TEMPERATURE EFFECTS ON THE ACTIVITY COEFFICIENT OF THE BICARBONATE ION

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ABSTRACT

Natural waters may be chemically studied as mixed electrolyte solutions. Some important equilibrium properties of natural waters are intimately related to the activity-concentration ratios (i.e., activity coefficients) of the ions in solution. An Ion Interaction Model, which is based on Pitzer's (1973) thermodynamic model, is proposed in this dissertation. The proposed model is capable of describing the activity coefficient of ions in mixed electrolyte solutions. The effects of temperature on the equilibrium conditions of natural waters and on the activity coefficients of the ions in solution, may be predicted by means of the Ion Interaction Model presented in this work.

The bicarbonate ion, HCO_3^-, is commonly found in natural waters. This anion plays an important role in the chemical and thermodynamic properties of water bodies. Such properties are usually directly related to the activity coefficient of HCO_3^- in solution. The Ion Interaction Model, as proposed in this dissertation, is used to describe indirectly measured activity coefficients of HCO_3^- in mixed electrolyte solutions.

Experimental pH measurements of MCl-$MHCO_3$ and MCl-H_2CO_3 solutions at 25^oC (where $M = K^+$, Na^+, NH_4^+, Ca^{2+} or Mg^{2+}) are used in this dissertation to evaluate indirectly the $MHCO_3$ virial coefficients. Such coefficients permit the prediction of the activity coefficient of HCO_3^- in mixed electrolyte solutions. The Ion Interaction Model is found to be an accurate method for predicting the activity coefficient of HCO_3^-

within the experimental ionic strengths (0.2 to 3.0 m). The virial coefficients of $KHCO_3$ and $NaHCO_3$ and their respective temperature variations are obtained from similar experimental measurements at 10^o and 40^oC. The temperature effects on the NH_4HCO_3, $Ca(HCO_3)_2$, and $Mg(HCO_3)_2$ virial coefficients are estimated based on these results and the temperature variations of the virial coefficients of 40 other electrolytes.

Finally, the Ion Interaction Model is utilized to solve various problems of water chemistry where bicarbonate is present in solution.

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LIST OF SYMBOLS

Roman Capital Letters

A	Debye-Huckel coefficient
B	Interaction function
C	Third virial coefficient
D	Finite pH difference
E	pH calibration error
G^{ex}	Excess Gibbs energy of mixing
I	Ionic strength
I^*	Pseudo-ionic strength
$\overline{J}$	Apparent molal heat capacity
K	Thermodynamic dissociation constant
K_{ip}	Thermodynamic ion product
K_{sp}	Thermodynamic solubility product
$\overline{L}$	Relative partial molal enthalpy
M	Specific cation
M_1	Molecular weight of solvent
P	Pressure
R	Gas constant
S	Solubility ratio
T	Absolute temperature
W	Power consumption/flow rate
X	Specific anion
Y	Virial coefficient temperature function
Z	Valence of an ion

Roman Lower-Case Letters

a, a'	Any anion in solution
a_1	Activity of water
b	Coefficient
c, c'	Any cation in solution
d	Coefficient
e	Coefficient
f	Debye-Hückel function
g	Ionic strength function
m	Molal concentration
q, r, s	Coefficients
t	Temperature in ^{o}C
v_1	Partial molal volume of water

Greek Letters

α	Coefficient
β	Virial coefficient
γ	Activity coefficient
δ	Incomplete dissociation factor
ϵ	Dielectric constant of water
θ	Like-charge virial coefficient
ν	Number of moles
Π	Osmotic pressure
ρ	Alkalinity fraction

σ	Standard deviation
ϕ	Osmotic coefficient
ϕ_J	Molal heat capacity
ϕ_L	Apparent molal enthalpy
Ψ	Triplets interaction coefficient
Ω	Osmotic membrane constant

Operators

[ ]	Molal concentration
( )	Molal activity
Σ	Summation
Δ	Difference
∂	Difference, partial derivative
$\vert\ \vert$	Absolute value

Chapter 1

INTRODUCTION

1.1 The Bicarbonate Ion as a Main Component of Natural Waters

The bicarbonate ion is commonly found in natural waters, and its intrinsic properties are of importance in the study of water chemistry equilibrium. Some of the basic chemical and physical properties of this anion are reviewed below.

In nature the bicarbonate ion leaves or enters a solution via one or more of many mechanisms. Among these are the processes of photosynthesis-respiration, contact with the atmosphere and precipitation-dissolution of carbonate and bicarbonate minerals. Due to the common occurrence of these processes the bicarbonate ion is a ubiquitous component of natural waters.

The bicarbonate ion exhibits amphoteric properties in aqueous solutions, being the intermediate state of protonation of the carbonate system. These important properties are directly related to the acid and base neutralizing capacities of aqueous solutions. Often in nature the bicarbonate ion is the main acid-neutralizing agent of the water (i.e., alkalinity). The pH of a water solution is therefore dependent on the concentration of bicarbonate ion.

Several thermodynamic models have been proposed to evaluate the intrinsic characteristics of mixed electrolyte solutions. The general principles of the two most commonly used models are presented in the following section. Natural waters may be considered as aqueous multicomponent electrolyte solutions and therefore may be studied as such. Quantitatively, the concentration of the individual ions in natural waters varies widely from place to place, but their main components are usually the same. In natural waters the most commonly found cations are H^+, Na^+, K^+, Ca^{2+} and Mg^{2+}, and in polluted waters NH_4^+. The anions usually present in natural water are OH^-, Cl^-, HCO_3^-, NO_3^-, $H_2PO_4^-$, F^-, SO_4^{2-}, CO_3^{2-}, HPO_4^{2-} and PO_4^{3-}. Therefore, the equilibrium properties of bicarbonate in natural waters may be studied by considering HCO_3^- as an individual component in a mixed electrolyte solution. A method is proposed in this work to evaluate accurately some important equilibrium characteristics of the bicarbonate ion in natural waters.

1.2 Thermodynamic Models

Several thermodynamic models have been proposed to predict the activity coefficients of mixed electrolyte solutions. These models give reasonable results for relatively simple multicomponent systems; however, few of them may be utilized in the calculation of the activity coefficients of electrolytes having more than four different ions in solution. The two most common methods of evaluating activity coefficients of such complex electrolytes are the Ion Association Model and the Ion Interaction Model. The general characteristics and basic assumptions of these equilibrium models are presented below.

The more widely used equilibrium model is the Bjerrum Ion

Association Model, which assumes the formation of ion pairs by oppositely charged ions (i.e., counter-ions). The Brønsted-Guggenheim Ion Interaction Model is the alternate procedure employed in the evaluation of several thermodynamic properties of aqueous solutions, including the activity coefficients of the individual ions in solution. The latter method approaches this problem by assuming interactions among the ions in solution.

The activity coefficient of any solute is defined as the dimensionless ratio between its activity and concentration in solution. Under very dilute conditions this ratio approaches unity. Stumm and Morgan (1970) report that the Debye-Hückel theory, which considers only long-range electrostatic interactions between the ions, is accurate in most cases for ionic strengths below 0.01 M. Deviations from the ideal Debye-Hückel theory at higher ionic strengths are attributed to short-range interionic forces. Different assumptions are used by the two basic models to account for deviations from ideality in concentrated solutions.

The Ion Association Model assumes that deviations from the Debye-Hückel theory are caused by differences in the ion sizes and/or by the relatively strong binding of counter-ions to form ion pairs. According to this model, the concentration of a specific type of ion pair is directly proportional to the activity of its free counter-ion components. The ion association criterion implies, then, a distinction between the thermodynamic properties of both free ions and ion pairs. The introduction of more variables into the system, to take into consideration the presence of ion pairs, complicates considerably the equilibrium calculations of mixed electrolyte solutions. Furthermore, tedious approximations have to be executed in order to satisfy the electroneutrality and mass balance conditions.

Several alternate methods are used in the Ion Association Model to compute the activity coefficients of free ions in solution. The following methods are widely used in the computation of these parameters:

i) The extended Debye-Hückel equation, and

ii) The Mean Salt method (MacInnes convention).

The first method, which utilizes an adjustable parameter (ion size parameter), permits one to evaluate analytically the activities of the individual free ions. The accuracy of this method is dubious at ionic strengths above 0.05 m, and should be used cautiously in concentrated solutions.

The Mean Salt method for obtaining the individual free ion activity coefficients has lately come under strong criticism. By convention, this method assumes that the activity coefficient of the potassium ion is equal to that of the chloride ion at a given ionic strength, regardless of the nature of the other ions in solution. Whitfield (1974a), mentions, among others, the following disadvantage of of this method:

> "The widely employed MacInnes convention is ambiguous at ionic strengths greater than 0.1 M and contradicts a number of conventional definitions of single ion properties in implying that the activity coefficient of the chloride ion is the same in all solutions of alkali and alkaline earth metal chlorides at constant ion strengths."

A thermodynamic property of aqueous solutions, which is not well understood, is the ion-pair activity coefficient. A great number of techniques have been proposed to evaluate this parameter. The lack of common grounds for the computation of the activity coefficients of ion pairs is directly reflected on many other thermodynamic properties of the solution as a whole.

Finally, in order to compute accurately the free ion activity coefficients, it becomes necessary to know precisely the value of the ionic strength of the solution. Some researchers who utilize the Ion Association Model evaluate the ionic strength of a solution by adding the individual contribution of free ions to the contribution of ion pairs. Other investigators claim that this is incorrect and evaluate this parameter from the contribution of the individual ions' total concentrations. This discrepancy may lead to wide differences in the predicted value of the activity coefficients of both free ions and ion pairs.

The osmotic and activity coefficients of single electrolyte solutions may be accurately predicted by the use of the Ion Interaction Model. These parameters are evaluated by the addition of an interaction term to the Debye-Hückel function. (This theory is studied in more detail in the next chapters.) The interaction term is a semilinear relationship of the molality of the solution, which rapidly tends to linearity as the concentration of the electrolyte increases. At a fixed temperature and pressure the slope of the interaction term depends only on the nature of the electrolyte, and its absolute value (i.e., deviation from ideality) is usually higher for multivalent electrolytes. Both the osmotic and activity coefficients of mixed electrolytes may be accurately predicted by assuming that the multiple interactions upon a specific ion are additive (Lewis and Randall (1961)).

The simplest method to predict short-range interactions among the ions is to assume linearity in the ion interaction term. This approach has yielded reasonable results for the activity coefficients of systems as complex and concentrated as sea water (Whitfield (1973)). Recently Pitzer (1973) has proposed a more detailed, but at the same time more complex, approach for the description of the osmotic and activity coefficients of single electrolytes from infinite dilution to 6.0 m. The value of the interaction term in Pitzer's method is described by three virial coefficients which multiply an equal number of functions of the ionic strength of the solution. Pitzer and Mayorga (1973) have evaluated and published the values of the virial coefficients of over 200 1:1, 1:2 and 1:3 electrolytes. The evaluation of these coefficients was performed from measurements of the activity and osmotic coefficients of single electrolyte solutions. In another publication Pitzer and Mayorga (1974) propose a mathematical approach to the evaluation of these two thermodynamic properties in solutions containing 2:2 electrolytes.

The activity and osmotic coefficients of mixed electrolytes are accurately described by a method presented by Pitzer and Kim (1974). The accuracy of this method is increased by considering interaction between like-charged ions as well as triple-ion interaction. Higher order electrostatic terms for multivalent electrolytes may be described by the technique proposed by Pitzer (1975). Many ambiguities existing in the theory of strong acids may be resolved by using Pitzer's method in the analytical studies of these electrolytes (Pitzer and Silvester (1976)).

1.3 Evaluation of the Thermodynamic Models

The main objection to the use of the Ion Interaction Model in aquatic chemistry is the execution of lengthy mathematical manipulations, but the accuracy of the model more than compensates this objection. In single electrolyte solutions the calculations involved in the Ion Interaction Model are probably more complex than those required by the Ion Association Model. However, for mixed electrolyte solutions, the opposite condition is often observed. This condition is due to the cumbersome approximations necessary to satisfy both the mass balance and electroneutrality constraints in the Ion Association Model.

The superiority of the Ion Interaction Model is also revealed by its reliability to predict the activity and osmotic coefficients of an extensive variety of mixed electrolytes over a wide range of ionic strengths. The evaluation in this chapter obviously leads to the selection of the Ion Interaction Model as a more effective means to describe the thermodynamic properties of the main ions present in natural waters.

1.4 Thermodynamic Properties of M-HCO_3 Salts

In view of the chemical importance of the bicarbonate ion in natural waters it becomes necessary to describe its thermodynamic behavior by means of a sound equilibrium model. The model chosen in this work was the Ion Interaction Model utilizing the latest modifications by Pitzer and co-workers.

Many investigations have dealt with the problem of predicting the activity coefficient of the bicarbonate ion in the presence of various cations. Nonetheless, most of these investigations have dealt with the problem according to the Ion Association Model. The validity of this approach is directly related to the prediction accuracy of the free bicarbonate ion activity coefficient. This parameter is usually evaluated by means of either one of two techniques: by the extended Debye-Hückel equation or by interpolation of tabulated values. A previous discussion of the effectiveness of the first technique to describe activity coefficients reveals that its validity is limited to very dilute solutions. The tabular values of the free bicarbonate ion activity coefficient are presented in an early work by Walker, Bray and Johnston (1927). The reliability of these values is dubious for they are computed from inexact titrametric alkalinity measurements in sodium and potassium chloride solutions. Many discrepancies in the reported thermodynamic properties of bicarbonate salts solutions are possibly due to the incapability of the two above techniques to predict accurately the activity coefficient of the free bicarbonate ion.

In lieu of the Ion Association Model, Butler and Huston (1970) have studied the activity of HCO_3^- in NaCl solutions according to Harned's Rule. Harned's Rule reduces to the simplified Interaction Model at high ionic strengths. Other than this study little is known about the interaction properties of the bicarbonate ion in natural waters.

This dissertation presents a theoretical approach to the determination of the virial coefficients of HCO_3^- in natural waters at various temperatures. Based on this approach the virial coefficients of various bicarbonate salts are evaluated from experimental results. These salts included the following bicarbonate compounds: $NaHCO_3$, $KHCO_3$, NH_4HCO_3, $Ca(HCO_3)_2$, and $Mg(HCO_3)_2$. The cations of these salts are the most important positively charged ions in natural and polluted waters. Thus, the knowledge of their respective interaction characteristics permits a more precise understanding of the equilibrium conditions of most water bodies.

1.5 Effects of Temperature on Aqueous Solutions' Equilibria

Local, seasonal and diurnal temperature variations are often observed in most natural phenomena. Temperature changes are of special interest in natural waters because, in general, their thermodynamic properties are temperature dependent. An example of these properties is the ion activity coefficient, which has a strong temperature dependence. In the activity coefficient equation both the long-range electrostatic function and the short-range interaction term are temperature functions.

Included in this work is a detailed study of the thermodynamic effects of temperature on the activity and osmotic coefficients of aqueous solutions. Finally, a computer program which takes into consideration temperature effects in the Ion Interaction Model is also included. Some of the many common water chemistry problems which may be solved with the aid of this computer program are studied in the chapter on Practical Applications.

Chapter 2

THE ION INTERACTION MODEL

2.1 Literature Review

The Ion Interaction Model was originally developed by Brønsted (1927) who proposed that the thermodynamic properties of aqueous solutions could be evaluated from the interactive forces between the ions in solution. He assumed that interactions between oppositely charged ions would be dominant, thus neglecting like-charge ion interaction. Guggenheim (1936) made a distinction between the two terms in the activity coefficient equation: the electrostatic interaction function and the short-range interaction term. He described the first function by the Debye-Hückel equation, which he assumed depended only on the ionic strength and the temperature of the solution. He also assumed that the second term might be described by a polynomial function in concentration with a linear leading term.

The emphasis of more recent publications has been the study of the short-range interaction term. Many researchers, including Guggenheim and Turgeon (1955), and Lewis and Randall (1961), have used a simple approach to this problem. They have assumed that the interaction term may be described by a linear function in concentration. Whitfield (1973) has utilized this assumption, which yielded reasonable results for the activity and osmotic coefficients of concentrated electrolytes. Marked deviations from linearity in the short-range interaction term may be observed at low ionic strengths.

Pitzer (1973) has developed a mathematical model which takes into consideration deviations from linearity. By considering like-charge interactions Pitzer and Kim (1974) have obtained excellent agreement between calculated and experimental measurements of the activity and osmotic coefficients of mixed electrolytes. The theory developed by Pitzer (1973) for the Ion Association Model appears to be the most accurate technique for predicting the equilibrium conditions of mixed electrolytes. The basic principles of Pitzer's theory, along with some temperature considerations, are presented in this dissertation. For more detailed information the reader is referred to the original publications.

2.2 General Equations

By convention, the ionic strength of a mixed electrolyte solution, I, is defined as follows:

$$I = \tfrac{1}{2}\sum_i m_i Z_i^2 \tag{2.1}$$

where m_i represents the molal concentration of any ion i in solution, and

Z_i represents the valence of any ion i in solution.

The osmotic coefficient of a solution is intimately related to various thermodynamic properties of its component solvent and solutes. The activity coefficients of the solvent and the ions in solution are, for example, related to the osmotic coefficient of the solution. Due to the importance and interdependence of these thermodynamic properties, a detailed study of the osmotic coefficient of mixed electrolyte solutions is presented in this dissertation.

Based on the Ion Interaction Theory, Pitzer and Kim (1974) propose the following equation for the osmotic coefficient, ϕ, of a mixed electrolyte solution:

$$\phi - 1 = \frac{1}{\sum_i m_i} \left\{ 2If^{\phi} + 2\sum_c \sum_a m_c m_a \left[B^{\phi}_{ca} + 2\left(\sum_c m_c Z_c\right) C_{ca} \right] \right.$$
$$+ \sum_c m_c \sum_{c'} m_{c'} \left[\theta_{cc'} + I\theta'_{cc'} + \sum_a m_a \Psi_{cc'a} \right]$$
$$\left. + \sum_a m_a \sum_{a'} m_{a'} \left[\theta_{aa'} + I\theta'_{aa'} + \sum_c m_c \Psi_{caa'} \right] \right\} \quad (2.2)$$

where $f^{\phi} = \dfrac{-A\sqrt{I}}{1 + 1.2\sqrt{I}}$ (Debye-Hückel function) (2.3)

A represents the Debye-Hückel coefficient. This coefficient is a function of the temperature of the solution, T, and is equal to 0.392 at 25°C,

$$B^{\phi}_{MX} = \beta^{o}_{MX} + \beta^{1}_{MX} e^{-\alpha_1\sqrt{I}} \quad (2.4)$$

c, c' and M represent the names of the cations in solution,

a, a' and X represent the names of the anions in solution.

$\sum_c m_c Z_c = -\sum_a m_a Z_a$ represents the total molal charge of the solution,

β^o and β^1 represent the first and second virial coefficients, C represents the third virial coefficient,

θ represents the interaction coefficient between like-charge ions.

$$\theta' = \partial\theta/\partial I \tag{2.5}$$

Ψ represents the interaction coefficient for triplets.

α_1 equals 2.0 for 1:1, 1:2 and 1:3 electrolytes, or

α_1 equals 1.4 for 2:2 electrolytes.

The virial coefficients of 227 pure aqueous 1:1, 1:2 and 1:3 electrolytes at 25°C are evaluated and presented by Pitzer and Mayorga (1973). Numerical values for some like-charge and triplets interaction coefficients are listed by Pitzer and Kim (1974).

The long-range interaction effects on the osmotic coefficient of a solution are mathematically simulated by the Debye-Huckel function, which is represented by the first term in equation (2.2). The remaining terms in this equation simulate the short-range interaction effects on the osmotic properties of a solution.

Two important thermodynamic properties of aqueous mixed electrolytes, the osmotic pressure of a solution and the activity coefficient of the solvent, may be computed from the osmotic coefficient of the solution. Lewis and Randall (1961) propose the following two equations for the osmotic pressure of mixed electrolytes, Π, and the activity of water, a_1:

$$\Pi = \frac{RT}{v_1} \frac{M_1}{1000} \phi \sum_i m_i \tag{2.6}$$

$$\ln a_1 = -\frac{M_1}{1000} \phi \sum_i m_i \tag{2.7}$$

where R represents the gas constant and equals 1.98726 cal/^{o}K - mole,

T represents the absolute temperature in Kelvin degrees,

v_1 represents the partial volume of water. ($v_1 \cong 18.0$ cc/mol for an infinite dilution at standard temperature and pressure.)

M_1 represents the molecular weight of the solvent (18.0 g/mol for water).

An electrolyte composed of a cation M with valence Z_M and an anion X with valence Z_X dissociates in water according to the reaction

$$M^{Z_M}_{\nu_M} X^{Z_X}_{\nu_X} \longrightarrow \nu_M M^{Z_M} + \nu_X X^{Z_X} \tag{2.8}$$

where ν_M represents the number of cations of M per molecule of MX, and

ν_X represents the number of anions of X per molecule of MX.

To satisfy the electroneutrality condition of the electrolyte MX it is necessary that

$$\nu_M Z_M = \nu_X \left| Z_X \right| \tag{2.9}$$

The activity coefficient of the electrolyte MX in solution, γ_{MX}, is computed from the geometric mean of the activity coefficient of the cation γ_M and the activity coefficient of the anion γ_X :

$$\gamma_{MX} = \left(\gamma_M^{\nu_M} \gamma_X^{\nu_X} \right)^{1/\nu} \tag{2.10}$$

where $\nu = \nu_M + \nu_X$ (2.11)

Based on the Ion Interaction Theory, Pitzer and Kim (1974) propose an equation for the computation of the activity coefficient of an electrolyte MX in a multicomponent solution. This equation may be easily resolved by symmetry into its two individual components, the activity coefficients of the cation and the anion. The two equations obtained by this procedure are presented below:

$$\begin{aligned}\ln \gamma_M = {} & Z_M^2 f + 2\sum_a m_a \left[B_{Ma} + \left(\sum_c m_c Z_c \right) C_{Ma} \right] \\ & + 2\sum_c m_c \theta_{Mc} + \sum_c m_c \sum_a m_a \left(Z_M^2 B'_{ca} + Z_M C_{ca} + \Psi_{Mca} \right) \\ & + \tfrac{1}{2} \sum_a m_a \sum_{a'} m_{a'} \left(\Psi_{Maa'} + Z_M^2 \theta'_{aa'} \right) \\ & + \frac{Z_M^2}{2} \sum_c m_c \sum_{c'} m_{c'} \theta'_{cc'}\end{aligned} \qquad (2.12)$$

and

$$\begin{aligned}\ln \gamma_X = {} & Z_X^2 f + 2\sum_c m_c \left[B_{cX} + \left(\sum_c m_c Z_c \right) C_{cX} \right] \\ & + 2\sum_a m_a \theta_{Xa} + \sum_c m_c \sum_a m_a \left(Z_X^2 B'_{ca} + \left| Z_X \right| C_{ca} + \Psi_{caX} \right) \\ & + \tfrac{1}{2} \sum_c m_c \sum_{c'} m_{c'} \left(\Psi_{cc'X} + Z_X^2 \theta'_{cc'} \right) \\ & + \frac{Z_X^2}{2} \sum_a m_a \sum_{a'} m_{a'} \theta'_{aa'}\end{aligned} \qquad (2.13)$$

where

$$f = - A \left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2} \ln (1 + 1.2\sqrt{I}) \right] \qquad (2.14)$$

$$B_{MX} = \beta^{o}_{MX} + \beta^{1}_{MX} \, g_1 (I) \qquad (2.15)$$

$$B'_{MX} = \beta^{1} g'_1 (I) \qquad (2.16)$$

$$g_1(I) = \frac{2}{\alpha_1^2 I}\left[1 - \left(1 + \alpha_1\sqrt{I}\right)e^{-\alpha_1\sqrt{I}}\right] \quad (2.17)$$

$$g_1'(I) = \frac{2}{\alpha_1^2 I^2}\left[-1 + \left(1 + \alpha_1\sqrt{I} + \tfrac{1}{2}\alpha_1^2 I\right)e^{-\alpha_1\sqrt{I}}\right] \quad (2.18)$$

Seemingly, the equations to calculate the osmotic and activity coefficients of a solution are very lengthy. Nevertheless, it must be remembered that at the given ionic strength of the electrolyte solution, f^{ϕ}, f, g_1 and g_1' are constant. Therefore, the Ion Interaction Model is a simple and accurate technique to calculate the equilibrium properties of mixed electrolyte solutions.

The above equations are somewhat simplified in the case of the dissolution of a single electrolyte. Since only one anion and one cation are present in this type of solution, the contributions of θ, θ' and Ψ are non-existent. The equations which describe the thermodynamic properties of pure salt solutions are given by Pitzer and Mayorga (1973). It was previously mentioned that these authors report the values of the first, second and third virial coefficients of 227 1:1, 1:2 and 1:3 electrolytes. These parameters were obtained by least square analyses of various thermodynamic properties of single electrolyte solutions.

Pitzer and Kim (1974) suggest that in most practical cases θ may be assumed to be constant over the ionic strength. In other words, they assume θ' to be equal to 0. Based on the above assumption they are able to predict accurately the activity and osmotic coefficients of 69 multicomponent solutions. They also report the values of θ and

Ψ utilized in such predictions.

The effect of θ' on the thermodynamic properties of most mixed electrolytes is minor. However, if maximum accuracy is desired in the prediction of these properties it becomes necessary to consider the variation of θ with the ionic strength. For complete information on the dependence of the like-charge interaction coefficient with ionic strength, the reader is referred to work of Pitzer (1975).

2.3 The Ion Interaction Theory for 2:2 Electrolyte Solutions

The capability of an electrolyte to completely dissociate in a solvent is directly related to the electrostatic attraction between the counterions in solution. Obviously, this electrostatic attraction increases as the absolute value of the counterions' charges increase. The model presented thus far may be used to describe the thermodynamic properties of electrolyte solutions only in the case where the absolute values of the valences of one or both counterions are equal to one. The particular case of 2:2 electrolytes (which do not completely dissociate in aqueous solutions) is considered in this section.

The osmotic coefficients of various single divalent cation sulfates at 25^{o}C, as experimentally determined by various researchers, were summarized by Pitzer (1972). These coefficients were successfully predicted by Pitzer and Mayorga (1974) by means of an interaction model, which takes into consideration incomplete electrolyte dissociation. Their approach consisted in adding an extra interaction term to the B^{ϕ}, B and B' equations. Even though this approach gave excellent results for single divalent cation sulfates it failed to predict their solubility product in seawater (Whitfield (1975a,b)). In these publications Whitfield utilizes a hybrid model (a combination between the Ion Association Model and the Ion Interaction Model) which permits a reasonable explanation of the difference between measured and calculated solubility products of sulfate salts in seawater. The hybrid model proposed by Whitfield assumes simultaneously Pitzer and Mayorga's compensation for ion association, as well as the existence of ion pairs as individual entities.

Three conclusions may be drawn from the above works:

a) Pitzer and Mayorga's interaction model for incomplete dissociation of divalent cation sulfates in aqueous solutions works satisfactorily in the case of single salt solutions, but fails to predict the thermodynamic properties of such sulfate salts in mixed electrolyte solutions.

b) The inclusion of the extra interaction term in Whitfield's hybrid model is redundant, for the purpose of this term is to compensate for ion association.

c) The simplicity of the Ion Interaction Model is destroyed when the particular problem of incomplete dissociation is approached from the point of view of ion association. In other words, if a hybrid model is utilized (by considering ion pairs as individual components of the solution) tedious iterations must be performed to satisfy both the mass balance and electroneutrality conditions of the solution.

A modification to Pitzer and Mayorga's work is proposed in this dissertation. This modification permits one to compensate for incomplete dissociation without implicitly considering ion pairing. The thermodynamic solubility product of gypsum (i.e., $CaSO_4 \cdot 2H_2O$) in a variety of mixed electrolyte solutions is studied in Chapter 5. The prediction accuracy of this thermodynamic constant confirms the validity of the proposed modification. Following is presented the proposed Ion Interaction Model for 2:2 electrolyte solutions.

The activity of an individual ion is reduced by a factor δ if incomplete dissociation occurs. The value of this factor varies from unity for complete dissociation, to zero for nil dissociation. It is assumed in this dissertation that 2:2 electrolytes in solution associate to some extent, while 1:1, 1:2 and 1:3 electrolytes do not experience this phenomenon. The following empirical equation is proposed for δ:

$$\ln \delta_i = \beta^2_{ij}\, m_j\, g_2\,(I^*) \tag{2.19}$$

where i represents the divalent cation M or the divalent anion X,

j represents the divalent anion X or the divalent cation M,

β^2 represents the association virial coefficient, which must be determined experimentally,

I^* represents the pseudo-ionic strength of M and X. I.e.,

$$I^* = \tfrac{1}{2}\left(m_M Z_M{}^2 + m_X Z_X{}^2\right) \tag{2.20}$$

and $$g_2(I^*) = \frac{2}{\alpha_2^2 I^*}\left[1 - \left(1 + \alpha_2\sqrt{I^*} - \frac{\alpha_2^2 I^*}{2}\right)e^{-\alpha_2\sqrt{I^*}}\right] \quad (2.21)$$

Thus, the individual ion activity coefficient, compensated for incomplete electrolyte dissociation, γ_i^c, may be computed as follows:

$$\ln\gamma_i^c = \ln\gamma_i + \ln\delta_i \quad (2.22)$$

An extra term must be added to the B^ϕ equation to compensate the osmotic coefficient for incomplete electrolyte dissociation. The proposed equation is as follows:

$$B_{MX}^\phi = \beta_{MX}^o + \beta_{MX}^1 e^{-\alpha_1\sqrt{I}} + \beta_{MX}^2 e^{-\alpha_2\sqrt{I^*}} \quad (2.23)$$

Values of β^2 for various divalent cation sulfates are presented in Pitzer and Mayorga's work. The values of α, which are also those recommended in the aforementioned work are listed in Table 2.1.

TABLE 2.1

α VALUES

Electrolyte	α_1	α_2
1:1	2.0	0
1:2	2.0	0
1:3	2.0	0
2:2	1.4	12.0

Examination of equations (2.19) through (2.23) reveals that these equations reduce to those proposed by Pitzer and Mayorga for the particular case of a pure salt solution. It is interesting to note that due to the large value of α_2, the exponential terms in both equations (2.21) and (2.23) rapidly tend to zero as the ionic strength increases. In relatively concentrated single electrolyte solutions ($I > 0.1m$) the equations proposed in this dissertation predict that the effect of β^2 on the solution osmotic coefficient is nil, while this effect reduces the $\ln \gamma_i$ by a constant equal to $2\beta^2_{ij} m_j / \alpha_2^2 I^*$ Experimental measurements of the osmotic and activity coefficient of divalent cation sulfate solutions confirm these trends (Pitzer (1972)).

2.4 Example

The purpose of the numerical example in this section is to apply the Ion Interaction Model in order to calculate the thermodynamic properties of a mixed electrolyte solution.

Statement: Marshall and Slusher (1966) report that the solubility of gypsum ($CaSO_4 \cdot 2H_2O$) in a 0.548 m NaCl solution at 25°C is 0.0372 m/1. Calculate the thermodynamic solubility product of gypsum.

Solution: The molal concentrations of the ions in solution are:

$$m_{Na} = m_{Cl} = 0.548$$

and

$$m_{Ca} = m_{SO_4} = 0.0372.$$

The ionic and pseudo-ionic strengths of this solution are, according to equations (2.1) and (2.20), respectively:

$$I = \tfrac{1}{2}\sum_i m_i z_i^2 = 0.6968\,m$$

$$I^* = \tfrac{1}{2}\left(m_M Z_M{}^2 + m_X Z_X{}^2\right) = 0.1488\,m$$

where, for this particular case, i represents all the ions in solution (i.e., Na, Ca, Cl, SO_4), M represents Ca and X represents SO_4.

The functions f(I), and f^{ϕ} may be computed from equations (2.14) and (2.3) respectively (at 25°C A = 0.392):

$$f = -A\left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2}\ \ln(1+1.2\sqrt{I})\right] = -0.6169$$

$$f^{\phi} = \frac{-A\sqrt{I}}{1+1.2\sqrt{I}} = -0.1635$$

The functions g_1 (I), g_1' (I), and g_2 (I*) are then computed from equations (2.17), (2.18) and (2.21) respectively. The values of α_1 and α_2 (which are presented in Table 2.1) and the previously calculated magnitudes of I and I* are the input parameters for these equations.

$$g_1(I) = \frac{2}{\alpha_1{}^2 I}\left[1 - \left(1+\alpha_1\sqrt{I}\right)e^{-\alpha_1\sqrt{I}}\right]$$

$$= 0.3568 \text{ for } \alpha_1 = 2.0$$

$$= 0.4774 \text{ for } \alpha_1 = 1.4$$

$$g_1'(I) = \frac{2}{\alpha_1{}^2 I^2}\left[-1 + \left(1+\alpha_1\sqrt{I} + \tfrac{1}{2}\alpha_1{}^2 I\right)e^{-\alpha_1\sqrt{I}}\right]$$

$$= -0.2417 \text{ for } \alpha_1 = 2.0$$

$$= -0.2391 \text{ for } \alpha_1 = 1.4$$

$$g_2(I^*) = \frac{2}{\alpha_2{}^2 I^*}\left[1 - \left(1+\alpha_2\sqrt{I^*} - \frac{\alpha_2{}^2 I^*}{2}\right)e^{-\alpha_2\sqrt{I^*}}\right]$$

$$= 0.0980 \text{ for } \alpha_2 = 12.0$$

The virial coefficients for the various sets of oppositely charged ions in solution, as determined by Pitzer and Mayorga (1973), are as follows:

M	X	β^o	β^1	β^2	C
Na	Cl	0.0765	0.266		6.4×10^{-4}
Na	SO_4	0.0196	1.113		2.0×10^{-3}*
Ca	Cl	0.3159	1.614		-1.2×10^{-4}
Ca	SO_4	0.2000	2.650	-55.7	0.0

*Improved value by Pitzer and Kim (1974)

The values of most like-charge and triplet interaction coefficients, which are required in this example, are given by Pitzer and Kim (1974) and Downes and Pitzer (1976). These values are as follows:

$$\theta_{Na,Ca} = 0.000$$

$$\theta_{Cl,SO_4} = -0.020$$

$$\Psi_{Na,Cl,SO_4} = 0.004$$

$$\Psi_{Na,Ca,Cl} = 0.000$$

The B^ϕ, B, B' and δ parameters are described by the next four equations (equations (2.23), (2.15), (2.16) and (2.19) respectively):

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

$$B_{MX} = \beta^o_{MX} + \beta^1_{MX} \; g_1(I)$$

$$B'_{MX} = \beta^1 g'_1(I)$$

$$\ln\delta_i = \beta^2_{ij} m_j g_2(I^*)$$

The results obtained by applying these equations to the mixed electrolyte solution yield the following:

M	X	B^{ϕ}	B	B'
Na	Cl	0.127	0.172	-0.045
Na	SO_4	1.878	0.417	-0.187
Ca	Cl	3.010	0.892	-0.272
Ca	SO_4	1.021	1.465	-0.441

$$\ln\gamma_{Ca} = \ln\gamma_{SO_4} = -0.2031$$

In order to solve the stated problem it is not necessary to compute the activities of the sodium and chloride ions. Therefore, only the activities of the calcium and sulfate ions are calculated in this exercise. The osmotic coefficient of the solution and the activity of calcium and sulfate may be computed from equations (2.2), (2.12) and (2.13) respectively. The net effect of θ' on the calculated osmotic and activity coefficients is usually minor, and for most practical applications may be ignored. Without much loss of accuracy one may assume that θ' and the unavailable Ψ values are equal to zero. Therefore, the osmotic coefficient of the solution, and the uncompensated activity coefficients of the calcium and sulfate ions are computed as follows:

$$\phi - 1 = \frac{1}{\sum_i m_i} \left\{ 2If^{\phi} + 2\sum_c \sum_a m_c m_a \left[B^{\phi}_{ca} + 2 \left(\sum_c m_c Z_c \right) C_{ca} \right] \right.$$

$$+ \sum_c m_c \sum_{c'} m_{c'} \left[\theta_{cc'} + \cancelto{0}{I\theta'_{cc'}} + \sum_a m_a \Psi_{cc'a} \right]$$

$$\left. + \sum_a m_a \sum_{a'} m_{a'} \left[\theta_{aa'} + \cancelto{0}{I\theta'_{aa'}} + \sum_c m_c \Psi_{caa'} \right] \right\}$$

$$= - 0.09961$$

Therefore, $\phi = 0.90039$

$$\ln \gamma_M = Z_M^2 f + 2\sum_a m_a \left[B_{Ma} + \left(\sum_c m_c Z_c \right) C_{Ma} \right]$$

$$+ 2\sum_c m_c \theta_{Mc} + \sum_c m_c \sum_a m_a \left(Z_M^2 B'_{ca} + Z_M C_{ca} + \Psi_{Mca} \right)$$

$$+ \tfrac{1}{2} \sum_a m_a \sum_{a'} m_{a'} \left(\Psi_{Maa'} + \cancelto{0}{Z_M^2 \theta'_{aa'}} \right)$$

$$= - 1.5063$$

$$\ln \gamma_X = Z_X^2 f + 2\sum_c m_c \left[B_{cX} + \left(\sum_c m_c Z_c \right) C_{cX} \right]$$

$$+ 2\sum_a m_a \theta_{Xa} + \sum_c m_c \sum_a m_a \left(Z_X^2 B'_{ca} + \left| Z_X \right| C_{ca} + \Psi_{caX} \right)$$

$$+ \tfrac{1}{2} \sum_c m_c \sum_{c'} m_{c'} \left(\Psi_{cc'X} + \cancelto{0}{Z_X^2 \theta'_{cc'}} \right)$$

$$= - 2.0638$$

Where, for this particular case, the subscripts in the above equations represent:

$M = Ca$

$X = SO_4$

$c = Na, Ca$

$c' = Ca, Na$

$a = Cl, SO_4$

$a' = SO_4, Cl$

$i = Na, Ca, Cl, SO_4$

The compensated activity coefficients of the calcium and sulfate ions are computed by inserting the appropriate values into equation (2.21):

$$\ln \gamma_i^c = \ln \gamma_i + \ln \delta_i = \begin{cases} -1.7094 & \text{for } i = Ca \\ -2.2669 & \text{for } i = SO_4 \end{cases}$$

Therefore, $\gamma_{Ca}^c = 0.1810$

$\gamma_{SO_4}^c = 0.1036$

The activity of the solvent, water, may be evaluated from the knowledge of the solution osmotic coefficient and the molality of the species in solution. From equation (2.7) one obtains:

$$\ln a_1 = -\frac{M_1}{1000} \phi \sum_i m_i \qquad \text{(where } M_1 = 18.0\text{)}$$

$$= -0.0190$$

Therefore, $a_1 = 0.9812$

Finally, it is now possible to calculate the thermodynamic solubility product of gypsum at 25°C from the above parameters. This thermodynamic constant is evaluated as follows:

$$K_{sp} = m_{Ca}\, m_{SO_4}\, \gamma^c_{Ca}\, \gamma^c_{SO_4}\, a_1^2 \tag{2.24}$$

$$= 2.498 \times 10^{-5}$$

Chapter 3

TEMPERATURE EFFECTS ON THE THERMODYNAMIC PROPERTIES OF ELECTROLYTE SOLUTIONS

3.1 Thermal Effects on Electrostatic Interactions

The thermodynamic properties of aqueous solutions are usually strongly dependent on temperature. The assumption that natural waters may be treated as mixed electrolytes under ideal conditions of standard temperature and pressure is often incorrect. Although pressure variations are of importance in chemical equilibrium, such variations are of little importance in the study of surface waters, which are the main concern of Environmental Engineering. The scope of this chapter is the study of the temperature effects on the thermodynamic equilibrium properties of aqueous solutions at one atmosphere total pressure.

Literature information on the temperature effects on electrolyte solutions equilibria is abundant. This information is usually analyzed from the Ion Association Model point of view. Perhaps one of the most complete works in this area is that of Helgeson (1967), who calculates several thermodynamic properties of various electrolyte solutions as a function of temperature. Among these properties he includes the thermodynamic dissociation constants of Brønsted acids and ion pairs. Helgeson's work is an important reference when the Ion

Interaction Model is utilized to estimate thermal effects on Brønsted acids' equilibria.

The Ion Interaction Model may be used to describe the thermodynamic properties of aqueous solutions at variable temperatures. Lewis and Randall (1961) conclude that both the long-range electrostatic attraction and the short-range interaction between ions in solution are temperature dependent. The electrostatic attraction terms for the osmotic and activity coefficients may be computed from equations (2.3) and (2.14) respectively. The only temperature dependent parameter in these equations is the parameter A, which has a triple dependence on temperature. This parameter is a direct function of temperature, the solvent dielectric constant and the coefficient of thermal expansion of the solvent (Lewis and Randall (1961)). The effect of temperature on the volumetric expansion for water is unimportant when compared with the two other dependences, and it is ignored in this dissertation.

The dielectric constant of water may be expressed as a polynomial function of temperature. A least-square criterion for curvilinear regression may be utilized to evaluate the coefficients of this polynomial. Utilizing the above criterion to fit a third-degree polynomial to the tabulated values of the dielectric constant of water (Weast (1975)), the following equation is obtained:

$$\epsilon = 87.924 - 0.40873\, t + 1.01465 \times 10^{-3}\, t^2 - 1.9365 \times 10^{-6}\, t^3 \tag{3.1}$$

where ϵ represents the dielectric constant of water, and

t represents the water temperature in centigrade degrees.

$$t = T - 273.16 \tag{3.2}$$

The coefficients in equation (3.1) are in close agreement with the values reported earlier by Harned and Owen (1958). The equation which describes the dependence of A with respect to temperature is given below (Robinson and Stokes (1959)):

$$A = \frac{1.400 \times 10^6}{(\epsilon T)^{3/2}} \tag{3.3}$$

The temperature effects on the long-range electrostatic interaction terms (in the osmotic and activity coefficients equations) may be calculated by means of the three above relationships and equations (2.3) and (2.14). These thermal effects are often of higher magnitude than the ones observed for the short-range interaction terms. Following is presented a thermodynamic analysis of these secondary temperature effects on the activity and osmotic coefficients of electrolyte solutions.

3.2 Thermal Effects on Short-Range Interactions

Several thermodynamic parameters are intimately related to the temperature effects on the interactive properties of ions in solution. Direct or indirect measurements of these properties may be utilized to compute the dependence of short-range interactions with respect to temperature. A general summary of some temperature related thermodynamic properties not listed in this dissertation is available in the works by Fortier and Desnoyers (1976) and Lewis and Randall (1961).

Pitzer and Mayorga (1973) propose the following relationship for the excess Gibbs energy of mixing of single electrolyte solutions:

$$\frac{G^{ex}}{n_1RT} = -\frac{4AI}{1.2}\ \ln\,(1 + 1.2\sqrt{I})$$
$$+\ 2m^2\,\nu_M\nu_X\left[\beta^o_{MX} + \beta^1_{MX}\,g_1\,(I) + \beta^2_{MX}\left(g_2\,(I^*) - e^{-\alpha_2\sqrt{I^*}}\right)\right]$$
$$+\ 2m^3\,z_M\,\nu_M\,C_{MX} \qquad (3.4)$$

where G^{ex} represents the excess Gibbs energy of mixing,

m represents the molality of the solution, and

I* equals I for single electrolyte solutions.

The excess Gibbs energy of mixing is related to the relative apparent molal enthalpy of an electrolyte in solution by the following partial differential equation:

$$\phi_L = \frac{1}{m}\ \frac{\partial(G^{ex}/T)}{\partial(1/T)}\Bigg|_{T,m} \qquad (3.5)$$

where ϕ_L represents the apparent molal enthalpy of an electrolyte in solution relative to infinite dilution.

Combining equations (3.4) and (3.5) one may express the temperature variation of the virial coefficients as a function of ϕ_L:

$$-\frac{1}{2m\,\nu_M\nu_X T^2}\left\{\frac{\phi_L}{R} + 3.333\,\frac{I}{m}\,\ln(1 + 1.2\sqrt{I})\,\frac{\partial A}{\partial(1/T)}\right\}_T$$
$$=\left\{\frac{\partial\beta^o_{MX}}{\partial T} + \frac{\partial\beta^1_{MX}}{\partial T}\,g(I) + \frac{\partial\beta^2_{MX}}{\partial T}\left(g_2\,(I^*) - e^{-\alpha_2\sqrt{I^*}}\right) + m\,\frac{z_M}{\nu_X}\,\frac{\partial C_{MX}}{\partial T}\right\}_T \qquad (3.6)$$

In general, calculations of activity and osmotic coefficients show that the relative importance of the parameters C, θ and Ψ is secondary. The variation of these parameters with temperature is probably even of less importance. It is therefore assumed in this work that $\partial C/\partial T = \partial \theta/\partial T = \partial \Psi/\partial T = 0$. Assuming no variation of the C virial coefficient with temperature, equation (3.6) may be represented by a linear polynomial of the form:

$$Y = b_o + b_1 X_1 + b_2 X_2 \tag{3.7}$$

where Y represents the left side terms of equation (3.6),

X_1 and X_2 represent the respective functions of I and I* in equation (3.6), and

b_o, b_1 and b_2 represent $\partial\beta^o/\partial T$, $\partial\beta^1/\partial T$ and $\partial\beta^2/\partial T$ respectively.

It is important to remember that β^2 represents the ion pairing virial coefficient. In this study this coefficient differs from zero only in the case of 2:2 interaction. Thus, $\partial\beta^2/\partial T$ is equal to zero for 1:1, 1:2 and 1:3 electrolyte solutions. For such solutions, graphs of Y with respect to X_1 should yield points lying on straight lines in which the intercept, b_o, represents $\partial\beta^o/\partial T$ and the slope of the line, b_1, represents $\partial\beta^1/\partial T$. This graphical technique permits one to evaluate readily the variation of the first two virial coefficients with respect to temperature. A more complete graphical method, which permits the simultaneous evaluation of b_o, b_1 and b_2 for 2:2 electrolyte solutions, is discussed later in this section.

Another important thermodynamic property, the relative partial molal enthalpy of an electrolyte in solution, is related to the activity coefficient of the electrolyte as follows:

$$\bar{L}\Big|_{T,m} = -\nu RT^2 (\partial \ln \gamma_{MX}/\partial T) \tag{3.8}$$

where $\overline{L}$ represents the partial molal enthalpy of an electrolyte in solution relative to infinite dilution.

In single electrolyte solutions, the rate of variation of the virial coefficients with respect to temperature may be also computed from experimental measurements of $\overline{L}$. This is obtained by differentiating the individual components of equation (2.10) with respect to temperature. Then by rearranging the terms in equation (3.8), the following expression is obtained:

$$\frac{\nu}{4m\nu_M\nu_X}\left\{-\frac{\overline{L}}{\nu RT}+\left|Z_MZ_X\right|\left[\frac{\sqrt{I}}{1+1.2\sqrt{I}}+\frac{2}{1.2}\ln\left(1+1.2\sqrt{I}\right)\right]\right\}_T$$

$$=\frac{\partial\beta^{o}_{MX}}{\partial T}+\frac{\partial\beta^{1}_{MX}}{\partial T}\left(\frac{g_1(I)+e^{-\alpha_1\sqrt{I}}}{2}\right)$$

$$+\ g_2(I^*)\frac{\partial\beta^{2}_{MX}}{\partial T}+\frac{3m}{2}\nu_MZ_M\frac{\partial C_{MX}}{\partial T} \qquad (3.9)$$

If the last term in the previous expression is ignored, this expression may be represented by a linear polynomial of the form of equation (3.7). Obviously, the values of Y, X_1 and X_2 are those of their corresponding functions in equation (3.9). As in the previous case, plots of Y against X_1 values (for 1:1, 1:2 and 1:3 electrolyte solutions) should yield points on straight lines. The significance of the slope and intercept of the lines is the same as before.

Theoretically, the second derivative of the virial coefficients with respect to temperature may be evaluated if either the relative partial molal heat capacity or the relative apparent molal heat capacity are known. The respective equations for these two thermodynamic properties are:

$$\phi_J = \frac{\partial \phi_L}{\partial T}\bigg|_m \tag{3.10}$$

and
$$\bar{J} = \frac{\partial \bar{L}}{\partial T}\bigg|_m \tag{3.11}$$

where ϕ_J represents the molal heat capacity relative to infinite dilution, and

$\bar{J}$ represents the apparent molal heat capacity relative to infinite dilution.

Literature information on the numerical values of the heat capacity functions is rather limited. This information suggests that the variations of ϕ_L and $\bar{L}$ with respect to temperature are small in comparison with their respective values, and for most electrolytes they may be ignored. It is assumed throughout this dissertation that both ϕ_L and $\bar{L}$ do not vary with temperature. In other words, it is assumed that the second partial derivatives of the virial coefficients with respect to temperature are equal to zero.

The functions Y, X_1 and X_2 in equation (3.7) may be evaluated from their respective terms in equations (3.6) and (3.9). The numerical values of Y, X_1 and X_2 for some important electrolytes are presented in tabular forms in the Appendix. Experimental results of ϕ_L and $\bar{L}$ at various ionic strengths are reported in several literature sources. Y values (computed from the experimental results of the 1:1 and 1:2 electrolytes listed in the Appendix) are plotted in Figures 3.1 and 3.2 respectively. As expected, the data points follow a linear correlation, especially for values of X_1 between 0.15 and 0.6. This domain corresponds to values of I approximately between 2.0 and 0.15 m. Devia-

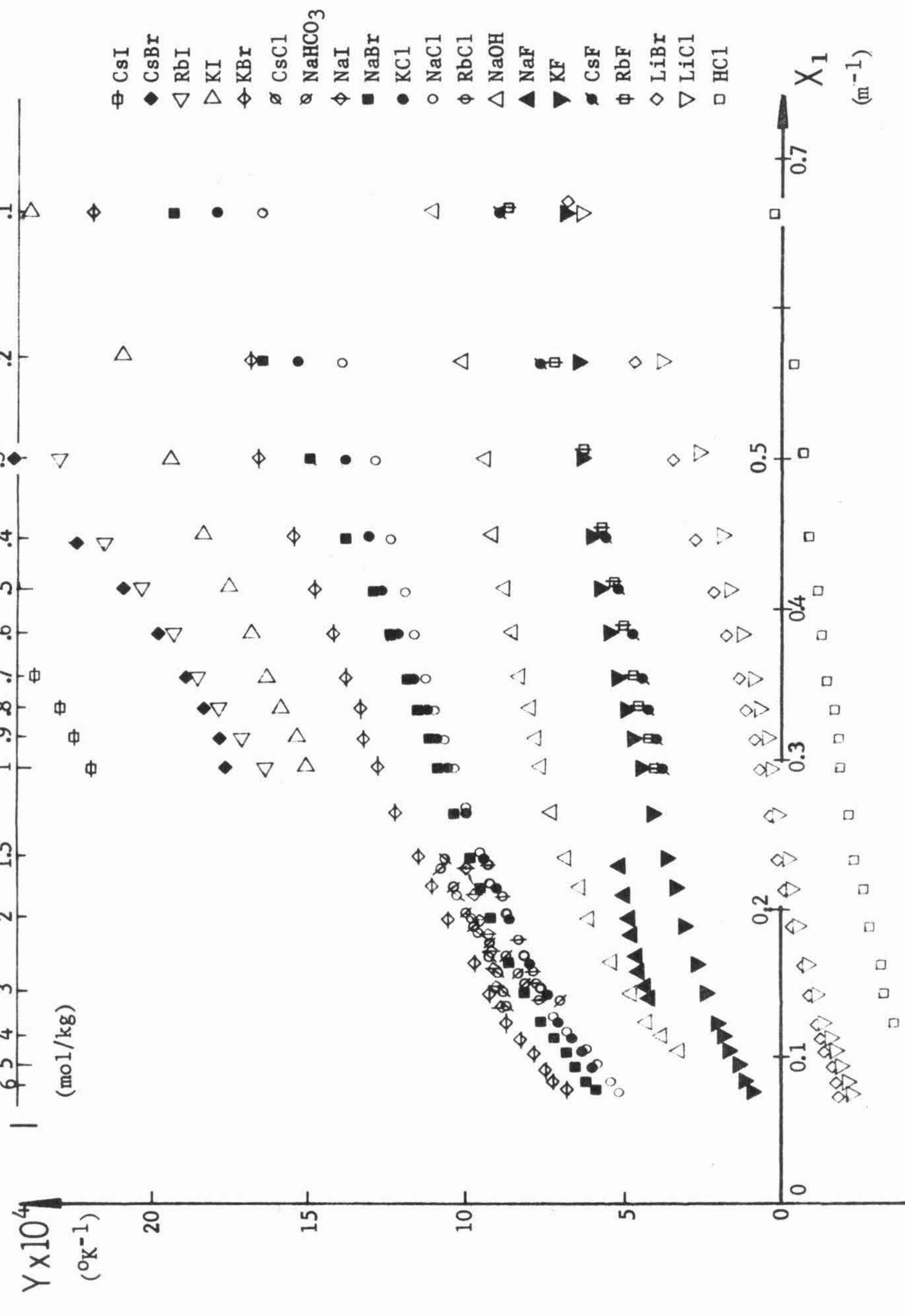

Figure 3.1 Y vs. X_1 Values for 1:1 Electrolytes

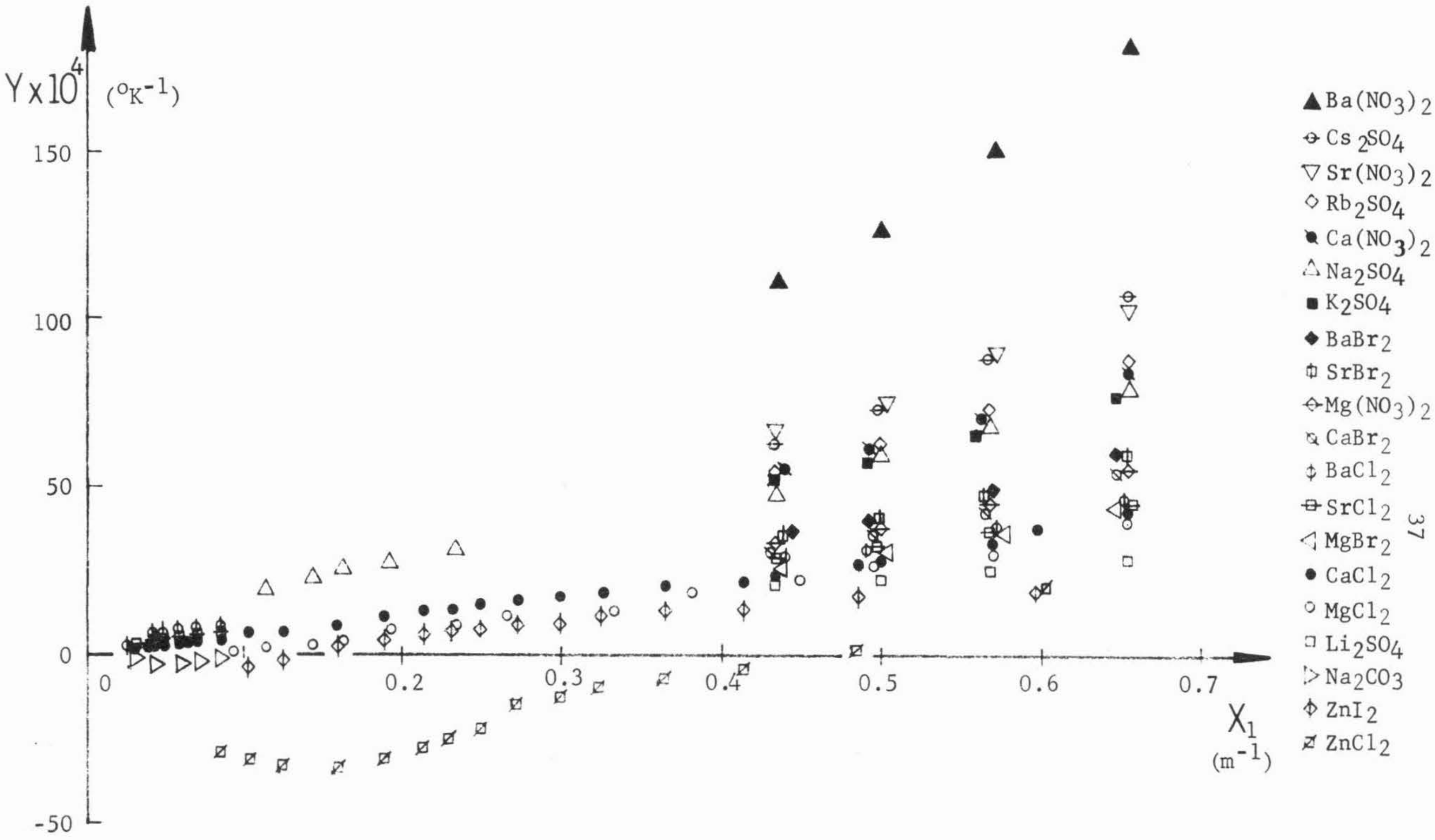

Figure 3.2 Y vs. X_1 Values for 1:2 Electrolytes

tions in the dilute range may be explained by imprecisions in the Ion Interaction Model or more probably to minor experimental errors. Regardless of the actual source of error in the graphical estimation of b_o and b_1, its effect on the computation of both activity coefficients and osmotic coefficients of very dilute solutions is, for all practical purposes, insignificant. Deviations from ideality for extremely concentrated 1:1 electrolyte solutions (X_1 less than 0.15) in Figure 3.1 suggest that the assumption that $\partial C/\partial T$ is equal to zero is probably incorrect. However, for less concentrated solutions linearity is preserved. Thus, the above assumption is sound for ionic strengths below 3.0 m.

The values of b_o and b_1 (i.e., $\partial\beta^o/\partial T$ and $\partial\beta^1/\partial T$) for 1:1 and 1:2 electrolytes were graphically calculated over the linear region in Figures 3.1 and 3.2 respectively. These values were then plotted against their respective virial coefficients at 25°C in Figures 3.3 and 3.4. The points in these figures were not labeled due to their relative closeness.

Figures 3.3 and 3.4 illustrate that there exists a definite correlation between a specific virial coefficient and its variation with temperature. Further, this correlation appears to be linear within the studied range. Assuming that the correlation is linear over the whole plane, it is possible to express a virial coefficient variation with temperature as a linear function of its corresponding virial coefficient. Such linear function is extremely adventageous to calculate the temperature effects on the thermodynamic properties of a

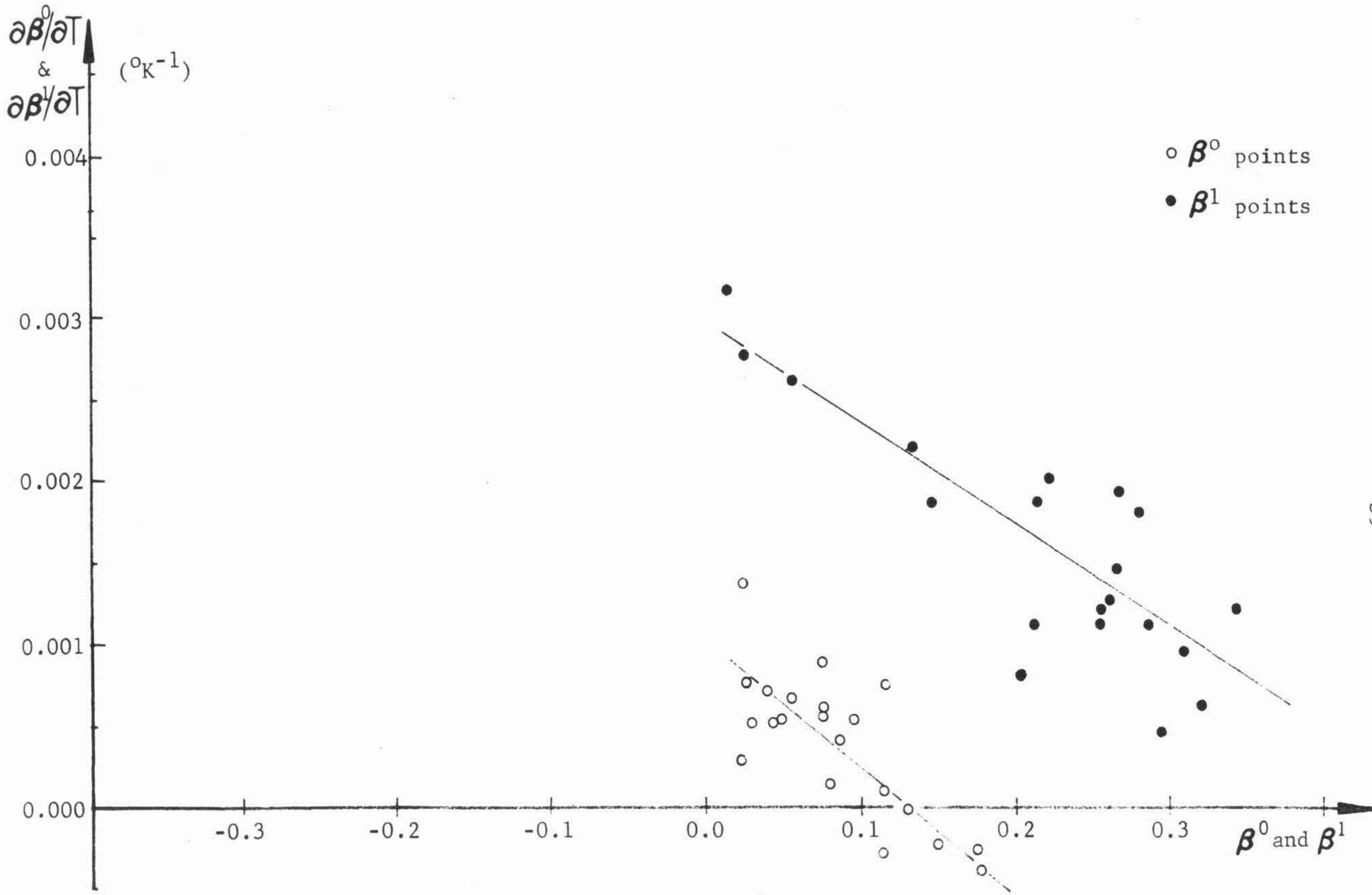

Figure 3.3 Temperature Variation of the First and Second Virial Coefficients of 1:1 Electrolytes

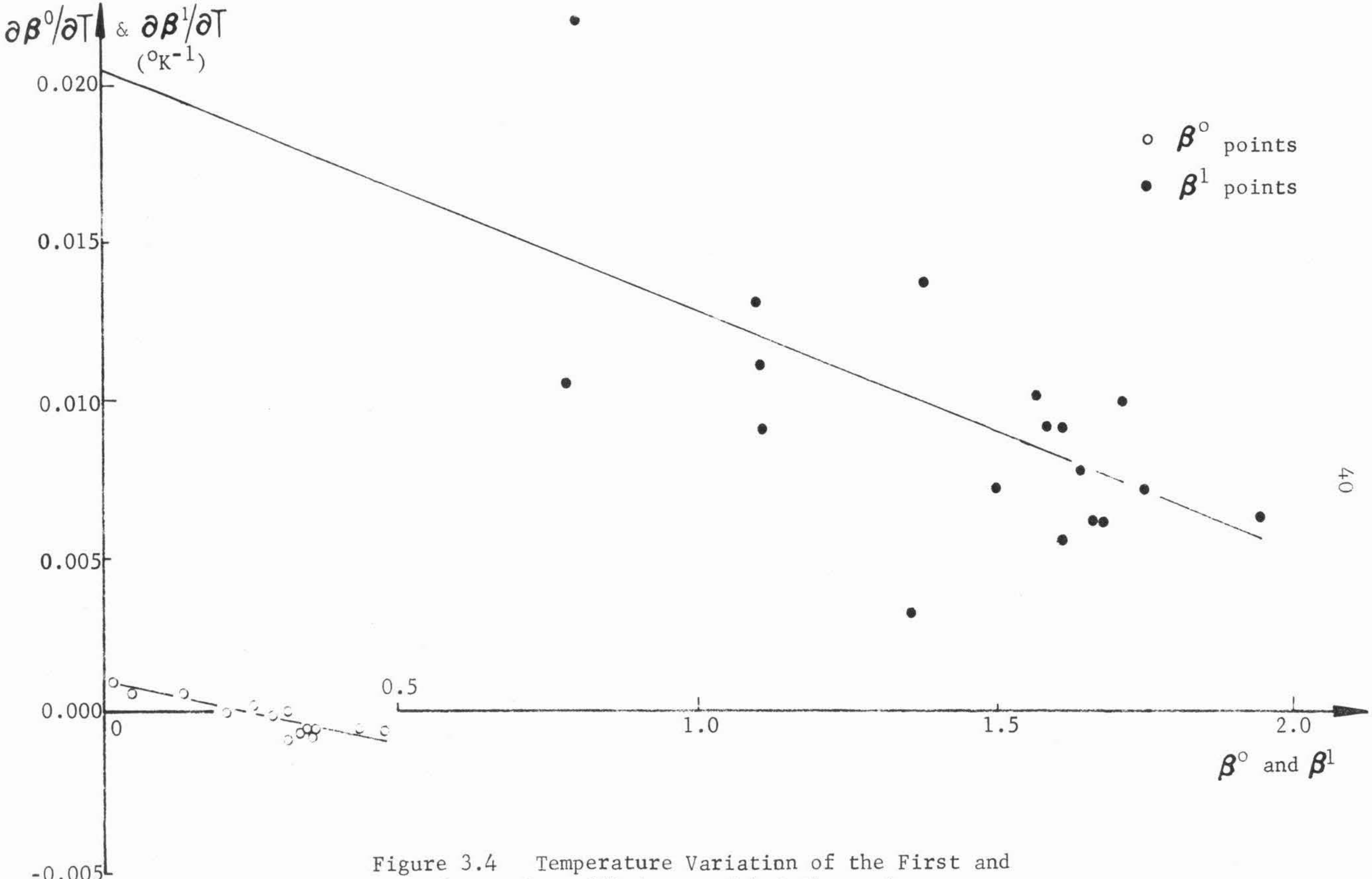

Figure 3.4 Temperature Variatinn of the First and Second Virial Coefficients of 1:2 Electrolytes

solution without implicitly knowing the rates of change of the individual virial coefficients with temperature.

The following linear equation approximately describes the relationship between the i^{th} virial coefficient, β^i, and $\partial\beta^i/\partial T$:

$$\frac{\partial\beta^i_{MX}}{\partial T} = d^i_{MX} + e^i_{MX}\beta^i_{MX}\Big|_{25^oC} \tag{3.12}$$

where $i = 0, 1$.

In the previous equation, d and e correspond to the intercept and the slope of the lines in Figures 3.3 and 3.4. Integration of equation (3.13) with respect to temperature leads to the following simple relationship:

$$\beta^i_{MX}\Big|_t = \left(d^i_{MX} + e^i_{MX}\ \beta^i_{MX}\Big|_{25^oC}\right)(t - 25) + \beta^i_{MX}\Big|_{25^oC} \tag{3.13}$$

Equation (3.13) permits the evaluation of a virial coefficient at any temperature as a function of its virial coefficient at 25°C and the solution temperature. The values of d and e for 1:1 and 1:2 electrolytes, as evaluated from a least-square analysis of the data points in Figures 3.3 and 3.4, are presented in Table 3.1. The magnitudes of d and e for 2:2 electrolytes are also presented in this Table. The evaluation procedure for this last case is discussed later in this section.

The linear correlation coefficients of the various sets of data suggest that the assumptions which led to the derivation of equations (3.12) and (3.13) are reasonable. The degree of accuracy of the proposed model may be sensed in more practical terms by comparing the calculated osmotic and activity coefficients of electrolyte solutions against the experimental ones. Publications on laboratory determinations of the activity and osmotic coefficients of electrolyte solutions at temperatures other than 25°C are rather scarce and often incongruent. Literature information on the thermodynamic properties of sodium chloride solutions at various temperatures is somewhat more reliable for these properties have been thoroughly studied by several investigators. The reported experimental activity and osmotic coefficients of sodium chloride solutions at temperatures between 0°C and 80°C and at concentrations as high as 1.0 m are listed in Table 3.2. These two coefficients are calculated in this dissertation by means of the d and e parameters for 1:1 electrolytes in Table 3.1. The results of these calculations are presented in Table 3.2.

TABLE 3.1

d AND e VALUES x 10^4

	Electrolyte					
	1:1	LCC*	1:2	LCC*	2:2	LCC*
d^o	9.80	0.76	10.89	0.92	0.0	
e^o	-70.92		-42.17		0.0	
d^1	29.54	0.80	205.08	0.61	-232.0	0.93
e^1	-61.92		-77.76		14.5	

*Linear Correlation Coefficient

TABLE 3.2

TEMPERATURE DEPENDENCE ON THE ACTIVITY AND OSMOTIC COEFFICIENTS OF NaCl SOLUTIONS

t, ^{o}C	I	γ_{Calc}	γ_{Exp}	ϕ_{Calc}	ϕ_{Exp}
0	0.1	0.781	0.781[a]	0.932	0.933[b]
	0.2	0.735	0.731	0.923	0.921
	0.5	0.680	0.673	0.921	0.911
	1.0	0.650	0.635	0.935	0.915
25	0.1	0.776	0.778[c]	0.932	0.932[c]
	0.2	0.732	0.735	0.923	0.925
	0.5	0.679	0.681	0.921	0.921
	1.0	0.655	0.657	0.935	0.936
40	0.1	0.783	0.774[d]	0.934	0.932[d]
	0.2	0.727	0.729	0.922	0.924
	0.5	0.676	0.677	0.922	0.923
	1.0	0.655	0.658	0.939	0.940
80	0.1	0.755	0.758[d]	0.926	0.927[d]
	0.2	0.710	0.711	0.918	0.919
	0.5	0.660	0.659	0.921	0.918
	1.0	0.644	0.640	0.964	0.939

[a] Harned and Owen (1958)

[b] Gibbard et al (1974)

[c] Robinson and Stokes (1959)

[d] Ensor and Anderson (1973)

The calculated activity coefficients of NaCl in Table 3.2 are in excellent agreement with the experimental ones over the studied temperature domain. At 80^{o}C a considerable discrepancy between experimental and calculated osmotic coefficients is observed. This discrepancy is probably a result of assuming that $\partial^2\beta/\partial T^2$ is unimportant.

Nonetheless, for the range of temperature of most natural waters, the above assumption yields reasonable results. One may conclude from the results in Table 3.2 that the proposed simplified model may be used with high degree of certainty to compute the thermodynamic properties of aqueous solutions at temperatures between $0^{o}C$ and $40^{o}C$. At higher temperatures the usage of the model should be discreet.

Harned and Owen (1958) compiled the relative partial molal enthalpies of dilute divalent cation sulfate solutions at $25^{o}C$. These values were used in this dissertation to calculate the Y variables, which correspond to the left side of equation (3.9). The Y variables, as well as their corresponding X_1 and X_2 values, were computed in the Appendix. It was previously discussed in this section that for most practical cases the last term in equation (3.9) can be ignored. This assumption holds in the following mathematical derivations.

Equation (3.9) is represented by the linear polynomial equation (3.7). It is initially assumed in this dissertation that the b_o term (i.e., $\partial\beta^{o}/\partial T$), in equation (3.7) is equal to zero. Ignoring b_o, the following relationship is obtained when one divides this equation by X_1:

$$\frac{Y}{X_1} = b_1 + b_2\left(\frac{X_2}{X_1}\right) \tag{3.14}$$

If the above assumptions are correct over the studied ionic strength range, for a given electrolyte solution, a plot of Y/X_1 against X_2/X_1 should yield points lying along a straight line. Figure 3.5 graphically illustrates the results of this type of plots.

In all cases linearity is preserved for X_2/X_1 between 0.04 and 0.27. This domain of the abscissa corresponds to ionic strengths from 0.36 to 0.026 m. Therefore, one may conclude that for this interval the above assumptions are valid.

The intercept, b_1, and the slope of any straight line, b_2, in Figure 3.5 correspond to $\partial\beta^1/\partial T$ and $\partial\beta^2/\partial T$ respectively. Only two points are plotted for calcium sulfate in Figure 3.5 due to the limited solubility of gypsum. It is unreasonable to attempt to evaluate b_1 and b_2 for $CaSO_4$ from this limited information. The b_1 and b_2 parameters for $CaSO_4$ were predicted according to a procedure described later in this section.

Experimental enthalpy information of concentrated divalent cation sulfate solutions is extremely limited. The only available publication on this type of information seems to be the work by Snipes et al (1975). These researchers have evaluated the relative apparent molal enthalpies of $MgSO_4$ at $40^\circ C$ and up to 8.0 m. The values of Y, X_1 and X_2 for these $MgSO_4$ solutions are evaluated in the Appendix. An attempt is now made to determine the actual magnitude of b_o for $MgSO_4$ solutions. The objective of such a determination is to demonstrate that for most practical cases the net effect of b_o on the thermodynamic properties of aqueous solutions is negligible. Subtracting b_2X_2 from equation (3.7) yields:

$$Y - b_2X_2 = b_o + b_1X_1 \tag{3.15}$$

Graphically calculating b_2 from Figure 3.5 one obtains that b_2 equals - 0.2475/deg. The left side of the previous equation may be

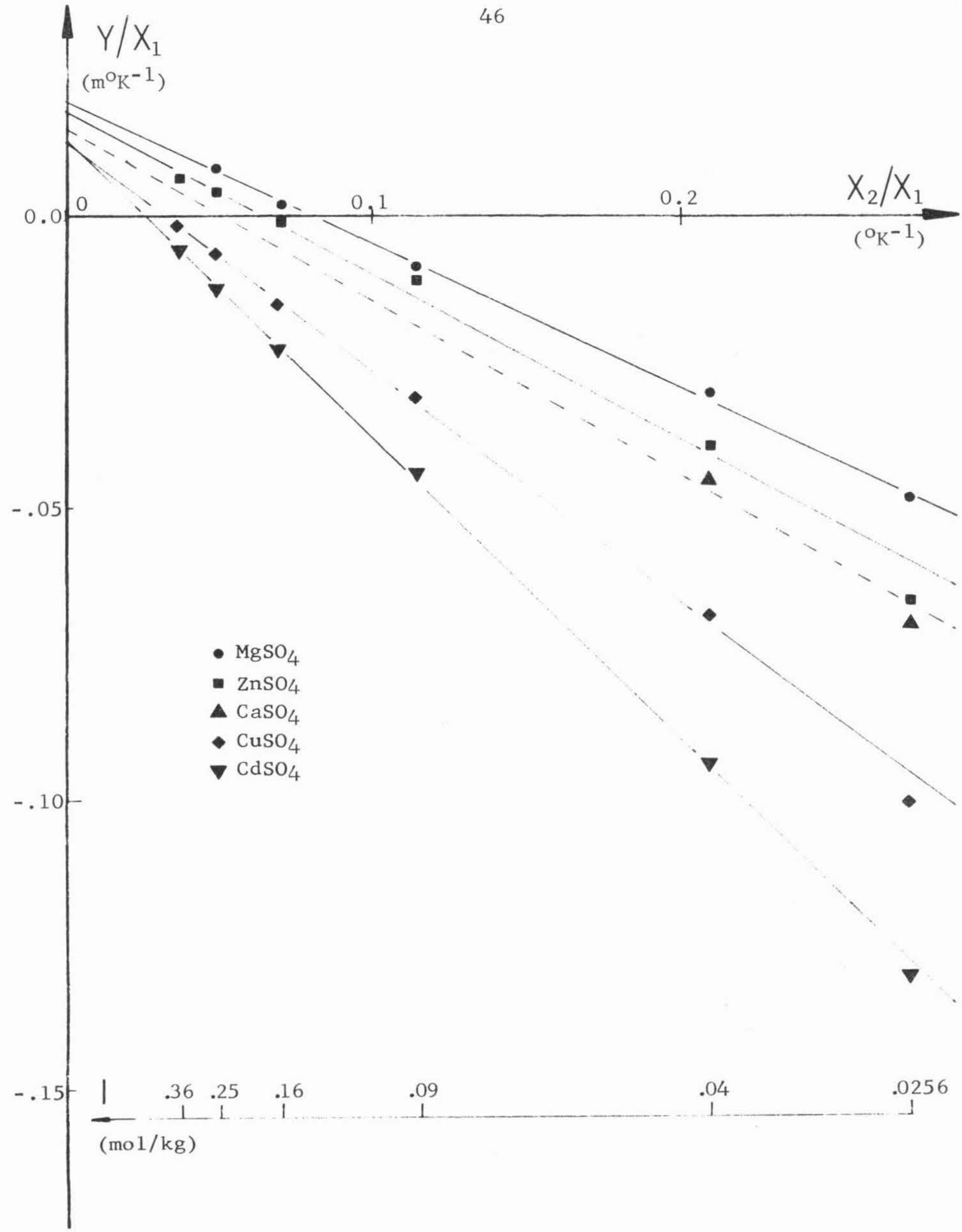

Figure 3.5 Y/X_1 vs. X_2/X_1 for 2:2 Electrolytes

then computed from the available information. The results of this computation are plotted as a function of X_1 in Figure 3.6. The intercept and slope of the best fit straight line in this figure correspond to b_o and b_1 respectively. The effect of b_2 on the value of the dependent variable in equation (3.15) may be visualized from the difference between the continuous and the dashed lines in Figure 3.6. The latter line represents a plot of the left side of equation (3.15) ignoring the contribution of b_2 (i.e., $b_2 = 0.$). The following important conclusions may be drawn from the graphical results in Figure 3.6:

a) The effects of b_2X_2 on the left side of equation (3.15) are of importance, especially at low ionic strength. These effects are reflected on the linearity of the full points in Figure 3.6. The excellent linear correlation of such points demonstrates the validity of the proposed magnitude of b_2.

b) A least-square analysis of $Y + b_2X_2$ as a function of X_1 shows that b_o and b_1 equal 0.0006/deg and 0.0272/deg. The assumption that one may neglect the effects of b_o in dilute solutions is confirmed by the relatively small value of b_o in comparison with b_1. This assumption should yield accurate results up to ionic strengths as high as 2.0 or 3.0 m.

c) The value of b_1 calculated from the intercept of Figure 3.5 equals 0.0210/deg. This value is slightly different than the one calculated from the slope of Figure 3.6. However,

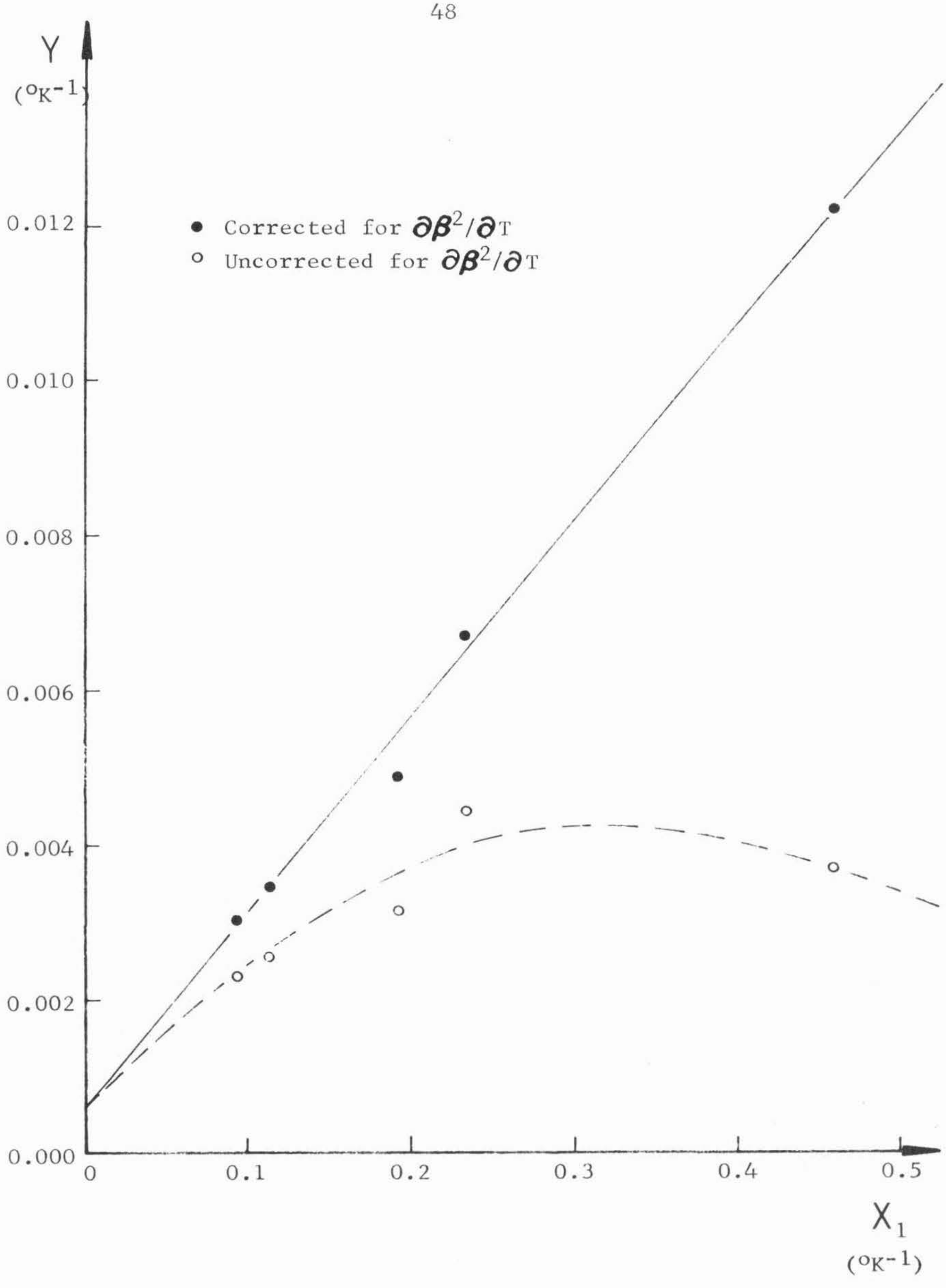

Figure 3.6 Y vs. X_1 Values for $MgSO_4$

considering that data from two literature sources were utilized to compute these two values, the agreement between both values is remarkable.

The values of b_1 (i.e., $\partial\beta^1/\partial T$) for 2:2 electrolyte solutions, as graphically calculated from Figures 3.5 and 3.6, are plotted as a function of their corresponding β^1 values in Figure 3.7. An excellent linear correlation coefficient of 0.93 is obtained for these data. The magnitudes of d_1 and e_1, which are listed in Table 3.2, are evaluated from a least-square analysis of the points in Figure 3.7.

The value of β^1 for $CaSO_4$ was utilized to estimate, from Figure 3.7, its corresponding magnitude of b_1. The b_2 value of $CaSO_4$ was then graphically evaluated from Figure 3.5 by assuming a best fit line (dashed line) with an intercept equal to b_1.

No apparent correlation was observed between the values of β^2 and b_2 for divalent cation sulfates. Table 3.3 shows the calculated b_2 values (i.e., $\partial\beta^2/\partial T$) for this type of electrolytes.

TABLE 3.3

DEPENDENCE OF β^2 ON TEMPERATURE

Elect.	β^2	$\partial\beta^2/\partial T$ (deg^{-1})
$CaSO_4$	-55.70	-0.284
$CdSO_4$	-48.07	-0.515
$CuSO_4$	-47.35	-0.393
$MgSO_4$	-37.23	-0.248
$ZnSO_4$	-32.81	-0.280

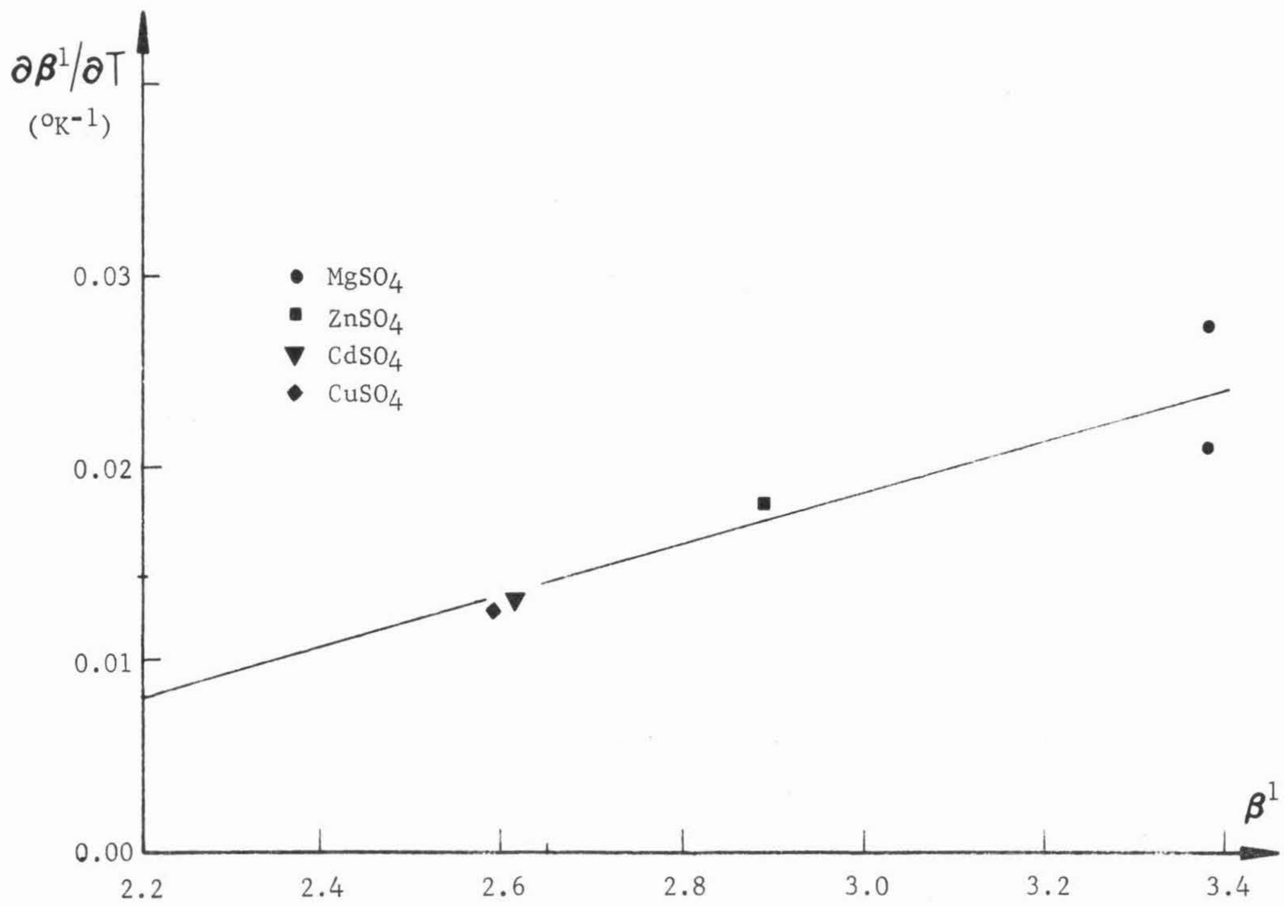

Figure 3.7 Temperature Variation of the Second Virial Coefficient of 2:2 Electrolytes

3.3 Example

The purpose of this example is to illustrate the use of the equations developed in the two previous sections as applied to the Ion Interaction Model.

Statement: Calculate the osmotic coefficient of a 1.0 m NaCl solution at $t = 40^oC$.

Solution: According to equation (3.1) at $t = 40^oC$ the dielectric constant of water equals:

$$\epsilon = 87.924 - 0.40873\,t + 1.01465 \times 10^{-3}t^2 - 1.9365 \times 10^{-6}t^3$$

$$= 73.074$$

The Debye-Hückel coefficient may be evaluated from equation (3.3) as follows:

$$A = \frac{1.400 \times 10^6}{(\epsilon T)^{3/2}} = 0.4044$$

For a 1:1 electrolyte I is equal to the molality of the solution. Knowing that I = 1.0 m and A = 0.4044, the following result is obtained for the Debye-Hückel function (equation (2.3)):

$$f^{\phi} = -0.1838$$

The first and second virial coefficients of MX electrolyte solutions at t^oC may be calculated from their corresponding values at 25^oC. From equation (3.13) one obtains for sodium chloride solutions at 40^oC:

$$\beta^i_{MX}\Big|_t = \left(d^i_{MX} + e^i_{MX}\,\beta^i_{MX}\Big|_{25^oC}\right)(t - 25) + \beta^i_{MX}\Big|_{25^oC}$$

$$= \begin{cases} 0.0831 & \text{for } i = 0 \\ 0.2856 & \text{for } i = 1 \end{cases}$$

the values of d and e for the above calculations were obtained from Table 3.1 and the β values at 25°C from Pitzer and Mayorga (1973).

One may proceed to calculate the interaction function for osmotic coefficients. From equation (2.4) one obtains

$$B^{\phi} = 0.1218$$

Finally, inserting the appropriate variables into equation (2.2), the following result is obtained for the osmotic coefficient:

$$\phi = 0.939$$

Chapter 4

THE ACTIVITY COEFFICIENTS OF ALKALI AND ALKALINE EARTH BICARBONATES

4.1 The Carbonate System in Aqueous Solutions

The thermodynamic properties of the bicarbonate ion are of major importance in the study of the chemical equilibrium of aqueous solutions. However, the existing information on its behavior in such solutions is confusing and often inconsistent. The purpose of this section is to elucidate the chemical theory of the bicarbonate ion in aqueous solutions.

The bicarbonate ion, HCO_3^-, is the intermediate protonation state of the carbonate system. The most protonated state of this system being carbonic acid, H_2CO_3, and the least being carbonate itself, CO_3^{2-}. Carbonic acid is the direct result of the dissolution and hydration of carbon dioxide, CO_2. Although carbon dioxide exists as a dissolved component in aqueous solutions, its occurrence is often ignored in most chemical models (the reason being that dissolved CO_2 is readily hydrated and available as carbonic acid).

The chemical reactions which describe the various protonation states of the carbonate system in an aqueous medium, as well as their corresponding mass action equilibrium equations, are listed in Table 4.1. (The adoption of the following convention greatly simplifies the nomenclature of the equations in this dissertation: Variables enclosed in parentheses represent molal activities while those enclosed in brackets (beginning on page 58) represent molal concentrations.)

TABLE 4.1

CHEMICAL REACTIONS AND EQUILIBRIUM EQUATIONS FOR THE CARBONATE SYSTEM IN WATER

$H_2O = H^+ + OH^-$	(4.1)
$K_w = (H^+)(OH^-)$	(4.2)
$CO_{2(g)} + H_2O = H_2CO_3$	(4.3)
$K_H = (H_2CO_3)/PCO_2\ a_1$	(4.4)
$H_2CO_3 = H^+ + HCO_3^-$	(4.5)
$K_1 = (H^+)(HCO_3^-)/(H_2CO_3)$	(4.6)
$HCO_3 = H^+ + CO_3{}^{2-}$	(4.7)
$K_2 = (H^+)(CO_3{}^{2-})/(HCO_3^-)$	(4.8)

where PCO_2 represents the partial pressure of CO_2,

K_w represents the ionization constant of water,

K_H represents the thermodynamic Henry's Law constant for CO_2, and

K_1 and K_2 represent the first and second thermodynamic ionization constant of the carbonate system.

The thermodynamic constants in Table 4.1 are temperature dependent and may be calculated from semi-empirical relationships of the form:

$$\log K = q + r/T + s/T \qquad (4.9)$$

where q, r and s represent the temperature coefficients.

The values of the temperature coefficients, as presented in the literature, are listed in Table 4.2. These coefficients may be used with confidence within the recommended temperature limits, 0 to 50^oC (Harned and Owen (1958)).

TABLE 4.2

TEMPERATURE COEFFICIENTS FOR THE CARBONATE SYSTEM IN WATER

K	q	r	s	Reference
K_w	6.0875	-4470.99	0.01706	Harned and Owen (1958)
K_H	-13.4170	2299.60	0.01422	Harned and Owen (1958)
K_1	14.8435	-3404.71	-0.03279	Harned and Davis (1943)
K_2	6.4980	-2902.39	-0.02379	Harned and Scholes (1941)

One observes from equations (4.4) and (4.6) that the activity of the bicarbonate ion may be expressed as a function of two variables: the partial pressure of carbon dioxide and the activity of the hydrogen ion. The latter property of a solution may be determined from experimental measurements of the hydrogen potential (i.e., pH). The theory of the bicarbonate ion activity coefficient in alkali and alkaline earth chloride solutions, under a constant partial pressure of CO_2, is studied in the following section.

4.2 General Principles of the Bicarbonate Ion Activity Coefficient

At a specific temperature the activity of a specific ion in a mixed electrolyte solution is a function of the molality of the various ions in solution and the virial coefficients of counter-ions, like-charge ions and triplets. Obviously, in order to estimate the bicarbonate ion activity coefficient in mixed electrolyte solutions, one needs to know the virial coefficients for cation-bicarbonate salts. For maximum accuracy it is also desirable to know the virial coefficients for anion-bicarbonate and cation-bicarbonate-cation virial coefficients.

The effect of like-charge and triplet interactions on the activity of an ion in solution is usually minor in comparison with opposite charge interactions. For the above reason, the emphasis of this chapter is the exclusive study of cation-bicarbonate interactions. The objective of this chapter is to experimentally obtain the virial coefficients between bicarbonate and the most common cations present in natural and contaminated waters. These cations are Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}.

The virial coefficients of an electrolyte MX are usually determined by one of the two following experimental methods (Pitzer and Mayorga (1973)):

a) by measurements of the osmotic coefficients of single MX solutions, or

b) by potentiometric measurements of the activity of M or X in single MX solutions.

The first experimental method requires the equilibration between the osmotic (or vapor) pressures of a sample MX solution and a solution with known osmotic (or vapor) pressure. Due to the long periods of equilibration (up to several days) and the presence of the carbon dioxide gas phase, this experimental technique cannot be employed to evaluate the $MHCO_3$ virial coefficients.

The activity of bicarbonate in an aqueous solution is intimately related to the activity of the hydrogen ion. Theoretically, the $MHCO_3$ virial coefficients can be determined from potentiometric measurements of the hydrogen ion activity in $MHCO_3$ solutions under a constant partial pressure of carbon dioxide. Unfortunately, due to the amphiprotic properties of HCO_3^-, the carbonate ion constitutes a considerable proportion of the total negative charge of the solution at pH values as low as 8.0. Therefore, the presence of this last anion in concentrated $MHCO_3$ solutions affects the electroneutrality condition of the solution and hinders any attempt to evaluate the viral coefficients of $MHCO_3$. Two alternate experimental procedures to evaluate these coefficients are proposed in.the following sections.

4.3 Theoretical Approach to γ_{MHCO_3} in MCl-$MHCO_3$ Solutions

At pH values below 7.0 the two anions of importance in a MCl - $MHCO_3$ solution are chloride and bicarbonate. At a known temperature and partial pressure of CO_2, the pH of a MCl solution containing a fixed concentration of $MHCO_3$ and a variable concentration of MCl is a function of the MCl and $MHCO_3$ virial coefficients. The electroneutrality condition (ENC) for this type of solution is as follows:

$$z_M[M^+] + [H^+] = [HCO_3^-] + [Cl^-] \tag{4.10}$$

Assuming that the hydrogen ion concentration is small (relative to the bicarbonate ion concentration) and that the cation M is monovalent, one obtains the following relationships for the mass balance conditions (MBC) of the particular problem:

$$[Cl^-] = [MCl] \tag{4.11}$$

$$[M^+] = [MHCO_3] + [MCl] \tag{4.12}$$

Simultaneously solving the three previous equations, the following simple equality is obtained:

$$[MHCO_3] = [HCO_3^-] \tag{4.13}$$

The bicarbonate ion concentration may be expressed as a function of its activity and activity coefficient:

$$[MHCO_3] = (HCO_3^-)/\gamma_{HCO_3} \tag{4.14}$$

One observes from equations (4.4) and (4.6) that the activity of bicarbonate ion equals $PCO_2K_HK_1\, a_1/(H^+)$. In the ideal conditions of infinite dilution the natural logarithm of a_1 is, according to equation (2.7), equal to $-0.036\,[M]$. Due to the minor effects of a_1 on the solution equilibrium conditions one may confidently assume that its natural logarithm behaves ideally. Inserting the appropriate values into equation (4.14) and taking the natural logarithms of the resulting relationship one obtains:

$$\ln [MHCO_3] = \ln (PCO_2K_HK_1E) - 0.036I + 2.303pH - \ln \gamma_{HCO_3} \tag{4.15}$$

where $I = [M]$ for 1:1 electrolytes, and

pH represents the negative logarithm (base 10) of the measured hydrogen ion activity,

$$pH = pH^o - pE \tag{4.16}$$

pH^o represents the actual pH of the solution, and

$pE = -\log_{10}E$ represents the pH calibration error.

Expressing the natural logarithm of the bicarbonate ion as a function of the ionic concentrations and the appropriate virial coefficients (equation (2.13)), one obtains:

$$2.303\,pH - f - 0.036I - I(I-[MHCO_3])(\beta^1_{MCl}g_1' + C_{MCl})$$
$$= b + 2I\beta^o{}_{MHCO_3} + 2Ig_1\beta^1{}_{MHCO_3} + 2I^2\;C_{MHCO_3} \tag{4.17}$$

where $b = \ln (PCO_2K_HK_1E/[MHCO_3])$ (4.18)

Equation (4.17) is a polynomial of the form

$$Y = b + \beta^o{}_{MHCO_3}X_1 + \beta^1{}_{MHCO_3}X_2 + C_{MHCO_3}X_3 \tag{4.19}$$

where Y represents the left side of equation (4.17), and

X_1, X_2 and X_3 represent their respective functions of I in equation (4.17)

Equation (4.17) describes the behavior of a measured pH function as one increases the ionic strength of a $MHCO_3$-MCl solution by the addition of MCl. (The temperature of the solution and partial pressure of CO_2 must be constant.)

Experimental pH measurements with accuracies greater than 0.01 pH unit are difficult to obtain (Bates (1973)). However, the precision of most modern digital meters is 0.001 pH unit. In other words, the accuracy of an individual pH reading is often below 0.01 unit, but the accuracy of pH variations (i.e., ΔpH) is as high as 0.001 unit. The method proposed in this work estimates the $MHCO_3$ virial coefficients not based on absolute pH measurements, but on relative values. Any least-square analysis of Y as a function of X_1, X_2 and X_3 must yield, regardless of the magnitude of the calibration error, constant calculated $MHCO_3$ virial coefficients (i.e., the pE is only reflected on the calculated b value).

The described theoretical approach to the evaluation of the $MHCO_3$ virial coefficients was derived for solutions containing concentrations of bicarbonate ion much greater than the concentrations of hydrogen ion (pH values between six and seven). Due to the limited solubility of calcium, magnesium and ammonia under these alkaline conditions, the virial coefficients for $Ca(HCO_3)_2$, $Mg(HCO_3)_2$ and NH_4HCO_3 have to be determined by the alternate model described in the following section. The applicability of the previously derived equations is therefore limited to the evaluation of the virial coefficients of sodium and potassium bicarbonate.

4.4 Theoretical Approach to γ_{MHCO_3} in MCl-H_2CO_3 Solutions

A second chemical model, which is able to predict the activity of bicarbonate ion in the presence of any of the studied cations, is presented below. This model relies on experimental pH measurements of single cation chloride solutions under a constant partial pressure of

CO_2. Even though this method is more versatile, its accuracy is lower due to the following reasons:

a) Most chloride salts contain trace amounts of alkalinity, which may considerably affect the equilibrium conditions of the system. Therefore, a salt alkalinity correction must be included in the model.

b) Under the proposed conditions, the activity of the bicarbonate ion is strongly dependent on the activity coefficient of the hydrogen ion. The latter ion exhibits unusual behavior in the presence of other cations. Thus, like-charge interactions must be considered in the model to explain the behavior of the hydrogen ion.

The trace alkalinity of a single MCl solution may be expressed as a fraction, ρ, of the ionic strength. The ENC for this type of solution under a constant partial pressure of carbon dioxide is

$$Z_M[M] + [H^+] = [HCO_3^-] + [Cl^-] \tag{4.20}$$

and the MBC is

$$Z_M[M] = [Cl^-] + \rho I \tag{4.21}$$

Subtracting equation (4.21) from (4.20) one obtains

$$[H^+] = [HCO_3^-] - \rho I \tag{4.22}$$

It is commonly accepted that the hydrogen ion exists hydrated by one or more water molecules (Bates (1973)). In the following derivation it is assumed that the hydrogen ion is present as hydronium ion, H_3O^+. Expressing concentrations as activities and rearranging terms in the previous equations, the following relationship is obtained. (In order to simplify nomenclature in the derivations H_3O^+ is expressed as H^+.)

$$(H^+)\ a_1 \left\{1 + \rho I/[H]\ a_1\right\} / \gamma_H = (HCO_3^-) / \gamma_{HCO_3} \tag{4.23}$$

Calculating the activity of the bicarbonate ion in equation (4.23) as a function of PCO_2, a_1 and (H^+) (equations (4.4) and (4.6)), and expressing the activity coefficients according to equations (2.12) and (2.13) one obtains the following relationship:

$$\begin{aligned} &1.151\, Z_M(Z_M + 1)\, pH - \frac{Z_M}{4}(Z_M + 1) \ln \left\{1 + \rho I/[H]\right\} + I\theta_{HM}^{+} \\ &= \frac{-Z_M}{4}(Z_M + 1) \ln \left\{PCO_2 K_H K_1 E^2\right\} + (\beta^o{}_{MHCO_3} - Z_M \beta^o{}_{HCl})\, I \\ &+ (\beta^1_{MHCO_3} - Z_M \beta^1_{HCl})\, I\, g(I) + (C_{MHCO_3} - Z_M C_{HCl})\, 2 I^2/(Z_M + 1) \end{aligned} \tag{4.24}$$

where $I = Z_M(Z_M + 1)\ [M]/2$

The alkalinity fraction, ρ, may be determined from pH measurements of aqueous MCl solutions under two different partial pressures of carbon dioxide, $PCO_2{}^1$ and $PCO_2{}^2$. It can be demonstrated that

$$\rho I = (w - 1) / \left(\frac{1}{[H^+]_2} - \frac{w}{[H^+]_1}\right) \tag{4.25}$$

where $$w = \frac{PCO_2{}^2}{PCO_2{}^1} \exp \left\{4.605(pH_2 - pH_1)\right\} \tag{4.26}$$

For symmetric mixing (i.e., mixing of two or more electrolytes whose anionic and cationic valences are equal) the like-charge virial coefficients may be assumed to be constant over the ionic strength of the solution (Pitzer and Kim (1974)). Pitzer (1975) has observed marked deviations from this ideal behavior for unsymmetrical electrolyte mixing. The like-charge interaction coefficient, for cases of unsymmetrical mixing, may be expressed as a function of the ionic strength of the solution. Therefore, for $MCl-H_2CO_3$ mixing the H-K, H-Na and $H-NH_4$ interactions, θ_{HM} may be assumed to be constant. (Pitzer and Kim report θ values for these types of interactions.) The non-ideal dependence of θ with the ionic strength of the solution for H^+Ca and H^+Mg interactions may be evaluated from pH measurements of $HCl-CaCl_2$ and $HCl-MgCl_2$ solutions. Ignoring triple ion interactions the following is true for a solution containing a fixed concentration of HCl, $[Cl_o^-]$, and a variable concentration of MCl_2:

$$\begin{aligned}2[M]\theta_{HM}^{+}(I) &= 2.303\ pH + f + \ln\{[Cl_o]E\} + 0.036(I/Z) \\ &+ [Cl^-]\{2(B_{HCl} + [Cl^-]C_{HCl}) + [M](B'_{MCl} + C_{MCl}) \\ &+ [H^+](B'_{HCl} + C_{HCl})\} \qquad (4.27)\end{aligned}$$

The ionic strength in the above equation may be assumed to be equal to the value utilized in equation (4.24) for values of I much larger than $[Cl_o^-]$. Equations (4.25) and (4.27) require the knowledge of the hydrogen ion concentration. This parameter is computed by dividing the hydrogen ion activity by its activity coefficient (calculated from equation (2.12)).

The $MHCO_3$ virial coefficients may be estimated by the use of the chemical model studied in this chapter. This estimation requires the following information:

a) pH measurements of MCl solutions under two different carbon dioxide partial pressures, and

b) in the case of M divalent, pH measurements of MCl_2-HCl solutions.

Due to the many mathematical manipulations and assumptions involved in the derivation of this model, it is expected that its accuracy will be lower than the model studied in the previous section (which can only be utilized to evaluate the virial coefficients of $NaHCO_3$ and $KHCO_3$).

4.5 Experimental Procedures

The virial coefficients of $MHCO_3$ salts may be evaluated from pH measurements of MCl-$MHCO_3$ and MCl-H_2CO_3 solutions, as discussed in the two prior sections. The experimental procedures required for this type of evaluation are considered in this section.

The experimental pH measurements of the aforementioned solutions are performed in the chemical reactor shown in Figure 4.1. (A complete listing of the equipment and instruments utilized in the experimental phase of this dissertation is given in Table 4.3.) This figure illustrates the reactor in a disassembled form, so that its individual parts may be clearly seen. By means of the access port, 250 grams of double distilled water are added into the previously washed and assembled reactor. The access port is also used when a known amount of salt needs to be added into the reactor. At any other time, this port is kept closed. A constant solution temperature is achieved by means of a constant temperature circulator which pumps water through the double wall bath. The thermometer in Figure 4.1 is used to confirm that the solution temperature is the desired one.

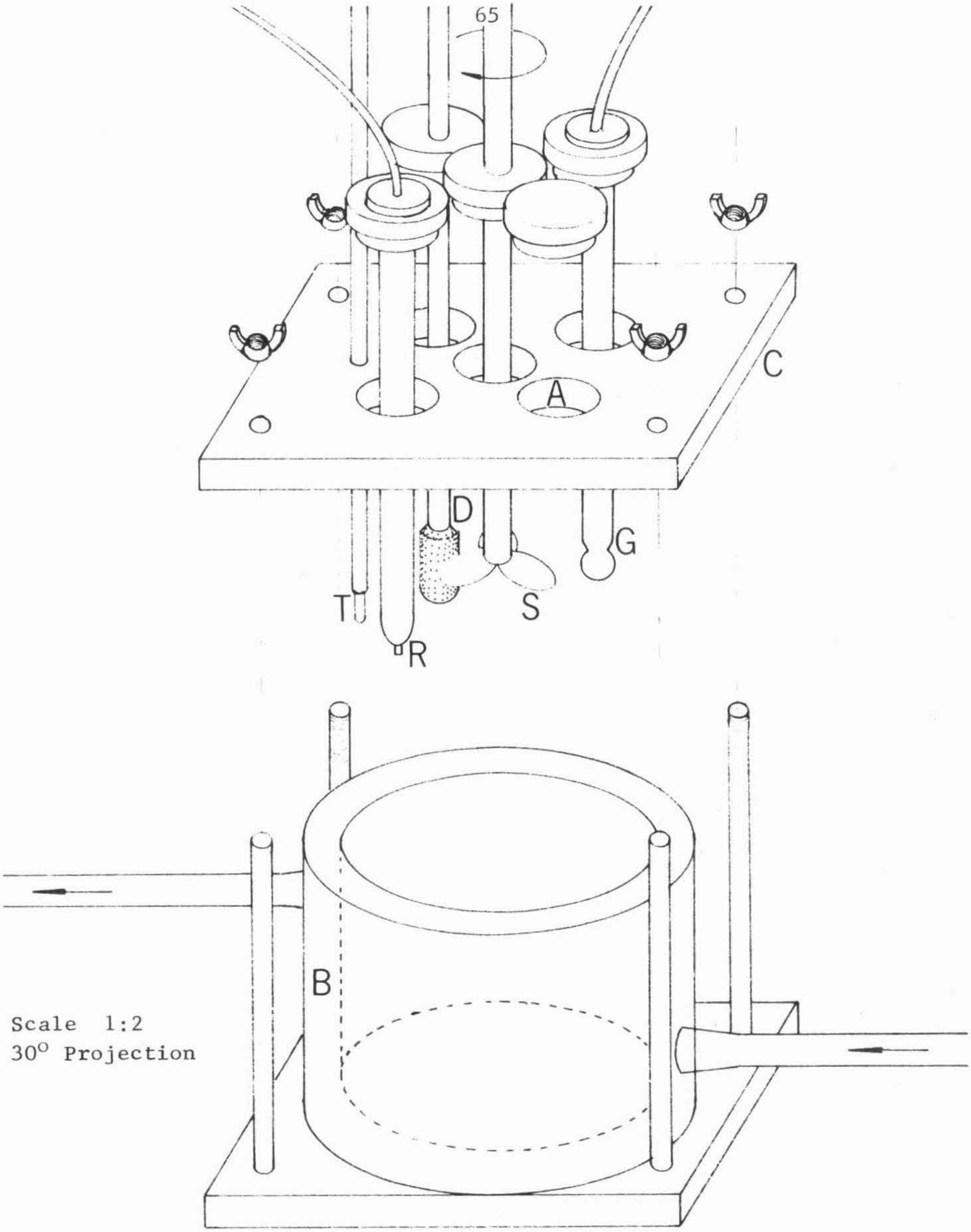

Figure 4.1 Chemical Reactor. A) Access Port, B) Constant Temperature Bath (1 liter), C) Cover, D) Glass Diffuser, G) Glass Electrode, R) Reference Electrode, S) Stirrer, T) Thermometer

TABLE 4.3

EQUIPMENT AND INSTRUMENTS USED
IN THE EXPERIMENTAL PROCEDURE

- Calomel reference electrode (Beckman 1170-5, fiber type)
- Constant temperature baths (1 liter and 0.25 liter)
- Constant temperature circulator (Haake F K, approximate precision: 0.05°C)
- Digital pH meter (Orion 801, precision: 0.001 pH unit)
- Gas flow meter (Matheson R-2-15-B)
- Glass diffusers (Pyrex ASTM 40.60 12 C)
- Low sodium E2 glass (pH) electrode (Beckman 39099)
- Propeller stirrer (Talboys 0-5000 RPM 30W)
- Thermometer (ERTCO 84627 -20 to 110°C)

The propeller-like stirrer is used for the following purposes:

a) To guarantee constant temperature and homogeneity throughout the solution,

b) To facilitate the dissolution of salts and carbon dioxide in the reactor, and

c) To avoid false pH readings, especially in low buffer capacity solutions.

A common misconception in the experimental determination of the pH of a solution is that the solution should not be stirred while readings are taken. This procedure is erroneous; in fact, the sample should be rapidly agitated around the electrodes. Bates (1973) mentions that "the pH of water can perhaps best be measured in a flow cell that permits a high rate of flow past the electrodes." For the described reactor, estimates of flow velocities around the electrodes yielded values of approximately 30 cm/sec.

In order to maintain a constant partial pressure of CO_2 within the reactor, 300 cc/min of a CO_2-N_2 mixture were bubbled into the solution by means of the glass diffuser shown in Figure 4.1. (The partial pressure of carbon dioxide in the gas mixture was known.) Prior to its introduction into the system, the gas mixture was bubbled in a distilled water constant temperature bath. The purpose of this pretreatment of the gas mixture was twofold: first, to saturate the gas with respect to water, and second, to equalize the gas temperature with the solution temperature.

The reference calomel electrode and glass (pH) electrode are shown in Figure 4.1. These electrodes are connected to an 801 Orion digital pH meter (not shown). The precision of this apparatus is 0.001 unit. The pH measurement procedure is as follows:

a) The temperature dial is set at the appropriate solution temperature, and the slope set at 100 per cent.

b) The electrodes are immersed in a constant temperature bath prior to the pH meter calibration.

c) The pH meter is calibrated with a 6.84 standard pH buffer solution. The slope of the electrodes is calibrated by adjusting the temperature dial until the pH reading equals the pH of a second 4.01 standard pH buffer solution. (The temperatures of the buffers and electrodes must be equal to the solution temperature.) The measured slope in the particular set of electrodes utilized in this research was never below 98.5 per cent.

d) The electrodes are inserted in their corresponding openings located in the cover of the reactor. The concentration of salt, MCl, in solution is increased by incremental additions of MCl. pH measurements are taken after the displayed pH readings have reached a constant value (i.e., equilibrium).

4.6 Experimental Determination of the $MHCO_3$ Virial Coefficients

The theoretical approach to the evaluation of the $MHCO_3$ virial coefficients were studied in sections 4.3 and 4.4. It was found in these two sections that, according to the Ion Interaction Model, the $MHCO_3$ virial coefficients could be evaluated by means of a least-square analysis of a function Y(pH) against functions $X_1(I)$ and $X_2(I)$. The experimental procedures involved in the determination of the pH of MCl-$MHCO_3$ and MCl-H_2CO_3 solutions under constant temperature and PCO_2 were discussed in the previous section. The purpose of this section is to obtain the $MHCO_3$ virial coefficients from experimental measurements of the pH in these types of solutions. The cations (M) studied in this research include K^+, Na^+, $NH_4{}^+$, Ca^{2+} and Mg^{2+}.

The virial coefficients of $KHCO_3$ and $NaHCO_3$ may be determined from experimental pH measurements of $MHCO_3$-MCl solutions (where M = K, Na). The temperature and PCO_2 of such solutions are kept constant throughout the experimentation period, which is approximately one hour. Tables 4.4 and 4.5 contain the experimental pH^o measurements of $MHCO_3$ solutions as one increases the ionic strength by adding reagent grade MCl. (The pH^o of a solution is the actual pH value, which is obtained by adding the calibration error to the pH reading. The calibration error is easily calculated from the first coefficient of the least-square analysis.) The $MHCO_3$ virial coefficients, as calculated from least-square analyses of each set of data, are given in Tables 4.4 and 4.5.

The pH^o of the solutions in Tables 4.4 and 4.5 may be calculated as a function of the ionic strength of the solution, once the $MHCO_3$ virial coefficients are known. Next to the measured pH^o values are also included the difference between the measured and calculated pH^o values.

Two different gas mixtures were utilized in this experimental phase. The mixtures, as prepared by the manufacturer (Matheson Gas Products) contained 100:0 and 50:50 CO_2:N_2 aquarator grade. The actual PCO_2 over the solution, was approximately three per cent lower than the dry mixture due to its saturation with respect to water vapor in the reactor.

The following important conclusions are obtained from the experimental results in Table 4.4 and 4.5:

TABLE 4.4

pH^o VALUES IN $KHCO_3$-KCl SOLUTIONS

PCO_2	0.97		0.97		0.48		0.97	
t^o	10^o		25^o		25^o		40^o	
$[KHCO_3]$	0.1		0.1		0.05		0.1	
I(m)	pH^o	D*	pH^o	D*	pH^o	D*	pH^o	D*
0.2	6.574	0	6.656	2	6.656	2	6.751	0
0.4	6.516	0	6.602	-1	6.602	0	6.703	1
0.6	6.479	-1	6.567	0	6.570	0	6.668	-2
0.8	6.456	2	6.545	0	6.547	1	6.646	-1
1.0	6.432	-2	6.527	0	6.528	0	6.630	1
1.2	6.417	-1	6.511	1	6.513	0	6.615	0
1.4	6.406	1	6.501	0	6.501	0	6.605	1
1.6	6.394	0	6.491	1	6.490	-1	6.596	1
1.8	6.385	1	6.484	1	6.483	0	6.579	-1
2.0	6.376	-1	6.476	0	6.475	0	6.579	-1
2.2	6.369	-1	6.471	-1	6.469	0	6.573	-1
2.4	6.365	1	6.463	0	6.464	0	6.569	0
2.6	6.359	-1	6.461	0	6.460	1	6.564	0
2.8	6.356	1	6.457	0	6.455	0	6.560	0
3.0	6.352	0	6.453	0	6.451	-1	6.557	1
β^o	0.0336		0.0550		0.0252		0.0445	
β^1	-0.1731		-0.1968		-0.0699		-0.0943	
C	-0.00130		-0.00658		-0.00168		-0.00480	

* D = (pH^o observed - pH^o calculated) x 10^3

TABLE 4.5

pH^o VALUES IN $NaHCO_3$-NaCl SOLUTIONS

PCO_2	0.97		0.97		0.48		0.97	
t^oC	10^o		25^o		25^o		40^o	
$[NaHCO_3]$	0.1		0.1		0.05		0.1	
I(m)	pH^o	D*	pH^o	D*	pH^o	D*	pH^o	D*
0.2	6.562	2	6.644	2	6.642	0	6.730	1
0.4	6.494	0	6.581	1	6.579	0	6.664	1
0.6	6.450	0	6.537	-1	6.538	0	6.621	-1
0.8	6.415	-1	6.505	0	6.506	0	6.590	0
1.0	6.389	1	6.479	0	6.480	-1	6.565	0
1.2	6.365	0	6.457	0	6.460	1	6.544	1
1.4	6.345	0	6.439	1	6.442	1	6.525	0
1.6	6.328	0	6.423	1	6.425	0	6.509	0
1.8	6.313	0	6.408	0	6.411	0	6.494	0
2.0	6.300	0	6.395	0	6.398	0	6.481	0
2.2	6.288	0	6.383	-1	6.386	0	6.470	0
2.4	6.317	0	6.373	0	6.376	0	6.458	-1
2.6	6.266	0	6.373	0	6.366	0	6.449	0
2.8	6.258	0	6.355	0	6.352	0	6.439	0
3.0	6.249	0	6.346	0	6.349	0	6.431	0
β^o	0.00731		0.0064		0.0016		0.0059	
β^1	-0.2559		-0.2169		-0.1592		-0.1486	
C	-0.00141		-0.00246		-0.00221		-0.00302	

* D = (pH^o observed - pH^o calculated) x 10^3

a) The addition of a neutral MCl salt to an $MHCO_3$ buffer causes a decrease of the solution pH. This decrease may be accurately described by the proposed Ion Interaction Model, whose precision in all cases was at least 0.002 pH unit.

b) Two sets of experimental pH^o measurements of $MHCO_3$-MCl solutions at 25^oC were performed at PCO_2 values of 0.97 and 0.48. The ratios of both PCO_2 were approximately equal to 2.0. The ratios of the bicarbonate concentrations in both solutions also equaled 2.0. Under these experimental conditions the theoretical model predicts that, for all practical purposes, the measured pH^o values in both cases should be equal. The validity of the model is experimentally demonstrated for the given conditions in that the absolute differences between both sets of pH^o values at 25^oC never exceeded 0.002 pH units. The excellent reproducibility of the measurements confirms the accuracy of the experimental procedures.

c) The calculated $MHCO_3$ virial coefficients at 25^oC are somewhat different for the two given conditions. These differences are due to minor pH^o measurement errors in the low ionic strength range. The effect of these errors on the calculated virial coefficients is considerable on the values of the β^1 coefficients. Nonetheless, the pH^o of both sets of solutions may be accurately predicted by using either one of the sets of calculated $MHCO_3$ virial coefficients.

d) The temperature variation of the $MHCO_3$ virial coefficients is positive as predicted by equation (3.12). The experimentally determined variations of β^1 with temperature are very similar to those predicted by equation (3.13). However, the experimental variations of β^o with temperature are slightly different than the ones calculated by equation (3.13). Such differences may be due to HCO_3^- - Cl^- interactions, whose effects are directly reflected on the value β^o.

The virial coefficients of $MHCO_3$ salts may be evaluated from pH measurements of MCl-H_2CO_3 solutions according to the model proposed in Section 4.4. In order to apply this model it is necessary to consider H^+M interactions. For M monovalent, the H^+M interaction coefficients may be assumed to be constant with the ionic strength and temperature. The values of θ_{H^+M} for the studied monovalent cations, as presented by Pitzer and Kim (1974), are 0.005, 0.036 and -0.016 for H-K, H-Na and H-NH_4 interactions.

Due to the low buffering capacity of H_2CO_3 solutions, one needs to consider the alkalinity effects of the salt MCl on the equilibrium conditions of the system. According to Section 4.4, the MCl alkalinity content may be estimated from pH measurements of H_2CO_3-MCl solutions under two different partial pressures of CO_2. The effectiveness of the method proposed in Section 4.4 may be evaluated by computing the virial coefficients of $KHCO_3$ and $NaHCO_3$ from pH measurements of KCl and NaCl solutions under two different PCO_2. The results for these types of measurements are given in Table 4.6. The MCl and HCl virial coefficients utilized for the calculation of the $MHCO_3$ virial coefficients are taken from Pitzer and Mayorga (1973).

The values of ρ in Table 4.6 are not calculated for ionic strengths below 1.0 m due to imprecisions of the theoretical model and pH^o measurements in dilute solutions. The average value of the alkalinity factor, $\bar{\rho}$, is used to calculate the $MHCO_3$ virial coefficients according to the model derived in Section 4.4.

A comparison between the values of the $MHCO_3$ virial coefficients calculated by the method in Section 4.3 and the one in Section 4.4 reveals that the latter method yields reasonable estimates for the first two virial coefficients. The validity of the Ion Interaction Model, as applied to bicarbonate solutions, may be sensed in practical terms by comparing the calculated pH^o of $MCl\text{-}H_2CO_3$ solutions utilizing the $MHCO_3$ virial coefficients of each method. This comparison is shown in Table 4.7, which contains the ΔpH^o between both methods. The accuracy of pH^o prediction of the Ion Interaction Model is represented by the ΔpH^o values in Table 4.7. This accuracy is higher than 0.01 pH unit for ionic strengths below 3.0 M.

The NH_4HCO_3 virial coefficients may be determined from pH^o measurements of $NH_4Cl\text{-}H_2CO_3$ solutions. Table 4.8 contains the results of these measurements at 25° and 40°C. The alkalinity fraction of NH_4Cl is evaluated from the two sets of measurements at 25°C.

TABLE 4.6

pH^o VALUES IN $KCl-H_2CO_3$ AND $NaCl-H_2CO_3$ SOLUTIONS AT 25°C

M	K			Na		
P_{CO_2}	0.48	0.97	$\rho \times 10^5$	0.48	0.97	$\rho \times 10^5$
I(m)						
0.2	4.041	3.887		4.031	3.880	
0.4	4.022	3.867		4.011	3.850	
0.6	4.006	3.851		3.984	3.824	
0.8	3.993	3.837		3.962	3.803	
1.0	3.982	3.823		3.945	3.784	
1.2	3.971	3.811	1.68	3.928	3.766	2.47
1.4	3.961	3.800	1.57	3.911	3.749	2.11
1.6	3.952	3.789	1.66	3.898	3.734	2.18
1.8	3.945	3.780	1.65	3.886	3.720	2.21
2.0	3.937	3.771	1.55	3.875	3.706	2.39
2.2	3.931	3.762	1.66	3.864	3.694	2.25
2.4	3.924	3.754	1.57	3.855	3.683	2.24
2.6	3.919	3.746	1.64	3.847	3.674	2.11
2.8	3.914	3.738	1.62	3.843	3.667	2.19
3.0	3.911	3.733	1.66	3.840	3.660	2.32
$\beta^o_{MHCO_3}$	0.0266			-0.0166		
$\beta^1_{MHCO_3}$	-0.0840			-0.1414		
C	0.00112			0.00159		
$\bar{\rho}$	1.63×10^{-5}			2.25×10^{-5}		

Similarly, one may evaluate the virial coefficients of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ salts from pH^o measurements in $MCl_2-H_2CO_3$ solutions. In order to perform this evaluation it is necessary to know the inter-

TABLE 4.7

ΔpH^o VALUES FOR MCl-H_2CO_3 SOLUTIONS AT 25°C*

M	K	Na
I(m)		
0.2	-0.001	0.000
0.4	-0.002	0.000
0.6	-0.002	0.000
0.8	-0.003	-0.001
1.0	-0.003	-0.001
1.2	-0.003	-0.002
1.4	-0.003	-0.003
1.6	-0.004	-0.003
1.8	-0.005	-0.003
2.0	-0.005	-0.003
2.2	-0.007	-0.004
2.4	-0.008	-0.004
2.6	-0.009	-0.004
2.8	-0.010	-0.004
3.0	-0.012	-0.004

*ΔpH^o = pH^o calculated from $MHCO_3$ virial coefficients of the MCl-H_2CO_3 method minus the pH^o calculated from the $MHCO_3$ coefficients of the MCl-$MHCO_3$ method.

action characteristics between H^+ and M (where M = Ca^{2+}, Mg^{2+}). These characteristics are easily obtained from pH^o measurements of HCl-MCl_2 solutions. The experimental pH^o measurements in these types of solutions and in MCl_2-H_2CO_3 solutions at 25°C are presented in Tables 4.9 and 4.10. Due to the uncertainty of both the theoretical model and

TABLE 4.8

pH^o MEASUREMENTS IN $NH_4Cl-H_2CO_3$ SOLUTIONS

PCO_2	0.48	0.97	0.97	$\rho \times 10^5$
t^oC	25	25	40	
I(m)				
0.2	4.044	3.884	3.934	
0.4	4.014	3.861	3.901	
0.6	3.993	3.841	3.977	
0.8	3.974	3.822	3.856	
1.0	3.957	3.806	3.836	
1.2	3.941	3.790	3.820	-0.28
1.4	3.926	3.776	3.804	-0.39
1.6	3.911	3.761	3.788	-0.34
1.8	3.896	3.747	3.773	-0.41
2.0	3.881	3.732	3.759	-0.37
2.2	3.867	3.718	3.745	-0.33
2.4	3.854	3.706	3.731	-0.37
2.6	3.841	3.693	3.718	-0.33
2.8	3.829	3.681	3.705	-0.30
3.0	3.817	3.669	3.692	-0.27
$\beta^o_{MHCO_3}$	-0.0011		0.0250	
$\beta^1_{MHCO_3}$	-0.0336		-0.1205	$\overline{\rho} = -0.34 \times 10^{-5}$
C_{MHCO_3}	0.00024		0.0002	

experimental procedures involved in the evaluation of the $M(HCO_3)_2$ virial coefficients, one may assume, without much loss of accuracy, that the third virial coefficient has a value of zero.

Pitzer and Mayorga (1973) mention that the degree of uncer-

TABLE 4.9

pH^o VALUES IN $CaCl_2$-H_2CO_3 SOLUTIONS AT 25°C

PCO_2	0.48	0.97	pH^*	$\rho \times 10^5$
I(m)				
0.2	4.044	3.886	1.338	
0.4	4.042	3.869	1.323	
0.6	4.044	3.858	1.303	
0.8	4.047	3.851	1.281	
1.0	4.052	3.845	1.257	
1.2	4.056	3.843	1.234	20.1
1.4	4.061	3.840	1.211	21.1
1.6	4.065	3.838	1.187	21.3
1.8	4.069	3.836	1.164	21.8
2.0	4.072	3.834	1.141	22.0
2.2	4.074	3.832	1.117	21.8
2.4	4.077	3.831	1.093	21.8
2.6	4.079	3.830	1.070	21.4
2.8	4.080	3.829	1.047	20.5
3.0	4.080	3.827	1.024	19.8
$\beta^o_{Ca(HCO_3)_2}$	0.0886			
$\beta^1_{Ca(HCO_3)_2}$	1.2670			$\bar{\rho}$ = 21.2
$C_{Ca(HCO_3)_2}$	0.0000			

*pH of a solution containing ~0.05 m HCl and I/3 m $CaCl_2$

tainty of the virial coefficients of electrolytes increases with the valences of the counter-ion components. It is therefore expected that the virial coefficients of the bicarbonate salts will be more accurate for M monovalent than for the divalent case. As expected, the confi-

TABLE 4.10

pH^o VALUES IN $MgCl_2$-H_2CO_3 SOLUTIONS AT 25°C

PCO_2	0.48	0.97	pH*	$\rho \times 10^5$
I(m)				
0.2	4.022	3.870	1.248	
0.4	3.976	3.823	1.233	
0.6	3.938	3.786	1.210	
0.8	3.906	3.752	1.182	
1.0	3.877	3.722	1.159	
1.2	3.849	3.693	1.136	1.72
1.4	3.823	3.667	1.113	1.55
1.6	3.798	3.643	1.089	1.15
1.8	3.775	3.619	1.064	1.30
2.0	3.753	3.596	1.038	1.44
2.2	3.730	3.573	1.013	1.38
2.4	3.709	3.552	0.988	1.27
2.6	3.690	3.531	0.965	1.58
2.8	3.670	3.510	0.941	1.69
3.0	3.650	3.491	0.916	1.42
$\beta^o_{Mg(HCO_3)_2}$	-0.0461			
$\beta^1_{Mg(HCO_3)_2}$	0.9159			$\bar{\rho} = 1.45$
$C_{Mg(HCO_3)_2}$	0.0000			

*pH of a solution containing ~0.05m HCl and I/3m $MgCl_2$

dence degree of the method described in Section 4.4 is low in the case of M divalent. One concludes that this method is not accurate enough to estimate the temperature variations of the virial coefficients of divalent cation bicarbonate salts. It is assumed throughout this dissertation that the temperature effects on the values of these coefficients may be described by equation (3.13).

4.7 Temperature Effects on the $MHCO_3$ Virial Coefficients

The virial coefficients at 25°C of various $MHCO_3$ electrolytes were experimentally determined in the previous section. These coefficients were also determined at other temperatures for the case of M monovalent. Two experimental methods were utilized to estimate the $KHCO_3$ and $NaHCO_3$ virial coefficients. The first one, and more accurate, was based on pH measurements of NaCl solutions under alkaline conditions. The second one required pH measurements of NaCl solutions under acidic conditions. Due to the higher reliability of the first method, the $KHCO_3$ and $NaHCO_3$ virial coefficients summarized in this section are those determined under alkaline conditions.

The experimentally determined $MHCO_3$ virial coefficients are compiled in Table 4.11 (in which the values at 25°C are averaged). It is assumed in this dissertation that the third virial coefficient, C, does not change with temperature. The C magnitudes reported in Table 4.11 are the average of the values at various temperatures. It is also assumed in this work that the value of C for M divalent is equal to zero.

The variations of the $MHCO_3$ virial coefficients with temperature have been calculated from the data in Table 4.11 and are included in this Table. These values have been plotted as a function of their

TABLE 4.11

SUMMARY OF THE $MHCO_3$ VIRIAL COEFFICIENTS

M	10°C	$\left(\frac{\Delta\beta}{\Delta T}\right) \times 10^4$	25°C	$\left(\frac{\Delta\beta}{\Delta T}\right) \times 10^4$	40°C
			β^o		
K^+	0.0336	4.33	0.0401	2.93	0.0445
Na^+	0.0073	-2.21	0.0040	1.27	0.0059
NH_4^+			-0.0011	7.43	0.0250
Ca^{2+}			0.0886		
Mg^{2+}			-0.0461		
			β^1		
K^+	-0.1731	26.5	-0.1334	26.1	-0.0943
Na^+	-0.2559	45.2	-0.1881	26.3	-0.1486
NH_4^+			-0.0336	-57.9	-0.1205
Ca^{2+}			1.267		
Mg^{2+}			0.9159		
			C		
K^+			-0.00359		
Na^+			-0.00228		
NH_4^+			0.00022		

respective virial coefficients in Figure 4.2.

The best-fit lines in Figure 4.2 were calculated in Chapter 3 from thermodynamic information of 20 1:1 electrolytes. The temperature variation of the $NaHCO_3$ virial coefficients were estimated from the respective points in Figure 3.3. These points were obtained from the literature values of dilution enthalpies of $NaHCO_3$ (Leung and Millero

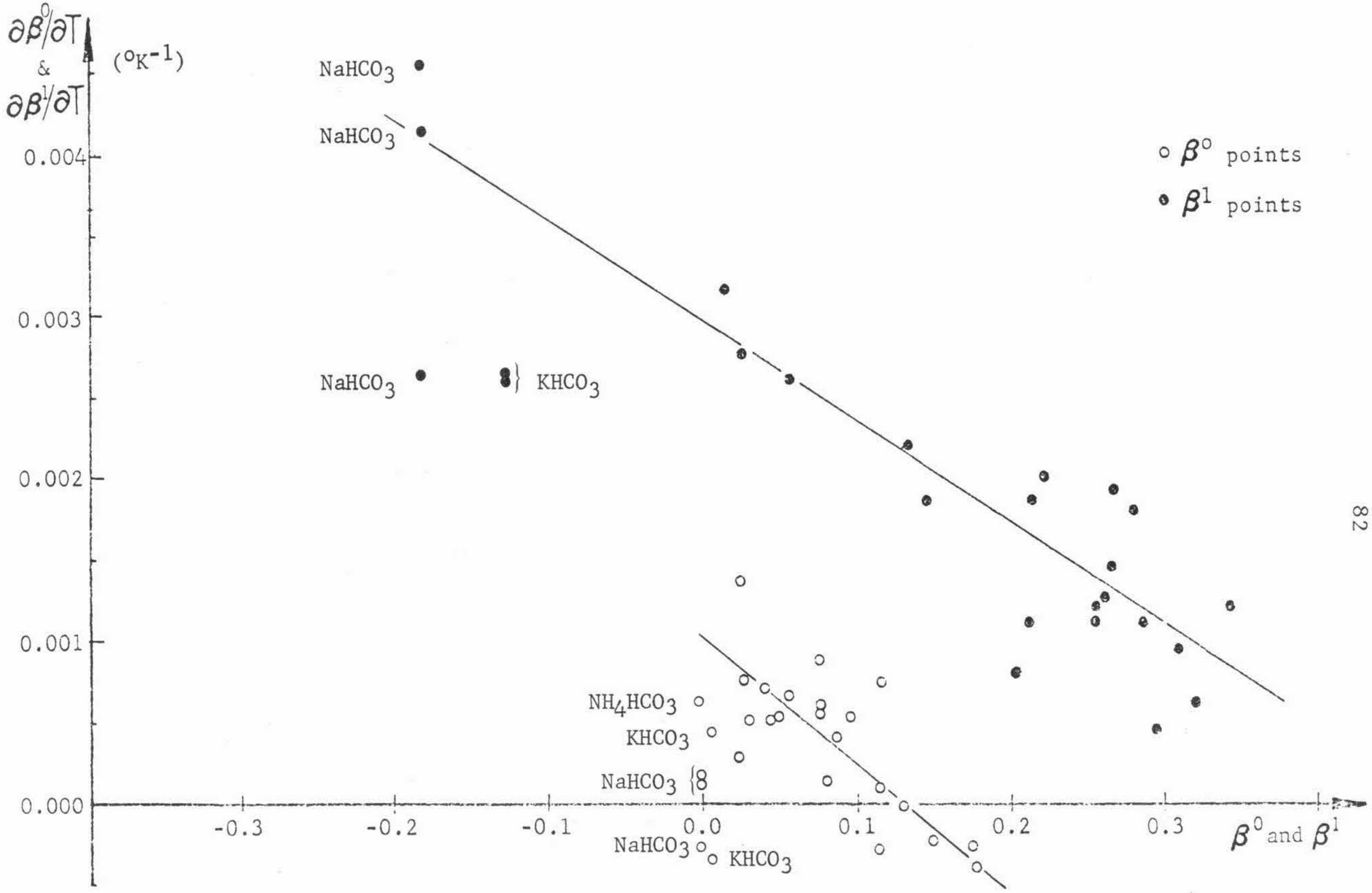

Figure 4.2 Temperature Variation of the First and Second $MHCO_3$ Virial Coefficients

(1975)). From Figure 3.3 one obtained $1.75 \times 10^{-4}/^{o}K$ for the temperature variation of the first virial coefficient of $NaHCO_3$, and $41.5 \times 10^{-4}/^{o}K$ for the second one. These values were also plotted in Figure 4.2 as a function of their corresponding virial coefficients.

It is important to remember that $\Delta\beta/\Delta T$ equals $\partial\beta/\partial T$ when β is a linear function of temperature. It is assumed in this dissertation that this linearity condition holds over the studied range of temperature. (The operators Δ and ∂ are used interchangeably throughout this dissertation.)

The following important conclusions are obtained from the results in Figure 4.2:

a) The experimentally determined values of $\Delta\beta/\Delta T$ of $NaHCO_3$ solutions are in excellent agreement with those calculated from the data by Leung and Millero. This agreement confirms the validity of the Ion Interaction Model as applied to $MHCO_3$ solutions.

b) The $\Delta\beta^{o}/\Delta T$ points for $MHCO_3$ electrolytes are somewhat lower than the expected values. The reason for this deviation is not well understood. A possible explanation for this deviation is that no HCO_3-Cl interactions were considered in this work. If such like-charge interactions are included in the models in Sections 4.3 and 4.4, one finds that as θ_{Cl-HCO_3} decreases, $\beta^{o}_{MHCO_3}$ increases. Therefore, the $MHCO_3$ points in Figure 4.2 move toward the right, closer to the expected values. However, the consideration of an extra variable in the models does not increase its accuracy and complicates the calculations. The HCO_3-Cl interactions are not implicitly considered but they are absorbed by the value of the first virial coefficient.

c) The NH_4HCO_3 virial coefficients are calculated by means of the model described in Section 4.4. The reliability of these coefficients is not very high due to the many assumptions involved in the model. The unreliability of the model is greatly magnified on the calculated $\Delta\beta/\Delta T$ of NH_4HCO_3 electrolytes. For example, the calculated $\Delta\beta^1/\Delta T$ is not plotted in Figure 4.2 because it falls off the graph. For the same obvious reason one cannot calculate the temperature effects on the virial coefficients of calcium and magnesium bicarbonate, but one may assume that these salts behave ideally according to equation (3.13).

The average temperature variations of the potassium and sodium bicarbonate virial coefficients are listed in Table 4.12.

TABLE 4.12

AVERAGE $\Delta\beta/\Delta T$ OF $MHCO_3$ ELECTROLYTES

	$KHCO_3$	$NaHCO_3$
$(\Delta\beta^o/\Delta T) \times 10^4$	3.63	0.27
$(\Delta\beta^1/\Delta T) \times 10^4$	26.3	37.7

4.8 Behavior of the Bicarbonate Ion in Mixed Electrolyte Solutions

The objective of this section is to test the validity of the proposed Ion Interaction Model in mixed electrolyte solutions. This is done by measuring pH^o values of K^+, Na^+-HCO_3^-, Cl^- solutions and then comparing these results with the calculated ones. The experimental procedures involved in the pH measurements have been previously described in Section 4.2.

The measured pH^o of two sets of K^+, Na^+-HCO_3^-, Cl^- solutions at 25°C and under 0.97 PCO_2 are reported in Table 4.13. The first set contains a constant concentration of $NaHCO_3$ and a variable concentration of KCl. In the second one the molality of $KHCO_3$ is kept constant while the molality of NaCl is increased.

The pH^o may be calculated by means of the Ion Interaction Model, the MBC and ENC of the solution. The virial coefficients used in these calculations are those presented by Pitzer and Mayorga (1973) and the $MHCO_3$ virial coefficients determined in this dissertation. The like-charge interaction coefficients used in the calculation of pH^o are listed by Pitzer and Kim (1974). The parameter D in Table 4.13 (in thousandths of a pH unit) is computed by ignoring any triplets' interaction and subracting the calculated pH^o value from the measured one.

One may conclude from the results in Table 4.13 that the Ion Interaction Model accurately describes the equilibrium conditions of the studied mixed electrolyte solutions. Further, the assumption that triplet interactions of the form K-HCO_3-Na are nil appears to be correct over the analyzed ionic strength range. This assumption is probably a good one for all types of triplet interactions where bicarbonate is one of the components.

TABLE 4.13

MEASURED pH^o VALUES IN THE SYSTEM
K^+, Na^+-HCO_3^-, Cl^-

	NaCl = 0.97m $NaHCO_3$ = 0.1m		KCl = 0.97m $KHCO_3$ = 0.1m	
MCl (m)	pH^o	D*	pH^o	D*
0.0	6.479	0	6.527	0
0.2	6.465	-1	6.502	-2
0.4	6.455	0	6.481	-2
0.6	6.446	0	6.463	-3
0.8	6.440	1	6.446	-4
1.0	6.434	1	6.432	-4
1.2	6.429	1	6.419	-5
1.4	6.427	3	6.408	-4
1.6	6.424	4	6.398	-4
1.8	6.421	4	6.388	-4
2.0	6.418	4	6.379	-4

$PCO_2 = 0.97$, $t = 25^oC$

$*D = (pH^o \text{ measured} - pH^o \text{ calculated}) \times 10^3$

4.9 Comparison of Experimental and Literature Values

Literature information of the activity coefficient of the bicarbonate ion is very limited. Perhaps the most reliable work in this area is the one by Butler and Huston (1970). These researchers have determined the mean activity coefficient of NaCl in $NaHCO_3$ solutions by means of sodium ion activity measurements. They claim that for their experimental results at 25°C "Harned's Rule is obeyed over the ionic strength from 0.5 to 3.0 with a coefficient of $\alpha_{12} = 0.047 \pm 0.003$." (Harned's Rule is a simplified form of the Ion Interaction Model.) According to Harned's Rule only one interaction coefficient, α_{12}, is required to predict the activity of an electrolyte in solution.

Equating the NaCl activity coefficient function proposed by Butler and Huston and the one determined by the Ion Interaction Model one obtains the following relationship:

$$2.303\,\alpha_{12} = \beta^{o}_{NaCl} - \beta^{o}_{NaHCO_3} + (\beta^{1}_{NaCl} - \beta^{1}_{NaHCO_3})\ e^{-2\sqrt{I}} + 2\,I\,(C_{NaCl} - C_{NaHCO_3}) \qquad (4.28)$$

The values of the NaCl and $NaHCO_3$ virial coefficients are respectively given by Pitzer and Mayorga (1973) and this dissertation. With these values one is able to calculate the Harned's Rule interaction coefficient as a function of the ionic strength of the solution. According to Butler and Huston's work, the value of α_{12} is approximately constant over the ionic strength range of 0.5 to 3.0 m. At these extreme values the α_{12} calculated by means of equation (4.28) is 0.081 and 0.051 respectively. The latter magnitude is comparable with the constant 0.047 ± 0.003 proposed by Butler and Huston. One observes that due to the exponential nature of the second term on the right side of the prior equation, the magnitude of this term rapidly decreases with the ionic strength. In other words, the values of α_{12} calculated from equation (4.28) quickly tends to the value computed at $I = 3.0$ as one increases the ionic strength from 0.5 to 3.0 m.

The similarity between the α_{12} value reported by Butler and Huston and those calculated in this dissertation is a positive indication of the effectiveness of both the theoretical model and the experimental results presented in this work.

The effectiveness of the experimental procedures may be also determined by comparing the pH^o measurements in $NaCl$-$NaHCO_3$ solutions at 25^oC presented in this dissertation with those by Garrels et al (1961). These investigators have measured the pH of 0.1 m $NaHCO_3$ solutions with variable concentrations of NaCl and constant 0.97 PCO_2. Table 4.14 contains a partial list of the pH^o (i.e., pH + pE) presented by Garrels et al. The last column in this table gives the interpolated pH^o values from Table 4.5.

TABLE 4.14

COMPARISON OF EXPERIMENTAL
pH^o VALUES

I(m)	pH^o a	pH^o b
0.35	6.59	6.597
0.60	6.54	6.537
0.85	6.50	6.499
1.10	6.47	6.468
1.60	6.42	6.423
2.10	6.40	6.389
3.10	6.33	6.342*

* Extrapolated value
a Garrels et al (1961), pE = 0.044
b This dissertation

The agreement between both sets of experimental pH^{o} values in Table 4.14 is remarkable. The minor discrepancy between values at high ionic strength is probably caused by alkaline errors in the pH measurements by Garrels et al. Bates (1973) describes the alkaline error as the lowering of the measured pH due to high concentrations of cations of the alkaline and alkaline earth series. These errors are minimized by using a low sodium electrode, such as the Beckman "E-2" glass electrode used in this dissertation.

Chapter 5

PRACTICAL APPLICATIONS

5.1 Objective

The scope of this chapter is to apply the proposed Ion Interaction Model to the solution of various chemical and engineering problems. These problems were partially solved with the aid of the FORTRAN IV program SOL. This program calculates the osmotic and activity coefficients of mixed electrolytes in aqueous solutions at any given temperature. By using the program SOL, one may also estimate the equilibrium conditions of solutions open to any atmosphere with known PCO_2. The theoretical approach of this program is based on the Ion Interaction Model and the carbonate system equations described in Chapters 2, 3 and 4 of this dissertation.

The program SOL may simultaneously handle up to 15 different ions in solution. These ions include the following common cations and anions:

a) Cations: H^+, K^+, Na^+, NH_4^+, Ca^{2+} and Mg^{2+}

b) Anions: OH^-, Cl^-, NO_3^-, HCO_3^-, $H_2PO_4^-$, SO_4^{2-}, CO_3^{2-}, HPO_4^{2-} and PO_4^{3-}

The 25^oC like-charge and virial coefficients employed in the program SOL are those reported by Pitzer and Mayorga (1973, 1974), Pitzer and Kim (1974), Pitzer and Silvester (1976) and this dissertation. The effect of triple ion interactions on the equilibrium conditions of mixed electrolytes is not considered in the program. Temperature variations of the first and second virial coefficients of 1:1 and 1:2 electrolytes (except $NaHCO_3$ and $KHCO_3$) are assumed to behave ideally according to equation (3.12) The rates of change with temperature of the $NaHCO_3$ and $KHCO_3$ virial coefficients are taken from Table 4.12. A copy of program SOL and its function, block data and subroutines (FG, DATA, AC, AC2, CB, BB, FG) are presented in Appendix II.

The usage of SOL requires the following input parameters:

a) The partial pressure of CO_2 and temperature of the solution. (If the system is closed to the atmosphere, $PCO_2 = 0.$)

b) The names of the cations and anions in solution.

c) The molal concentrations of cations (excluding H^+) and anions (excluding OH^-, HCO_3^- and CO_3^{2-}).

Once the computer calculates the equilibrium conditions of the solution, the terminal types out the following thermodynamic properties:

a) The pH, osmotic coefficient, and ionic strength of the solution,

b) The activity of the water in solution,

c) The concentrations and activity coefficients of the individual ions, and

d) The mean electrolyte activity coefficients.

5.2 The Thermodynamic Solubility Product of Gypsum

The Ion Interaction Model was described in Chapter 2. In that chapter some important assumptions were proposed in order to resolve the inconsistencies of the Ion Interaction Model when calculating the thermodynamic properties of 2:2 electrolytes in aqueous solutions. The accuracy of the Ion Association Model, as proposed in this dissertation, is tested by determining the thermodynamic solubility product of gypsum (i.e., $CaSO_4 \cdot 2H_2O$) in seawater and NaCl solutions.

Marshall and Slusher (1966) present experimental gypsum solubilities in NaCl solutions at various temperatures. Their results at 25^{o}C are presented in Table 5.1. One may obtain the thermodynamic properties of the solutions in this table by means of the program SOL. The experimental solubility products, K_{sp}, of gypsum reported in Table 5.1 are easily computed by inserting the appropriate variables into equation (2.24). The thermodynamic solubility product of gypsum is also calculated from experimental measurements of the solubility of $CaSO_4 \cdot 2H_2O$ in seawater (Briggs and Lilley (1973)).

Considering that there is a two-fold variation in the ionic strength of the solutions in Table 5.1 and the multiple components of seawater, the agreement between the calculated K_{sp} values is excellent. A statistical analysis of the calculated K_{sp} values in this table yields 2.466×10^{-5} and 0.068×10^{-5} for the mean and standard deviation respectively.

The thermodynamic solubility product of gypsum at temperatures other than 25^{o}C were calculated from Marshall and Slusher's data at ionic strengths below 1.0m. Statistical analyses of the calculated K_{sp} values yielded the results in Table 5.2.

TABLE 5.1

THERMODYNAMIC SOLUBILITY PRODUCT
OF GYPSUM AT 25°C

NaCl [a] (m)	$CaSO_4$ [a] (m)	$K_{sp} \times 10^5$
0.0000	0.0151	2.499
0.0117	0.0162	2.461
0.0257	0.0175	2.459
0.0513	0.0194	2.442
0.1147	0.0231	2.430
0.1921	0.0266	2.435
0.2319	0.0281	2.435
0.5480	0.0372	2.482
0.6890	0.0388	2.350
0.8340	0.0430	2.527
1.005	0.0457	2.539
1.024	0.0452	2.466
2.024	0.0540	2.478
2.870	0.0560	2.466
4.125	0.0560	2.638
Seawater saturated with gypsum[b]		2.356

[a]Marshall and Slusher (1966)

[b]Briggs and Lilley (1973)

The low variation coefficient (i.e., σ/K_{sp}) of the results in Table 5.2 is a good indicator of the accuracy of the proposed Ion Association Model as applied to mixed electrolyte solutions at temperatures from freezing point to 60°C.

Further, the K_{sp} of gypsum at 25°C, 2.466×10^{-5}, is in excellent agreement with other literature values, which vary from 2.45 x 10^{-5} (Moreno and Osborn (1963)) to 2.50 x 10^{-5} (Nakayama and Rasnik (1967)).

TABLE 5.2

THERMODYNAMIC SOLUBILITY PRODUCT OF GYPSUM FROM 0.5 TO 60°C

Temp. C°	Mean $K_{sp} \times 10^5$	$\sigma \times 10^5$	No. of Points
0.5	2.270	0.064	14
5.0	2.374	0.050	7
10.0	2.470	0.055	7
15.0	2.492	0.024	6
20.0	2.475	0.042	6
25.0	2.466	0.068	18
30.0	2.404	0.041	9
40.0	2.290	0.055	8
60.0	1.887	0.096	8

5.3 The Solubility Product of Calcite

In nature the most common carbonate solid phase is calcite (i.e., $CaCO_3$). This mineral plays a special role in the study of natural waters' equilibrium. Its dissolution in and precipitation from an aquatic medium produces important repercussions on the equilibrium conditions of water solutions. For example, these processes of dissolution-precipitation of calcite are directly related to the pH of the solutions and their bicarbonate content (i.e., alkalinity).

In order to understand the chemistry of calcite in water solutions it is convenient to know its thermodynamic solubility product. Most literature determinations of this thermodynamic constant are based on Frear and Johnston's (1929) experimental measurements of the solubility of calcite in water at 25°C. By using these and other literature data, Jacobson and Langmuir (1974) attempted to evaluate the K_{sp} of calcite in water. Their theoretical approach was based on the Ion Association Model. In this approach they considered the existence of $CaHCO_3^+$ and $CaCO_3^o$ ion pairs. Interestingly, they found that when these ion pairs are considered in their computations, the calculated K_{sp} at a given temperature is not constant; rather, it decreases with the ionic strength of the solution. In fact, their results were closer to a constant value when they ignored the presence of ion pairs. The K_{sp} values, as calculated by assuming ion association, are presented in the third column of Table 5.3.

In this dissertation, the thermodynamic solubility product of calcite is calculated according to the Ion Interaction Model. For Frear and Johnston's data, the computer program SOL yields the K_{sp} values listed in the fourth column of Table 5.3. This program utilizes $Ca(HCO_3)_2$ virial coefficients, which are experimentally evaluated in this dissertation.

It is observed from Table 5.3 that the standard deviation of the calculated K_{sp} values is significantly lower for the results of the Ion Interaction Model than for those of the Ion Association Model. One may conclude that for the particular set of experimental data, the former model is superior over the latter.

TABLE 5.3

THE THERMODYNAMIC SOLUBILITY PRODUCT OF CALCITE AT 25°C[a]

PCO_2[b] (atm)	Ca x 10^3[b] (m)	K_{sp}[c]	K_{sp}[d]
0.00031	0.52	3.89	4.07
0.00038	0.56	3.98	4.13
0.00093	0.76	3.98	4.12
0.00334	0.17	3.80	3.95
0.00690	1.51	3.80	3.93
0.01600	2.01	3.63	3.78
0.04320	2.87	3.55	3.74
0.11160	4.03	3.39	3.65
0.96840	8.91	3.09	3.47
Mean		3.68	3.87
σ		0.30	0.23

[a]Values of K_{sp} x 10^9

[b]Frear and Johnston (1929)

[c]Jacobson and Langmuir (1974), considering ion association

[d]This dissertation

5.4 Heat Exchanger Problem

Statement: A "once-through" nuclear power plant utilizes water from a nearby lake for cooling purposes. The annual average temperature of the lake, t, is 15°C. The lake water is pumped through the heat exchanger of the power plant, and its temperature is increased by Δt °C. Determine the maximum theoretical Δt allowable in the heat exchanger before precipitation of calcite or gypsum occurs. Assume that the lake water is in equilibrium with the atmosphere (PCO_2 = 0.00035). The molal concentrations of the main components in solution are: $[Na^+] = 0.1520$, $[Ca^{2+}] = 0.00085$, $[Cl^-] = 0.0295$ and $[SO_4{}^{2-}] = 0.0620$.

Solution: Assuming no ion association, Jacobson and Langmuir (1974) have proposed the following temperature function for the thermodynamic solubility product of calcite K_{sp}^C:

$$\log K_{sp}^C = 13.870 - (3059/T) - 0.04035\,T \qquad (5.1)$$

The ion product of a salt, K_{ip}, is defined as the activity product of the individual components of the salt. This thermodynamic variable equals K_{sp} under saturated conditions. The ion products of calcite, K_{ip}^C, and gypsum, K_{ip}^G, for the lake water are calculated at various temperatures by means of the program SOL and are presented in Table 5.4. This table also includes the K_{sp}^C values as calculated from equation (5.1) and the thermodynamic solubility product of gypsum, K_{sp}^G, which was evaluated in Section 5.2.

The solubility ratios of calcite, S^C, and gypsum, S^G, in Table 5.4 are calculated by dividing their respective K_{ip} by K_{sp}. One notices from the values of S^C that the lake water quickly saturates with respect to calcite as the temperature increases. The solution becomes saturated with calcite at approximately 39°C. Therefore, $\Delta t = 39 - 15 = 24°C$.

One observes from Table 5.4 that S^G is less than 1.0 over the range of temperatures from 25 to 60°C. Therefore, the solubility of gypsum is not a dominant parameter in the design of the heat exchanger.

TABLE 5.4

SOLUBILITY PROPERTIES OF CALCITE AND GYPSUM IN A LAKE WATER

t^oC	$K_{ip}^C \times 10^9$	$K_{sp}^C \times 10^9$	$K_{ip}^G \times 10^5$	$K_{sp}^G \times 10^5$	S^C	S^G
25.0	2.09	3.80	2.09	2.47	0.55	0.85
30.0	2.37	3.41	1.99	2.40	0.70	0.83
40.0	2.97	2.90	1.83	2.29	1.02	0.80
60.0	4.09	1.76	1.51	1.89	2.32	0.80

5.5 Reverse Osmosis Problem

Statement: A reverse osmosis process is to be utilized to desalinate seawater. The desired salt rejection through the process is 99 per cent. At the operation condition of 102 Atm. and 25°C, the membrane constant, Ω, equals 0.75×10^{-5} g/(cm^2-atm-sec). Calculate the energy consumption per unit volume of product and the water flux through the membrane.

Solution: According to Garrels and Thompson's seawater model (1962) the main components of ocean waters and their respective molal concentrations are: $Na^+ = 0.4752$, $K^+ = 0.0100$, $Ca^{2+} = 0.0104$, $Mg^{2+} = 0.0540$, $Cl^- = 0.5543$, $HCO_3^- = 0.00238$ and $SO_4^{2-} = 0.0284$.

Let us assume that the membrane's salt rejection properties are equal for all the above ions. Therefore, for the desired efficiency, the ionic concentrations in the product water are reduced by a factor of 0.01 from those in seawater.

Riley et al (1971) propose the following equation for the water flux, J, across an osmotic membrane:

$$J = \Omega\{P_s + \Pi_o - (P_o + \Pi_s)\} \tag{5.2}$$

where P_s and P_o represent the pressures on the seawater and product water sides, and

Π_s and Π_o represent the osmotic pressures of seawater and product water.

According to equations (2.6) and (2.7) the osmotic pressure of a solution is related to the activity coefficient of water as follows:

$$\Pi = -\frac{RT}{v_1} \ln a_1 \tag{5.3}$$

Without much loss of accuracy in the equation, one may assume that v_1 equals 18.0 cc/mol. Then, RT/v_1 = 1359.23 Atm. One may easily obtain the activities of water in both seawater and product water by means of the computer program SOL. The input data for this program are the PCO_2 over the solution, which is assumed to be atmospheric, the solution temperature and the molal concentration of the dissolved species. The values of a_1 as calculated by SOL are presented in Table 5.5. The corresponding osmotic pressures are also included in this table.

Assuming that the pressure on the product side is atmospheric, one may calculate the water flux from equation (5.2):

$$J = 0.75 \times 10^{-5} (102 + 0.27 - 25.17)$$
$$= 5.78 \times 10^{-4} \text{ g/cm}^2\text{-sec}$$
$$= 500 \text{ l/m}^2\text{-day}$$

The power consumption per unit of products, therefore, is as follows:

$$W = 102 \text{ atm} \times 0.0199 \text{ kw/m}^3\text{-day-atm}$$
$$W = 2.03 \text{ kw/m}^3\text{-day}$$

TABLE 5.5

OSMOTIC PROPERTIES OF SEAWATER AND PRODUCT WATER

Water	a_1	Π(atm)
Seawater	0.98165	25.17
Product	0.99980	0.27

Chapter 6

CONCLUSIONS

The purpose of this chapter is to summarize the most important conclusions of this dissertation, as follows:

a) The main objection to the use of the Ion Interaction Model in aquatic chemistry is the execution of lengthy mathematical manipulations, but the accuracy of the model more than compensates this objection. In single electrolyte solutions the calculations involved in the Ion Interaction Model are probably more complex than those required by the Ion Association Model. However, the opposite condition is usually the case in mixed electrolyte solutions, where cumbersome approximations are necessary to satisfy both the ENC and MBC constraints in the Ion Association Model. The superiority of the Ion Interaction Model is also revealed by its reliability in predicting the activity and osmotic coefficients of mixed electrolytes over a wide range of ionic strengths

b) An empirical modification of the thermodynamic model at $25^{o}C$ by Pitzer and Mayorga (1974) is proposed in this dissertation. This modification permits one to calculate the activity coefficients of an incompletely dissociated electrolyte in mixed electrolyte solutions. The accuracy of the proposed modification is tested by the computation of the thermodynamic solubility product of gypsum in a variety of mixed electrolyte solutions.

c) The Ion Interaction Model proposed in this work may be used to predict accurately the activity coefficient of any individual ion in mixed electrolyte solutions at temperatures ranging from 0^{o} to $40^{o}C$. Thermal effects on both electrostatic and short-range interactions are studied in this dissertation. Two simple temperature functions are required to calculate the thermal effects on the Debye-Hückel functions (i.e., electrostatic interactions). The dependence of a determinate virial coefficient (i.e., short-range interaction) on temperature is found to follow approximately a linear function of the magnitude of the virial coefficient and the solution temperature.

d) The virial coefficients at $25^{o}C$ of $MHCO_3$ electrolytes (where M = K^+, Na^+, NH_4^+, Ca^{2+} or Mg^{2+}) were experimentally determined from pH measurements of MCl-$MHCO_3$ and/or MCl-H_2CO_3 solutions. An excellent agreement was found between the $MHCO_3$ virial coefficients calculated from the results of both experimental techniques.

e) The virial coefficients of $KHCO_3$ and $NaHCO_3$ at 10^{o}, 25^{o} and $40^{o}C$ were determined from pH measurements of NaCl solutions under alkaline conditions. The calculated temperature variations of the $KHCO_3$ and $NaHCO_3$ were found in good agreement with those determined experimentally. This agreement led to the conclusion that the temperature variations of NH_4HCO_3, $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ behave ideally according to the equations proposed for the temperature variations of 1:1 and 1:2 virial coefficients.

Appendix I

VIRIAL COEFFICIENTS DEPENDENCE ON TEMPERATURE

The temperature effects on the thermodynamic properties of aqueous solutions were studied in Chapter 3. It was found in this chapter that both the electrostatic and the short-range interaction functions are temperature dependent. The temperature effects on the former type of interactions is reflected only on the value of the Debye-Hückel coefficient. Therefore, at a given ionic strength, the electrostatic interactions depend only on the solution temperature and are independent of the nature of the electrolytes in solution. On the other hand, the virial coefficients, which describe the short-range interactions, are a function of both temperature and the nature of the electrolyte. The purpose of this appendix is to present the Y and X parameters for various 1:1 and 1:2 electrolytes. For a specific electrolyte, the temperature variation of its first virial coefficient is the intercept of the linear function of Y against X. The slope of such function represents the temperature variation of the second virial coefficient.

TABLE A.1a

Y VALUES[a] OF SOME 1:1 ELECTROLYTE SOLUTIONS[b]

I(m)	X	HCl	LiCl	LiBr	NaCl	NaBr	NaOH	KF	KCl	KBr
0.1	0.664	0.3	6.2	6.8	16.4	19.2	11.0	6.8	17.8	21.8
0.2	0.564	-0.4	3.7	4.6	13.9	16.5	10.1	6.4	15.2	16.7
0.3	0.499	-0.7	2.6	3.4	13.0	14.9	9.5	6.3	13.7	16.5
0.4	0.451	- .	1.9	2.7	12.4	13.8	9.1	6.0	13.1	15.5
0.5	0.413	-1.2	1.5	2.1	12.0	12.9	8.8	5.7	12.5	14.7
0.6	0.382	-1.4	1.2	1.7	11.6	12.3	8.5	5.4	12.0	14.2
0.7	0.356	-1.5	0.9	1.4	11.3	11.8	8.2	5.1	11.6	1 .7
0.8	0.334	-1.7	0.7	1.1	11.0	11.4	8.0	4.8	11.2	13.4
0.9	0.314	-1.8	0.5	0.9	10.7	11.1	7.8	4.6	10.9	13.2
1.0	0.297	-1.9	0.3	0.7	10.4	10.8	7.6	4.4	10.	12.7
1.2	0.268	-2.2	0.1	0.4	10.0	10.4	7.2	4.0	10.0	12.2
1.5	0.234	-2.5	-0.3	0.0	9.5	9.8	6.8	3.5	9.3	11.5
1.7	0.216	-2.6	-0.4	-0.1	9.1	9.5	6.4	3.3	9.0	11.1
2.0	0.193	-2.8	-0.6	-0.4	8.7	9.2	6.0	3.0	8.5	10.5
2.5	0.165	-3.1	-0.9	-0.7	7.8	8.6	5.4	2.6	8.0	9.7
3.0	0.143	-3.3	-1.2	-0.9	7.5	8.1	4.8	2.3	7.4	9.2
3.5	0.127	-3.5	-1.4	-1.1	7.0	7.6	4.3	2.1	7.0	8.7
4.0	0.114		-1.6	-1.3	6.6	7.2	3.8	1.8	6.7	8.3
4.5	0.103		-1.8	-1.4	6.1	6.8	3.3	1.6	6.3	7.9
5.0	0.094		-2.0	-1.6	5.8	6.5		1.3	5.9	7.5
5.5	0.086		-2.2	-1.7	5.4	6.2		1.1		7.2
6.0	0.078		-2.4	-1.9	5.1	5.9		0.9		6.8
$(\Delta\beta^0/\Delta T)^c$		-4.0	-2.5	-2.8	6.0	5.3	4.0	1.3	5.3	6.5
$(\Delta\beta^1/\Delta T)^c$		4.5	9.5	12.0	14.5	18.0	11.0	8.0	18.5	20.0

[a]Y values x 10^4 calculated from ϕ_L at 25°C

[b]Harned and Owen (1958)

[c]Values x 10^4

TABLE A.1b

Y VALUES[a] OF SOME 1:1 ELECTROLYTE SOLUTIONS[b]

I(m)	X	RbF	CsF	CsBr	KI	RbI	CsI
0.1	0.664	8.7	8.9	31.0	23.7	29.2	37.5
0.2	0.564	7.0	7.1	26.9	20.8	25.1	32.5
0.3	0.499	6.2	6.2	24.3	19.3	22.3	29.4
0.4	0.451	5.7	5.5	22.3	18.3	21.4	27.3
0.5	0.413	5.3	5.1	20.8	17.5	20.2	25.7
0.6	0.382	4.9	4.7	19.7	16.8	19.3	24.5
0.7	0.356	4.7	4.4	18.8	16.3	18.5	23.5
0.8	0.334	4.4	4.2	18.2	15.8	17.8	22.8
0.9	0.314	4.2	4.0	16.8	15.4	17.0	22.2
1.0	0.297	4.0	3.8	17.6	15.0	16.3	21.8
$(\Delta\beta^{o}/\Delta T)^{c}$		0.8	-0.2	7.5	8.8	7.0	13.8
$(\Delta\beta^{1}/\Delta T)^{c}$		11.0	12.5	31.5	21.0	22.0	28.0

[a]Y values x 10^4 calculated from ϕ_L at 25°C

[b]ϕ_L calculated from empirical equations by Fortier and Desnoyers (1976)

[c]Values x 10^4

TABLE A.2

Y VALUES OF SOME 1:1 AND 1:2 ELECTROLYTE SOLUTIONS

1:1 Electrolytes

I(m)	X	RbCl	CsCl	NaF	NaI	$NaHCO_3$
0.2	0.230	9.3	10.6	5.2	9.9	10.8
0.3	0.211	8.9	10.2	5.0	9.7	10.4
0.4	0.194	8.7	9.8	4.9	9.5	9.9
0.5	0.181	8.3	9.5	4.7	9.3	9.6
0.6	0.169	8.2	9.2	4.6	9.2	9.3
0.7	0.159	7.9	9.0	4.5	9.0	8.7
0.8	0.151	7.7	8.8	4.4	8.9	8.4
0.9	0.142	7.6	8.6	4.2	8.7	7.0
$(\Delta\beta^0/\Delta T) \times 10^4$		5.0	5.0	2.8	7.3	1.8
$(\Delta\beta^1/\Delta T) \times 10^4$		18.5	26.0	11.0	12.0	4.15

1:2 Electrolytes

I(m)	X	$CaCl_2$	$SrCl_2$	$BaCl_2$	Na_2CO_3	
0.6	0.084	4.3	6.6	7.9	-0.6	
0.9	0.070	3.6	5.7	7.3	-1.7	
1.2	0.060	3.1	5.1	6.9	-2.4	
1.5	0.053	2.8	4.7	6.5	-2.7	
1.8	0.047	2.8	4.2	6.1	-2.8	
2.1	0.042	2.0	3.6	5.8	-2.6	
2.4	0.038	1.8	2.8	5.5	-2.8	
2.7	0.034	2.2	2.1	2.6	-1.6	
$(\Delta\beta^0/\Delta T) \times 10^4$		0.0	1.0	3.0	-2.0	
$(\Delta\beta^1/\Delta T) \times 10^4$		54.0	62.0	70.0	0.0	

* Calculated from $\Delta\phi_L$ values at 30°C by Leung and Millero (1975)

TABLE A.3a

Y VALUES[a] OF SOME 1:2 ELECTROLYTE SOLUTIONS[b]

I(m)	X	$LiSO_4$	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4	$MgCl_2$	$MgBr_2$	$Mg(NO_3)_2$	$CaCl_2$
0.068	9.653	28.15	79.07	78.76	87.81	106.87	39.40	44.40	54.70	42.52
0.120	0.569	25.03	68.22	66.80	73.71	88.04	29.28	34.76	45.38	32.99
0.188	0.497	22.24	60.32	57.49	62.13	73.54	23.49	28.91	38.17	27.67
0.270	0.435	21.13	47.33	51.57	54.09	63.06	20.66	25.54	33.32	24.59
$(\Delta\beta^o/\Delta T) \times 10^4$		7.0	10.0	6.0	7.0[c]	7.0[c]	-5.0	-5.0	-5.0	0.0
$(\Delta\beta^1/\Delta T) \times 10^4$		31.0	30.0	104.0	110.0[c]	130.0[c]	60.0	70.0	90.0	54.0

I(m)	X	$CaBr_2$	$Ca(NO_3)_2$	$SrCl_2$	$SrBr_2$	$Sr(NO_3)_2$	BaClx	$BaBr_2$	$Ba(NO_3)_2$
0.068	0.653	54.39	84.07	44.40	59.39	102.81	45.33	61.58	180.90
0.120	0.569	42.38	70.70	36.53	47.15	86.45	37.95	49.10	149.46
0.188	0.497	35.35	61.11	31.96	39.76	74.44	33.32	41.00	127.32
0.270	0.435	30.73	54.88	28.37	34.55	66.29	29.55	35.37	111.14
$(\Delta\beta^o/\Delta T) \times 10^4$		-8.0	0.0	1.0	-7.0	7.0[c]	3.0	-8.0	15.0[c]
$(\Delta\beta^1/\Delta T) \times 10^4$		90.0	124.0	62.0	98.0	136.0[c]	70.0	100.0	220.0[c]

[a] Y values x 10^4 calculated from ϕ_L at 25°C

[b] Harned and Owen (1958)

[c] Slopes calculated by assuming intercept

TABLE A.3b

Y VALUES[a] OF SOME 1:2 ELECTROLYTE SOLUTIONS

I (m)	X	$CaCl_2$[b]	ZnI_2[b]	$ZnCl_2$
0.1	0.597	37.4	18.3	19.3
0.2	0.486	20.8	17.5	1.1
0.3	0.417	21.5	15.5	-4.0
0.4	0.367	20.3	12.7	-7.0
0.5	0.328	18.7	10.9	-10.1
0.6	0.297	17.4	9.3	-12.4
0.7	0.272	16.1	8.2	-14.8
0.8	0.250	14.9	7.1	-22.4
0.9	0.232	13.9	6.1	-26.0
1.0	0.216	12.8	5.3	-27.8
1.2	0.190	11.1	3.8	-30.8
1.5	0.160	9.0	2.0	-34.2
2.0	0.126	6.9	-1.3	-32.8
2.5	0.104	5.7	-4.4	-31.0
3.0	0.087	4.8		-29.6
4.0	0.066	3.2		
5.0	0.053	2.4		
$(\Delta\beta^o/\Delta T) \times 10^4$		0.0	-6.0	-35.0[d]
$(\Delta\beta^1/\Delta T) \times 10^4$		54.0	62.0	76.0

[a]Y values x 10^4 calculated from I values

[b]Lewis and Randall (1961)

[c]Harned and Owen (1958)

[d]Not plotted or used in least-square analysis

TABLE A.3c

Y VALUES[a] OF SOME 1:2 ELECTROLYTE SOLUTIONS[b]

I (m)	X	$CaCl_2$	$SrCl_2$	$BaCl_2$	Na_2CO_3
0.6	0.084	4.3	6.6	7.9	-0.6
0.9	0.070	3.6	5.7	7.3	-1.7
1.2	0.060	3.1	5.1	6.9	-2.4
1.5	0.053	2.8	4.7	6.5	-2.7
1.8	0.047	2.8	4.2	6.1	-2.8
2.1	0.042	2.0	3.6	5.8	-2.6
2.4	0.038	1.8	2.8	5.5	-2.8
2.7	0.034	2.2	2.1	2.6	-1.5
$(\Delta\beta^o/\Delta T) \times 10^4$		0.0	1.0	3.0	-2.0
$(\Delta\beta^1/\Delta T) \times 10^4$		54.0	62.0	70.0	0.0

[a]Y values $\times 10^4$ calculated from $\Delta\phi_L$

[b]Leung and Millero (1975)

TABLE A.3d

Y VALUES[a] OF SOME 1:2 ELECTROLYTE SOLUTIONS[b]

I (m)	X_1	$MgCl_2$	Na_2SO_4
0.3	0.499	26.8	
0.4	0.451	22.4	
0.6	0.382	18.3	
0.8	0.334	14.9	
1.0	0.297	12.8	
1.2	0.268	11.0	
1.5	0.234	9.1	30.2
2.0	0.193	6.8	27.3
2.5	0.165	4.7	25.2
3.4	0.143	3.0	23.5
4.0	0.114	1.7	18.8
5.0	0.094	0.6	18.8
$(\Delta\beta^o/\Delta T) \times 10^4$		-5.0	10.0
$(\Delta\beta^1/\Delta T) \times 10^4$		60.0	90.0

[a]Y values x 10^4 calculated from ϕ_L

[b]Snipes et al (1975)

TABLE A.4

Y/X_1 VALUES[a] OF SOME 2:2 ELECTROLYTE SOLUTIONS[b]

I (m)	X_2/X_1	$MgSO_4$	$CaSO_4$	$ZnSO_4$	$CdSO_4$	$CuSO_4$
0.0256	0.2749	-485	-700	-663	-1305	-1004
0.0400	0.2084	-301	-456	-390	-935	-684
0.0900	0.1145	-84	c	-109	-440	-306
0.1600	0.0717	19	c	-10	-229	-152
0.2500	0.0504	80	c	35	-126	-68
0.3600	0.0385			64	-70	-18
$(\Delta\beta^1/\Delta T) \times 10^4$		210	143[d]	80	130	125
$(\Delta\beta^2/\Delta T) \times 10^4$		-2475	-2840[d]	-2800	-5150	-3925

[a] Y/X_1 values $\times 10^4$ calculated from $\bar{L}$ at 25°C

[b] Harned and Owen (1958)

[c] Saturated with respect to gypsum

[d] Calculated assuming intercept

TABLE A.5

Y VALUES[a] OF SOME 2:2 ELECTROLYTE SOLUTIONS[b]

I (m)	X_1	X_2	$MgSO_4$[c]	$MgSO_4$[d]
0.4	0.567	0.0346	37.7	123.3
1.5	0.348	0.0093	44.6	67.5
2.0	0.300	0.0069	31.8	49.0
4.0	0.1962	0.0035	25.8	34.4
5.0	0.1672	0.0028	23.5	30.4
$(\Delta\beta^o/\Delta T) \times 10^4$				6.0
$(\Delta\beta^1/\Delta T) \times 10^4$				272.0

[a]Y values x 10^4 calculated from ϕ_L

[b]Snipes et al (1975)

[c]Uncorrected for association virial coefficient

[d]Corrected for association virial coefficient

Appendix II

FORTRAN IV COMPUTER PROGRAMS

Three sets of independent computer programs are presented in this appendix. The first set is the group of programs required to run the program SOL. The input-output parameters of this program are described in Section 5.1.

The other two sets of programs, $MHCO_3$ and MX, are used to calculate the $MHCO_3$ virial coefficients. These programs are based on pH measurements of $MHCO_3$-MCl solutions and H_2CO_3-MCl solutions respectively. Both require the subroutines AMR, CB and FG. Their input parameters are: a) the solution temperature and PCO_2, and b) the ionic strength of the solutions and their respective pH values.

MAIN PROGRAM SOL

```
      REAL I,NCH,IP,NCH2,KW
      DIMENSION ACA(6),AAN(9),NA2(9),NC2(6),IC(6),IA(9),
     1 CCA(6),CAN(9),B(9,6),BP(9,6),GM(6),GX(9),BB1(9,6),
     2 R(9,6),BMX(4,9,6)
      COMMON/IN/ZC(6),ZA(9),
     3 BBB(4,9,6),TA(9,9),TC(6,6),TIC(2,6),TIA(2,9)
      NC=0
      DO 61 J=1,9
      CAN(J)=0
      IA(J)=0
   61 AAN(J)=0
      DO 62 K=1,6
      CCA(K)=0
      IC(K)=0
   62 ACA(K)=0
      IC(1)=1
      IA(1)=1
      IA(2)=4
      IA(3)=7
   26 NC=NC+1
      LC=0
      LA=0
      NCH=0
      NCH2=0
      PCH=0
      PCH2=0
      PHI=0
      DL=.001
      SM=0
      H=0
      IP=0
      CALL READ(IC,IA,NCAT,NAN,CCA,CAN,PCO2,NS,NC,NT,T)
      TK=273.15+T
      CKH=10.**(-13.417+2299.6/TK+0.01422*TK)
      CK1=10.**(14.8435-3404.71/TK-0.03279*TK)
      CK2=10.**(6.498-2902.39/TK-0.02379*TK)
      KW=10.**(6.0875-4470.99/TK-0.01706*TK)
      DT=(T-25.)/1.E4
      DO 74 J=1,NAN
      DO 74 K=1,NCAT
      IF(ZA(IA(J)).EQ.1..AND.ZC(IC(K)).EQ.1.)GO TO 70
      IF(ZA(IA(J)).EQ.2..AND.ZC(IC(K)).EQ.2.)GO TO 72
      A1=10.89
      B1=-42.17
      A2=205.08
      B2=-77.757
      GO TO 73
   70 A1=9.7979
```

```
      B1=-70.91
      A2=29.540
      B2=-61.915
      IF(IA(J).NE.4)GO TO 73
      A1=1.07
      B1=0
      A2=3.3757
      B2=-171.85
      GO TO 73
   72 A2=-232.
      B2=14.5
      A3=-1739.3
      B3=19.76
      A1=0
      B1=0
   73 BMX(1,IA(J),IC(K))=BBB(1,IA(J),IC(K))+(A1+B1*BBB(1,IA(J),
     1 IC(K)))*DT
      BMX(2,IA(J),IC(K))=BBB(2,IA(J),IC(K))+(A2+B2*BBB(2,IA(J),
     1 IC(K)))*DT
      BMX(3,IA(J),IC(K))=BBB(3,IA(J),IC(K))
      IF(ZA(IA(J)).EQ.2..AND.ZC(IC(K)).EQ.2.)BMX(3,IA(J),IC(K))=
     1 BBB(3,IA(J),IC(K))+(A3+B3*BBB(3,IA(J),IC(K)))*DT
   74 BMX(4,IA(J),IC(K))=BBB(4,IA(J),IC(K))
      DO 65 J=1,3
   65 CAN(IA(J))=0
      CCA(IC(1))=0
      DO 1 J=1,NAN
      SM=SM+CAN(IA(J))
      IF(ZA(IA(J)).EQ.1.)GO TO 4
      LA=LA+1
      NA2(LA)=IA(J)
    4 NCH=NCH+CAN(IA(J))*ZA(IA(J))
    1 NCH2=NCH2+CAN(IA(J))*ZA(IA(J))**2.
      DO 2 J=1,NCAT
      SM=SM+CCA(IC(J))
      IF(ZC(IC(J)).EQ.1.)GO TO 3
      LC=LC+1
      NC2(LC)=IC(J)
    3 PCH=PCH+CCA(IC(J))*ZC(IC(J))
    2 PCH2=PCH2+CCA(IC(J))*ZC(IC(J))**2.
      D=NCH-PCH
      I=0.5*(NCH2+PCH2)
      IF(PCO2.EQ.0.)GO TO 50
      ACA(1)=0.5*(D+(D*D+4.*PCO2*CKH*CK1)**0.5)
      CCA(1)=ACA(1)/(2.718**FG(I,T))
    5 PCH=0
      SM=0
      NCH=0
```

```
      NCH2=0
      PCH2=0
      DO 6 J=1,NAN
      SM=SM+CAN(IA(J))
      NCH=NCH+CAN(IA(J))*ZA(IA(J))
    6 NCH2=NCH2+CAN(IA(J))*ZA(IA(J))**2.
      DO 7 J=1,NCAT
      SM=SM+CCA(IC(J))
      PCH=PCH+CCA(IC(J))*ZC(IC(J))
    7 PCH2=PCH2+CCA(IC(J))*ZC(IC(J))**2.
      I=0.5*(NCH2+PCH2)
      IF(PHI.EQ.0.) AH2O=1.-.018*SM
      AAN(1)=KW/ACA(1)
      H=ACA(1)
      H2CO3=PCO2*CKH*AH2O
      AAN(4)=H2CO3*CK1/H
      AAN(7)=AAN(4)*CK2/H
      IF(DL.LE.0.0001) GO TO 15
      IF(DL.GE.ABS((IP-I)/I) )GO TO 15
   10 IP=I
   50 DO 11 J=1,NAN
   11 GX(IA(J))=2.718**(FG(I,T)*ZA(IA(J))**2.)
      DO 12 J=1,NCAT
   12 GM(IC(J))=2.718**(FG(I,T)*ZC(IC(J))**2.)
   15 CAN(1)=AAN(1)/GX(1)
      CAN(4)=AAN(4)/GX(4)
      CAN(7)=AAN(7)/GX(7)
      CCA(1)=ACA(1)/GM(1)
      DO 16 J=1,NAN
   16 AAN(IA(J))=CAN(IA(J))*GX(IA(J))
      DO 17 J=1,NCAT
   17 ACA(IC(J))=CCA(IC(J))*GM(IC(J))
      IF(PCO2.EQ.0.)GO TO 51
      E=CCA(1)-(CAN(1)+CAN(4)+D+2.*CAN(7))
      CHCO3=CAN(4)
      CAN(4)=CHCO3*(1.+E/(CHCO3+CCA(1)+2.*CAN(7)))
      ACA(1)=CK1*H2CO3/(CAN(4)*GX(4))
      IF(ABS((CHCO3-CAN(4))/CHCO3).GE.0.0001) GO TO 5
      IF(DL.EQ.0.0001)GO TO 20
      DL=0.0001
   51 CALL AC(I,ZC,ZA,IC,IA,NCAT,NAN,NC2,NA2,CAN,CCA,B,
     1 BP,AM,AX,BMX,GM,GX,BB1,LC,TA,TC,PCH,LA,LC,R)
      SI=I**0.5
      FF=FG(I,-1.)
      DO 44 K=1,NCAT
      DO 44 J=1,NAN
      IF(ZA(IA(J)).EQ.1..OR.ZC(IC(K)).EQ.1.)GO TO 43
      B(IA(J),IC(K))=BMX(1,IA(J),IC(K))+(BMX(2,IA(J),IC(K))*
```

```
     1 2.7183**(-1.4*SI))+BMX(3,IA(J),IC(K))*2.7183**
     2 (-12.*R(IA(J),IC(K))**0.5)
      GO TO 44
   43 B(IA(J),IC(K))=BMX(1,IA(J),IC(K))+BMX(2,IA(J),IC(K))*
     1 2.7183**(-2.*SI)
   44 B(IA(J),IC(K))=B(IA(J),IC(K))+2.*PCH*BMX(4,IA(J),IC(K))
      DO 42 K=1,NCAT
      DO 42 J=1,NAN
   42 PHI=PHI+CCA(IC(K))*CAN(IA(J))*B(IA(J),IC(K))
      PHI=((FF+2.*PHI+AM+AX)/SM)+1.
      AH2O=2.7183**(-.01802*PHI*SM)
   20 CAN(4)=AAN(4)/GX(4)
      IF(PCO2.NE.0.)GO TO 52
      PH=7.
      E=D
      GO TO 53
   52 IF(DL.LE.ABS((CHCO3-CAN(4))/CHCO3)) GO TO 5
      PH=-ALOG10(ACA(1))
   53 TYPE 27, PH,I,AH2O,PHI,E
      GK=CCA(5)*CAN(6)*AH2O*AH2O*BB1(6,5)*BB1(6,5)
      TYPE 101,GK,BB1(6,5),GM(5),GX(6)
      GC=CCA(5)*CAN(7)*BB1(7,5)*BB1(7,5)
      TYPE 101,GC,GM(5),GX(7),GX(4)
  101 FORMAT(5G13.5)
      IF(NT.EQ.0)GO TO 28
      TYPE 33
      DO 29 K=1,NCAT
      ACA(IC(K))=CCA(IC(K))*GM(IC(K))
   29 TYPE 34,(TIC(L,IC(K)),L=1,2),CCA(IC(K)),GM(IC(K)),ACA(IC(K))
      DO 30 J=1,NAN
      AAN(IA(J))=CAN(IA(J))*GX(IA(J))
   30 TYPE 34,(TIA(L,IA(J)),L=1,2),CAN(IA(J)),GX(IA(J)),AAN(IA(J))
      TYPE 35 ,((TIC(L,IC(K)),L=1,2),K=1,NCAT)
      DO 31 J=1,NAN
   31 TYPE 34,(TIA(L,IA(J)),L=1,2),(BB1(IA(J),IC(K)),K=1,NCAT)
   33 FORMAT(/,5X,'ION',8X,'CONC.',8X,'A.C.',8X,'ACT.')
   34 FORMAT(2A5,2X,5G13.5)
   35 FORMAT(/,'   MEAN A C',10(2A5,3X))
   27 FORMAT(5X,'PH',11X,'I',10X,'(H2O)',9X,'O.C.'12X,
     1 'E',/,6G13.5)
   28 IF(NC.LT.NS) GO TO 26
      STOP
      END
```

```
      SUBROUTINE CB(A,W,X,Y)
      P=A*W**0.5
      X=2.*(1.-(1.+P)*2.718**-P)/P**2.
      Y=2.*(-1.+(1.+P+0.5*P**2.)/2.718**P)/(A*W)**2.
      RETURN
      END


      BLOCK DATA
      REAL KW
      DIMENSION ZC(6),ZA(9),BMX(4,9,6),TA(9,9),TC(6,6),
     1 TIC(2,6),TIA(2,9)
      COMMON /IN/ZC,ZA,BMX,TA,TC,TIC,TIA
      DATA ZC/1.,1.,1.,1.,2.,2./,ZA/1.,1.,1.,1.,1.,
     4 2.,2.,2.,3./,(((BMX(M,L,K),K=1,6),L
     5 =1,9),M=1,4)/C.,.0864,.1298,3*0.,.1775,.0765,
     6 .04835,.0522,.3159,.3523,.1119,.0068,-.0816,
     7 -.0154,.2108,.3671,0.,.004,.0401,-.0011,.0886,
     8 -.0461,0.,-.0533,-.0678,4*0.,.01958,.05,.0409,.2,
     9 .221,4*0.,0.00,2*0.,-.0583,.0247,4*0.,.1781,.3729,3*0.,0.,
     1 .253,.32,3*0.,.2945,.2664,.2122,.1918,1.614,
     1 1.681,.3206,.1783,.0494,.112,1.409,1.584,0.,-.18812,
     2 -.1334,-.0336,1.267,.9159,0.,.0396,-.1042,4*0.,
     3 1.113,.7793,.6585,2.65,3.343,7*0.,1.466,1.274,
     4 4*0.,3.851,3.972,3*0.,22*0.,0.0,11*0.,-55.7,-37.23,18*0.,0.,
     5 .0022,.00205,3*0.,.0004,.00064,-.00042,-.001505,
     6 -.00012,.00183,.005,-.00036,.0033,-.00002,-.00712,
     7 -.00729,0.,-.00359,-.00413,.00022,0.,0.,
     8 0.,.00398,5*0.,.00202,0.,-.00041,0.,.00625,7*0.,
     9 .0104,.0058,4*0.,-.01487,-.02506,3*0./,
     1 TA/0.,-.05,7*0.,-.05,0.,.016,2*0.,-.02,4*0.,.016,
     1 26*0.,-.02,34*0./,
     2 TC/0.,.036,.005,-.016,2*0.,.036,0.,-.012,3*0.,
     3 .005,-.012,2*0.,-.04,0.,-.016,7*0.,-.04,2*0.,.01,
     4 4*0.,.01,0./,TIC/10H         H      ,
     5 10H       NA      ,10H        K      ,
     6 10H      NH4      ,10H       CA      ,
     7 10H       MG      /,TIA/
     8 10H       OH      ,10H       CL      ,
     9 10H      NO3      ,10H     HCO3      ,
     1 10H    H2PO4      ,10H      SO4      ,
     2 10H      CO3      ,10H     HPO4      ,
     3 10H      PO4      /
      END
```

```
      SUBROUTINE READ(IC,IA,NCAT,NAN,CCA,CAN,PCO2,NS,NC,NT,T)
      DIMENSION IC(6),IA(9),CCA(6),CAN(9)
      IF(NC.GT.1)GO TO 9
      PCO2=1.
      TYPE 25
   25 FORMAT(///,'  COMPLETE INFORMATION? (YES=1, NO=0)',
     1 /,'   *')
      ACCEPT 2, NT
      TYPE 1
    1 FORMAT(' NO. OF SOLS. W/ COMMON IONS',/,2X,'**')
      ACCEPT 2,NS
    2 FORMAT(1X,10I2)
      TYPE 3
    3 FORMAT('  ENTER CATIONS',/,'  NA=2 K=3 NH4=4 CA=5 MG=6',
     1 /,2X,5(' *'))
      ACCEPT 2,(IC(L),L=2,6)
      TYPE 4
    4 FORMAT('  ENTER ANIONS',/,'  CL=2 NO3=3 H2PO4=5',
     1 ' SO4=6 HPO4=8 PO4=9',/,2X,6(' *'))
      ACCEPT 2,(IA(L),L=4,9)
      DO 5 I=1,6
    5 IF(IC(I).EQ.0) GO TO 6
    6 NCAT=I-1
      DO 7 I=1,9
    7 IF(IA(I).EQ.0) GO TO 8
    8 NAN=I-1
    9 IF(PCO2.EQ.0.)GO TO 20
      TYPE 13
   13 FORMAT('   PCO2      T',/,' ******** ********')
      ACCEPT 14, PCO2,T
   14 FORMAT(1E9.3,1F9.3)
   20 TYPE 15
   15 FORMAT('  MOLAL CONCENTRATIONS OF CATIONS',/,
     1 5('   *.*****'))
      ACCEPT 17, (CCA(IC(I)),I=2,6)
   17 FORMAT(10F10.5)
      TYPE 18
   18 FORMAT('  MOLAL CONCENTRATIONS OF ANIONS',/,
     1 6('   *.*****'))
      ACCEPT 17,(CAN(IA(I)),I=4,9)
      RETURN
      END
```

```
      SUBROUTINE AC(I,ZC,ZA,IC,IA,NCAT,NAN,IC2,IA2,CAN,CCA,
     1 B,BP,C1,CP,BMX,GM,GX,BB1,I2,TA,TC,PCH,LA,LC,R)
      REAL I
      DIMENSION GCA(6),GAN(9),BB1(9,6),BB2(3,9,6),CCA(6),
     1 P(3,9),Q(3),GX(9),GM(6),ZC(6),ZA(9),IC(6),IA(9),
     2 IC2(6),IA2(9),CAN(9),B(9,6),BP(9,6),BMX(4,9,6),KZ(9),
     3 TA(9,9),TC(6,6),DBP(9,6),R(9,6)
      CALL CB(2.,I,C1,CP)
      CALL BB(IA,IC,B,BP,C1,CP,NAN,NCAT,BMX)
      IF(I2.EQ.0) GO TO 4
      CALL CB (1.4,I,C1,CP)
      CALL BB(IA2,IC2,B,BP,C1,CP,LA,LC,BMX)
    4 DO 5 L=1,3
      Q(L)=0.
      DO 5 J=1,NAN
      P(L,IA(J))=0.
      DO 5 K=1,NCAT
      AL=L
      BB2(L,IA(J),IC(K))=BP(IA(J),IC(K))*AL*AL
     1 +BMX(4,IA(J),IC(K))*AL
    5 CONTINUE
      DO 7 L=1,3
      DO 7 J=1,NAN
      DO 6 K=1,NCAT
    6 P(L,IA(J))=P(L,IA(J))+BB2(L,IA(J),IC(K))*CCA(IC(K))
    7 Q(L)=Q(L)+P(L,IA(J))*CAN(IA(J))
      C1=0
      CP=0
      DO 9 J=1,NAN
      TAA=0
      DO 8 K=1,NCAT
    8 BB1(IA(J),IC(K))=B(IA(J),IC(K))+PCH*BMX(4,IA(J),IC(K))
      DO 90 L=1,NAN
      CP=CAN(IA(J))*CAN(IA(L))*TA(IA(J),IA(L))+CP
   90 TAA=TAA+TA(IA(J),IA(L))*CAN(IA(L))
      KZ(J)=ZA(IA(J))
    9 GAN(IA(J))=Q(KZ(J))+2.*TAA
      DO 10 K=1,NCAT
      TCC=0
      DO 91 L=1,NCAT
      C1=CCA(IC(K))*CCA(IC(L))*TC(IC(K),IC(L))+C1
   91 TCC=TCC+TC(IC(K),IC(L))*CCA(IC(L))
      KZ(K)=ZC(IC(K))
   10 GCA(IC(K))=Q(KZ(K))+2.*TCC
      DO 12 J=1,NAN
      BC=0
      DO 11 K=1,NCAT
   11 BC=2.*BB1(IA(J),IC(K))*CCA(IC(K))+BC
```

```
      GAN(IA(J))=2.718**(GAN(IA(J))+BC)
   12 GX(IA(J))=GX(IA(J))*GAN(IA(J))
      DO 15 K=1,NCAT
      BC=0
      DO 14 J=1,NAN
   14 BC=2.*BB1(IA(J),IC(K))*CAN(IA(J))+BC
      GCA(IC(K))=2.718**(GCA(IC(K))+BC)
   15 GM(IC(K))=GM(IC(K))*GCA(IC(K))
      DB=0.
      DO 28 J=1,NAN
      DO 28 K=1,NCAT
      IF(ZA(IA(J)).EQ.1..OR.ZC(IC(K)).EQ.1.)GO TO 28
   24 IF(CAN(IA(J)).EQ.0..OR.CCA(IC(K)).EQ.0.)GO TO 28
   25 CALL AC2(IA(J),IC(K),CAN,CCA,ZA,ZC,BMX(3,IA(J),IC(K)),
     1 GX,GM,R(IA(J),IC(K)))
   28 CONTINUE
      DO 13 K=1,NCAT
      DO 13 J=1,NAN
   13 BB1(IA(J),IC(K))=((GM(IC(K))**ZA(IA(J)))*
     1 (GX(IA(J))**ZC(IC(K))))**(1./(ZC(IC(K))+ZA(IA(J))))
      RETURN
      END

      SUBROUTINE AC2(J,K,CAN,CCA,ZA,ZC,B,GX,GM,R)
      DIMENSION CCA(6),CAN(9),GM(6),GX(9),ZC(6),ZA(9)
      A=12.
      P=(CCA(K)*ZC(K)*ZC(K)+CAN(J)*ZA(J)*ZA(J))/2.
      R=A*SQRT(P)
      CALL CB(A,P,C,CP)
      GX(J)=GX(J)*2.718**(B*CCA(K)*(C+2.718**-R))
      GM(K)=GM(K)*2.718**(B*CAN(J)*(C+2.718**-R))
      RETURN
      END

      SUBROUTINE BB(IA,IC,B,BP,C1,CP,NAN,NCAT,BMX)
      DIMENSION IA(9),IC(6),BMX(4,9,6),B(9,6),BP(9,6)
      DO 1 J=1,NAN
      DO 1 K=1,NCAT
      B(IA(J),IC(K))=BMX(1,IA(J),IC(K))+
     1 BMX(2,IA(J),IC(K))*C1
    1 BP(IA(J),IC(K))=BMX(2,IA(J),IC(K))*CP
      RETURN
      END
```

```
   REAL FUNCTION FG(X,T)
   IF(T.GE.0.) GO TO 30
   FG=-2.*A*S*X/P
   GO TO 50
30 IF(X.EQ.XP)GO TO 50
   S=X**0.5
   P=1.+1.2*S
   IF(T.EQ.TP)GO TO 40
   E=87.924-0.40873*T+(1.01465E-3)*T*T
  1 -(1.9365E-6)*T*T*T
   A=1400000/(E*(T+273.15))**1.5
40 FG=-A*((S/P)+1.666667*ALOG(P))
   TP=T
   XP=X
50 RETURN
   END

       MAIN PROGRAM MHCO3
   REAL I,M
   DIMENSION PH(100),PHC(100),X(5,100),I(100),Y(100)
  1 ,B(5),CC(4),PP(100)
   TYPE 16
16 FORMAT(4X,'THO',/,' ******** ')
   ACCEPT 11,TH
   IF(TH.NE.0.)GO TO 2
   TYPE 18
   ACCEPT 12,NS,Z,B1MX,CMX,T,HCO3
18 FORMAT('  NS',4X,'ZM',7X,'B1MX',7X,'CMX',7X,'T',
  1 7X,'HCO3',/,'  **',5(' ******** '))
12 FORMAT(1I3,5F10.5)
   B1MX=(29.54-61.92*B1MX)*(T-25.)*(1.E-4)+B1MX
   TYPE 13
13 FORMAT(5X,'I',8X,'PH',/,2(' ******** '))
   ZZ=Z*(Z+1.)
   DO 10 J=1,NS
10 ACCEPT 11,I(J),PH(J)
 2 DO 1 J=1,NS
   M=2.*I(J)/ZZ
   AX=M*Z-HCO3
   CALL CB(2.,I(J),G,GP)
   PP(J)=-FG(I(J),T)-0.018*I(J)/Z-M*AX*(B1MX*GP+CMX)
  1 +2.*AX*TH*(0.638*G-1.)
   Y(J)=PP(J)+2.303*PH(J)
   X(1,J)=2.*M
   X(2,J)=2.*M*G
 1 X(3,J)=2.*Z*M*M
```

```
      TYPE 15
      CALL AMR(NS,4,X,Y,B,CC)
      DO 4 J=1,NS
      X(4,J)=Y(J)
      Y(J)=B(1)
      DO 3 L=1,3
    3 Y(J)=Y(J)+B(L+1)*X(L,J)
      PHC(J)=(Y(J)-PP(J))/2.303
    4 TYPE 11,PH(J),(X(L,J),L=1,4),Y(J),PHC(J)
      TYPE 14,(B(L),L=1,4),(CC(L),L=1,3)
   11 FORMAT(10G10.4)
   14 FORMAT(/,3X,'K',9X,'B0',8X,'B1',9X,'C',7X,
     1 'CC1',7X,'CC2',7X'CC3',/,10G10.4,//)
   15 FORMAT(//,3X,'PH',8X,'X1',7X,'X2',8X,'X3',
     1 8X,'Y',9X,'YC',7X,'PHC')
      STOP
      END


      SUBROUTINE AMR(N,M,X,Y,B,CC)
      DIMENSION CC(4),XX(5,5),Y(100),X(5,100),YY(5),
     1 SX(5),SX2(5),B(5),A(50,5),BX(50)
      SY=0
      SY2=0
      AN=N
      DO 10 I=1,N
   10 X(M,I)=1
      DO 20 J=1,M
      SX(J)=0
      YY(J)=0
      SX2(J)=0
      DO 16 K=1,M
      XX(K,J)=0
      DO 15 I=1,N
   15 XX(K,J)=XX(K,J)+X(J,I)*X(K,I)
   16 A(J,K)=XX(K,J)
      DO 19 I=1,N
      SX(J)=SX(J)+X(J,I)
      SX2(J)=SX2(J)+X(J,I)*X(J,I)
   19 YY(J)=YY(J)+X(J,I)*Y(I)
   20 BX(J)=YY(J)
      DO 25 I=1,N
      SY=SY+Y(I)
   25 SY2=SY2+Y(I)*Y(I)
      DO 29 J=1,M-1
      cc(j)=0
      if(sx(j).eq.0.)go to 29
      CC(J)=(AN*YY(J)-SX(J)*SY)/((AN*SX2(J)-SX(J)*
     1 SX(J))*(AN*SY2-SY*SY))**0.5
```

```
  1 SX(J))*(AN*SY2-SY*SY))**0.5
29 continue
   CALL MATINV(A,M,BX,1,D)
   B(1)=BX(M)
   DO 30 J=1,M-1
30 B(J+1)=BX(J)
   RETURN
   END
```

MAIN PROGRAM MX

```
   REAL I
   DIMENSION PH(100),PHC(100),X(5,100),I(100),Y(100),
  1 B(5),CC(4),H(100),RC(100),RO(100),A(6),PHS(100),CY(100)
   DATA A/0.1775,0.2945,0.0004,0.1119,0.3206,0.0005/
   TYPE 12
   L=0
   ACCEPT 10,NS,Z,A2,R,T
   TYPE 10,NS,Z,A2,R,T
   IF(Z.LT.0.)L=3
   NC=NS
   ZZ=Z*(Z+1.)
   NP=2
   IF(NS.GT.0)GO TO 30
   NS=NN
   GO TO 20
30 TYPE 13
   NN=NS
   DO 1 J=1,NS
   RO(J)=0
 1 ACCEPT 11,I(J),PH(J),PH(J+NS),PHS(J)
   IF(PH(1+NS).EQ.0.)NP=1
20 DO 8 J=1,NS
   CY(J)=0
   X(1,J)=I(J)
   X(1,J+NS)=I(J)
   CALL CB(2.,I(J),C1,CP)
   IF(PHS(J).NE.0.)CY(J)=-2.303*ZZ*PHS(J)/4.
  1 +.009*I(J)*(Z+1.)-Z*(Z+1.)*FG(I(J),    )/2.-2.*I(J)
  2 *CP*A2/(Z+1.)
   X(2,J)=I(J)*C1
   X(2,J+NS)=X(2,J)
   X(3,J)=0
   CL=2.0*I(J)/(Z+1.)
   GH=2.718**(FG(I(J),T)+2.*CL*(A(1+L)+A(2+L)*C1
  1 +CL*A(3+L))+CL*CL*A2*CP/Z)
   DO 9 K=1,NP
   JK=J+NS*(K-1)
   H(JK)=(10.**-PH(JK))/GH
```

```
 9 RC(JK)=ALOG(1.+R*I(J)/H(JK))/2.
   IF(NP.EQ.1)GO TO 8
   W=0.5*2.718**(4.605*(PH(J)-PH(J+NS)))
   RO(J)=(W-1.)/(I(J)*((1./H(J))-W/H(J+NS)))
 8 CONTINUE
   TYPE 11,(RO(J),J=1,NS),PH(1),PH(1+NS)
   ACCEPT 11,D50,D100
   DO 17 J=1,NS
   PH(J)=PH(J)+D50
   CY(J+NS)=CY(J)
17 PH(J+NS)=PH(J+NS)+D100
   IF(D50.NE.0..OR.D100.NE.0.)GO TO 20
 6 TYPE 15
   DO 26 K=1,NP
   U=(K-2)*(NP-1)
28 DO 26 J=1,NS
   JK=J+NS*(K-1)
 3 IF(NC.GE.0)GO TO 5
   X(4,JK)=0
   GO TO 26
 5 X(4,JK)=2.*I(J)*I(J)/(Z+1.)
26 Y(JK)=ZZ*(2.303*PH(JK)-RC(JK)+0.3466*U)/2.+CY(JK)
   CALL AMR(NS*NP,5,X,Y,B,CC)
   DO 4 K=1,NP
   U=(K-2)*(NP-1)
   DO 4 J=1,NS
   JK=J+NS*(K-1)
   X(5,JK)=Y(JK)
   Y(JK)=B(1)
   DO 7 L=1,4
 7 Y(JK)=Y(JK)+B(L+1)*X(L,JK)
   PHC(JK)=(2.*(Y(JK)-CY(JK))/ZZ+RC(JK)-0.3466*U)/2.303
 4 TYPE 11,PH(JK),(X(L,JK),L=1,3),X(5,JK),Y(JK),PHC(JK),RO(J)
18 TYPE 14,(B(J),J=1,5),(CC(J),J=1,2)
10 FORMAT(1I3,5G12.5)
11 FORMAT(10G10.4)
12 FORMAT('  NS',5X,'ZM',9X,'B1MX',9X,'RO',10X,'T',/,
  1 '  **',4('  ********   '))
13 FORMAT('       I        PH50       PH100',7X,'PH*',/,
  13('    *.*****'))
14 FORMAT(/,3X,'K',8X,'DB0',7X,'DB1',8X,'B2',8X,'DC',
  1 7X,'CC1',7X,'CC2',/,10G10.4,//)
15 FORMAT(//,3X,'PH',7X,'I=X1',7X,'X2',8X,'X3',
  1 8X,'Y',9X,'YC',7X,'PHC',9X,'RO')
   STOP
   END
```

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