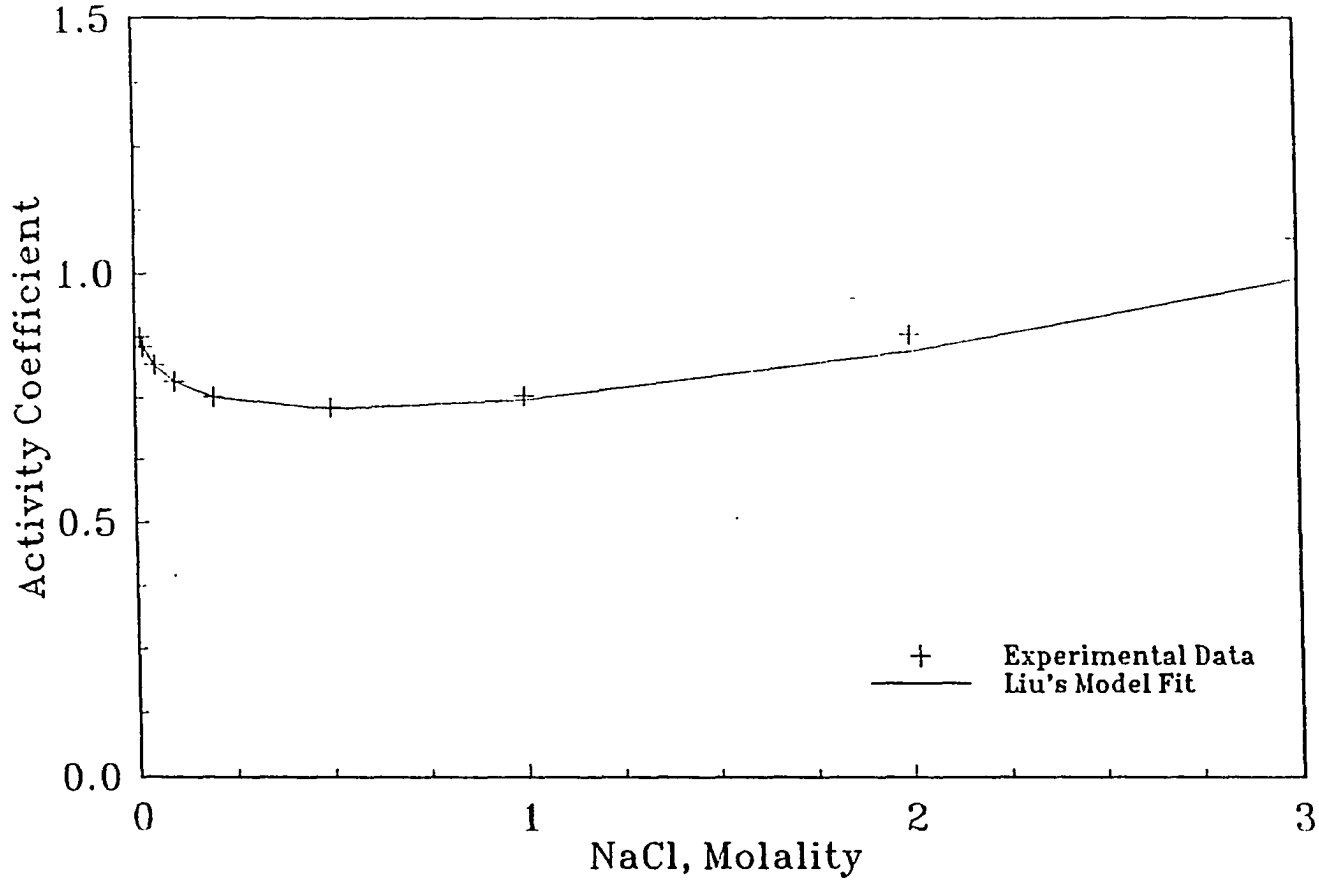

Figure 4.1: Activity coefficient of HCl in NaCl at 298.15 K (HCl = 0.01 m)

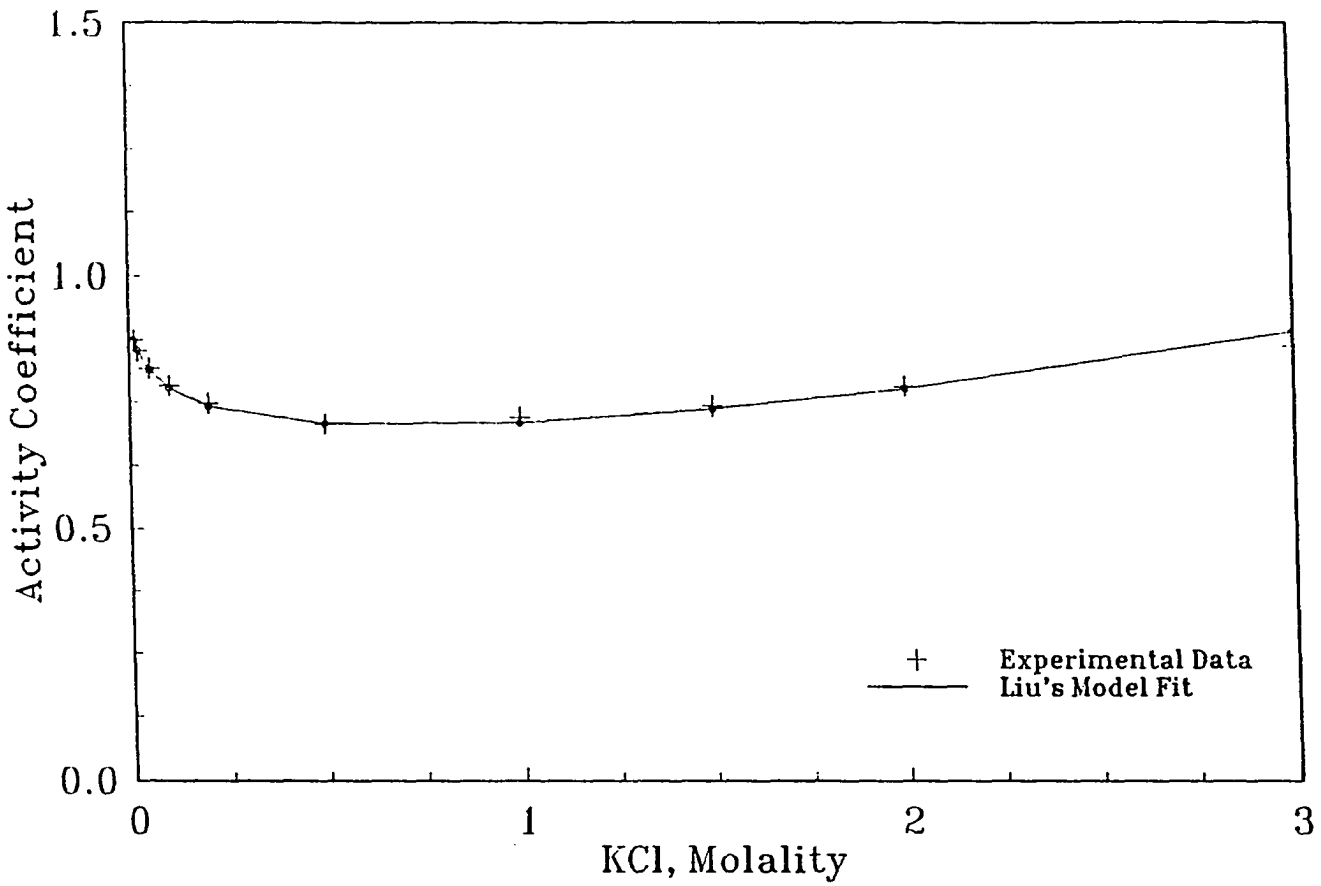

Figure 4.2: Activity coefficient of HCl in KCl at 298.15 K (HCl = 0.01 m)

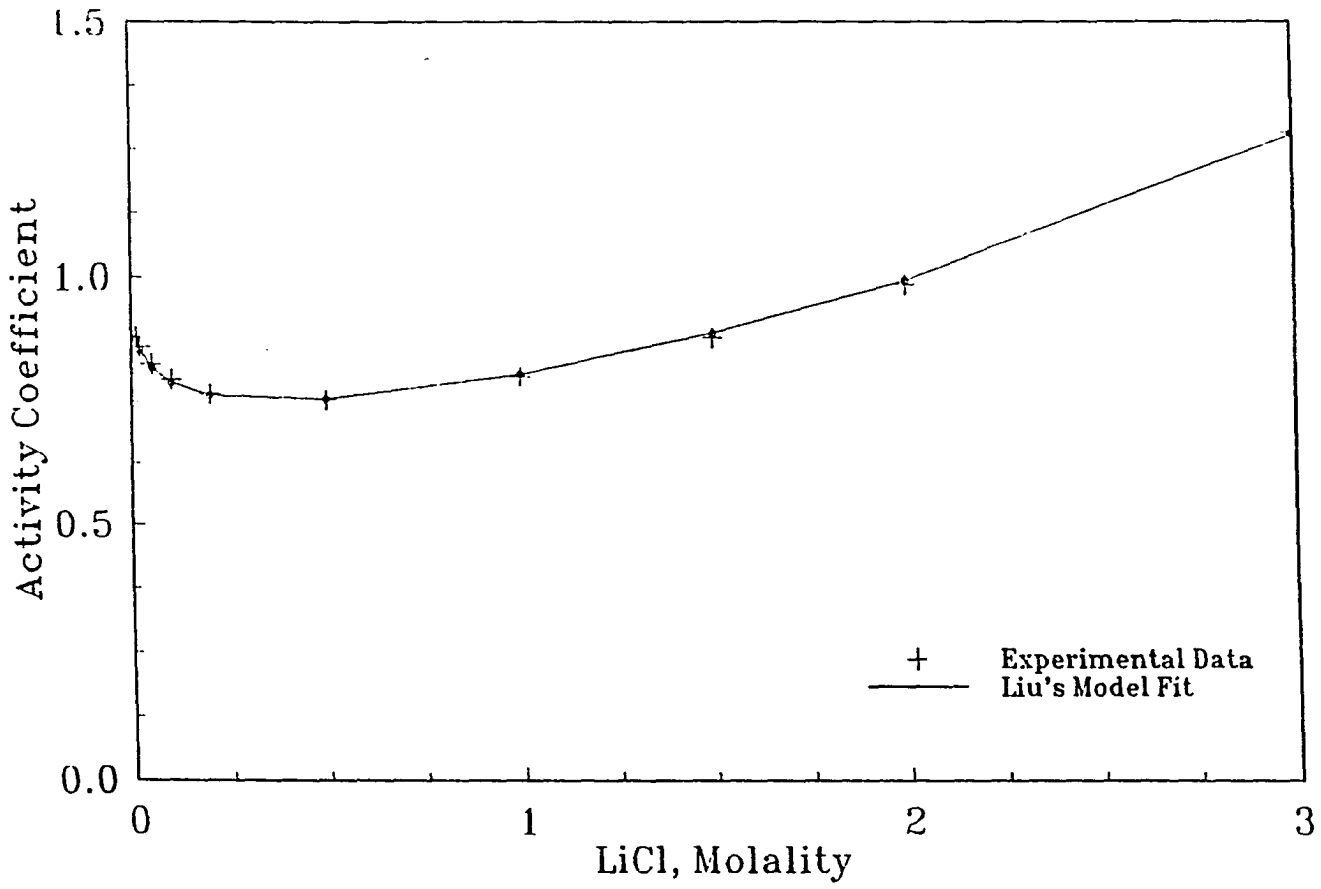

Figure 4.3: Activity coefficient of HCL in LiCl at 298.15 K (HCl = 0.01 m)

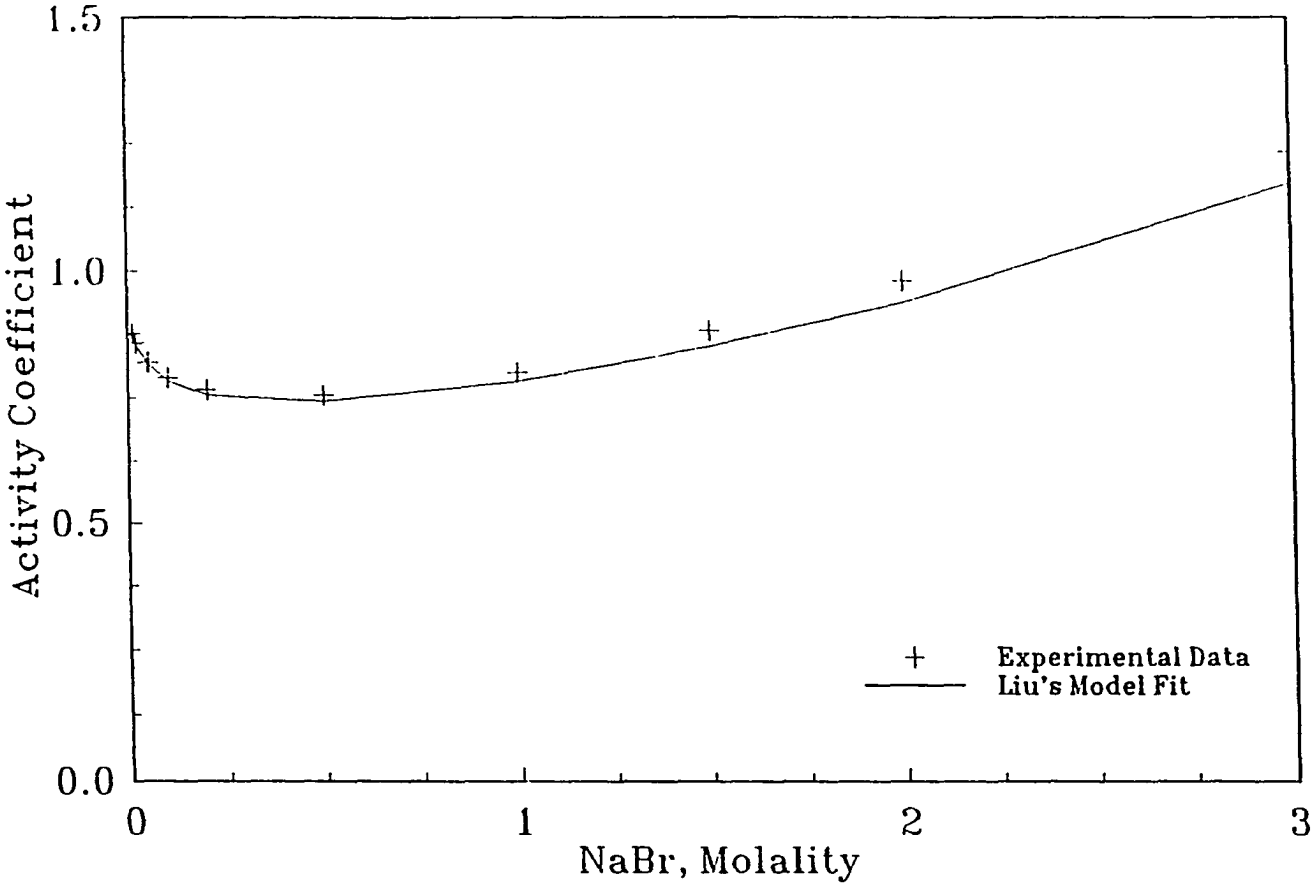

Figure 4.4: Activity coefficient of HBr in NaBr at 298.15 K (HBr = 0.01 m)

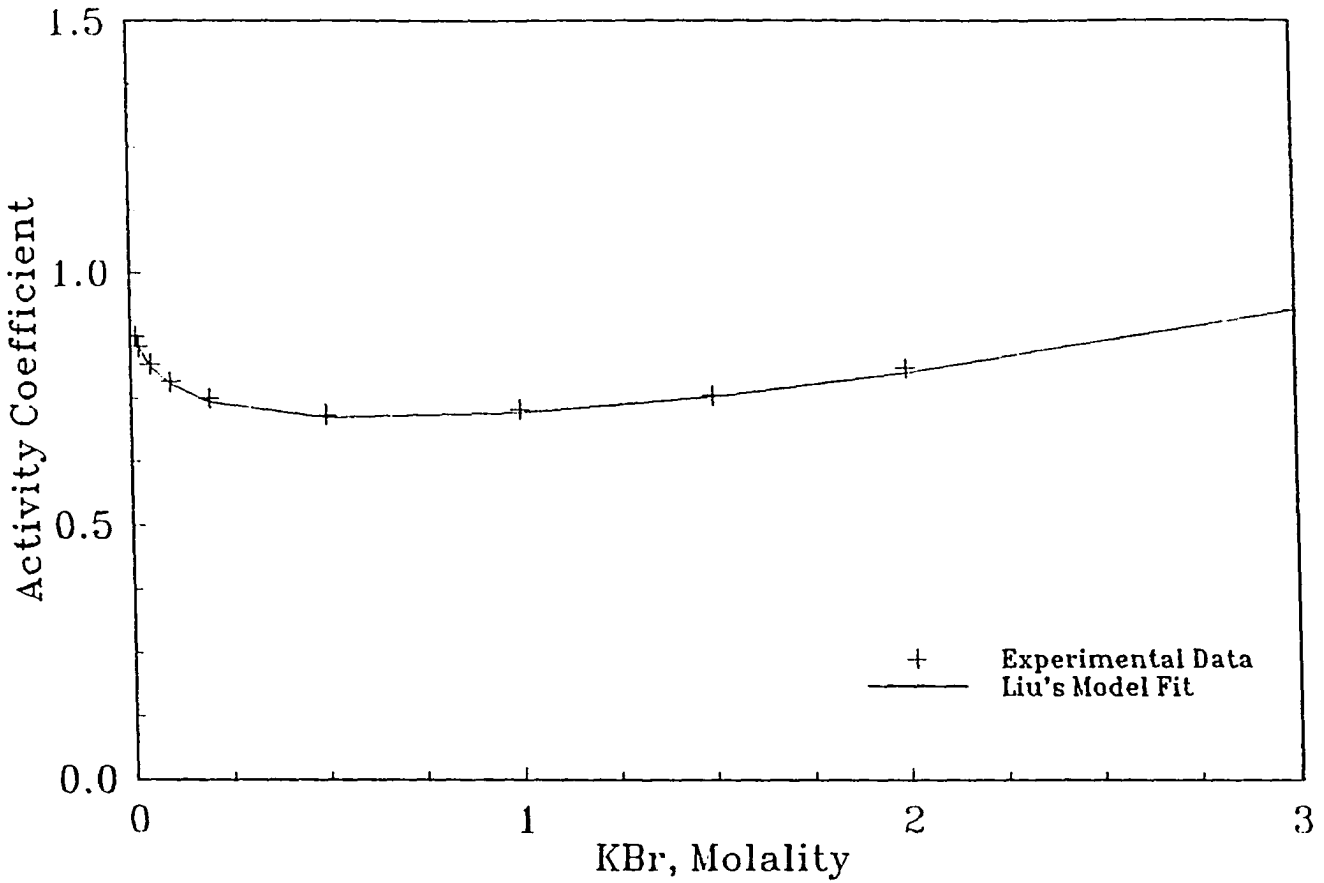

Figure 4.5: Activity coefficient of HBr in KBr at 298.15 K (HBr = 0.01 m)

5. CONCLUSION

The modified Liu et al.'s NRTL model gave a practical method for correlating the model parameters from the available binary experimental data. No additional parameters were needed for predicting the activity coefficients of the multicomponent solutions. The salt-salt interaction parameters were directly calculated from the binary parameters.

It is worth pointing out that the model parameters, as well as the λ values given in this study may not be the best ones because multiroots exist for this highly nonlinear least square analysis. The best values should be selected in light of the multicomponent experimental data.

6. NOMENCLATURE

C = coordination number,

D = dielectric constant,

G = Gibbs free energy,

$G_{ji,ki}$ = defined quantity,

R = gas constant,

T = temperature (K),

e = protonic charge,

g_{ji} = interaction energy parameter of j-i pair,

k = Bolzmann constant,

m = molality,

n_i = number density of species i,

r_c, r_a = ionic radius of cations, anions,

x_i = true mole fraction of species i based on all species (ionic and molecular),

z_c, z_a = algebraic valences of cations and anions, respectively.

Greek Letters

α = defined quantity,

γ = activity coefficient,

λ = size constant,

σ = standard deviation of the correlation,

ν_c, ν_a = number of cations and anions, respectively, produced by the complete dissociation of one electrolyte molecule.

τ, τ' = defined quantities.

Superscripts

cal. = calculated value,

exptl = experiment value.

Subscripts

a = anion,

c = cation,

ca = electrolyte ca,

LR = long-range interaction,

SR = short-range interaction,

w = water.

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PART II.

PHASE EQUILIBRIUM CALCULATION BY USING LARGE-SCALE OPTIMIZATION TECHNIQUE

1. ABSTRACT

A new multicomponent solid-liquid phase equilibrium calculation algorithm is described. The algorithm has the following features: (1) the phase selection procedure is easy. No stability test is needed; (2) the optimum solution satifies Gibbs phase rule; and (3) the mathematical procedures have thermodynamic meanings. Numerical examples for $NaCl-KCl-MgCl_2-CaCl_2-H_2O$ quinary system and its quaternary subsystems illustrate the capability of this algorithm. The comparison between this algorithm and the SQP (Sequential Quadratic Programming) method for $NaCl-KCl-MgCl_2-H_2O$ system at 298.15 K and 273.15 K demonstrates the advantage of the new algorithm over SQP method.

2. INTRODUCTION

The use of optimization techniques has been of considerable value in chemical and phase equilibria calculations. One of the early applications of optimization procedure for equilibrium calculations was proposed by White, Johnson and Dantzig (1958). They used the efficient linear programming (LP) technique, in particular, the Simplex method, developed by George B. Dantzig in 1947. The method was limited by the necessary of prior knowledge of the phases presented at equilibrium before the phase compositions could be determined. In order to circumvent this limitation many other optimization techniques have been employed. Most of them involve nonlinear programming (NLP) since the Gibbs free energy is nonlinear in nature. These techniques are fully reviewed by Luenberger (1984), Van Zeggeren and Storey (1970) and Smith and Missen (1982).

The equilibrium problem is generally not well defined in the sense that the actual phases exist at the equilibrium are not known at the start of the calculations. The mathematical procedures are designed to search among all the possible phases in some systematic way.

In the "phase-splitting" method proposed by Gautam and Seider (1979), a small number of phases is assumed at the beginning of the calculation. The candidate phases are tested against the stability criterion. If the phases are stable and including

them will lower the Gibbs free energy of the whole system, they are included in the phase assemblage. This "phase-splitting" approach, based on the stability test, has been used by several authors (Sander et al., 1986; Walraven and Rompay, 1988).

An alternative approach was used by Castillo and Grossmann (1981), which is a "phase-elimination" method. All possible phases were assumed at the beginning of the calculation. The equilibrium compositions were obtained by analyzing the optimal solution. For the non-existing phases or species the corresponding mole number is zero. Unlike the "phase-splitting" method, the nonlinear programming problem was solved once and the stability test was not used. The algorithm used was the variable metric projection method of Sargent and Murtagh (1973).

Harvie and Weare (1980) solved the dual problem of the general chemical and phase equilibrium problem for the $Na - K - Mg - Ca - Cl - SO_4 - H_2O$ system. The cutting plane algorithm (Kelley, 1960) was used. The derivation of the dual problem was given in detail by Greenberg (1986). By transforming to the dual problem the objective function becomes linear while the constraints are the minimization subproblem for the solution phase.

Geometric programming approach was proposed by Ohanomah and Thompson (1984). In this method the free energy minimization was transformed to a set of nonlinear equations, which were solved by the classical Newton-Raphson method.

Since the chemical and phase equilibrium problem is linearly constrained, direct minimization also can be performed (Harvie, Greenberg and Weare, 1987; Castier, Rasmussen and Fredensland, 1989). The whole class of linear constrained linear and nonlinear minimization methods are discussed by Gill et al. (Gill, Murray and Wright, 1981). The algorithm most often used is the SQP (Sequential Quadratic Pro-

gramming) algorithm. An alternative approach to solve the constrained minimization problem is penalty function method, which transforms the constrained problem into an unconstrained problem. The comparison study using the penalty function method and the SQP method was given by Lantagne, Marcos and Cagrol (1988).

Of all the existing methods for the chemical and phase equilibrium computation discussed above, the phase stability test and mathematical programming are considered separately. By carefully analyzing the optimization algorithm it can be shown that there is a more unified approach toward this problem. The mathematical condition for optimization is identical with the thermodynamic stability criterion. The phase selection procedure based on thermodynamic criteria is the same as the mathematical considerations that find the optimum solution. The optimum solution will always satisfy Gibbs phase rule. The algorithm is based on the large-scale optimization technique developed by Murtagh and Saunders (1978). The reason for using this method is not because the problem is very large, but because it offers the properties discussed above. Clearly, this algorithm has advantages over other algorithm for a very large problems.

3. SOME TERMINOLOGY OF LINEAR PROGRAMMING (LP)

3.1 Basic Solution

Consider the system of equalities:

$$A\mathbf{x} = \mathbf{b}$$

where A is a $m \times n$ matrix, $\mathbf{x}$ is a vector with dimension n, and $n \geq m$.

Let B be any $m \times m$ nonsingular matrix made up of columns of A. Then, if all (n - m) variables $\mathbf{x}$ not associated with B are set to be zero, the solution to the resulting set of equations is said to be a basic solution with respect to the basis B. The variables of $\mathbf{x}$ associated with the basis are called basic variables while the rest are called nonbasic variables.

3.2 Basic Feasible Solution of Linear Programming (LP)

Now consider the system of equations:

$$\begin{aligned} A\mathbf{x} &= \mathbf{b} \\ \mathbf{x} &\geq \mathbf{0}. \end{aligned}$$

that made up of the constraints of the LP problem. If a vector $\mathbf{x}$ satisfies the above constraints and is basic, it is called basic feasible solution.

3.3 Simplex Method

The basic idea of the simplex method is that one proceeds from one basic feasible solution to another so that the objective function value will be decreased (or increased) until the minimum (or maximum) is reached.

3.4 Revised Simplex Method

The revised simplex method is actually the simplex method in matrix form.

Consider the linear programming problem of the standard form:

$$\begin{aligned} Min \quad & \mathbf{c}^T\mathbf{x} \\ s.t. \quad & A\mathbf{x} = \mathbf{b} \\ & \mathbf{x} \geq \mathbf{0} \end{aligned} \tag{3.1}$$

where A is a $m \times n$ matrix. m is the number of constraints and n is the number of variables. Assume B consists of the first m columns of A and forms a basis. Then by partition A,$\mathbf{x}$ and $\mathbf{c}^T$ as:

$$A = [B \quad D]$$

$$\mathbf{x} = (\mathbf{x}_B \quad \mathbf{x}_D) \quad \mathbf{c}^T = (\mathbf{c}_B^T \quad \mathbf{c}_D^T)$$

where subscripts B and D denote basis and nonbasis, respectively.

Then the linear programming problem becomes:

$$\begin{aligned} Min \quad & z = \mathbf{c}_B^T\mathbf{x}_B + \mathbf{c}_D^T\mathbf{x}_D \\ s.t. \quad & B\mathbf{x}_B + D\mathbf{x}_D = \mathbf{b} \\ & \mathbf{x}_B \geq \mathbf{0} \quad , \quad \mathbf{x}_D \geq \mathbf{0} \end{aligned} \tag{3.2}$$

The basis feasible solution of the LP can be expressed as:

$$\mathbf{x}_B = B^{-1}\mathbf{b} - B^{-1}D\mathbf{x}_D \tag{3.3}$$

Substitution into the objective function yields:

$$\begin{aligned} z &= \mathbf{c}_B^T(B^{-1}\mathbf{b} - B^{-1}D\mathbf{x}_D) + \mathbf{c}_D^T\mathbf{x}_D \\ &= \mathbf{c}_B^T B^{-1}\mathbf{b} + (\mathbf{c}_D^T - \mathbf{c}_B^T B^{-1}D)\mathbf{x}_D \end{aligned} \tag{3.4}$$

Equation 3.3 and Equation 3.4 express the variable $\mathbf{x}$ and objective function value z in terms of $\mathbf{x}_D$. The term

$$\lambda_D^T = \mathbf{c}_D^T - \mathbf{c}_B^T B^{-1}D$$

is called *the reduced cost vector* (nonbasic variables).

3.5 Duality of LP

The dual of problem (1) is defined as follows

$$\begin{aligned} Min \quad & \pi^T\mathbf{b} \\ s.t. \quad & \pi^T A \leq \mathbf{c}^T \end{aligned} \tag{3.5}$$

where π is the dual variables.

By the duality theorem of LP, if either of the Equation 3.2 and Equation 3.5 has a finite optimal solution, so does the other, and the corresponding optimal objective function values are equal.

It can be shown that $\pi^T = \mathbf{c}_B^T B^{-1}$, which is called *the pricing vector.* Thus the reduced cost vector can also be written as:

$$\lambda_D = \mathbf{c}_D - D^T\pi$$

3.6 Optimality Conditions

If for some basic feasible solution, $\lambda_D \geq \mathbf{0}$, then that solution is optimal. This is the direct result of Equation 3.4:

$$z = \mathbf{c}_B^T B^{-1}\mathbf{b} + \lambda_D^T \mathbf{x}_D$$

since if $\lambda_D < \mathbf{0}$, it is still possible to increase $\mathbf{x}_D$ so that the value of the objective function is decreased. For some basic feasible solution with $\lambda_D \geq \mathbf{0}$, the optimal solution is found as:

$$\begin{aligned} z^* &= \mathbf{c}_B^T B^{-1}\mathbf{b} = \pi^{*T}\mathbf{b} = \mathbf{c}^T\mathbf{x}^* \\ \mathbf{x}^* &= (\mathbf{x}_B^* \quad \mathbf{0}) \end{aligned}$$

4. OPTIMIZATION CONDITIONS FOR PHASE EQUILIBRIUM PROBLEM

The Gibbs free energy of a closed system at constant pressure and temperature can be expressed as:

$$G = \sum_{i=1}^{NSP} n_i \mu_i$$

where

NSP = total species in the system,

n_i = mole number of species i,

μ_i = chemical potential of species i, or $\frac{\partial G}{\partial n_i}$.

The phase equilibrium problem then can be expressed as the following minimization problem:

$$\begin{aligned} Min \quad G &= \sum_{i=1}^{NSP} n_i \mu_i \\ s.t. \quad A\mathbf{n} &= \mathbf{b} \\ \mathbf{n} &\geq \mathbf{0} \end{aligned} \tag{4.1}$$

The linear constraints are the charge and mass balance. From numerical calculation point of view, the rows of matrix A should be linearly independent.

For the electrolyte solid-liquid phase equilibrium with NS solid phases and NI completely dissociated ionic species in the aqueous solution phase, Equation 4.2 may be rewritten as (assume pure solid phases):

$$\begin{aligned} Min \quad G &= \sum_{i=1}^{NI+1} n_i\mu_i + \sum_{i=NI+2}^{NSP} n_i\mu_i^o \\ s.t. \quad A\mathbf{n} &= \mathbf{b} \\ \mathbf{n} &\geq \mathbf{0} \end{aligned} \tag{4.2}$$

where NSP = NS + NI + 1, μ_i^o = the standard chemical potential of the solid phase i which is assumed to be pure and one represents the solvent water.

4.1 First-Order Necessary Conditions (Kuhn-Tucker Conditions)

Suppose the constraints of Equation 4.3 are linearly independent. Let $\mathbf{n}^*$ be a local minimum point for Equation 4.3. Then there is a vector π and a vector $\lambda \geq \mathbf{0}$ such that:

$$\begin{aligned} \nabla G(\mathbf{n}^*) + (A^T \quad I)\begin{pmatrix} \pi^* \\ -\lambda^* \end{pmatrix} &= \mathbf{0} \\ \lambda^{*T}\mathbf{n}^* &= \mathbf{0} \end{aligned} \tag{4.3}$$

Equation 4.3 has significant consequences. It states:

- $\lambda_j > 0$, if jth solid phase does NOT exist at equilibrium;
- $\lambda_j = 0$, if jth solid phase exists at equilibrium.

4.2 Second-Order Conditions

If $\mathbf{n}^*$ is a local minimum point of Equation 4.3, then the Hessian:

$$H = \left(\frac{\partial^2 G}{\partial n_i \partial n_j} \right)_{T,P}$$

of Gibbs free energy is *positive semidefinite.*

5. UNIQUENESS OF CHEMICAL AND PHASE EQUILIBRIUM PROBLEM

The uniqueness of chemical and phase equilibrium problem defined by Equation 4.2 or Equation 4.3 is related to the conditions of finding the global minimum of Equation 4.2 or Equation 4.3. The optimality condition discussed in last section are all local properties. The only assurance of the global optimality of Equation 4.2 or Equation 4.3 is by the theorem which states that if a function is a convex function defined on convex set, then any local minimum of the function is also a global minimum.

The thermodynamic models (empirical or semi-empirical) of the Gibbs free energy available may not be convex functions. Thus the global minimum may or may not be found during the optimization processes. It has been proved that the unique solution exists for a single ideal-solution phase system (Shapiro and Shapley, 1965). The non-uniqueness for nonideal system has been discussed by many authors (Othmer, 1976; Caram and Scriven, 1976; Heidemann, 1978).

It can be shown, however, that the local minimum of the Equation 4.3 corresponds to a stable phase assemblage. This is the result of the second-order optimality condition and the stability criteria. The proof is given in Appendix A.

6. PHASE EQUILIBRIUM ALGORITHM USING LARGE-SCALE OPTIMIZATION TECHNIQUES

The motivation of the development of a large-scale optimization technique arises because in many nonlinear problems only a small percentage of the variables are in the nonlinear part of the objective function. This is the case for the solid-liquid equilibrium problem. The nonlinear portion of the Gibbs free energy arises from the solution phase only, which consists of a predetermined small number of ionic species and solvent, water. The remaining parts of the Gibbs energy arise from pure solid phase, which has a linear form. It is not known *a priori* how many of the possible solid phases are present at equilibrium. The actual number of solid phases is determined by the Gibbs phase rule, and will not exceed the number of ionic species or the number of constraints.

Almost all the practical large-scale optimization techniques utilize linear programming as part of their procedures. Griffith and Stewart (1961) proposed the Approximation Programming, in which they linearized the nonlinear part of the objective function and the nonlinear constraints, then solved the posed problem with a LP procedure. An iteration method is performed in order to get the desired accuracy.

Taking a second order approximation of the nonlinear part of the objective function, another method was proposed by Murtagh and Saunders (1978). Although

it was originally intended for linealy constrained problems, it has been generalized to handle nonlinear constraints as well (Murtagh and Saunders, 1987). It is the combination of the revised simplex method of LP and the quasi-Newton method of unconstrained NLP.

Since the chemical potential of species i is defined as:

$$\mu_i = \mu_i^o + RT \ln \gamma_i m_i$$

where γ_i, and m_i are activity coefficient and molality of i.

Rearrange Equation 4.3 as follow:

$$\begin{aligned} Min \quad G = F(\mathbf{n}) \; &+ \; \sum_{i=1}^{NSP} n_i \mu_i^o \\ s.t \qquad A\mathbf{n} \; &= \; \mathbf{b} \\ \mathbf{n} \; &\geq \; \mathbf{0} \end{aligned} \tag{6.1}$$

The nonlinearity is due to the logarithm in the chemical potential of the solution phase which is represented as function F(**n**). The number of nonlinear variables is (NI+1), corresponding to the number of dissolved ionic species in the solution plus water.

Similar to the LP case, we partition the variables into basic, superbasic and nonbasic variables. The basic and nonbasic variables have the same definition as in LP. The superbasic variables are the variables that lie between their bounds. The introduction of the notion of superbasic variables came from the knowledge that the optimum point is not a basic solution in NLP but it is "rather near" basic by realizing the number of nonlinear variables is small.

In the solid-liquid phase equilibrium situation, it seems reasonable to assume that the basic variables consist the moles of ionic species and moles of water since they

are usually not zero at equilibrium. The variables corresponding to the precipitated solid phase are superbasic variables and the non- precipitated solid phase are nonbasic variables.

We now partition the constraints as follows:

$$A\mathbf{n} = [B \quad S \quad N] \begin{bmatrix} \mathbf{n}_B \\ \mathbf{n}_S \\ \mathbf{n}_N \end{bmatrix} \tag{6.2}$$

where

B is $m \times m$ non-singular basic matrix,

S is $m \times s$ superbasic matrix,

N is $m \times (NSP - m - s)$ nonbasic matrix.

Consider the Taylor series of the Gibbs free energy

$$G(\mathbf{n} + \Delta\mathbf{n}) = G(\mathbf{n}) + \mu^T \Delta\mathbf{n} + \frac{1}{2}\Delta\mathbf{n}^T \mathbf{H}(\mathbf{n} + \theta\Delta\mathbf{n})\Delta\mathbf{n}$$

where $0 \leq \theta \leq 1$, and H is the Hessian matrix.

Then we have the following properties:

Property 1 (Feasible Direction):

$$\begin{bmatrix} B & S & N \\ \mathbf{0} & \mathbf{0} & I \end{bmatrix} \begin{bmatrix} \Delta\mathbf{n}_B \\ \Delta\mathbf{n}_S \\ \Delta\mathbf{n}_N \end{bmatrix} = \mathbf{0} \tag{6.3}$$

Property 2 (Kuhn-Tucker Condition):

For $\lambda \geq \mathbf{0}$,

$$\begin{bmatrix} \mu_B \\ \mu_S \\ \mu_N \end{bmatrix} + H \begin{bmatrix} \Delta \mathbf{n_B} \\ \Delta \mathbf{n_S} \\ \Delta \mathbf{n_N} \end{bmatrix} = \begin{bmatrix} B^T & \mathbf{0} \\ S^T & \mathbf{0} \\ N^T & I \end{bmatrix} \begin{bmatrix} \pi \\ \lambda \end{bmatrix} \tag{6.4}$$

where π and λ are the Lagrangian multipliers corresponding to general linear constraints and variable constraints, respectively.

From Property 1, we obtain:

$$\Delta \mathbf{n}_N = \mathbf{0}$$

$$\Delta \mathbf{n}_B = -B^{-1} S \Delta \mathbf{n}_S$$

Let $W = B^{-1}S$, then:

$$\Delta \mathbf{n} = \begin{pmatrix} -W \\ I \\ \mathbf{0} \end{pmatrix} \Delta \mathbf{n}_S \tag{6.5}$$

which implies that only superbasic variables $\mathbf{n}_S$ are independent variables.

Multiplying Equation 6.4 by the matrix:

$$\begin{bmatrix} I & \mathbf{0} & \mathbf{0} \\ -W^T & I & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & I \end{bmatrix}$$

yields:

$$B^T \pi = \mu_B + [I \quad \mathbf{0} \quad \mathbf{0}] \begin{bmatrix} -W \\ I \\ \mathbf{0} \end{bmatrix} \Delta \mathbf{n}_B$$

$$\lambda = \mu_N - N^T\pi + [\mathbf{0} \quad \mathbf{0} \quad I]H \begin{bmatrix} -W \\ I \\ \mathbf{0} \end{bmatrix} \Delta \mathbf{n}_S$$

At stationary point where $\|\Delta \mathbf{n}_S\| = \mathbf{0}$, we have:

$$B^T\pi = \mu_B \tag{6.6}$$

Or

$$\pi^T = \mu_B^T B^{-1}$$

$$\lambda = \mu_N - N^T\pi = \mu_N - N^T(B^T)^{-1}\mu_B \tag{6.7}$$

It is not difficult to realize from the previous LP discussion that π is the pricing vector and λ is reduced cost vector. The only difference is that the derivatives of the objective function with respect to basic and nonbasic variables, μ_B and μ_N, are not constant. The significant impact of these two equations, Equation 6.6 and Equation 6.7, will be clearer in the following discussion.

The third result obtained from the multiplication is:

$$\begin{bmatrix} -W^T & I & \mathbf{0} \end{bmatrix} H \begin{bmatrix} -W \\ I \\ \mathbf{0} \end{bmatrix} \Delta \mathbf{n}_S = -\mathbf{h} \tag{6.8}$$

where

$$\mathbf{h} = [-W^T \quad I \quad \mathbf{0}]\mu = \mu_S - W^T\mu_B = \mu_S - S^T\pi \tag{6.9}$$

Now $\|h\| = \mathbf{0}$ becomes the necessary condition for the stationary point $\|\Delta n\| = \mathbf{0}$ for the current basis and superbasis. Note that the Equation 6.8 gives a Newton step with respect to superbasic variables, $\mathbf{n}_S$.

The thermodynamic implication of Equation 6.7 and Equation 6.9 are rather significant. By thermodynamic principles, the chemical potential of the pure solid phases should have the following relations at the equilibrium

$$\mu^{o}_{Solid} = \sum_i \nu_i \mu_i \quad \textit{for precipitated phases} \tag{6.10}$$

and

$$\mu^{o}_{Solid} > \sum_i \nu_i \mu_i \quad \textit{for nonexisting phases} \tag{6.11}$$

where ν is the stoichiometric coefficients for the solid formation reaction.

The Equation 6.10 is the necessary condition for stationary point. Also Equation 6.10 and Equation 6.11 are the Kuhn-Tucker conditions for Lagrangian multiplier λ ($\lambda = 0$ for precipitate phases and $\lambda > 0$ for not precipitated phases). This in turn is the counterpart of the LP optimality conditions.

In the case of $\lambda < 0$, or

$$\mu^{o}_{Solid} < \sum_i \nu_i \mu_i$$

this suggests that the solid phase is more stable than solution phase, thus the corresponding solid should precipitate, i.e. add a new element to the superbasis. This is exactly the simplex procedure.

It can also be shown mathematically that if NL is the number of nonlinear variables in the objective function, there is at most NL superbasic variables at optimal (Lasdon and Waren, 1978). Thermodynamically, this is nothing but the Gibbs phase rule for solid-liquid equilibrium.

Based on the above discussion, the numerical algorithm is summarized as follows:

STEP 1 : Convergence Test ($\|\mathbf{h}\| = \mathbf{0}$). If no, go to STEP 3. (In terms of thermodynamics, solve for the compositions of each phase for current phase assemblage.)

STEP 2 : Phase selection (Revised simplex procedure). Select the most negative λ, add to the current superbasis. If all $\lambda \geq 0$, stop. Optimal found.

STEP 3 : Direction search (Quasi-Newton step) Compute Δn.

STEP 4 : Linear Search (Optimal step size) Find step size α , which solves

$$Min \quad G(\mathbf{n} + \alpha \mathbf{\Delta n})$$

for $0 \leq \alpha \leq \alpha_{max}$, α_{max} is the largest α value for which $(\mathbf{n} + \alpha \mathbf{\Delta n})$ is feasible. If $\alpha \leq \alpha_{max}$, go to STEP1. If $\alpha > \alpha_{max}$, change basis or superbasis according to the actual situation. Go to STEP 1.

7. NUMERICAL EXAMPLES

The solubilities of $NaCl - KCl - MgCl_2 - CaCl_2 - H_2O$ system have been measured over the years by many authors. Among recent studies, Motayama et al. (1972, 1975) reported extensive experimental results for this system as well as ternary and quaternary subsystems. Therefore we take this system as as example to show our computation scheme and compare our calculation results with the experimental data. The nonideality of the electrolyte solution was calculated by using Pitzer's model (Pitzer, 1973). The equations for calculating activity coefficients of ionic species and the osmotic coefficient of water are given in Appendix B. The Pitzer model parameters and the standard chemical potentials of ion, water and the pure solid phases at 25^oC and 0^oC were taken from Harvie and Weare (1980) and Spencer, Moller and Weare (1990), respectively. The "computer experiments" were performed by gradually removing water so that univariant lines and invariant points could be found. The simulation results for different systems at 25^oC and 0^oC were then plotted to show the corresponding phase diagrams.

As from the numerical consideration, a low bound for each mole number of ionic species was given since the chemical potential is not defined at zero concentration. The low bound of 10^{-4} or less is found appropriate.

The minimization problem was set up by assuming all the possible phases with-

out considering the Gibbs phase rule at the beginning of the calculation. The actual phase(s) presented at the equilibrium were then obtained through the optimization procedure discussed in previous section. If certain possible phases are not considered at the beginning of the computation, a correct answer can be obtained only if those phases are really absent from the phase assemblage at the equilibrium.

It is worth pointing out that deleting or adding a phase to the phase assemblage during the optimization procedure is based on the revised simplex method, which is also identical to the thermodynamic criteria. Therefore, it is expected that the phase selection procedure will be stable and accurate. Comparing with the SQP method, SQP is active working set method. It deletes or adds a phase to the phase assemblage by examining the estimated corresponding Lagrangian multiplier value. A phase is deleted or added if the corresponding Lagrangian multiplier,λ, is positive or zero, respectively. An inaccurate estimate of the Lagrangian multiplier values might cause incorrect deleting or adding a phase (Gill et al., 1981). Therefore, extra care is needed for the SQP calculations.

7.1 $NaCl - KCl - MgCl_2 - H_2O$ system at 298.15 K and 273.15 K

The problem was set up by assuming the following possible solid phases: Halite (NaCl), Sylvite (KCl), Bischofite ($MgCl_2.6H_2O$) and Carnallite ($KMgCl_3.6H_2O$).

According to the Gibbs phase rule, at most three out of those four solids can precipitate at the same time.

As discussed in previous section, the phase selection criteria for all four possible solid phases are:

$$\mu^o_{NaCl} < \mu_{Na^+} + \mu_{Cl^-}$$

Table 7.1: Invariant points of $NaCl - KCl - MgCl_2 - H_2O$ at 298.15K. Molality

	NaCl	KCl	$MgCl_2$	Solid Phase
(1)	0.49	0.56	4.05	
(2)	0.49	0.56	4.05	$NaCl + KCl + KMgCl_3.6H_2O$
(3)	0.52	0.65	3.94	
(1)	0.09	0.02	5.70	
(2)	0.003	0.08	2.47	$NaCl + MgCl_2.6H_2O + KMgCl_3.6H_2O$
(3)	0.09	0.03	5.84	

where (1) = This work, (2) = SQP method, (3) = Experimental data.

Table 7.2: Invariant points of $NaCl - KCl - MgCl_2 - H_2O$ at 273.15 K. Molality

	NaCl	KCl	$MgCl_2$	Solid Phase
(1)	0.58	0.43	3.62	
(2)	0.79	0.63	3.39	$NaCl + KCl + KMgCl_3.6H_2O$
(3)	0.49	0.43	3.59	
(1)	0.056	0.008	5.52	
(2)	0.052	0.015	5.59	$NaCl + MgCl_2.6H_2O + KMgCl_3.6H_2O$
(3)	0.052	0.010	5.36	

where (1) = This work, (2) = SQP method, (3) = Experimental data.

$$\begin{aligned}
\mu^o_{KCl} &< \mu_{K^+} + \mu_{Cl^-} \\
\mu^o_{MgCl_2.6H_2O} &< \mu_{Mg^{2+}} + 2\mu_{Cl^-} + 6\mu_{H_2O} \\
\mu^o_{KMgCl_3.6H_2O} &< \mu_{K^+} + \mu_{Mg^{2+}} + 3\mu_{Cl^-} + 6\mu_{H_2O}
\end{aligned}$$

If any of above four inequalities hold, the corresponding solid phases will precipitate out and the inequalities become equality after the algorithm converges to the optimum solution (Equation 6.9 or Equation 6.10).

The calculated invariant points of the phase diagram for 298.15 K and 273.15 K are listed in the Table 7.1 and Table 7.2 together with the results calculated by using SQP and the experimental values. All the experimental data are taken from Motoyama et al (1972, 1975). The calculated phase diagram is given in Figure 7.1

and Figure 7.2

The results obtained by using described algorithm agrees with the experimental data very well. The result obtained from SQP method is far from satisfactory both at 298.15 K and 273.15 K.

7.2 $NaCl - KCl - CaCl_2 - H_2O$ system at 298.15 K

The problem was set up by assuming the following possible solid phases: Halite (NaCl), Sylvite (KCl), Antarcticite ($CaCl_2.6H_2O$).

The precipitation criterion for antarcticite is:

$$\mu^o_{CaCl_2.6H_2O} < \mu_{Ca^{2+}} + 2\mu_{Cl^-} + 6\mu_{H_2O}$$

Since the current form of Pitzer's model will not give reliable answer for the osmotic coefficients of $CaCl_2$ at concentration above 5 molal due to the possible structure change of the Ca^{2+} in the solution (Phutela and Pitzer,1983), which is also illustrated in Figure 7.3, the calculation of the concentration region of $CaCl_2$ higher than 5 molal is not considered here.

The calculated results and the experimental values were plotted in Figure 7.4 for the univariant line for the precipitation of halite and sylvite. Although there are not many experimental data available in this region, the calculated results seem to be reliable.

7.3 $NaCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K

Again, the problem was set up by assuming the following pure solid phases: Halite (NaCl),Bischofite ($MgCl_2.6H_2O$), Antarcticite ($CaCl_2.6H_2O$) and Tachyhy-

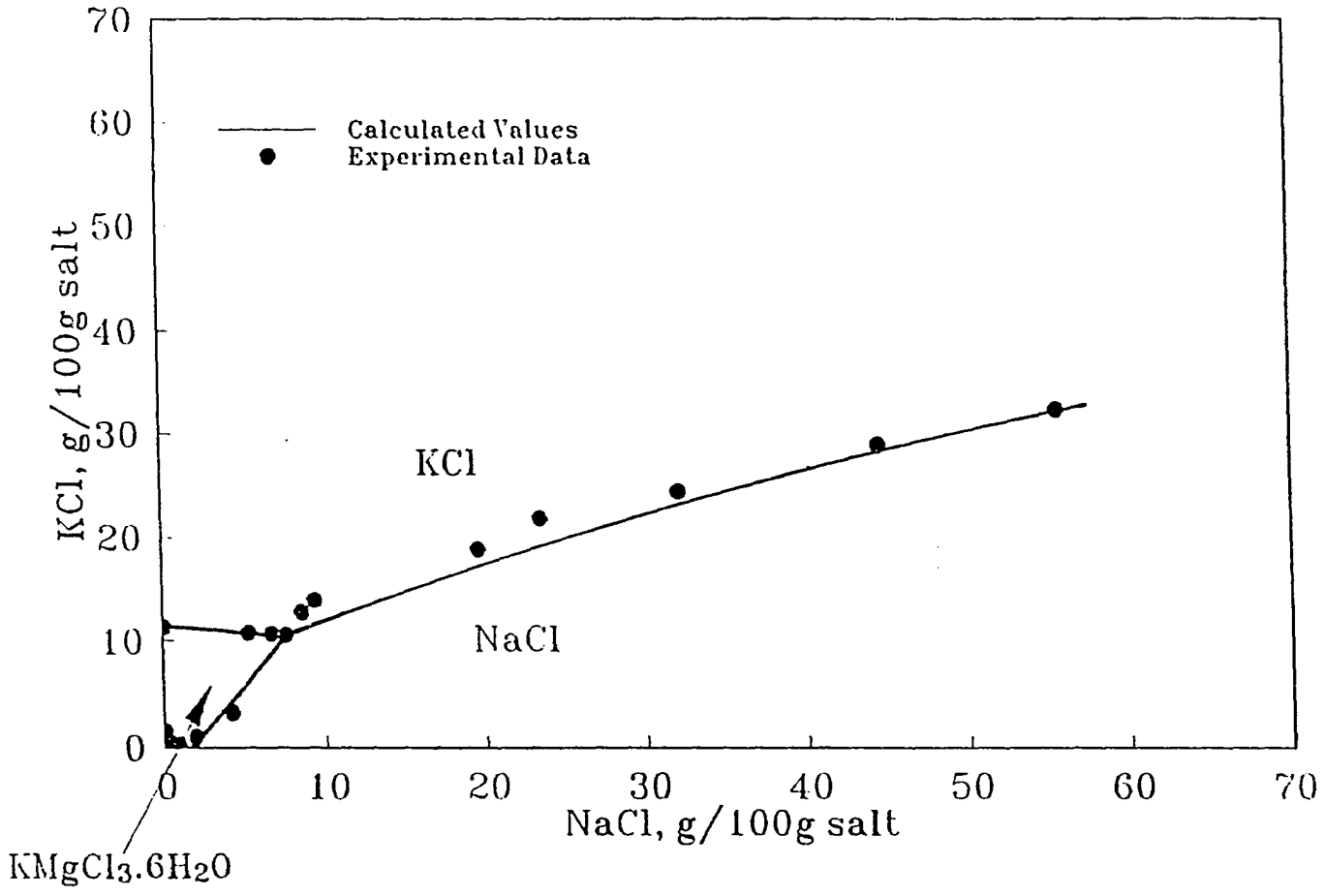

Figure 7.1: $NaCl - KCl - MgCl_2 - H_2O$ system at 298.15 K

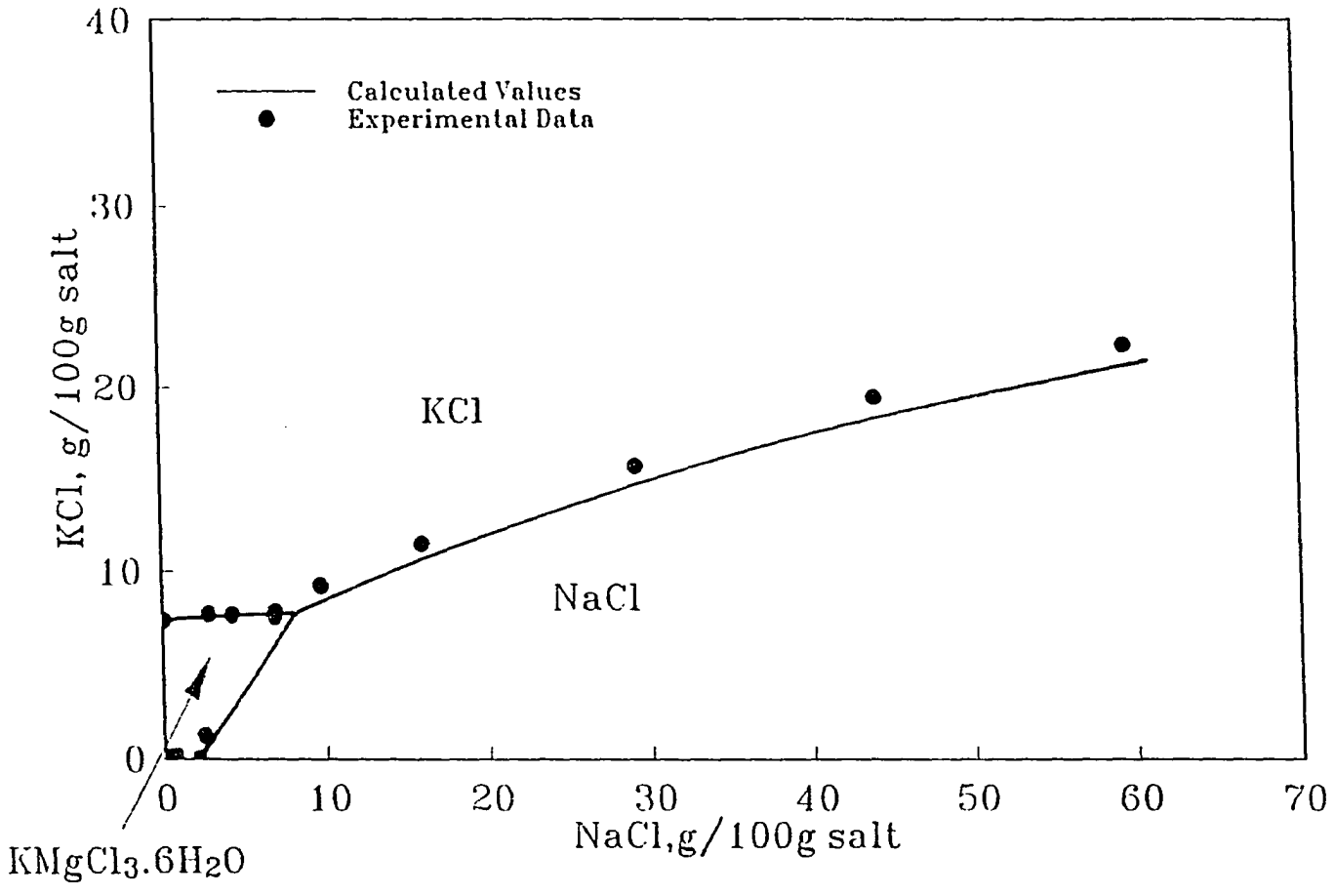

Figure 7.2: $NaCl - KCl - MgCl_2 - H_2O$ system at 273.15 K

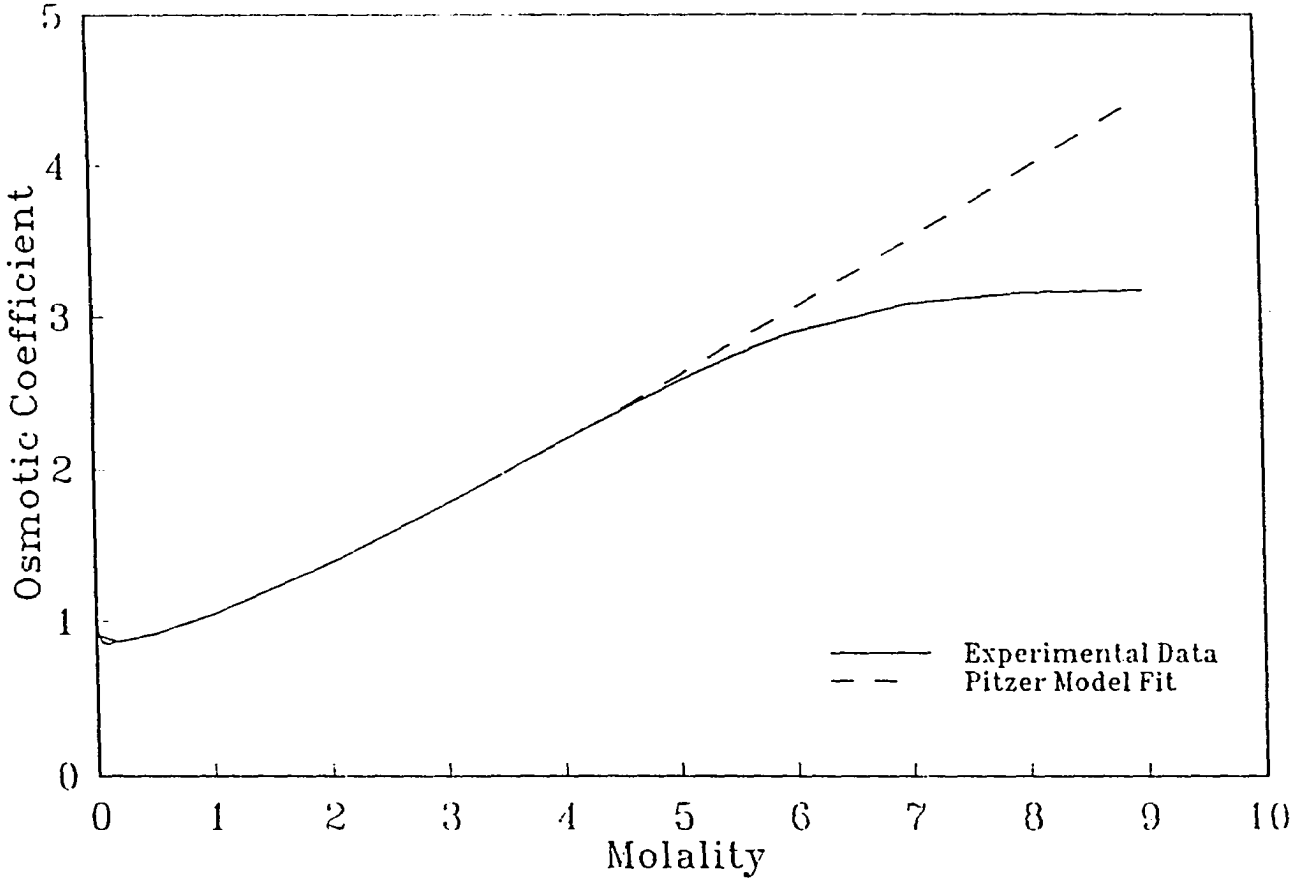

Figure 7.3: Comparison of Pitzer model fit of osmotic coefficients of $CaCl_2$ with experimental data

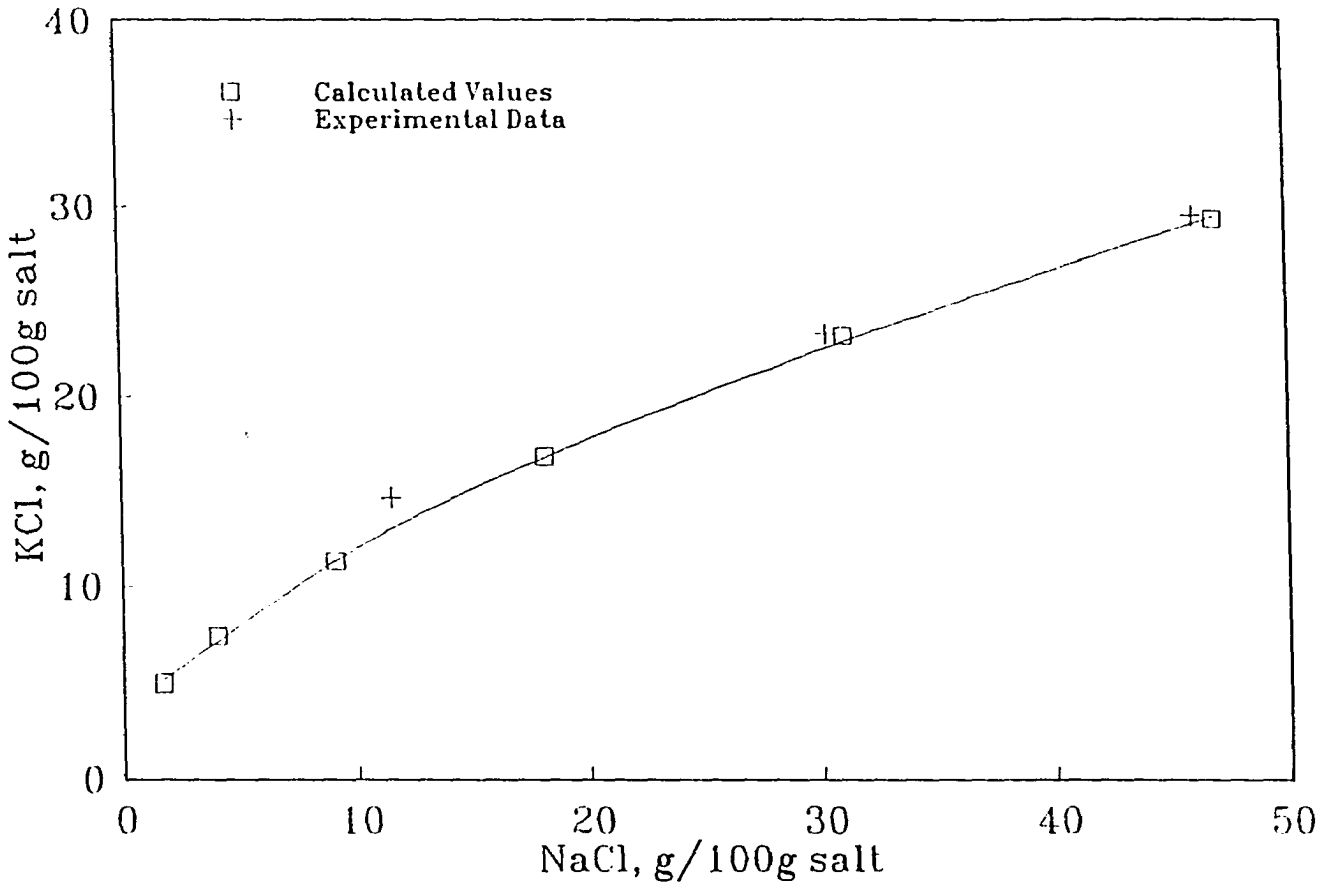

Figure 7.4: $NaCl - KCl - CaCl_2 - H_2O$ system at 298.15 K. Solid phase: NaCl + KCl

drite ($Mg_2CaCl_6.12H_2O$).

The precipitation critrion for tachyhydrite is:

$$\mu^o_{Mg_2CaCl_6.12H_2O} < 2\mu_{Mg^{2+}} + \mu_{Ca^{2+}} + 6\mu_{Cl^-} + 12\mu_{H_2O}$$

The calculated univariant line (with the precipitation of halite and bischofite) is presented in Figure 7.5. The univariant line is almost a straight line because the concentrations of NaCl in solution phase are nearly unchanged (about 0.09 molal). The calculated results agree with the experimental observations quite well.

7.4 $KCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K

There are more possible phases for this systems than previous ones. They are Sylvite (KCl),Bischofite ($MgCl_2.6H_2O$),Antarcticite ($CaCl_2.6H_2O$), Carnallite ($KMgCl_3.6H_2O$) and Tachyhydrite ($Mg_2CaCl_6.12H_2O$).

The solid phases precipitation criteria are the same as before. The calculated univariant line (with solid phases bischofite and carnallite) is given in Figure 7.6. The straight line is due to the constant KCl concentration in solution phase.

7.5 $NaCl - KCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K

For this quinary system, all the possible solid phases mentioned in previous calculation are assumed here. The equilibrium concentrations of the solution phase with the precipitation of halite, carnallite and bischofite were calculated. The calculated values were then compared with the experimental data of Motoyama et al. (1972) as well as the most recently published data of Korln and Roy (1988). The results were plotted in Figure 7.7. The agreement is quite good.

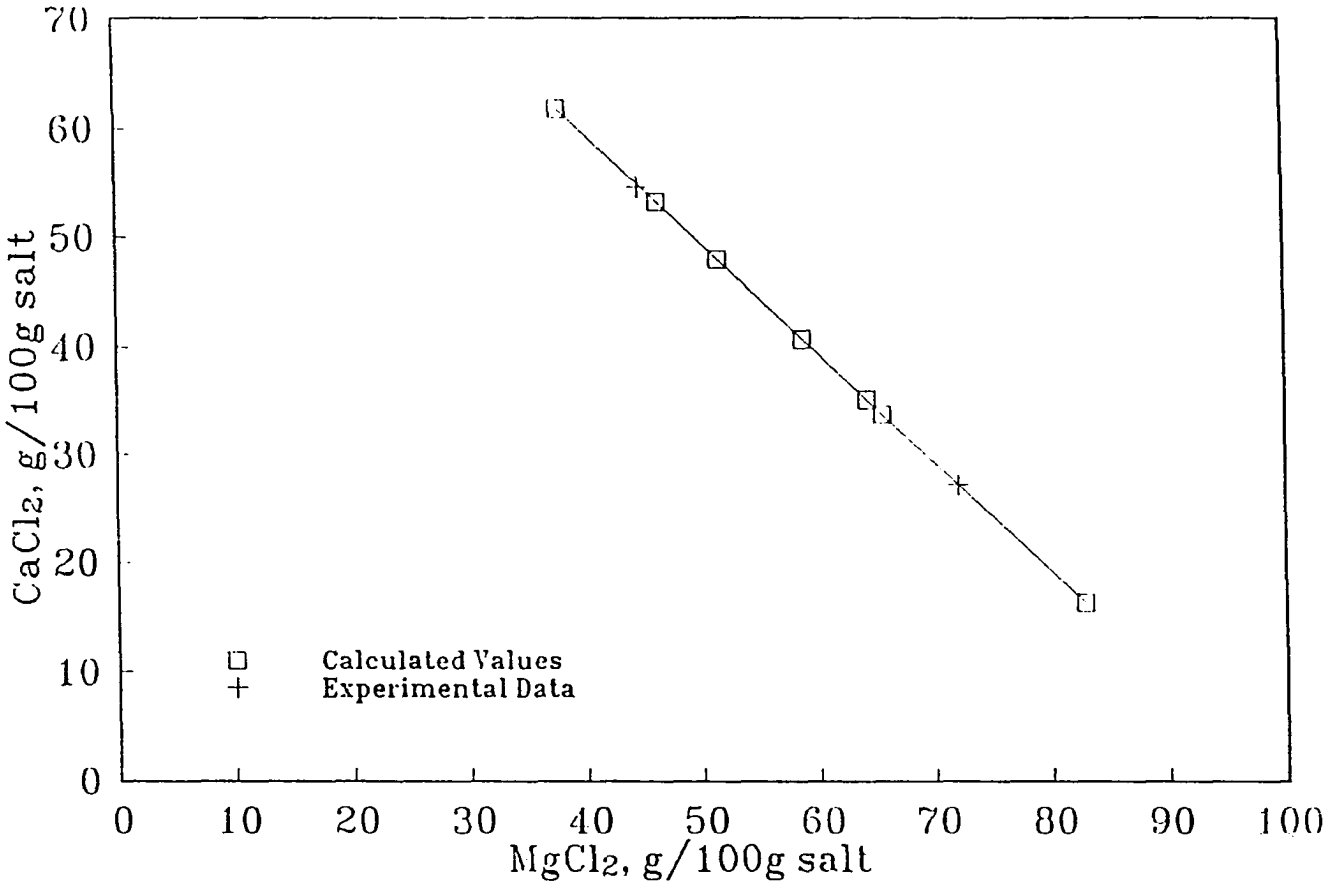

Figure 7.5: $NaCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K. Solid phase: NaCl + $MgCl_2.6H_2O$

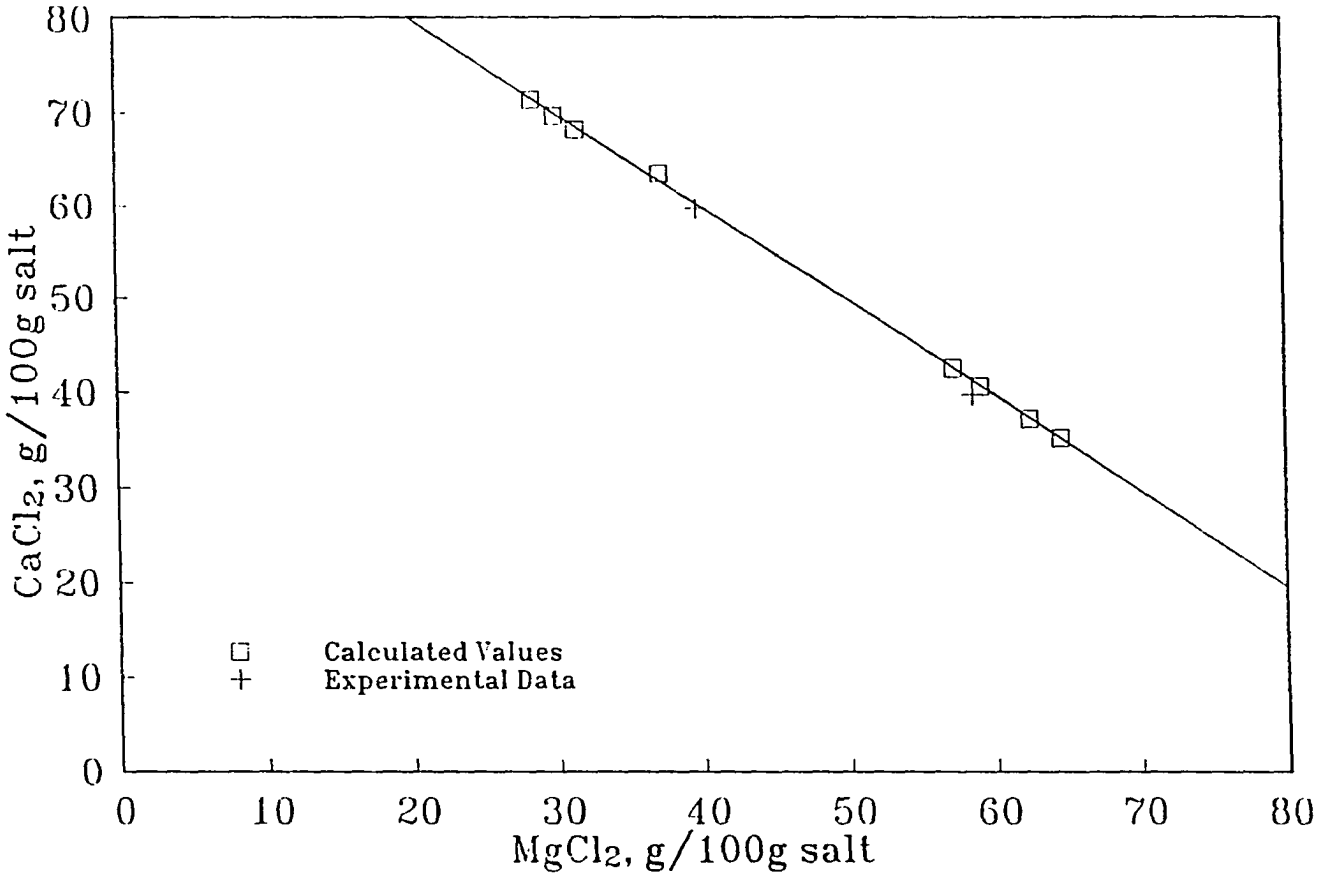

Figure 7.6: $KCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K. Solid phase: KCl + $KMgCl_3.6H_2O$

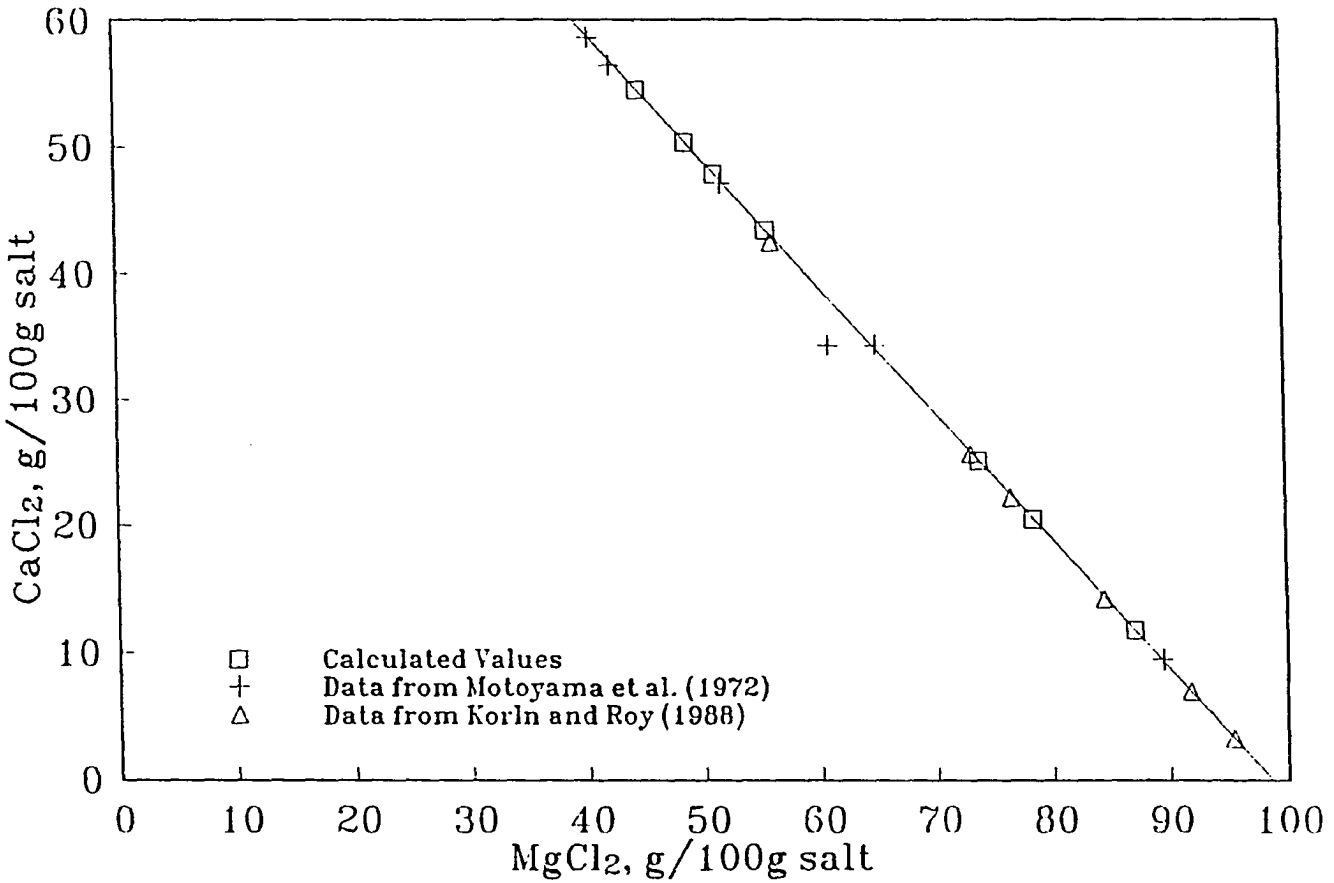

Figure 7.7: $NaCl - KCl - MgCl_2 - CaCl_2 - H_2O$ system at 298.15 K. Solid phase: NaCl + $KMgCl_3.6H_2O$ + $MgCl_2.6H_2O$

It should be pointed out that our assumption of the possible solid phases at the beginning of the calculation was based on the experimental results. For the actual prediction case when the phase equilibrium information is not available, all possible phases should be considered. Since the magnesium and calcium chloride crystallized in various forms, the following solid phases might also be considered: $MgCl_2.12H_2O, MgCl_2.4H_2O, MgCl_2.2H_2O, CaCl_2.4H_2O$ and $CaCl_2.2H_2O$.

As the list of the possible solid phases goes on, the dimension of the optimization problem increases. But the nonlinear part of the Gibbs free energy, i.e. the solution phase, is left unchanged. The advantage of the large-scale optimization technique as described in this work is then fully realized.

8. CONCLUSIONS

The phase equilibrium calculation algorithm described above combined the chemical thermodynamic principles with the mathematical procedures. By considering the maximum number of possible phases at the beginning of the calculation, the phase selection criteria are identical to the mathematical considerations towards minimization. The Gibbs phase rule was satisfied by the mathematical theorem. The comparison between this algorithm and SQP method at 298.15 K and 273.15 K for $NaCl - KCl - MgCl_2 - H_2O$ system demonstrated the advantage of this algorithm over the SQP method. For the complicated quinary system $NaCl - KCl - MgCl_2 - CaCl_2 - H_2O$ at 298.15 K, the current algorithm gave accurate predictions.

9. NOMENCLATURE

b = Right hand side; The initial system input,

m = Number of constraints,

m_i = Molality of species i,

n = Mole number,

A = Coefficient matrix,

B = Basis matrix,

D = Non-basis matrix in LP,

G = Gibbs free energy,

I = Ionic strength,

H = Hessian matrix,

N = Nonbasis matrix in NLP,

NI = number of dissolved ionic species in solution,

NS = number of possible solid phases at equilibrium,

NSP = total number of species (ion, molecular and solid) in solution,

S = Superbasis matrix,

W = defined quantity.

Greek Letters

γ = Activity coefficients,

ϕ = Osmotic coefficients,

λ = Lagrangian multiplier for variable constraints,

μ = Chemical potential,

ν = Stoichiometric coefficients for the solid formation reactions,

π = Lagrangian multiplier for linear constraints.

Subscripts

a, a' = anion,

c, c' = cation,

ca = salt ca,

B = Basis,

M = cation,

N = Nonbasis,

S = Superbasis,

X = anion.

Superscripts

T = Transpose,

o = standard state,

$*$ = Optimum solution.

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APPENDIX A. STABILITY AND OPTIMUM CRITERIA

Let $y^{(0)}$ be the total internal energy of a system:

$$y^{(0)} = f(S, V, n_1, n_2, ..., n_n) = f(\mathbf{x})$$

where S and V are entropy and volume of the system,respectively. Then the necessary conditions for a stable system are:

$$y_{kk}^{(k-1)} > 0,$$

$$y_{(k+1)(k+1)}^{k} = 0, \qquad k = 1, 2, ..., NSP + 1$$

where

$$y_{kk}^{(k-1)} = \left(\frac{\partial^2 y^{(k-1)}}{\partial x_k^2} \right)$$

(For more detail, see Modell and Reid (1983))

For k = 3, we have

$$y_{33}^{(2)} = \frac{\partial^2 G}{\partial n_1^2} > 0$$

For k = 4, we have

$$y_{44}^{(3)} = \frac{\begin{vmatrix} \frac{\partial^2 G}{\partial n_1^2} & \frac{\partial^2 G}{\partial n_1 \partial n_2} \\ \frac{\partial^2 G}{\partial n_2 \partial n_1} & \frac{\partial^2 G}{\partial n_2^2} \end{vmatrix}}{\frac{\partial^2 G}{\partial n_1^2}} > 0$$

Thus

$$\begin{vmatrix} \frac{\partial^2 G}{\partial n_1^2} & \frac{\partial^2 G}{\partial n_1 \partial n_2} \\ \frac{\partial^2 G}{\partial n_2 \partial n_1} & \frac{\partial^2 G}{\partial n_2^2} \end{vmatrix} > 0$$

It can be shown that:

For k = n + 1

$$\begin{vmatrix} \frac{\partial^2 G}{\partial n_1^2} & \frac{\partial^2 G}{\partial n_1 \partial n_2} & \cdots & \frac{\partial^2 G}{\partial n_1 \partial n_{n-1}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial^2 G}{\partial n_{n-1} \partial n_1} & \frac{\partial^2 G}{\partial n_{n-1} \partial n_2} & \cdots & \frac{\partial^2 G}{\partial n_{n-1}^2} \end{vmatrix} > 0$$

For k = n + 2

$$\begin{vmatrix} \frac{\partial^2 G}{\partial n_1^2} & \frac{\partial^2 G}{\partial n_1 \partial n_2} & \cdots & \frac{\partial^2 G}{\partial n_1 \partial n_n} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial^2 G}{\partial n_n \partial n_1} & \frac{\partial^2 G}{\partial n_n \partial n_2} & \cdots & \frac{\partial^2 G}{\partial n_n^2} \end{vmatrix} = 0$$

This also means that the Hessian of the Gibbs free energy should be positive semidefinite.

APPENDIX B. PITZER'S EQUATIONS

The osmotic coefficients ϕ are calculated as follows

$$
\begin{aligned}
(\phi - 1) &= (2/\sum_i m_i)[-A_\phi I^{3/2}/(1 + bI^{1/2}) + \sum_c \sum_a m_c m_a (B^\phi_{ca} + ZC_{ca}) \\
&+ \sum_{c<} \sum_{c'} m_c m_{c'} (\Phi^\phi_{cc'} + \sum_a m_a \psi_{cc'a}) + \sum_{a<} \sum_{a'} m_a m_{a'} (\Phi^\phi_{aa'} + \sum_c m_c \psi_{cac'})
\end{aligned}
$$

The activity coefficients of cation M and anion X are

$$
\begin{aligned}
\ln \gamma_M &= z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\Phi_{Mc} + \sum_a m_a \psi_{Mca}) \\
&+ \sum_{a<} \sum_{a'} m_a m_{a'} \psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca}
\end{aligned}
$$

$$
\begin{aligned}
\ln \gamma_X &= z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a (2\Phi_{Xa} + \sum_c m_c \psi_{cXa}) \\
&+ \sum_{c<} \sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca}
\end{aligned}
$$

where c and c' are actions and a and a' are anions. The ion charges are indicated by z_M and z_X.

The quantity F is as follows:

$$
\begin{aligned}
F &= -A_\phi [I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] \\
&+ \sum_c \sum_a m_c m_a B'_{ca} + \sum_{c<} \sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_{a<} \sum_{a'} m_a m_{a'} \Phi'_{aa'}
\end{aligned}
$$

where I is the ionic strength, B's, C's Φ's and ψ's are Pitzer model parameters. b is a model constant, 1.2. A_ϕ is Pitzer -Debye-Huckel limiting slope. The definitions of those parameters were given by Pitzer (1973). They are not repeated here.

PART III.

PHASE EQUILIBRIUM OF THE Na-K-Mg-Cl-NO_3-H_2O SYSTEM AT THE TEMPERATURES BELOW 25^oC

1. ABSTRACT

The phase equilibria of the $Na - K - Mg - Cl - NO_3 - H_2O$ system at the temperatures below 25^oC were studied. The Pitzer model was used to calculate the activity and osmotic coefficients. The revised Helgeson, Kirkham and Flowers (revised HKF model) was used to calculate the standard state chemical potential of the aqueous ionic species. The standard state chemical potentials of the solids were correlated from the single salt solubility calculations. The multicomponent salt system phase equilibria were then calculated and compared with the experimental data when available. Reasonable agreements were obtained.

2. INTRODUCTION

Many industrial process and waste streams consist of aqueous mixtures of chloride, nitrate and sulfate salts of alkali metals and alkaline earths. Frequently these streams also contain dissolved organics. As a consequence these streams pose problems in separation and these waste streams of this nature must be incinerated, a very expensive process considering that the streams are mostly water. An alternative process is the concentration of the streams by freezing out pure water. Often this results in the generation of supersaturated solutions with consequent precipitation or crystallization of the dissolved salt. Suitable techniques can be developed to produce the ice and salt crystals which then may be recovered. Such a process has a significant energy advantage over incineration.

One of the problems associated with the development of such a process is the prediction of the composition of the remaining liquor and the quantity and composition of the solids produced. As the process must be carried out at temperatures below the freezing point of water it is of interest to provide a means of determining the phase equilibrium of mixed aqueous salt solutions at temperatures below 0°C. Little solubility data exists for pure salts at these temperatures and far less data are available for mixed salt phase equilibria. The following analysis provides a means for predicting the phase equilibria of aqueous mixed salt solutions of chloride and

nitrate salts of sodium, potassium and magnesium down to 0^oC. One would expect for temperatures say 5° or 10° below 0^oC that extrapolation of these results would provide usable information for design purposes.

In general, the phase equilibrium problem can be formulated as the following minimization problem:

$$\begin{aligned} Min \quad G &= \sum_{i=1}^{NSP} n_i \mu_i \\ s.t \quad A\mathbf{n} &= \mathbf{n_T} \\ \mathbf{n} &\geq \mathbf{0} \end{aligned} \tag{2.1}$$

where the linear constraints are the charge and mass balance, NSP is the total number of species (ion and molecule) in the system and the chemical potential of species i, μ_i, is defined as usual:

$$\mu_i = \mu_i^o + RTln\gamma_i m_i$$

The following thermodynamic information is necessary so that the phase equilibrium calculation can be carried out.

(1). A thermodynamic model for the activity coefficient calculation;

(2). The model parameter values at the temperature and pressure concerned;

(3). The standard state chemical potential of all the species (ion and molecule) in the system at the temperature and pressure concerned.

During the past decade, many empirical or semi-empirical thermodynamic models for calculating the activity and osmotic coefficients of electrolyte solutions have been proposed (Pitzer, 1973; Cruz and Renon (1978); Chen et al. (1982) and Sander

et al. (1986)). But Pitzer's model has remained the most widely used one. It has been used in predicting the mineral solubilities of natural waters with great success. Harvie and Weare (1980), Harvie, Moller and Weare (1984) calculated the phase equilibria of the Na-K-Mg-Ca-Cl-SO_4-H_2O and Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system at 25°C. The studies of the natural water systems at temperatures other than 25°C also can be found in Pabalan and Pitzer (1987), Moller (1988), Greenberg and Moller (1989) and Spencer et al. (1990).

In this study, we calculated the phase equilibria of the electrolyte mixtures including NO_3^- ion, which is an important component in chemical industrial wastewater and other systems. The Pitzer's model was used for the osmotic and activity coefficients. The revised Helgeson, Kirkham, and Flowers (revised HKF model, Tanger and Holgeson, 1988) was used for the temperature dependence of the standard chemical potential of the aqueous ionic species. The solubilities were obtained through the minimization of the Gibbs free energy. The minimization procedure was described in detail in authors' previous publication (Song and Larson, in press). The calculated results were then compared with the experimental data, which showed satisfactory results.

3. GENERAL EQUATIONS FOR ACTIVITY AND OSMOTIC COEFFICIENTS (PITZER MODEL)

The osmotic coefficients ϕ are calculated as follows (Pitzer, 1973):

$$\begin{aligned}(\phi - 1) &= (2/\sum_i m_i)[-A_\phi I^{3/2}/(1+bI^{1/2}) + \sum_c \sum_a m_c m_a (B^\phi_{ca} + ZC_{ca}) \\ &+ \sum_{c<} \sum_{c'} m_c m_{c'} (\Phi^\phi_{cc'} + \sum_a m_a \psi_{cc'a}) \\ &+ \sum_{a<} \sum_{a'} (\Phi^\phi_{aa'} + \sum_c m_c \psi_{aa'c})\end{aligned} \tag{3.1}$$

The activity coefficients of cation M and anion X are:

$$\begin{aligned}\ln \gamma_M &= z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\Phi_{Mc} + \sum_a m_a \psi_{Mca}) \\ &+ \sum_{a<} \sum_{a'} m_a m_{a'} \psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca}\end{aligned} \tag{3.2}$$

$$\begin{aligned}\ln \gamma_X &= z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a (2\Phi_{Xa} + \sum_c m_c \psi_{cXa}) \\ &+ \sum_{c<} \sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca}\end{aligned} \tag{3.3}$$

where c and c' are cations and a and a' are anions. The ion charges are indicated by z_M and z_X.

The quantity F is as follows:

$$\begin{aligned}F &= -A_\phi [I^{1/2}/(1+bI^{1/2}) + (2/b)\ln(1+bI^{1/2})] \\ &+ \sum_c \sum_a m_c m_a B'_{ca} + \sum_{c<} \sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_{a<} \sum_{a'} m_a m_{a'} \Phi'_{aa'}\end{aligned} \tag{3.4}$$

where I is the ionic strength, B's, C's are the binary model parameters and Φ's and ψ's are the common-ion ternary model parameters. b is a fixed parameter, its value is assigned to be 1.2. A_ϕ is the Pitzer-Debye-Huckel limiting slopes for water, which is defined as:

$$A_\phi = 1/3(2\pi N_0 d/1000)^{1/2}[e^2/(DkT)]^{3/2}$$

where

d = the density of pure water,

N_0 = Avogadro number,

e = charge of electron,

D = the dielectric constant of water,

k = Boltzmann constant.

The A_ϕ values from 0 to 100°C have been given by Ananthaswamy and Atkinson (1984).

$$Z = \sum_i m_i |z_i|$$

The binary model parameters are defined as:

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} e^{-\alpha_1\sqrt{I}} + \beta^{(2)}_{MX} e^{-\alpha_2\sqrt{I}}$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g(\alpha_1\sqrt{I}) + \beta^{(2)}_{MX} g(\alpha_2\sqrt{I})$$

$$B'_{MX} = \beta^{(1)}_{MX} g'(\alpha_1\sqrt{I})/I + \beta^{2}_{MX} g'(\alpha_2\sqrt{I})/I$$

$$C_{MX} = C^\phi_{MX}/2\sqrt{|z_M z_X|}$$

where α_1 and α_2 are 2.0, except for 2-2 type electrolytes that α_1 = 1.4 and α_2 = 12.0. β_2 is zero for lower valence electrolytes.

The functions, $g(x)$ and $g'(x)$, are defined as follows

$$g(x) = 2[1 - (1 + x)e^{-x}]/x^2$$

$$g'(x) = -2[1 - (1 + x + \frac{1}{2}x^2)e^{-x}]/x^2$$

The ternary model parameter terms, Φ, which account for interactions between ions of like signs, are defined as follows:

$$\Phi^{\phi}_{ij} = \theta_{ij} + E_{\theta_{ij}}(I) + IE'_{\theta_{ij}}(I)$$

$$\Phi_{ij} = \theta_{ij} + E_{\theta_{ij}}(I)$$

$$\Phi'_{ij} = E'_{\theta_{ij}}(I)$$

where θ_{ij} is an adjustable parameter for each pair of cations or anions. The $E_{\theta_{ij}}(I)$ and $E'_{\theta_{ij}}(I)$ terms are calculated as follows.

$$E_{\theta_{ij}}(I) = \frac{z_i z_j}{4I}(J_0(x_{ij}) - 1/2J_0(x_{ii}) - 1/2J_0(x_{jj}))$$

$$E'_{\theta_{ij}}(I) = \frac{z_i z_j}{8I^2}(J_1(x_{ij}) - 1/2J_1(x_{ii}) - 1/2J_1(x_{jj})) - \frac{E_{\theta_{ij}}}{I}$$

where $x_{ij} = 6z_i z_j A^{\phi}\sqrt{I}$. The function $J_0(x)$ and $J_1(x)$ are given as:

$$J_0(x) = \frac{1}{4}x - 1 + \frac{1}{x}\int_0^{\infty}[1 - exp(-\frac{x}{y}e^{-y})]y^2\,dy$$

$$J_1(x) = \frac{1}{4}x - \frac{1}{x}\int_0^{\infty}[1 - (1 + \frac{x}{y}e^{-y})exp(-\frac{x}{y}e^{-y})]y^2\,dy$$

The integrals above were evaluated by using the NAG FORTRAN Library Routine D01AMF.

4. EQUATIONS OF STATE FOR THE STANDARD STATE CHEMICAL POTENTIAL OF AQUEOUS IONS

Tanger and Helgeson (1988) published the equations of state for the standard state partial molar properties of the aqueous ions. The standard state properties of the aqueous ions were assumed to be the sum of two contributions, an intrinsic property and an electrostriction contribution. The electrostriction contribution accounts for the ion-solvent interactions. The equation for the calculation of the standard partial Gibbs free energy or standard state chemical potential of the aqueous ions are as follows:

$$\begin{aligned}
\mu^o \; - \; & \mu^o_{P_r,T_r} = -\bar{S}^o_{P_r,T_r}(T - T_r) - c_1[Tln(\frac{T}{T_r}) - T + T_r] + a_1(P - P_r) \\
+ \; & a_2 ln(\frac{\Psi + P}{\Psi + P_r}) - c_2\{[\frac{1}{T - \Theta} - \frac{1}{T_r - \Theta}](\frac{\Theta - T}{\Theta}) - \frac{T}{\Theta^2} ln[\frac{T_r(T - \Theta)}{T(T_r - \Theta)}]\} \\
+ \; & (\frac{1}{T - \Theta})[a_3(P - P_r) + a_4 ln(\frac{\Psi + P}{\Psi + P_r})] + \omega(\frac{1}{D} - 1) \\
- \; & \omega_{P_r,T_r}(\frac{1}{D_{P_r,T_r}} - 1) + \omega_{P_r,T_r} Y_{P_r,T_r}(T - T_r) \qquad (4.1)
\end{aligned}$$

where $\bar{S}^o$ is the partial molar entropy. P_r and T_r are the reference pressure and temperature, which are taken as 1 bar and 298.15 K. c_1, c_2, a_1, a_2, a_3 and a_4 are the parameters, which are the properties of the individual aqueous ion. Those values were given in Table 3 (Tanger and Helgeson (1988)). Θ = 228 K, Ψ = 2600 bar and Y_{P_r,T_r} = - 5.81 $\times 10^{-5}$. D is the dielectric constant of water. The temperature and

pressure dependence of D is taken from Bradley and Pitzer (1979). For the jth ion ω_j is calculated as

$$\omega_j = \eta \left[z_j^2 [r_j + |z_j|(k_z + g)]^{-1} - z_j (3.082 + g)^{-1} \right]$$

where $\eta = 1.66027 \times 10^5 \mathring{A}$ cal/mole, z_j and r_j correspond to the charge and the crystallographic radius of the ion, which are also given in the Table 3 (Tanger and Helgeson (1988)), k_z is equal to 0.94 $\mathring{A}$ for cations and 0.0 $\mathring{A}$ for anions. The function g is further defined as:

$$g = 0.5[-b + \sqrt{b^2 - 4c}]$$

where

$$b = 3.72 - 2\eta \left[\sum_{i=-1}^{4} \sum_{j=0}^{4-i} a_{ij} T^i d^j \right]^{-1}$$

$$c = 3.4571 - 3.72\eta \left[\sum_{i=-1}^{4} \sum_{j=0}^{4-i} a_{ij} T^i d^j \right]^{-1}$$

In the above equations, d is the density of the water. The a_{ij} values were given in Table C-1 (Tanger and Helgeson (1988)).

5. RESULTS

As pointed out in the Introduction, the temperature dependence of the Pitzer model parameters and the standard state chemical potential of all the species are needed to calculate the phase equilibrium of the Na-K-Mg-Cl-NO_3-H_2O system from 0 to 25°C. Pitzer (1979) published an extensive array of the 25°C model parameters and the first order temperature derivatives of the binary parameters. For the ternary parameters, Pabalan and Pitzer (1987) suggested that it would fit many systems with constant θ's at their 25°C values and ψ's at the corresponding temperatures. We adopted this philosophy in this study. The standard state chemical potential of aqueous ions were calculated by using the revised HKF model discussed above.

Theoretically, the standard state chemical potentials of the pure solids at the temperature other than 25°C can be calculated if the temperature dependence of their heat capacities is known. Unfortunately, the heat capacities of many solids at the temperature below 25°C are not available. In this study, we chose to fit the standard state chemical potential of the pure solids with their solubility data at the corresponding temperatures. The standard state chemical potential of the double salt, $KMgCl_3.6H_2O$, was fitted with the common-ion ternary solubility data.

Table 5.1: Pitzer model parameters at 25°C (Pitzer, 1979)

	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
NaCl	0.0765	-0.2664	0.00127
$NaNO_3$	0.0068	0.1783	-0.00072
KCl	0.04835	0.2122	-0.00084
KNO_3	-0.0816	0.0494	0.00660
$MgCl_2$	0.3524	1.6815	0.00519
$Mg(NO_3)_2$	0.3671	1.5848	-0.02062

5.1 The Single Salt (Binary) Systems

The single salt solubilities from 0 to 25°C were fitted with the available experimental data in order to determine the standard state chemical potential of the pure solids. The pure salts solubilities were taken from Linke and Seidell (1965).

The Pitzer model parameters at 25°C and their first order temperature derivatives were listed in Table 5.1 and Table 5.2. Higher order temperature derivatives were not considered in this study because the data were not available.

The standard state chemical potentials of aqueous ions at 1 bar and various temperatures were calculated by using the revised HKF model. The obtained values were then fitted with the following equation.

$$\mu^o/RT = a + bt + ct^2$$

where t indicates the temperature. The results are listed in Table 5.3.

Those thermodynamic properties were then used to calculate the solubilities of the pure salts. The standard state chemical potentials of the solids were adjusted so that the calculated solubilities were close to the experimental data. The final results of the standard state chemical potential of the pure solids are also listed

Table 5.2: Temperature derivatives of Pitzer model parameters (Pitzer, 1979)

	$(\frac{\partial\beta^{(0)}}{\partial T}) \times 10^4$	$(\frac{\partial\beta^{(1)}}{\partial T}) \times 10^4$	$(\frac{\partial C^{\phi}}{\partial T}) \times 10^5$
NaCl	7.15	7.00	-10.54
$NaNO_3$	12.66	20.60	-23.16
KCl	5.79	10.71	- 5.09
KNO_3	2.06	64.50	39.7
$MgCl_2$	-4.29	36.53	–
$Mg(NO_3)_2$	5.15	44.93	–

Table 5.3: The standard state chemical potential of aqueous ions, water, and pure solids. μ^o/RT = a + bt + ct^2, t: ^{o} C

	a	b × 10	c $\times 10^3$
Na^+	-114.71	3.9392	-1.2923
K^+	-123.29	4.0564	-1.3334
Mg^{2+}	-201.41	7.8611	-2.2291
Cl^-	-57.151	1.7912	-0.4982
NO_3^-	-47.165	1.0551	-0.3223
H_2O	-103.69	3.4590	-1.0560
KCl	-179.03	6.1250	-1.8193
KNO_3	-171.90	5.6059	-1.7877
NaCl	-168.30	5.7810	-1.8174
$NaNO_3$	-160.31	6.1066	-4.8312
$MgCl_2.6H_2O$	-927.08	32.171	-10.115
$Mg(NO_3)_2.6H_2O$	-912.51	30.897	-8.7497
$KMgCl_3.6H_2O$	-1109.0	38.266	-10.666

in Table 5.3. The calculated solubilities of various salts between 0 and 25°C are presented in Figure 5.1. The calculated results agreed with the experimental data quite well. The double salt $KMgCl_3.6H_2O$ will be discussed in the later section.

It should be pointed out that the a, b, and c values in Table 5.3 for the solids were correlated between 0 and 25°C. They should not be used outside the temperature range. The standard state chemical potential values will be quite different from those obtained here if they are calculated from the heat capacity data found in Robie et al. (1978) because extrapolation is required.

Also, the 0°C $\beta^{(0)}$ value for $NaNO_3$ was adjusted to be -0.04785. This was done because the first order temperature derivative of the $\beta^{(0)}$ for $NaNO_3$ had the same order as its $\beta^{(0)}$ value. This meant that the higher order derivative terms were also important. Since the higher order terms were not available, the $\beta^{(0)}$ value was adjusted so that the calculated solubilities agreed with the experimental data.

5.2 Common-ion Ternary Systems

The temperature dependence of the ternary parameters, θ and ψ, in Pitzer's model are usually not available due to lack of the common-ion ternary activity coefficient data at various temperatures. But they can be correlated from the common-ion ternary solubility data. Following the suggestion by Pablan and Pitzer (1987), we used the constant θ at their 25°C values and correlated the ψ values from the common-ion ternary solubility data. The 25°C parameters were taken from Pitzer (1979) except where otherwise indicated.

Table 5.4: Ternary parameters

	θ	ψ					
		25°C	20°C	18.5^{o}C	15°C	10°C	0°C
Na-K-Cl	-0.012	-0.001	-0.001			-0.002	-0.003
Na-K-NO_3	-0.012	-0.0025	-0.001			0.004	0.0085
Na-Cl-NO_3	0.016	-0.006	-0.006			-0.006	-0.007
K-Cl-NO_3	0.016	-0.006	-0.006	-0.006		-0.003	-0.003
Mg-Cl-NO_3	0.016	0.000	0.000		-0.001	-0.005	-0.005
K-Mg-Cl	0.000	-0.022	-0.022		-0.018	-0.018	-0.018
K-Mg-NO_3	0.000	-0.015	-0.015			-0.030	0.000

5.2.1 NaCl-KCl-H_2O System

The phase diagrams of the NaCl-KCl-H_2O system at the temperature below 25°C have been calculated by Pabalan and Pitzer (1987) and Spencer et al. (1990). The temperature dependence of ψ was given as:

$$\psi_{ijk} = -6.81 \times 10^{-3} + 1.68 \times 10^{-5} T$$

by Pabalan and Pitzer. Spence et al. considered the temperature dependence of both θ and ψ. Those two values were obtained by fitting the solubility data and the freezing point data down to -20°C.

In this study, the ψ values were fitted with the solubility data from Linke and Seidell (1965). The results are listed in Table 5.4. The calculated solubilities at 0, 20 and 25°C are shown in Figure 5.2. The obtained ψ values agree with the values calculated from the equation given by Pabalan and Pitzer (1987). The 10°C ψ value will be discussed later.

5.2.2 NaCl-$NaNO_3$-H_2O System

The phase diagrams of the NaCl-$NaNO_3$-H_2O system at 0, 20 and 25°C were calculated by using the same strategy. The fitted ψ values are listed in Table 5.4. It appears that the ψ values do not change much within the 25°C temperature range. The calculated phase diagrams are shown in Figure 5.3.

5.2.3 KCl-KNO_3-H_2O System

The phase diagrams of the KCl-KNO_3-H_2O system at 0, 18.5 and 25°C were calculated and compared with the experimental data. The ψ values obtained are listed in Table 5.4 and the calculated phase diagrams are shown in Figure 5.4.

5.2.4 $NaNO_3$-KNO_3-H_2O System

The calculated phase diagrams of the $NaNO_3$-KNO_3-H_2O system at 0, 20 and 25°C are shown in Figure 5.5. Since there are very few experimental data, the ψ values were adjusted so that the calculated invariant points agreed with the available experimental data as close as possible. The ψ values are listed in Table 5.4.

5.2.5 $MgCl_2$-KCl-H_2O System

The calculated phase diagrams of the $MgCl_2$-KCl-H_2O system at 0, 15 and 25°C are shown in Figure 5.6. The 25°C ternary parameters were taken from Harvie and Weare (1980). The standard state chemical potential of the double salt $KMgCl_3.6H_2O$ were adjusted, together with the ψ values, in order to match with the experimental data. The standard state chemical potentials of the $KMgCl_3.6H_2O$ are listed in Table 5.3. The ψ values are given in Table 5.4.

The formation of the double salts and the multi-hydration salts such as magnesium chloride and sulfate makes the correlation of their standard state chemical potential and the ψ more difficult. Without the heat capacity data, the only way of obtaining those data is from the ternary solubility data provided that the solubility data for such system are available at the temperature concerned.

5.2.6 $MgCl_2$-$Mg(NO_3)_2$-H_2O System

The calculated phase diagrams of the $MgCl_2 - Mg(NO_3)_2 - H_2O$ system at 15 and 25°C are shown in Figure 5.7. The ψ values are given in Table 5.4. The 0°C ψ value was obtained from the quaternary solubility calculation presented below.

5.2.7 $Mg(NO_3)_2 - KNO_3 - H_2O$ System

The phase diagrams of the $Mg(NO_3)_2 - KNO_3 - H_2O$ system at 0 and 25°C were calculated and compared with the experimental data. The corresponding ψ values are given in Table 5.4. Both the 25°C and 0°C ψ values were obtained from fitting the experimental data. The calculated phase diagrams are plotted in Figure 5.8.

5.3 The Quaternary Systems

In order to test the model parameters and the solid standard state chemical potential values obtained above, the phase diagrams of two quaternary systems, $NaCl - KNO_3 - H_2O$ and $MgCl_2 - KNO_3 - H_2O$, were calculated at different temperatures and compared with available experimental data. For the $NaCl - KNO_3 - H_2O$ system, the phase equilibria were calculated at 0, 10, 20 and 25°C. The 10°C ψ values used are listed in Table 5.4. They were chosen to fit

Table 5.5: Invariant points for $NaCl - KNO_3 - H_2O$ system, in molality

	Experimental	data	Calculated	values
t (C)	NaCl	KNO_3	NaCl	KNO_3
0	6.5187	2.0410	6.4230	2.4408
10	6.4519	2.5944	6.4032	2.6133
20	6.4906	3.4108	6.5133	4.1874
25	6.6286	4.0991	6.6403	4.8431

the experimental invariant data. The calculated invariant points are listed in Table 5.5 together with the experimental data. The phase diagram calculated at 20^oC is compared with the experimental data in Figure 5.9 along with phase diagrams at 0 and 25^oC.

For the $MgCl_2 - KNO_3 - H_2O$ system, the phase diagrams were calculated at 0, 10 and 20^oC. All calculated values compared well with the experimental data. At 10^oC, four ψ values, $\psi_{Mg,K,Cl}$, ψ_{Mg,K,NO_3}, $\psi_{Cl,NO_3,Mg}$ and ψ_{Cl,K,NO_3} were adjusted to produce good agreement between the calculated values and the experimental data because those four ψ values had not been obtained from the common-ion ternary calculations. The results given in Figure 5.10 show good agreement for all three temperatures.

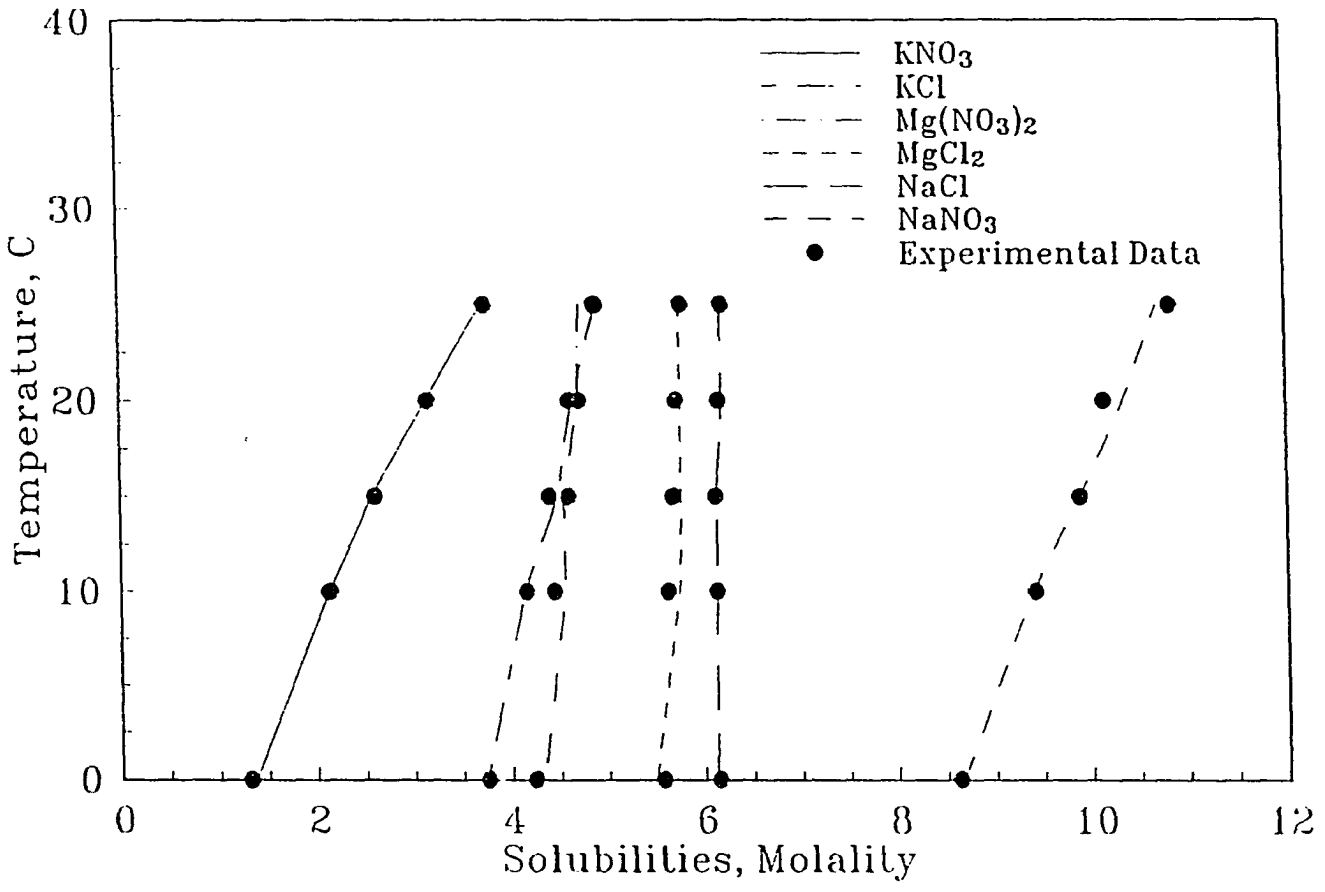

Figure 5.1: Solubilities of pure salts

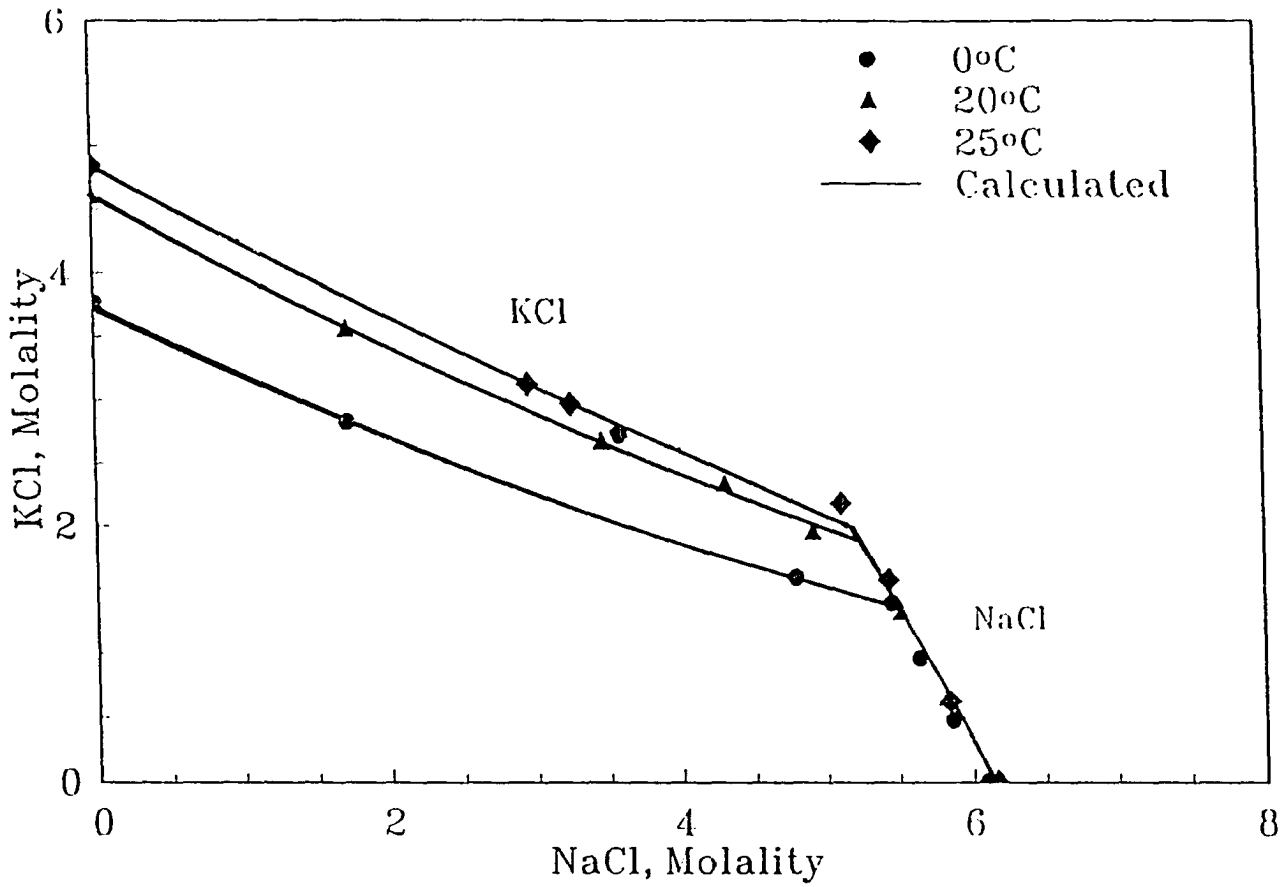

Figure 5.2: Solubilities of NaCl-KCl-H_2O system

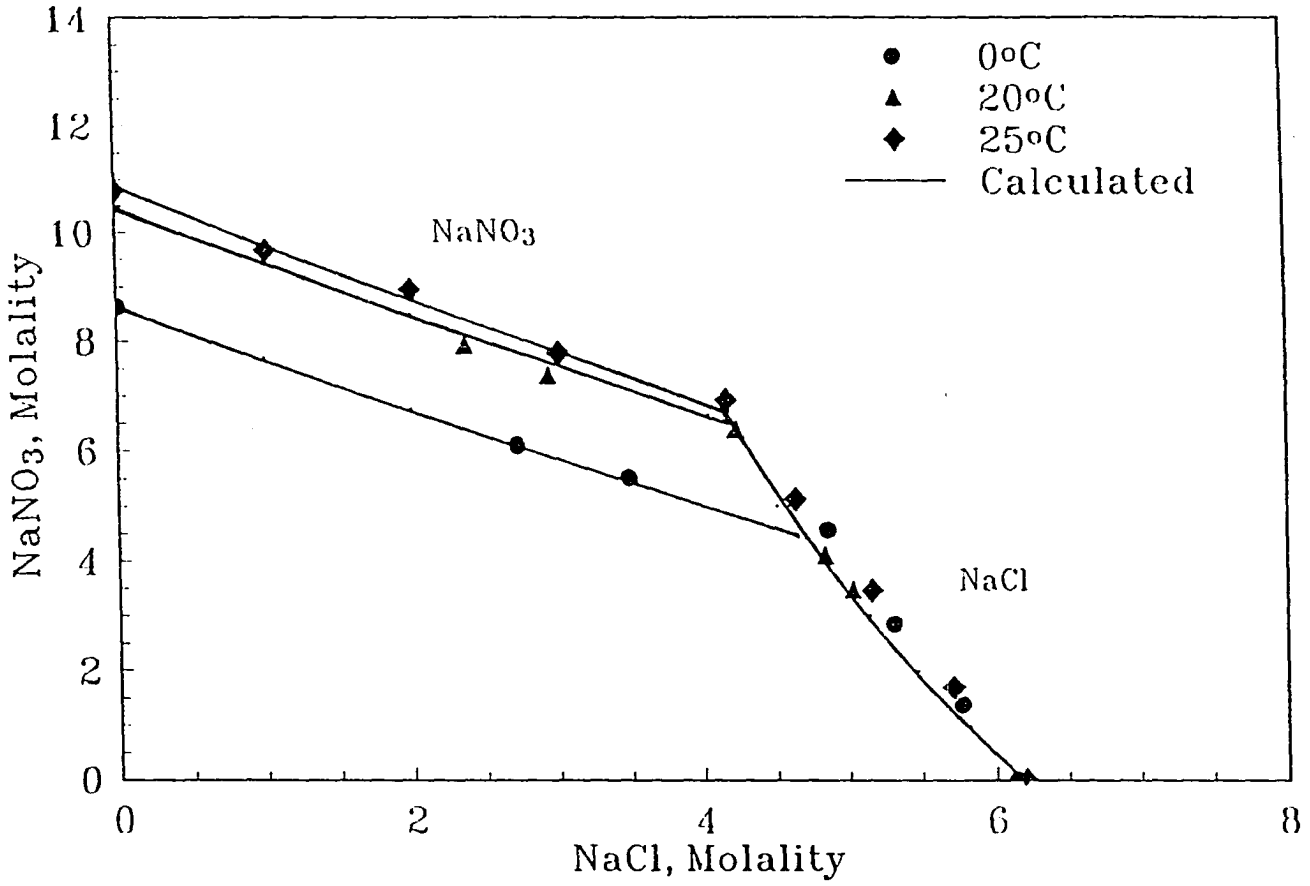

Figure 5.3: Solubilities of NaCl-$NaNO_3$ – H_2O system

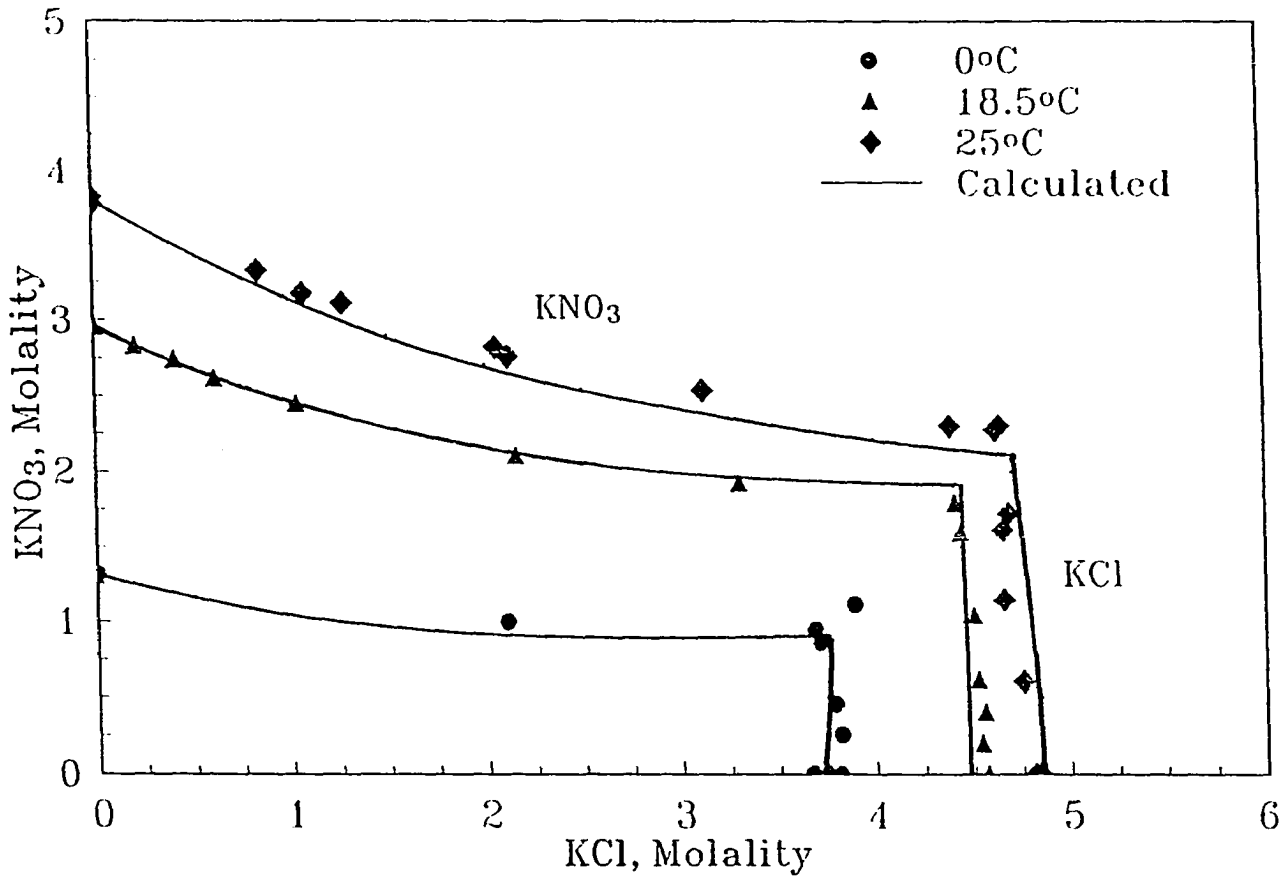

Figure 5.4: Solubilities of KCl-KNO_3 – H_2O system

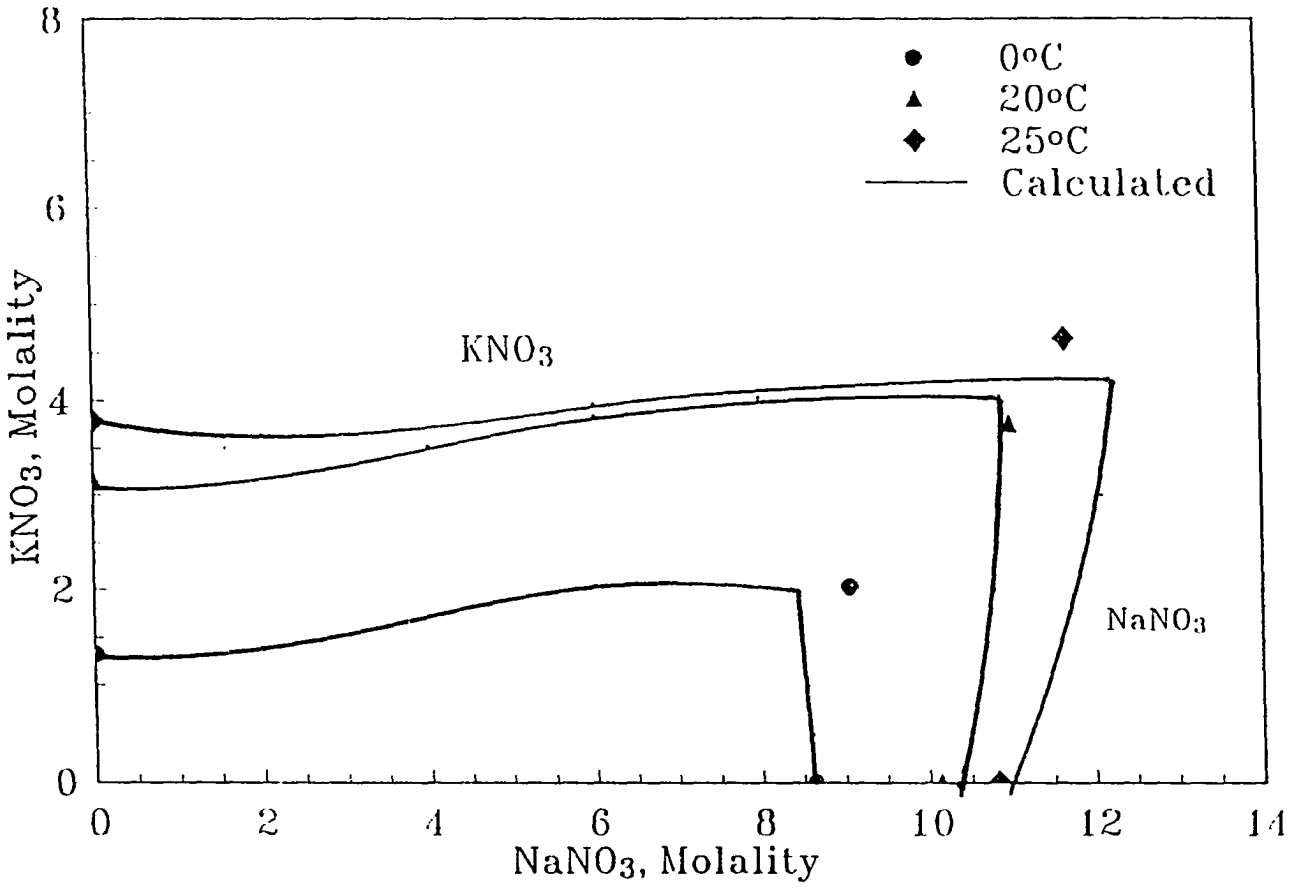

Figure 5.5: Solubilities of $NaNO_3 - KNO_3 - H_2O$ system

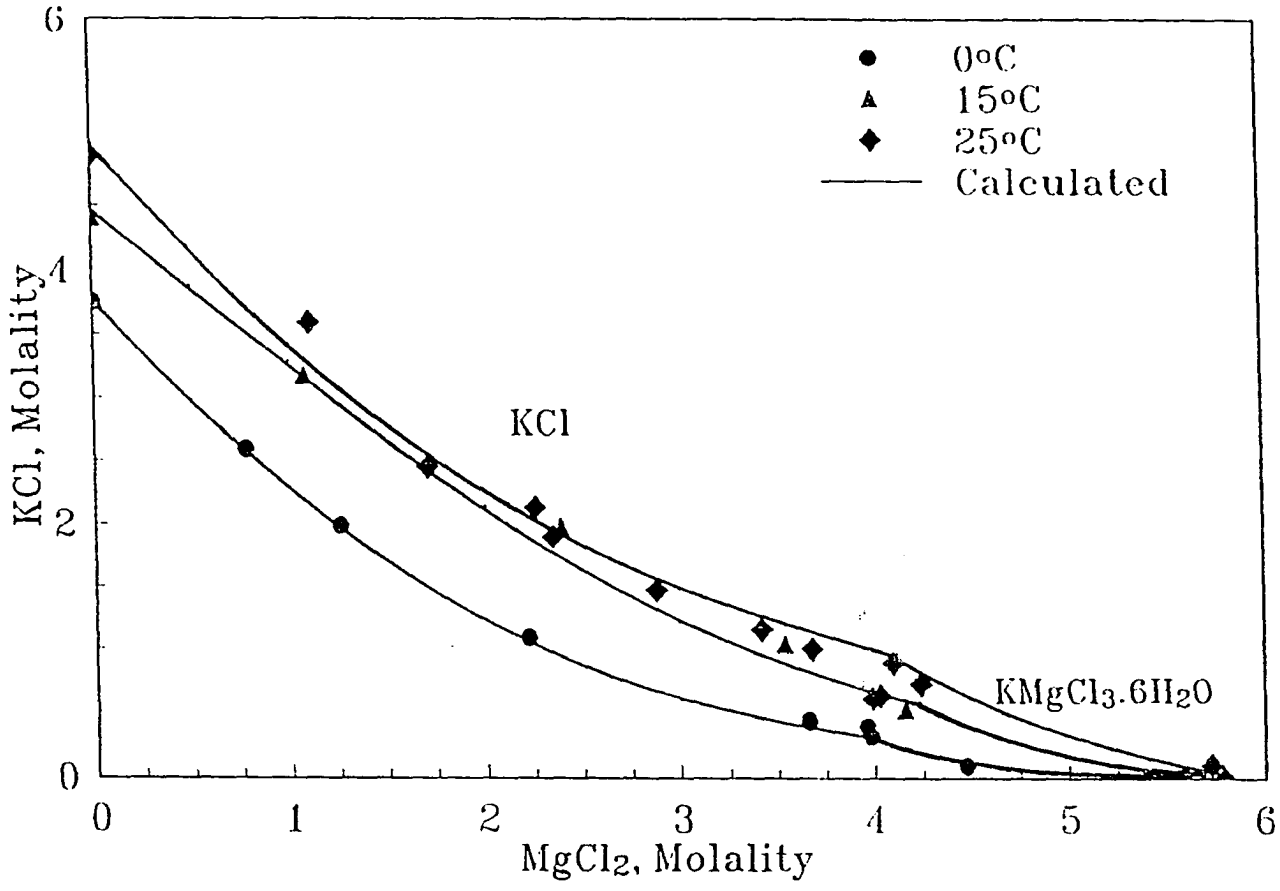

Figure 5.6: Solubilities of $MgCl_2 - KCl - H_2O$ system

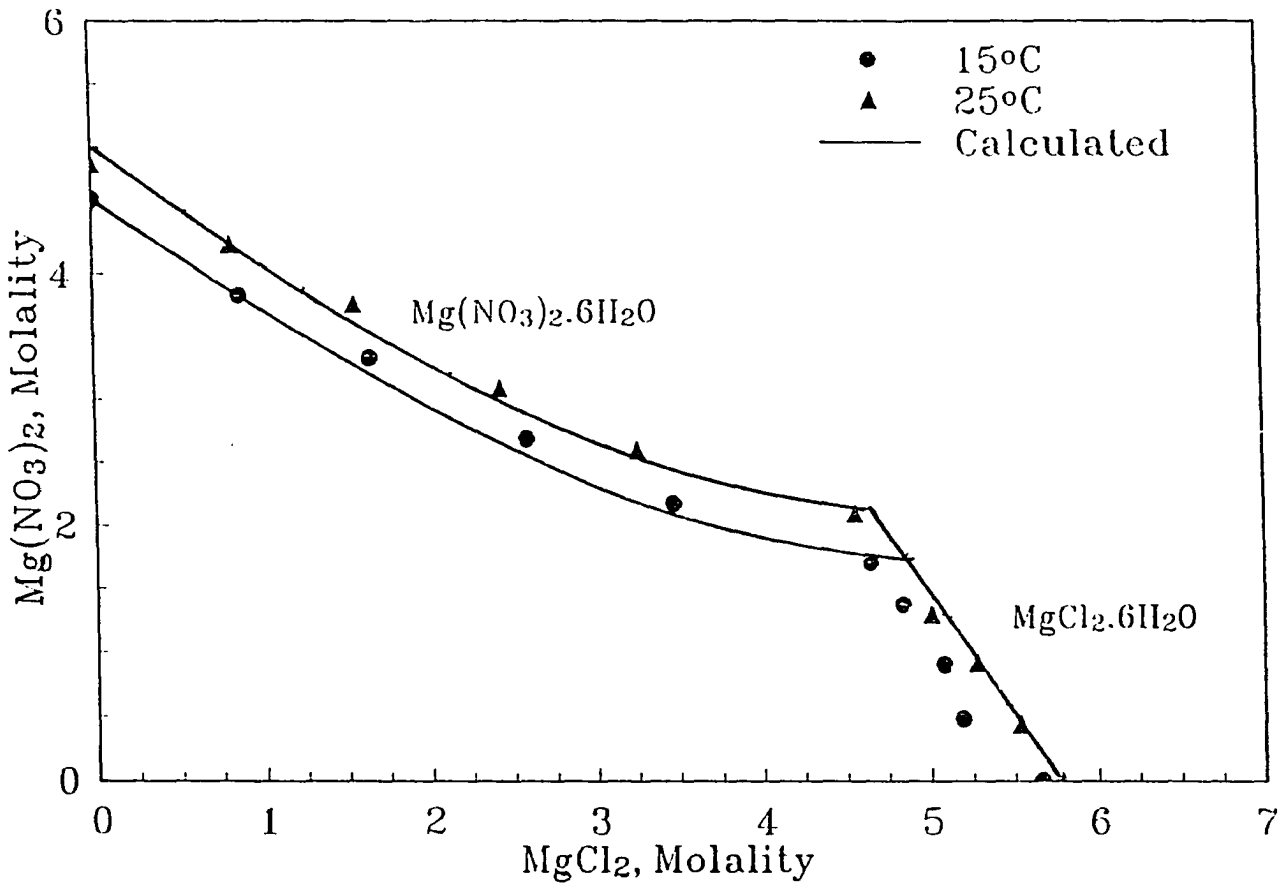

Figure 5.7: Solubilities of $MgCl_2 - Mg(NO_3)_2 - H_2O$ system

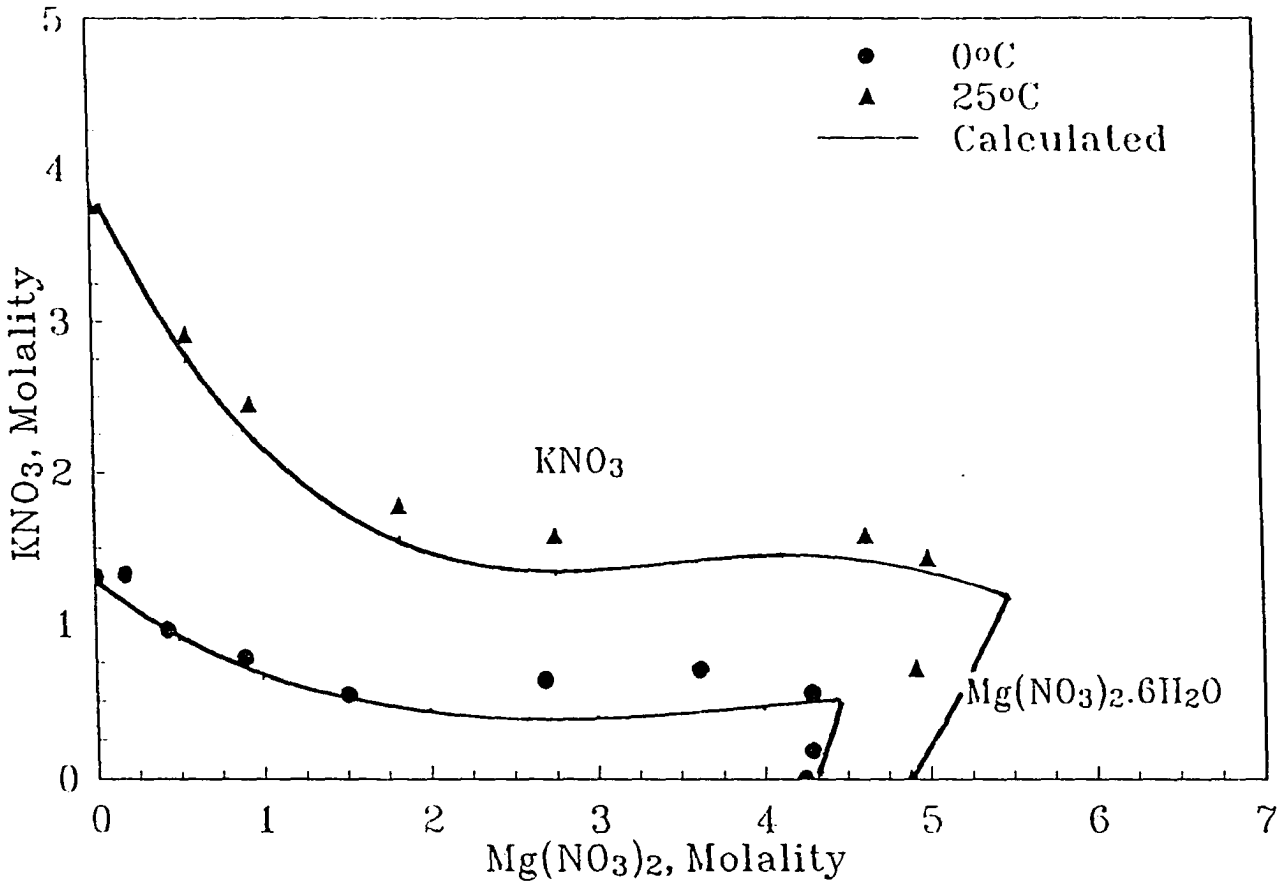

Figure 5.8: Solubilities of $Mg(NO_3)_2 - KNO_3 - H_2O$ system

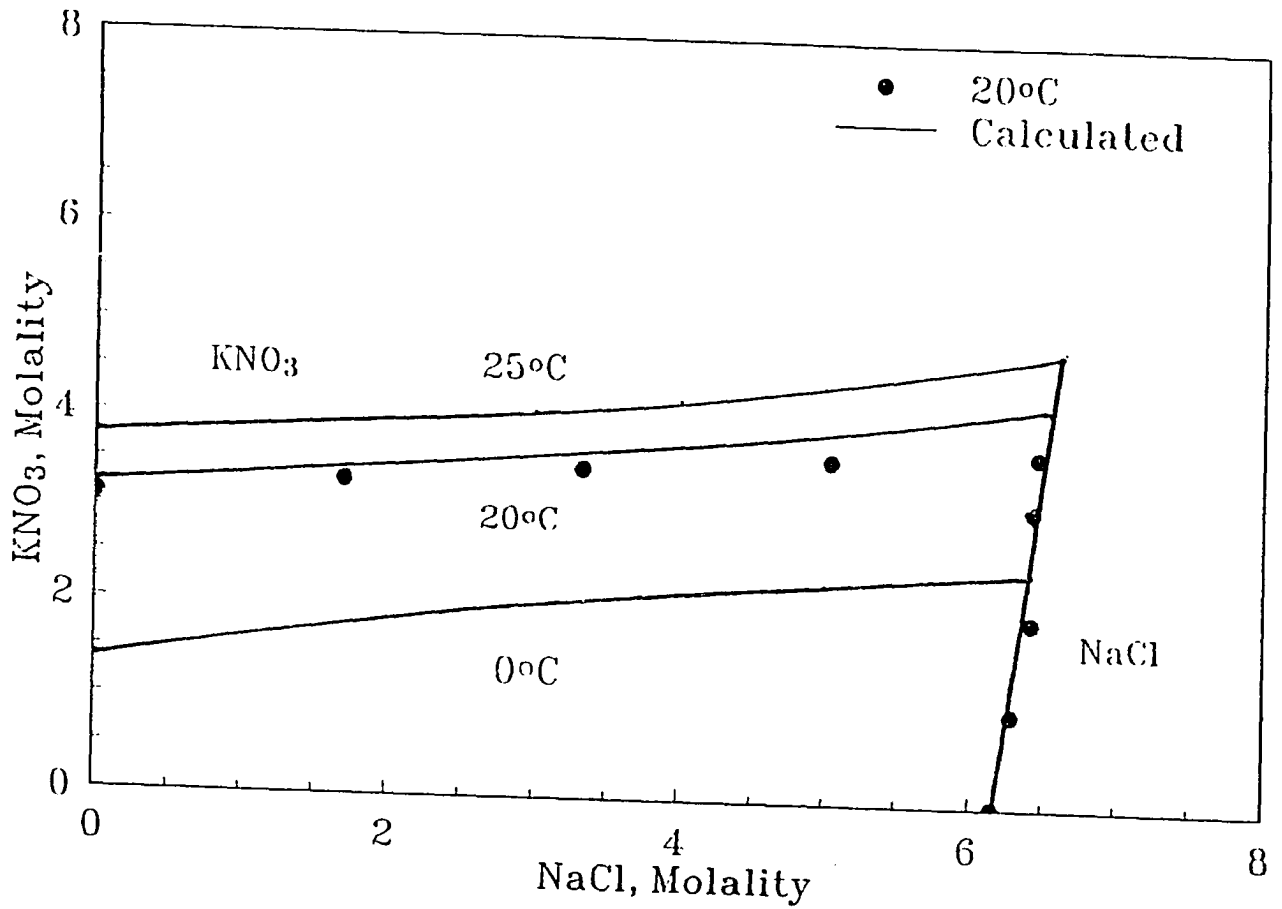

Figure 5.9: Solubilities of NaCl-$KNO_3 - H_2O$ system

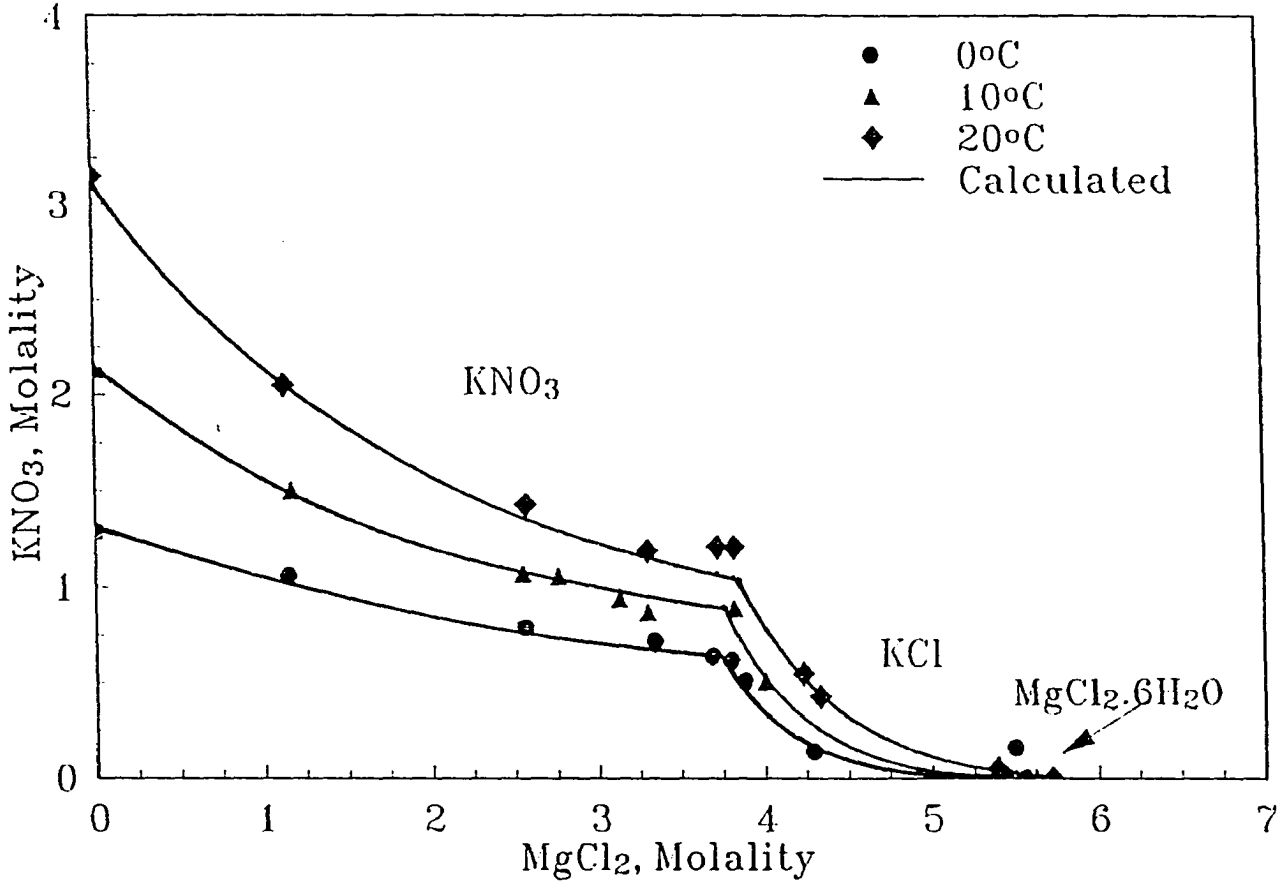

Figure 5.10: Solubilities of $MgCl_2 - KNO_3 - H_2O$ system

6. CONCLUSIONS

In this study, the Na-K-Mg-Cl-NO_3-H_2O phase equilibria were calculated by using the Pitzer's model for the activity and osmotic coefficients and a revised HKF model for the standard state chemical potential of aqueous ionic species and water. The pure solid standard state chemical potentials were obtained by fitting the solubility data. All phase equilibria were calculated by using the method of Song and Larson (in press).

Within the temperature range of this study (0 to 25°C), the first order temperature dependence of the binary parameters in the Pitzer model is sufficient for the phase diagram predictions with the exception of systems containing $NaNO_3$. Because of the small value of $\beta^{(0)}$ for $NaNO_3$ at 25°C, using only the first order temperature derivative is not sufficient for the accurate predications. Higher order terms are needed for a temperature range greater than 25 degrees.

The temperature dependence of the ternary ψ values were fitted from the common-ion ternary solubility data. It has been found that these ternary parameters are sensitive to the equilibrium calculation although they have very small values.

The calculated phase diagrams using the fitted model parameters and the solid standard state chemical potential values showed reasonable agreement with the experimental data. Care should be taken in the application of these calculations. The

presence of organic and other solutes in process of waste stream would be expected to affect the phase equilibria of these salt mixtures.

7. NOMENCLATURE

A = Coefficient Matrix,

A_ϕ = the Pitzer-Debye-Huckel limiting slope,

B_{ca} = Binary Pitzer model parameter for cation-anion interactions,

C_{ca} = Binary Pitzer model parameters,

D = Dielectric constant of pure water,

G = Gibbs free energy of the system,

I = ionic strength,

N_0 = Avogadro Number,

P = Pressure,

R = Gas constant,

T = Temperature, (K)

Z = Term in the Pitzer model,

b = Pitzer model constant, 1.2,

e = charge of electron,

k = Boltzmann constant,

m_i = molality of the ith species,

n_i = the mole number of ith species,

$\mathbf{n_T}$ = the initial system input vector,

t = temperature, ^{o}C,

z_i = ion charge.

Greek Letters

$\beta^{(0)}, \beta^{(1)}, \beta^{(2)}$ = Pitzer model parameters,

γ = Activity coefficients,

ϕ = Osmotic coefficients,

μ = Chemical potential,

ψ = Ternary Pitzer model parameters.

Subscripts

a, a' = anion,

c, c' = cation,

ca = salt ca,

r = reference state,

M = cation,

X = anion.

Superscripts

o = standard state.

8. LITERATURE CITED

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SUMMARY AND DISCUSSION

This work covers three aspects of the phase equilibrium calculation, namely (1) thermodynamic model, (2) numerical algorithm and (3) practical applications with the focus on the aqueous electrolyte mixtures. The success of a thermodynamic model relies on its flexibility and accuracy in predicting of solution properties such as activity, density and solubility. A large database of model parameters and their temperature and pressure dependence is the only way of making certain models have any engineering usefulness. Yet only the information obtained from a convincing numerical procedure can be used in the engineering design.

Despite the primary promising results obtained by using Liu et al. model, lack of temperature and pressure dependence of the model parameters prevent the further application of the model, which is true for all NRTL models. It is very difficult to predict volumetric properties using the NRTL model because the pressure derivative of the Gibbs free energy given by the NRTL model is mathematically very complex and the resulting equations will be highly nonlinear. But the advantage of these models is its capability of dealing with mixed solvent and systems involving molecular species.

The Gibbs free energy given by Pitzer's model is a linear model in terms of the model parameters. Any derivative of linear equation is still in linear form. Therefore,

Pitzer's model gives a simple model for the engineering purposes. As shown in Part III of this work, Pitzer's model can give fairly accurate predictions about the phase equilibrium of the aqueous electrolyte solutions.

Since the Gibbs free energy for nonideal system is highly nonlinear with respect to composition, being able to find the correct equilibrium composition of each phase is as important as having an accurate thermodynamic model. The algorithm described in Part II of this work provides an unified approach in solving the phase equilibrium problem. The mathematical procedures have thermodynamic meanings. The algorithm described in this part has the following advantages:

- The phase selection procedure is identical to the thermodynamic considerations;
- The phases selected are stable;
- The optimum solution will always satisfy Gibbs phase rule;
- The calculated phase diagrams agree well with experimental data.

One general neglected area in solid-liquid phase equilibrium problems is the study of the properties of individual solid phase, to be specific, the temperature dependence of the standard state chemical potential of the solid or the equilibrium constant of the solid formation reaction. Without those information, the solid-liquid phase equilibrium prediction could be very tedious and sometimes impossible.

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APPENDIX A. DEBYE-HUCKEL THEORY

In 1923 Debye and Huckel provided, in a simple theory, the correct equation for the behavior of electrolyte solutions in the limit of very low concentration. The theory can be divided into three parts, i.e. (1) the selection of the molecular model or the interionic potentials of mean force, (2) the calculation of the interionic radial distribution functions from the model, and (3) the calculation of thermodynamic functions from the potentials and the radial distribution functions.

Interionic potentials

A plausible model can be described as follows:

$$u_{ij}(r) = u^*_{ij}(r) + z_i z_j e^2/Dr$$

where $z_i e$ is the charge of ion i,r is the distance between ion i and j, and $u^*_{ij}(r)$ is short-range interaction function giving the difference between the true potential of mean force and the electrostatic term. All effects departure from this electrostatic term are combined in $u^*_{ij}(r)$. These include at intermediate distances a variety of effects related to the molecular natures of the solvent (solvation, dielectric saturation, etc.) as well as dispersion forces between ions and at shorter distances the direct repulsion of ions as their electron shells begin to overlap.

The simplest assumption for u^*, used by Debye and Huckel and frequently called

the primitive model, is:

$$u^*_{ij} = +\infty, r < a$$

$$u^*_{ij} = 0, r > a$$

where the hard-core diameter a is the same for all ions.

Radial Distribution Functions

The concentration of ionic species i near species j is given by the Boltzmann expression:

$$n_i(r)/N_i = \exp(-z_i e\phi_j/KT)$$

where $n_i(r)$ is the number of ions per unit volume at distance r, N_i is the total number of ion i per unit volume, ϕ_j is electrostatic potential associated with ion j, and K is Boltzmann constant. This implies the following radial distribution function:

$$g_{ij}(r) = \exp(-z_i e\phi_j/KT)$$

The summation over all ion i at distance r gives the charge density:

$$\begin{aligned} \rho_j(r) &= \sum_i z_i e n_i(r) \\ &= \sum_i z_i e N_i \exp(-z_i e\phi_j/KT) \end{aligned}$$

Take the expansion for the exponential function, yields:

$$\rho_j(r) = e\sum_i z_i N_i - (e^2\phi_j/KT)\sum_i z_i^2 N_i + ...$$

According to the electrical neutrality, the first term on the right is zero. For simplicity we only take the second term as an approximation. Substituting into

the Poisson equation for the electrostatic potential and using appropriate boundary conditions, yield:

$$\phi_j(r) = \frac{z_j e \exp(ka) \exp(-kr)}{D(1+ka)r}$$

where $k^2 = (4\pi e^2/DKT)\sum_i z_i^2 N_i$, and a is the diameter of the hard-core. Then the radial distribution function becomes:

$$g_{ij} = \exp(-q_{ij})$$

$$q_{ij} = \frac{z_i z_j \exp(ka)}{DKT(1+ka)} \frac{\exp(-ka)}{r}$$

Thermodynamic Equations

The osmotic coefficient for the solution is then:

$$\phi - 1 = -(6cKT)^{-1} \sum_i \sum_j \int_0^\infty \frac{\partial u_{ij}}{\partial r} g_{ij}(r)(4\pi r^2) dr$$

where c is the total concentration of solute. The activity coefficient can be calculated from the Gibbs-Duhem equation and the final result is:

$$\ln \gamma_j = -\frac{A z_j^2 I^{1/2}}{1 + BaI^{1/2}}$$

where A and B are Debye-Huckel constants, I is the ionic strength. At infinite dilution, the above equation becomes:

$$\ln \gamma_j = -A z_j^2 I^{1/2}$$

APPENDIX B. SOURCE PROGRAM

```
//EQUIL    JOB N1$WXS,WXS,MSGLEVEL=(1,1),CLASS=C
/*ACCOUNT  I5649
//* CHECKPOINT=YES
/*JOBPARM LINES=100
//SO EXEC SCRUNC,PARM='N1$WXS.SONG1'
//SO EXEC SCRUNC,PARM='N1$WXS.SONG2'
//SO EXEC SCRUNC,PARM='N1$WXS.SONG3'
//SFORT1 EXEC FORTVCL,FVPOPT=2
//FORT.SYSIN DD *
@PROCESS DC(ZCOMM)
      IMPLICIT REAL*8 (Z)
      COMMON/ZCOMM/Z(400000)
      DATA NWCORE/400000/

      CALL MINOS1( Z,NWCORE)
      STOP
      END
      SUBROUTINE FUNOBJ(MODE,N,X,F,G,NSTATE,NPROB,Z,NWCORE)
      IMPLICIT REAL*8(A-H,O-Z)
      DOUBLE PRECISION X(N),G(N),Z(NWCORE),MOL(4)
      EXTERNAL EQUIL
C
      CALL EQUIL(N,X,F,G)
C
      DO 10 I = 1, 4
 10     MOL(I) = X(I)*1000.0D0/(18.0D0*X(5))
      WRITE(6,*) 'THE EQUILIBRIUM CONCENTRATIONS ARE: '
      WRITE(6,111) (MOL(I), I = 1, 4)
 111  FORMAT(2X,4F10.4)
```

```
      RETURN
      END
C
C
C
C     ****************************************************
C     *  THE FOLLOWING SUBROUTINE IS FOR THE CALCULATION OF *
C     *       THE GIBBS FREE ENERGY AND ITS GRADIENTS       *
C     *       CHEMICAL POTENTIAL USING PITZER'S MODEL       *
C     ****************************************************
C
C
C
      SUBROUTINE EQUIL(N,X,G,DG)
      INTEGER NSP,NI,NC,NA,NS

      PARAMETER (NC=2,NA=2,NI=NC+NA)
      DOUBLE PRECISION BETA(NC,NA),BETA1(NC,NA),BETA2(NC,NA),
     $       SITAO(NI,NI),ALFA1(NC,NA),ALFA2(NC,NA),CFI(NC,NA),
     $       PUSI(NI,NI,NI),LNR(NI),ML(NI),Z(NI),SITA1(NI,NI)
      DOUBLE PRECISION U(NI+1),DG(N),X(N)
      DOUBLE PRECISION B,T,G,AFI,FI,I,MZ,LNW
      COMMON /PARA2/B,BETA,BETA1,BETA2,ALFA1,ALFA2,CFI,
     $    PUSI,SITAO,SITA1,Z,T,UO
      EXTERNAL ACTIVT,OSMOTC
      INTRINSIC DLOG
C
      B = 1.2D0
      T = 283.15D0
      AFI = 0.388D0
C
      Z(1) = 2.0D0
      Z(2) = 1.0D0
      Z(3) = 1.0D0
      Z(4) = 1.0D0
C
C     BINARY PARAMETERS
C
C     *** MG-CL ***
      BETA(1,1) = 0.3545D0
```

```
      BETA1(1,1) = 1.6632D0
      BETA2(1,1) = 0.0D0
      CFI(1,1) = 0.00519D0
      ALFA1(1,1) = 2.0D0
      ALFA2(1,1) = 2.0D0
C
C     *** MG-NO3 ***
      BETA(1,2) =  0.36460D0
      BETA1(1,2) = 1.5803D0
      BETA2(1,2) = 0.0D0
      CFI(1,2) = -0.02062D0
      ALFA1(1,2) = 2.0D0
      ALFA2(1,2) = 2.0D0
C
C     *** K-CL ***
      BETA(2,1) = 0.04546D0
      BETA1(2,1) = 0.2068D0
      BETA2(2,1) = 0.0D0
      CFI(2,1) = -0.0005860D0
      ALFA1(2,1) = 2.0D0
      ALFA2(2,1) = 2.0D0
C
C     *** K-NO3 ***
      BETA(2,2) = -0.08263D0
      BETA1(2,2) = 0.01715D0
      BETA2(2,2) = 0.0D0
      CFI(2,2) =  0.004615D0
      ALFA1(2,2)=2.0D0
      ALFA2(2,2) = 2.0D0
C
C     TERNEY PARAMETERS
C
      SITA0(1,2) =  0.000D0
      SITA0(3,4) = 0.016D0
      SITA1(1,2) = 0.0D0
      SITA1(3,4) = 0.0D0
      PUSI(1,2,3) = -0.022D0
      PUSI(1,2,4) = -0.020D0
      PUSI(3,4,1) = -0.000D0
      PUSI(3,4,2) = -0.006D0
```

```
C
C       CALCULATE THE MOLALITY FROM MOLE NUMBER
C
        MZ=0.0D0
        DO 17 K=1,NI
          ML(K)=1.0D+3/(1.8D+1*X(NI+1))*X(K)
            MZ=MZ+ML(K)*Z(K)**2
 17     CONTINUE
             I = 0.5D0*MZ
C
C       COMPUTE THE CHEMICAL POTENTIAL OF SPECIES j.
C
C       CALCULATE ACTIVITIES
          CALL ACTIVY(ML,I,AFI,LNR)
C       CALCULATE OSMOTICS
          CALL OSMOTC(ML,I,AFI,FI,LNW)
C
        DO 20 J=1,NI+1
          IF(J.LE.NI) THEN
              U(J)=LNR(J)+DLOG(ML(J))
          ELSE
              U(J)=LNW
          ENDIF
 20     CONTINUE
C
C       COMPUTE THE FREE ENERGY OF THE NONLINEAR PART
C
        G=0.0D0
        DO 30 L=1,NI+1
 30      G=G+U(L)*X(L)
C
C       CALCULATE DERIVATIVES OF THE OBJECTIVE FUNC.
C
        DO 60 L=1,NI+1
         DG(L) = U(L)
  60    CONTINUE
        RETURN
        END
C
C
```

```
C       CALCULATE THE ACTIVITY.
C
      SUBROUTINE ACTIVY(ML,I,AFI,LNR)
       COMMON /PARA2/B,BETA,BETA1,BETA2,ALFA1,ALFA2,CFI,
     & PUSI,SITAO,SITA1,Z
       DOUBLE PRECISION GX
       EXTERNAL GX,SITIA,FUNF
       INTRINSIC DSQRT
       INTEGER NI,NC,NA
       PARAMETER (NC=2,NA=2,NI=NC+NA)
       DOUBLE PRECISION Z(NI),LNR(NI),ML(NI),
     *  BETA(NC,NA),BETA1(NC,NA),BETA2(NC,NA),ALFA1(NC,NA),
     *  ALFA2(NC,NA),CFI(NC,NA),BA(NC,NA),C(NC,NA),
     *  PUSI(NI,NI,NI),SITAO(NI,NI),ESITA(NI,NI),
     *  ESITAP(NI,NI),FI(NI,NI),R1(NC,NC),R2(NA,NA),
     *  RI1(NI),RI2(NI),RI3(NI),SITA1(NI,NI)
       DOUBLE PRECISION  SI,I,B,F,AFI,RR,X1,X2,ZZ,SITAI
C
C
C     CALCULATE BA(NC,NA)
C
       SI=DSQRT(I)
      DO 5 K=1,NC
       DO 5 L=1,NA
         X1=ALFA1(K,L)*SI
          X2=ALFA2(K,L)*SI
           BA(K,L)=BETA(K,L)+BETA1(K,L)*GX(X1)
     *              +BETA2(K,L)*GX(X2)
 5    CONTINUE
C
       ZZ=0.0D0
      DO 6 K=1,NI
 6      ZZ=ZZ+ML(K)*Z(K)
      DO 10 K=1,NC
        DO 10 L=1,NA
        L1=L+NC
 10      C(K,L)=CFI(K,L)/(2.0D0*DSQRT(Z(K)*Z(L1)))
C
           CALL SITIA(Z,I,AFI,ESITA,ESITAP)
C
```

```
      DO 15 K=1,NC
       DO 15 L=1,NC
        IF(K.GE.L) GOTO 15
         SITAI=SITAO(K,L)+(2.0D0*SITA1(K,L)/4.0D0/I)*
     *          (1.0D0-(1.0D0+2.0D0*SI)*DEXP(-2.0D0*SI))
         FI(K,L)=SITAI+ESITA(K,L)
 15      CONTINUE
      DO 16 K=1,NA
       K1=K+NC
        DO 16 L=1,NA
         L1=L+NC
          IF(K.GE.L) GOTO 16
         SITAI=SITAO(K1,L1)+(2.0D0*SITA1(K1,L1)/4.0D0/I)*
     *          (1.0D0-(1.0D0+2.0D0*SI)*DEXP(-2.0D0*SI))
          FI(K1,L1)=SITAI+ESITA(K1,L1)
 16     CONTINUE
C
      CALL FUNF(ML,I,AFI,F)
C
C     COMPUTE CATION'S ACTIVITY COEFFICIENTS
C
      DO 20 J=1,NC
       RI1(J)=0.0D0
        DO 21 L=1,NA
         L1=L+NC
21        RI1(J)=RI1(J)+ML(L1)*(2.0D0*BA(J,L)+ZZ*C(J,L))
          RI2(J)=0.0D0
           DO 25 K=1,NC
            IF(K.EQ.J) GO TO 25
            IF(K.LT.J) FI(J,K)=FI(K,J)
             R1(J,K)=0.0D0
              DO 22 L=1,NA
               L1=L+NC
                IF(K.LT.J) PUSI(J,K,L1)=PUSI(K,J,L1)
22              R1(J,K)=R1(J,K)+ML(L1)*PUSI(J,K,L1)
              RI2(J)=RI2(J)+ML(K)*(2.0D0*FI(J,K)+R1(J,K))
25          CONTINUE
     RI3(J)=0.0D0
      DO 30 K=1,NA
       K1=K+NC
```

```
          DO 30 L=1,NA
           L1=L+NC
            IF(K.GE.L) GO TO 30
        RI3(J)=RI3(J)+ML(K1)*ML(L1)*PUSI(K1,L1,J)
 30    CONTINUE
        LNR(J)=Z(J)**2*F+RI1(J)+RI2(J)+RI3(J)
 20    CONTINUE
       RR=0.0D0
        DO 35 K=1,NC
         DO 35 L=1,NA
          L1=L+NC
 35       RR=RR+ML(K)*ML(L1)*C(K,L)
        DO 36 J=1,NC
 36      LNR(J)=LNR(J)+RR*Z(J)
C
C       COMPUTE ANION'S ACTIVITY COEFFICIENTS
C
       DO 60 J=1,NA
        J1=J+NC
         RI1(J1)=0.0D0
          DO 40 K=1,NC
 40        RI1(J1)=RI1(J1)+ML(K)*(2.0D0*BA(K,J)+ZZ*C(K,J))
         RI2(J1)=0.0D0
          DO 45 L=1,NA
           L1=L+NC
           IF (L.EQ.J) GOTO 45
           IF (L.LT.J)  FI(J1,L1)=FI(L1,J1)
            R2(J,L)=0.0D0
             DO 50 K=1,NC
             IF(L.LT.J) PUSI(J1,L1,K)=PUSI(L1,J1,K)
 50           R2(J,L)=R2(J,L)+ML(K)*PUSI(J1,L1,K)
         RI2(J1)=RI2(J1)+ML(L1)*(2.0D0*FI(J1,L1)+R2(J,L))
 45         CONTINUE
          RI3(J1)=0.0D0
        DO 55 K=1,NC
         DO 55 L=1,NC
          IF(K.GE.L) GO TO 55
            RI3(J1)=RI3(J1)+ML(K)*ML(L)*PUSI(K,L,J1)
 55     CONTINUE
        LNR(J1)=Z(J1)**2*F+RI1(J1)+RI2(J1)+RI3(J1)+Z(J1)*RR
```

```
 60     CONTINUE
        RETURN
        END
C
C
        FUNCTION GX(X)
        DOUBLE PRECISION  GX,X
        INTRINSIC DEXP
         GX=2.0D0*(1.0D0-(1.0D0+X)*DEXP(-X))/X**2
        RETURN
        END
C
C       CALCULATE F FUNCTION
C
       SUBROUTINE FUNF(M,I,AFI,F)
       COMMON /PARA2/B,BETA,BETA1,BETA2,ALFA1,ALFA2,CFI,
     *        PUSI,SITAO,SITA1,Z
       DOUBLE PRECISION GXP
       EXTERNAL GXP,SITIA
       INTRINSIC DSQRT,DLOG
       INTEGER NI,NC,NA
       PARAMETER (NC=2,NA=2,NI=NC+NA)
       DOUBLE PRECISION M(NI),Z(NI),BETA(NC,NA),BETA1(NC,NA),
     *    ALFA1(NC,NA),ALFA2(NC,NA),CFI(NC,NA),PUSI(NI,NI,NI),
     *    BP(NC,NA),ESITA(NI,NI),ESITAP(NI,NI),SITAO(NI,NI),
     *    BETA2(NC,NA),SI,I,F1,F2,F3,F4,F,B,AFI,X1,X2,SITA1(NI,NI)
C
       SI=DSQRT(I)
       F1=-AFI*(SI/(1.0D0+B*SI)+2.0D0/B*DLOG(1.0D0+B*SI))
       DO 5 K=1,NC
         DO 5 L=1,NA
           X1=ALFA1(K,L)*SI
            X2=ALFA2(K,L)*SI
             BP(K,L)=BETA1(K,L)*GXP(X1)/I
     *               +BETA2(K,L)*GXP(X2)/I
 5     CONTINUE
C
         CALL SITIA(Z,I,AFI,ESITA,ESITAP)
C
       F2=0.0D0
```

```
        DO 10 K=1,NC
          DO 10 L=1,NA
           L1=L+NC
 10         F2=F2+M(K)*M(L1)*BP(K,L)
C
C      FOR CATION
C
        F3=0.0D0
         DO 11 K=1,NC
           DO 11 L=1,NC
             IF(K.GE.L) GO TO 11
               F3=F3+M(K)*M(L)*ESITAP(K,L)
 11      CONTINUE
C
C      FOR ANION
C
        F4=0.0D0
         DO 12 K=1,NA
          K1=K+NC
           DO 12 L=1,NA
            L1=L+NC
             IF(K.GE.L) GO TO 12
               F4=F4+M(K1)*M(L1)*ESITAP(K1,L1)
 12      CONTINUE
        F=F1+F2+F3+F4
       RETURN
       END
C
C
       FUNCTION GXP(X)
       DOUBLE PRECISION GXP, X
       INTRINSIC DEXP
       GXP=-2.0D0*(1.0D0-(1.0D0+X+5.0D-1*X**2)*DEXP(-X))/X**2
       RETURN
       END
C
C
C
       SUBROUTINE SITIA(Z,I,AFI,ESITA,ESITAP)
       INTEGER NI,NC,NA
```

```
      PARAMETER (NC=2,NA=2,NI=NC+NA)
      DOUBLE PRECISION Z(NI),ESITA(NI,NI),ESITAP(NI,NI),
     *  JXO(NI,NI),JX1(NI,NI),XZ(NI,NI),XX,XO,X1,AFI,I
      EXTERNAL JXFUN
      INTRINSIC DSQRT
      COMMON /DATA/XX
C
C     FOR CATION
C
      DO 10 K=1,NC
        DO 10 L=1,NC
        IF(K.GT.L) GOTO 10
         XZ(K,L)=6.0DO*Z(K)*Z(L)*AFI*DSQRT(I)
          XX=XZ(K,L)
           CALL JXFUN(XO,X1)
            JXO(K,L)=XO
            JX1(K,L)=X1
 10   CONTINUE
      DO 11 K=1,NC
        DO 11 L=1,NC
        IF(K.GE.L) GO TO 11
         ESITA(K,L)=Z(K)*Z(L)/(4.0DO*I)*(JXO(K,L)-
     &              5.0D-1*JXO(K,K)-5.0D-1*JXO(L,L))
         ESITAP(K,L)=Z(K)*Z(L)/(8.0DO*I**2)*(JX1(K,L)-
     &      5.0D-1*JX1(L,L)-5.0D-1*JX1(K,K))-ESITA(K,L)/I
 11    CONTINUE
C
C     FOR ANION
C
      DO 12 K=1,NA
        K1=K+NC
        DO 12 L=1,NA
        L1=L+NC
       IF(K.GT.L) GOTO 12
         XZ(K1,L1)=6.0DO*Z(K1)*Z(L1)*AFI*DSQRT(I)
          XX=XZ(K1,L1)
           CALL JXFUN(XO,X1)
             JXO(K1,L1)=XO
             JX1(K1,L1)=X1
 12   CONTINUE
```

```
      DO 13 K=1,NA
       K1=K+NC
       DO 13 L=1,NA
       L1=L+NC
         IF(K.GE.L) GO TO 13
       ESITA(K1,L1)=Z(K1)*Z(L1)/(4.0D0*I)*(JX0(K1,L1)-
     &              5.0D-1*JX0(K1,K1)-5.0D-1*JX0(L1,L1))
       ESITAP(K1,L1)=Z(K1)*Z(L1)/(8.0D0*I**2)*(JX1(K1,L1)-
     &   5.0D-1*JX1(K1,K1)-5.0D-1*JX1(L1,L1))-ESITA(K1,L1)/I
 13    CONTINUE
       RETURN
       END
C
C
C     CALCULATE THE OSMOTIC.
C
      SUBROUTINE OSMOTC(ML,I,AFI,FI,LNW)
      COMMON /PARA2/B,BETA,BETA1,BETA2,ALFA1,ALFA2,CFI,
     &        PUSI,SITA0,SITA1,Z
      INTEGER NI,NA,NC
      PARAMETER (NC=2,NA=2,NI=NA+NC)
      DOUBLE PRECISION Z(NI),ML(NI),ALFA2(NC,NA),
     * BETA(NC,NA),BETA1(NC,NA),BETA2(NC,NA),ALFA1(NC,NA),
     * PUSI(NI,NI,NI),SITA0(NI,NI),ESITA(NI,NI),ESITAP(NI,NI),
     * FIFI(NI,NI),BFI(NC,NA),C(NC,NA),CFI(NC,NA),SITA1(NI,NI),
     * AFI,I,MZ1,B,FI1,FI2,FI3,FI31,FI4,FI41,FI,ZZ,LNW,SITAI,SI
C
      EXTERNAL SITIA
      INTRINSIC DSQRT,DEXP
C
C     CALCULATE THE TOTAL MOLALITY AND ION STRENGTH
C
       MZ1=0.0D0
      DO 3 K=1,NI
          MZ1=MZ1+ML(K)
 3    CONTINUE
       SI = DSQRT(I)
C
      FI1=-AFI*I**1.5/(1.0D0+B*DSQRT(I))
        ZZ=0.0D0
```

```
      DO 2 K=1,NI
 2     ZZ=ZZ+ML(K)*Z(K)
      DO 5 K=1,NC
      DO 5 L=1,NA
        L1=L+NC
         BFI(K,L)=BETA(K,L)+BETA1(K,L)*DEXP(-ALFA1(K,L)
     &    *DSQRT(I))+BETA2(K,L)*DEXP(-ALFA2(K,L)*DSQRT(I))
        C(K,L)=CFI(K,L)/(2.0D0*DSQRT(Z(K)*Z(L1)))
 5    CONTINUE
C
           CALL SITIA(Z,I,AFI,ESITA,ESITAP)
C
      DO 13 K=1,NC
        DO 13 L=1,NC
         IF(K.GE.L) GO TO 13
         SITAI=SITA0(K,L)+(2.0D0*SITA1(K,L)/4.0D0/I)*
     *          (1.0D0-(1.0D0+2.0D0*SI)*DEXP(-2.0D0*SI))
         FIFI(K,L)=SITAI+ESITA(K,L)+I*ESITAP(K,L)
 13    CONTINUE
       DO 14 K=1,NA
       K1=K+NC
        DO 14 L=1,NA
        L1=L+NC
         IF(K.GE.L) GO TO 14
         SITAI=SITA0(K1,L1)+(2.0D0*SITA1(K1,L1)/4.0D0/I)*
     *          (1.0D0-(1.0D0+2.0D0*SI)*DEXP(-2.0D0*SI))
       FIFI(K1,L1)=SITAI+ESITA(K1,L1)+I*ESITAP(K1,L1)
 14     CONTINUE
C
      FI2=0.0D0
       DO 15 K=1,NC
         DO 15 L=1,NA
          L1=L+NC
 15       FI2=FI2+ML(K)*ML(L1)*(BFI(K,L)+ZZ*C(K,L))
      FI3=0.0D0
       DO 20 K=1,NC
         DO 20 L=1,NC
           IF(K.GE.L) GO TO 20
            FI31=0.0D0
              DO 21 J=1,NA
```

```
              J1=J+NC
 21            FI31=FI31+ML(J1)*PUSI(K,L,J1)
          FI3=FI3+ML(K)*ML(L)*(FIFI(K,L)+FI31)
 20    CONTINUE
C
       FI4=0.0D0
        DO 25 K=1,NA
         K1=K+NC
          DO 25 L=1,NA
           L1=L+NC
            IF(K.GE.L) GO TO 25
             FI41=0.0D0
              DO 26 J=1,NC
 26             FI41=FI41+ML(J)*PUSI(K1,L1,J)
          FI4=FI4+ML(K1)*ML(L1)*(FIFI(K1,L1)+FI41)
 25    CONTINUE
         FI=1.0D0+2.0D0/MZ1*(FI1+FI2+FI3+FI4)
         LNW=-1.8D+1/1.0D+3*MZ1*FI
       RETURN
        END
C
C      CALL D01AMF, CALCULATE THE INTEGRAL IN PITZER'S MODEL.
C
       SUBROUTINE JXFUN(JX0,JX1)
       INTEGER  KOUNT
C      ... LOCAL SCALARS ...
       DOUBLE PRECISION A,ABSERR,EPSABS,EPSREL,EX,
     *                  EXACT,RESUT1,RESUT2,X,JX0,JX1
       INTEGER  IFAIL,INF,NOUT
C      ... LOCAL ARRAYS ...
       DOUBLE PRECISION W(800)
       INTEGER  IW(102)
C      .. FUNCTION REFERENCES ..
       DOUBLE PRECISION  X01AAF,FST1,FST2
C      .. SUBROUTINE REFERENCES ..
       EXTERNAL FST1,FST2,X01AAF
       COMMON /TELNUM/KOUNT
       COMMON /DATA/X
       DATA  NOUT/6/
       EPSABS = 0.0D0
```

```
      EPSREL = 1.0D-4
      A = 0.0D0
      EXACT = X01AAF(A)
      INF = 1
      KOUNT = 0
      IFAIL = 1
      CALL D01AMF(FST1,A,INF,EPSABS,EPSREL,RESUT1,ABSERR,W,
     *            800,IW,102,IFAIL)
      JX0 = 0.25D0*X-1.0D0+RESUT1/X
      EX = DABS(EXACT-RESUT1)
      CALL D01AMF(FST2,A,INF,EPSABS,EPSREL,RESUT2,ABSERR,W,
     *            800,IW,102,IFAIL)
      JX1 = 0.25D0*X-RESUT2/X
      EX = DABS(EXACT-RESUT2)
      RETURN
      END
C
      FUNCTION FST1(Y)
C     ... SCALAR ARGUMENTS ...
      DOUBLE PRECISION X,Y
C     ..
C     ... SCALARS IN COMMON ...
      INTEGER KOUNT
C     ... FUNCTION REFERENCES ...
      DOUBLE PRECISION DEXP,FST1
C     ..
      COMMON /TELNUM/KOUNT
      COMMON /DATA/X
      KOUNT = KOUNT + 1
      FST1 = (1.0D0-DEXP(-X/Y*DEXP(-Y)))*Y**2
      RETURN
      END
C
      FUNCTION FST2(Y)
C     ... SCALAR ARGUMENTS ...
      DOUBLE PRECISION X,Y
C     ..
C     ... SCALARS IN COMMON ...
      INTEGER KOUNT
C     ... FUNCTION REFERENCES ...
```

```
      DOUBLE PRECISION DEXP,FST2
C     ..
      COMMON /TELNUM/KOUNT
      COMMON /DATA/X
      KOUNT = KOUNT + 1
      FST2=(1.0D0-(1.0D0+X/Y*DEXP(-Y))*
     *                DEXP(-X/Y*DEXP(-Y)))*Y**2
      RETURN
      END
//LKED.SYSLMOD DD DSN=N1$WXS.SONG3(FUTCRQP),
//  DISP=(NEW,CATLG),SPACE=(TRK,(30,10,10),RLSE),UNIT=DISK,
// VOL=SER=UCC001
//LKED.MYLIB DD DSN=N1$WXS.MINOS51.LOAD,DISP=SHR
//LKED.SYSIN DD *
  MODE AMODE(31),RMODE(ANY)
  INCLUDE  MYLIB(MINOS)
  ENTRY MAIN
//STEP1  EXEC  PGM=FUTCRQP,REGION=5000K,TIME=60
//STEPLIB  DD  DSN=N1$WXS.SONG3,DISP=SHR
//            DD  DSN=SYS1.VSF2FORT,DISP=SHR
//FT06F001  DD  SYSOUT=A,
//             DCB=(RECFM=FBA,LRECL=133,BLKSIZE=3458,BUFNO=2)
//FT08F001  DD  UNIT=SYSDA,SPACE=(TRK,(4,4)),
//             DCB=(RECFM=FB,LRECL=8,BLKSIZE=1600)
//FT09F001  DD  SYSOUT=A,
//             DCB=(RECFM=FBA,LRECL=133,BLKSIZE=3458,BUFNO=2)
//*FT10F001 DD DSN=N1$WXS.SONG1,
//*        UNIT=DISK,DISP=SHR
//FT11F001  DD  UNIT=DISK,DISP=(,CATLG),
//          DSN=N1$WXS.SONG1,
//          SPACE=(TRK,(150,30)),
//          DCB=(RECFM=FB,LRECL=80,BLKSIZE=6160)
//FT13F001 DD DSN=N1$WXS.SONG2,UNIT=DISK,
//  DISP=(,CATLG),DCB=(LRECL=111,RECFM=FB,BLKSIZE=18981),
//  SPACE=(TRK,(50,30))
//FT05F001  DD  *
BEGIN MGCLKN03
   MINIMIZE
   OBJECTIVE =          GENERGY
```

```
   NONLINEAR VARIABLES     5
   SUPERBASICS LIMIT       5
   DERIVATIVE LEVEL        3
   ITERATION LIMIT         10

   LOG FREQUENCY           1
   SAVE FREQUENCY          1
   NEW BASIS FILE          11

END MGCLKNO3
NAME          MGCLKNO3
ROWS
 E  RMG
 E  RK
 E  RCL
 E  RNO3
 E  RH2O
 E  CONST1
 E  CONST2
 N  GENERGY
COLUMNS
    MG        RMG       1.0          GENERGY   -186.590
    MG        CONST1    2.0
    K         RK        1.0          GENERGY   -115.711
    K         CONST2    1.0
    CL        RCL       1.0          GENERGY   -53.7681
    CL        CONST1    -1.0
    NO3       RNO3      1.0          GENERGY   -45.1830
    NO3       CONST2    -1.0
    H2O       RH2O      1.0          GENERGY   -97.2389
    MGCL26    RMG       1.0          RH2O      6.0
    MGCL26    RCL       2.0          GENERGY   -867.100
    KNO3      RK        1.0
    KNO3      RNO3      1.0          GENERGY   -161.405
    KCL       RK        1.0
    KCL       RCL       1.0          GENERGY   -167.55
    MGNO36    RMG       1.0          RH2O      6.0
    MGNO36    RNO3      2.0          GENERGY   -854.500
RHS
    B         RMG       3.82
```

```
    B          RK        5.0
    B          RCL       10.64
    B          RNO3      2.0
    B          CONST1    0.0
    B          CONST2    0.0
    B          RH2O      55.5
BOUNDS
 PL BOUND01    MG        1.0E-4
 PL BOUND01    K         1.0E-4
 PL BOUND01    CL        1.0E-4
 PL BOUND01    NO3       1.0E-4
 PL BOUND01    H2O       1.0E-4
 FX INITIAL    MG        3.82
 FX INITIAL    K         5.0
 FX INITIAL    CL        10.64
 FX INITIAL    NO3       2.0
 FX INITIAL    H2O       55.5
 LO INITIAL    MGCL26
 LO INITIAL    KCL
 LO INITIAL    MGNO36
 LO INITIAL    KNO3
 LO INITIAL    KMGCL36
ENDATA
/*
```

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