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AN IMPROVED MODEL FOR CALCULATING HEATS OF DILUTION  
AND EQUILIBRIUM CONSTANTS FOR HIGH TEMPERATURE  
AQUEOUS ELECTROLYTE SOLUTIONS

by

Xiaoyun Lin

A thesis submitted to the faculty of

Brigham Young University

in partial fulfillment of the requirements for the degree of

Master of Science

Department of Chemical Engineering

Brigham Young University

April 2007



BRIGHAM YOUNG UNIVERSITY

GRADUATE COMMITTEE APPROVAL

of a thesis submitted by

Xiaoyun Lin

This thesis has been read by each member of the following graduate committee and by majority vote has been found to be satisfactory.

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BRIGHAM YOUNG UNIVERSITY

As chair of the candidate's graduate committee, I have read the thesis of Xiaoyun Lin in its final form and have found that (1) its format, citations, and bibliographical style are consistent and acceptable and fulfill university and department style requirements; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the graduate committee and is ready for submission to the university library.

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## ABSTRACT

# AN IMPROVED MODEL FOR CALCULATING HEATS OF DILUTION AND EQUILIBRIUM CONSTANTS FOR HIGH TEMPERATURE AQUEOUS ELECTROLYTE SOLUTIONS

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At high temperatures, the properties of aqueous electrolyte systems differ markedly from those at 25°C. For mixed-electrolyte dilute solutions at high temperatures, the degree of ion-association is sufficiently large that the association equilibrium must be incorporated in any model describing the solutions. These association reactions usually do not occur to a measurable extent at room temperature. Oscarson and co-workers<sup>1, 2, 3</sup> have designed a correlation model based on the excess Gibbs energy which can correlate  $\log K$  and  $\Delta H$  values as well as the heats of dilution for aqueous electrolyte systems as a function of temperature ( $T$ ) and ionic strength ( $I$ ) from 275 to 350°C. Use of calorimetric data to develop the model has been shown to be more accurate than using  $\Delta_{\text{dil}}H$  values from the variation of  $\log K$  with temperature because one less differentiation with respect to temperature is required.





In this study, the computer program developed by Oscarson and co-workers has been modified by incorporating the IAPWS-95 water equation of state<sup>4</sup> and Archer and Wang's correlation of the dielectric constant of water<sup>5</sup> into the excess Gibbs energy model. The difference between the present work and prior work is that it uses a more accurate equation of state for water, a more accurate dielectric constant for water and the best equilibrium constants currently available. The properties of water play a very important role in the calculation of  $\Delta_{\text{dil}}H$  values, and the modified program developed here using improved water equations is shown to be superior to the previous one.

The results of this modified model were tested by comparing the predicted heats of dilution with experimental measurements from Oscarson's work<sup>1, 2, 23</sup>. These experimental data cover the range from 523.15 K to 623.15 K and 103 bar to 128 bar. The nominal concentrations of the solutions used for the  $\Delta_{\text{dil}}H$  experiments<sup>1, 2, 23</sup> were 0.25, 0.5 and 1.0 m. Equilibrium constants  $K$  for  $\text{Na}_2\text{SO}_4$  (aq),  $\text{H}_2\text{SO}_4$  (aq),  $\text{NaAc}$  (aq), and  $\text{HCl}$  (aq) association were taken from conductivity values measured by Wood and co-workers<sup>6, 7, 8</sup> using a flow conductance apparatus. These  $\log K$  values were used to compare the predicted  $\log K$  values from Oscarson's model and those from this modified model.



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## NOMENCLATURE

a	coefficients of the equilibrium correlation ( Eq. (3.2) )
A	Debye-Hückel limiting law slope
b	(1) coefficients of the equilibrium correlation ( Eq. (3.2) ) (2) fitting parameters of equation for dielectric constant of water ( Eq. (2.15) )
c	coefficients of the equilibrium correlation ( Eq. (3.2) )
d	coefficients of the equilibrium correlation ( Eq. (3.2) ) IAPWS-95 parameters
e	the electronic charge
f	Helmholtz free energy
G	molar Gibbs energy
H	molar enthalpy
I	ionic strength
k	Boltzmann constant
K	equilibrium constant
n	number of moles parameters of the IAPWS-95 equation
$N_A$	Avogadro's number
P	pressure
q	parameters in Meissner's model (Eq. (2.7))

R	gas constant
S	molar entropy
T	temperature
t	parameters of the IAPWS-95 equation
$V_m$	the molar volume
W	the potential of average force acting on the arbitrary pair of molecules

### Greek Letters

$\alpha$	(1) Debye-Hückel parameter (2) parameters of the IAPWS-95 equation
$\beta$	(1) parameters of short-range interactions (2) parameters of the IAPWS-95 equation
$\gamma$	(1) activity coefficients (2) the angle between dipole moment (3) parameters of the IAPWS-95 equation
$\delta$	reduced density
$\epsilon_0$	permittivity of vacuum
$\epsilon$	water dielectric constant
$\tau$	reduced temperature
$\rho$	density of pure water
$\mu$	molecular dipole moment of an arbitrary molecule
$\Delta$	auxiliary function of the IAPWS-95 equation
$\Psi$	auxiliary function of the IAPWS-95 equation

$\Phi$  reduced Helmholtz energy

### Subscripts

c critical condition

i,j,k,l,m components i,j,k,l,m

ij binary mixture parameter

ijk triplet mixture parameter

m molal based

P constant pressure (isobaric)

T constant temperature (isothermal)

### Superscripts

ex excess

per perturbation

ref reference

<sup>0</sup> ideal

r residual



## CHAPTER 1

### INTRODUCTION: MODELS FOR ELECTROLYTE SYSTEMS

Development of models for electrolyte systems is an important subject of research in applied thermodynamics because it is essential for the design and simulation of a wide variety of important chemical processes including separation processes such as extractive distillation and seawater desalination, environmental applications such as waste water treatment or chemical waste disposal and electrochemical processes like mineral scaling in steam systems. A great deal of effort has gone into the investigation of the properties of electrolyte systems since the 1970s, and a large amount of experimental data has been reported, as many empirical and semi-empirical models that cover a wide range of conditions for various aqueous electrolytes have been developed.

The available electrolyte models have been classified with respect to the basic assumptions of solution chemistry<sup>9</sup>, i.e. (1) models that consider electrolytes as undissociated species; (2) models that assume all electrolytes dissociate completely into their constituent ions; and (3) speciation-based models, which explicitly account for the chemical equilibria occurring in solutions.

Models that consider electrolytes to be undissociated species are sometimes suitable for high temperature systems in which ions exhibit a high degree of association. Models that assume fully dissociated ions are the most common for electrolytes at ambient temperature and pressure. Speciation-based models are more realistic models because



thermodynamic calculations can be used for solutions containing mixed solutes. The superiority of speciation-based models becomes apparent when thermodynamic properties other than phase equilibria are considered. It has been shown that speciation is valuable in modeling electrolysis, corrosion and other natural processes, and in predicting accurate pH values. The use of speciation-based models requires a more detailed knowledge of the properties of various coexisting species. Speciation-based models have been developed by several workers<sup>10, 11, 12, 13</sup>.

Fundamental theories and application of theoretical and empirical results to engineering problems for electrolyte systems will now be reviewed.

### **Fundamental Theories for Models of Aqueous Electrolyte Systems**

Theoretical models have been used to correlate or predict the thermo-physical properties of electrolyte solutions over the past 70 years. Modern theories can be roughly grouped into four broad categories<sup>14</sup>. (1) The Debye-Hückel (DH) theory is based on the solution of the Poisson-Boltzmann equation. In the DH theory, the ions are assumed to be charged species with a fixed diameter in a continuous dielectric medium. (2) Perturbation theories use theoretical models to calculate the properties of a reference fluid and add a perturbation term to account for the difference between the real and reference fluid properties. In this method, the reference terms are based only on theory and the parameters in the perturbation term are adjusted to fit experimental data. (3) Integral equation theories are based on solution of the Ornstein-Zernicke (OZ) equation by using relationships between the direct- and pair-correlation functions. In these theories, the mean spherical approximation (MSA) has the practical advantage of relative simplicity

and is often used to solve the OZ equation. (4) Kirkwood-Buff (KB) theories relate concentration fluctuations in the statistical mechanical grand canonical ensemble to partial derivatives of thermodynamic functions.

These four theories have been applied to two basic types of models: continuum-solvent models and discrete-solvent models. The perturbation and KB theories are more often applied to the discrete-solvent models than the DH and integral theories approaches.

### **Models for Electrolyte Systems**

Significant advancement in modeling electrolyte systems has been achieved during the last three decades. Several excellent reviews of electrolyte solution models are available<sup>9, 14</sup>. According to Anderko<sup>9</sup> and Loehe and Donohue<sup>14</sup>, empirical and semi-empirical models for electrolyte solutions can be divided into the following categories.

#### Local composition models

Local composition models for electrolyte solutions were first developed by Chen<sup>15</sup> et al. and discussed in detail by Zemaitis<sup>16</sup> et al. In this approach, a short-range force is considered to be the only contribution for the interactions between the ions and the solvent, and then generalized to the entire solution. Improvement to this approach was achieved by Haghtalab and Vera<sup>17</sup>, and Liu, Harvey and Prausnitz<sup>18</sup> (LHP model). The LHP model included a modified Debye-Hückel term to account for the effect of long-range electrostatic forces on the local composition, and a short-range term that differs significantly from Chen's short-range interaction.

## Hydration models

Like local composition approaches, hydration models expand the effect of ion-solvent association over the entire system. In addition, they include specific terms for the hydration energy and hydration number. Such a model has been available for many years<sup>19</sup>. In 1990, Ghosh and Patwardhan<sup>20</sup> proposed the excess Gibbs energy as a combination of Pitzer's<sup>21</sup> long-range ion-ion interaction expression, a hydration term consisting of the energy of hydration, and a function of the total moles of water involved in ion hydration per kilogram of solution.

## Models for mixed electrolyte aqueous solutions

The properties of mixed electrolytes rapidly become very complicated as the number of species in solution increases beyond two. For some cases, many solutions with but a single dissolved electrolyte become mixtures of electrolytes as a result of ion pairing, hydrolysis, and complexation reactions. To treat mixed-electrolyte systems effectively, a careful choice of existing species is required.

Patwardhan and Kumar<sup>22</sup> have illustrated that a new set of mixing rules, based on the assumption that single-electrolyte systems of equal ionic strength mix ideally, reproduce exceptionally well experimental activity coefficients, vapor pressures, solution densities, heat capacities, enthalpies of mixing, and compressibilities for many two-salt systems. This method requires only the property equations for the single electrolytes. The authors have defined a reduced-activity coefficient, from which a number of important thermodynamic properties can be derived and the agreement between the predicted values and the data is impressive.

Several studies of ion-ion interactions in aqueous solution in the temperature range of 250 - 350°C have been conducted by Oscarson and co-workers<sup>1, 2, 3, 23</sup>. Their studies cover various aqueous solutions containing chemical species such as Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>-2</sup> and C<sub>2</sub>H<sub>3</sub>O<sup>-</sup>. These species are of interest in geological and industrial processes. For these solutions, enthalpies of dilution were measured using isothermal flow calorimetry. Parameters used in the excess Gibbs ion-interaction models were determined from the fits of the experimental heat data. Thermodynamic values such as equilibrium constants, enthalpy changes, entropy changes and heat capacity changes have been estimated based on calorimetric data. The specific details of the construction and operation of the calorimetry have been described<sup>24</sup> together with the mathematical procedure used to reduce the raw data.

For use in their study, Oscarson and co-workers<sup>1, 2, 3, 23</sup> have proposed a correlation approach to give equilibrium constants from calorimetric data of aqueous electrolyte solutions. In the calculations, the heats of dilution and heats of reaction vs. total mass flow of solvent data were analyzed by a computer program to correlate log  $K$  and  $\Delta H$  values for each reaction at different temperatures and zero ionic strength. Activity coefficients,  $\gamma_i$ , based on the Lindsay modification of the Meissner model<sup>25</sup> were calculated in the program and were used to extrapolate log  $K$  values at the experimental  $I$  value to log  $K$  values at  $I \rightarrow 0$  to account for the heats due to changes in ionic strength. The OPTDESX.BYU optimization routine was used to find the log  $K$  and  $\Delta H$  values which give the best agreement between the predicted and measured heats. For all systems studied<sup>1, 2, 3, 23</sup>, the enthalpy and entropy changes were positive and increased dramatically with an increase in temperature  $T$ .

One shortcoming of Oscarson's model is that it uses approximate equations for the density of water and the Debye-Hückel law limiting slopes, which lead to deviations of predicted  $\log K$  values from literature data.

#### Models for mixed-solvent electrolyte solutions

Development of models dealing with the thermodynamics of mixed-solvent electrolyte solutions has been an active area of research. Many of these approaches include three contributions to the excess Gibbs energy: (1) a long-range effect that accounts for electrostatic interactions between ions; (2) a short-range interaction contribution that accounts for water-cosolvent interactions; and (3) the Born model, which represents the chemical contribution to ion-solvent interactions.

A model for aqueous electrolyte systems containing a supercritical component at high temperatures and pressures appeared in the work of Harvey and Prausnitz<sup>26</sup>. The model consists of three contributions to the residual Helmholtz energy: a non-electrolyte term to represent all interactions except those involving ions, a term that arises from charging the ions, and a charge-charge interaction term. Agreement between predicted and measured values is poor for CO<sub>2</sub> in the NaCl system. The authors suggested that the poor agreement may be due to the Lennard-Jones term which does not explicitly define species formed in equilibria between CO<sub>2</sub> and other components.

More recently, a comprehensive mixed-solvent model which combines an excess Gibbs energy model with detailed speciation calculations has been developed by Wang et al. This model has proven to be accurate for mixed-solvent systems over full concentration ranges and works well to predict complex solid-liquid equilibrium<sup>12</sup>.

In this thermodynamic framework, the excess Gibbs energy is expressed as:

$$\frac{G^{ex}}{RT} = \frac{G_{LR}^{ex}}{RT} + \frac{G_{MR}^{ex}}{RT} + \frac{G_{SR}^{ex}}{RT} \quad (1.1)$$

where  $G_{LR}^{ex}$  designates the contribution of long-range electrostatic interaction calculated from the Pitzer-Debye-Hückel formula,  $G_{SR}^{ex}$  is the short range contribution resulting from intermolecular interactions by using a UNIQUAC model, and an additional (middle range) term  $G_{MR}^{ex}$  is of a second-virial-coefficient type for ion-ion and ion-neutral molecule interactions that are not accounted for by the long-range term.

#### Models for supercritical and high temperature electrolyte systems

The widely used equations based on excess Gibbs energy,  $G^{ex}$ , as a function of temperature,  $T$ , pressure,  $P$ , and concentration (mole fraction,  $x$ , or molality,  $m$ ) are less effective near the critical point of water because solution properties change dramatically with small changes in  $T$ ,  $P$ , or  $m$  in this region. A more stable function for this situation is the residual Helmholtz energy,  $f^{res}$ , with the independent variables  $T$ , solution density,  $\rho$ , and  $m$  or  $x$ . When expressed as a function of temperature and density, differentiation of the Helmholtz energy expression allows the calculation of all other thermodynamic properties.

Among various kinds of models, the  $f^{res}$  model developed by Anderko and Pitzer (AP) <sup>27</sup> is considered one of the best models for correlation of the densities and phase

equilibrium of the NaCl-H<sub>2</sub>O system in the near-critical and supercritical region. This comprehensive equation of state includes a reference part and a perturbation contribution:

$$f^{res} = f^{ref} + f^{per} \quad (1.2)$$

In this equation, the superscript *ref* denotes the reference contributions, which come from an idealized molecular model. While the reference term yields approximate properties of the real system, the perturbation contributions compensate for the deviation from the real system by fitting empirical data. This model assumes that NaCl is completely associated. Because this equation accurately describes the density and phase behavior of the NaCl-H<sub>2</sub>O system, it provides a useful reference for studying more complex high-temperature systems.

Models with explicit inclusion of solute speciation for dilute sodium chloride at near critical conditions was recently developed and tested by Oscarson and co-workers<sup>10,11</sup>. In 2001, Oscarson and Palmer<sup>8</sup> proposed a modified model (RI model) based on a Helmholtz expression developed by Anderko and Pitzer<sup>27</sup> (AP model) and the equilibrium constant equation for NaCl from conductivity measurements of Wood and co-workers<sup>28, 29</sup>. The basic assumption of the AP model is that all NaCl present is associated. This may cause a large error in the dilute region where a large fraction of the NaCl is dissociated. The RI model takes into account the effects of ionic dissociation, hard-sphere interactions, and dipole-dipole interactions, which make it more applicable for dilute solutions at lower temperature and higher pressure where ion association is least. Another model (RII model) reported by Oscarson and Liu<sup>11</sup> as an extension of the

RI model shows its usefulness in correlating the thermodynamics of NaCl solutions as a function of solution  $\rho$ ,  $T$  and  $m$  in the water critical region. The  $P$ ,  $T$  and  $m$  ranges were 18-40 MPa, 350-402°C, and 0-5m respectively. The RII model is superior to the AP and RI models since it incorporates terms for both ion dissociation and ion-ion interaction, resulting in accurate prediction of  $\Delta_{\text{dil}}H$  values over wide  $T$ ,  $P$  and  $m$  ranges.

### **Summary of Objectives**

Accurate predictions of thermodynamic properties of aqueous electrolyte solutions are needed in order to understand various geological and industrial processes. At elevated temperatures, the interactions of chemical species with the solvent and with each other differ significantly from those at room temperatures. Reactions occurring in high temperature aqueous solutions containing ions such as  $\text{Na}^+$ ,  $\text{Ac}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , etc. , are of great importance in the electric power industry because all of these ions are most likely to concentrate with time and cause corrosion problems to the construction materials of the power system. While chemical equilibria in aqueous solutions has been thoroughly studied near room temperature, investigations about thermodynamic values are scarce for temperatures above 250°C.

The objective of this research is to improve a correlation approach proposed by Oscarson and co-workers<sup>1,2,3</sup> to give more accurate values of equilibrium constants from calorimetric data. The objective of this work was accomplished by (1) finding the appropriate correlation for association equilibrium constants  $K$  at zero ionic strength in aqueous solutions from fits of existing experimental data, (2) using the appropriate derivatives and thermodynamic identities to derive enthalpy changes  $\Delta H^0$  valid at



infinite dilution ( $I \rightarrow 0$ ), (3) using the value of  $\log K$  and  $\Delta H^0$  at zero ionic strength and the  $\gamma$  values determined from the modified Meissner's activity coefficient model<sup>25</sup> to calculate the concentrations and heats of dilution at experimental ionic strengths, and (4) determining the  $\log K$  and  $\Delta H$  values at experimental conditions by minimizing differences between the calculated and experimental heats of dilution.

This work describes this modified correlation model by first presenting a background of Lindsay's modified Meissner model<sup>25</sup>, IAPWS-95 water equation of state<sup>4</sup> and the dielectric constant model<sup>5</sup> of Archer and Wang. This is followed by a review of the appropriate experimental data and delineation of the approach used in this study to incorporate the newer models. Correlation of equilibrium constants for ionization reactions is then described. Chapter 4 explains the procedure of calculation. Next, the heats of dilution predicted from the modified model are compared to experimental measurements and predicted heats of dilution from Oscarson's work, and, the predicted  $\log K$  values are compared to Wood's data<sup>6,7,8</sup>. Finally, conclusions are drawn from this comparison, and recommendations for future work are provided.

## CHAPTER 2

### BACKGROUND

This chapter contains a review of the pertinent literature concentrating primarily on Lindsay's modified Meissner model<sup>25</sup>, the best water equation of state<sup>4</sup> and water dielectric constant model<sup>5</sup> currently available. Following these discussions, a brief description of the approach used in this research will be given.

#### **Lindsay's Modified Meissner Model**

An activity coefficient can show the deviation of a solute from ideality. In fact, it is a quantitative measure of the difference between the chemical potential of the real solute in the actual solution and the chemical potential that a solute would have if it were in an ideal solution at the same temperature, pressure and composition. The excess Gibbs free energy  $G^{ex}$  of a system containing one kilogram of solvent and  $m_i$  mole of each solute specie is:

$$G^{ex} = RT \sum_i m_i \left[ (1 - \varphi) + \frac{\sum_i m_i \ln \gamma_i}{\sum_i m_i} \right] \quad (2.1)$$

In Eq.(2.1), subcript i represents each solute specie in the system,  $\gamma$  are the activity coefficients based on the 1 molal standard state, and  $\varphi$  is the osmotic coefficient. The

standard state is a hypothetical one molal solution at infinite dilution. The excess Gibbs free energy is useful in that it allows general correlation of thermodynamic data from measurements on both solutes and solvent.

Pitzer<sup>30</sup> has successfully developed equations for activity coefficients and osmotic coefficients of electrolyte solutions with superior theoretical foundations. However, these equations contain empirically determined parameters, which may introduce large errors when extrapolated to higher concentrations and they require a large number of parameters when applied to solutions containing many solutes.

Meissner<sup>31</sup> formulated a set of equations that successfully model the activity coefficients of a large variety of electrolytes over a wide range of ionic strength at 25°C. The correlation he proposed is shown in Eqs. (2.2) – (2.5),

$$\gamma_{\pm}^{1/z_+z_-} = [1 + B(1 + 0.1I)^q - B]\Gamma^* \quad (2.2)$$

$$B = 0.75 - 0.065q \quad (2.3)$$

$$\log \Gamma^* = -\frac{0.5107I^{1/2}}{1 + CI^{1/2}} \quad (2.4)$$

$$C = 1 + 0.055qe^{-0.023I^3} \quad (2.5)$$

where  $z^+$  and  $z^-$  are the charges on the cations and anions, respectively,  $\gamma_{\pm}$  is the mean activity coefficient of the electrolyte studied,  $I$  is the ionic strength and  $q$  is a fitting parameter, which is different for different electrolytes. When  $\gamma_{\pm}^{1/z_+z_-}$  is plotted against ionic strength for many different types of electrolytes at 25°C, a smooth family of curves is formed. Therefore, given a single experimental value of  $\gamma_{\pm}$  at a known ionic strength

for an electrolyte, its  $\gamma_{\pm}$  value can be estimated for the whole range of concentrations with reasonable accuracy.

The Meissner equation has a form similar to the extended Debye-Hückel equation, but distinguishes itself in the following items: (1) there is only one adjustable parameter,  $q$ ; (2) the equation extrapolates well to higher concentrations; (3) a reasonable shape is preserved up to high ionic strength. Meissner's model gives reasonably accurate sodium chloride activity coefficients from 25°C up to 120°C using a simple form. However, this approach is inappropriate over a wider range of temperatures because the constant 0.5107 in Eq. (2.4) must be replaced by the correct Debye-Hückel limiting slope.

Lindsay<sup>25</sup> modified Meissner's equation so that it could be used over a wide range of temperature, 0°C to 350°C. The numerical constant 0.5107 of Eq. (2.4) was replaced by  $A/2.0303$ , and the parameter  $A$  is the Debye-Hückel limiting law slope, was expressed as a fifth-order polynomial in  $t$  (°C):

$$\begin{aligned} A/2.303 = & 0.484582 + 0.158173(t/100) - 0.214065(t/100)^2 \\ & + 0.256199(t/100)^3 - 0.105332(t/100)^4 + 0.0157603(t/100)^5 \end{aligned} \quad (2.6)$$

The parameter  $q$  as a function of temperature for NaCl solutions is given by the following equation:

$$q = 2.95869 - 0.321502(t/100) - 0.17233(t/100)^2 \quad (2.7)$$

In Eq. (2.7),  $t$  is the temperature in ° C. This equation is applicable at temperatures from 100-350° C and at saturated pressure of water.

This correlation fits the mean activity coefficients of sodium chloride solutions as calculated by the accurate Silvester-Pitzer correlation over the full range of concentrations at temperatures of 100-300 °C at pressures near the vapor pressure of water.

Although Lindsay's equation was fitted to NaCl data, it works quite well at temperatures above 250 °C for other 1:1 strong electrolytes based on three assumptions.

(1) Activity coefficients for all 1-1 electrolytes exhibit similar trends and can be assumed to be a function only of  $I$ , temperature, species charges, and dielectric constant. This is because as the temperature increases, the long-range effects become more significant so the size of the ions becomes less important. The long-range effect is due to the charge on the ions. Therefore the values of the activity coefficients of 1:1 electrolytes approach each other at high temperatures. (2) Sodium chloride activity coefficient data are acceptable as standards for the behavior of strong electrolytes in high temperature water. (3) An approximation for higher charged electrolytes is:

$$\gamma_{|z|} = \gamma_{\pm(\text{NaCl})}^{z^2} \quad (2.8)$$

in which  $z$  is the ion charge ( $\pm 2, \pm 3$ ),  $\gamma_{|z|}$  is a single ion activity coefficient for a multiple-charged ion, and  $\gamma_{\pm(\text{NaCl})}$  is the mean molal activity coefficient for NaCl. Lindsay<sup>25</sup> pointed out that this model for multiple-charged ions is inadequate at higher ionic strength because pronounced differences with experimental data were observed.

Lindsay's model shows some uncertainty at higher temperature because of the way in which the limiting law slope was fitted: it is fitted only as a function of temperature. However, as water becomes more compressible,  $A$  is a function of pressure  $P$  as well as temperature  $T$ .

For use in this work, the numerical constant 0.5107 in Eq. (2.4) was replaced by the exact form of  $A/\ln(10)$ . The limiting law slope  $A$  is given by

$$A_{\gamma} = e^3 \cdot (2 \cdot \pi \cdot N_A \cdot \rho)^{\frac{1}{2}} \cdot (4 \cdot \pi \cdot \epsilon \cdot \epsilon_0 \cdot k \cdot T)^{\frac{-3}{2}} \quad (2.9)$$

where  $e = 1.6021773 \times 10^{-19}$  C is the charge of an electron,  $\epsilon_0 = 8.8541878 \times 10^{-12}$  C<sup>2</sup>J<sup>-1</sup>m<sup>-1</sup> is the permittivity of vacuum,  $\epsilon$  is the dielectric constant of water,  $\rho$  is the density of water with unit g/cm<sup>3</sup>, and  $N_A$ ,  $\pi$ ,  $k$  and  $T$  have their usual meaning. The values of limiting law slope  $A$  calculated from Eq. (2.9) and Eq. (2.4) were compared with accurate reported data<sup>5</sup>. For the limiting law slope calculated using Lindsay's fitting equation, differences from reported data<sup>5</sup> are as large as 2.5%, 8.5%, and 25% at the pressures of 10MPa, 20MPa and 30MPa, respectively. Meanwhile, the discrepancy between the limiting law slope calculated from Eq. (2.9) and the reported data<sup>5</sup> is a maximum of 0.16% at a pressure of 30MPa.

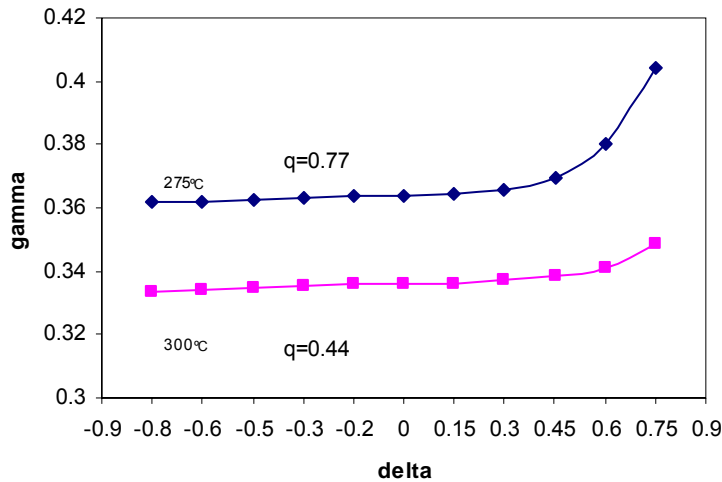
In Lindsay's modification of Meissner's model, the parameter  $q$  is only an empirical equation that does not have any physical interpretation or obvious dependence on pressure/density.

In order to investigate if  $q$  is dependent on pressure/density, a new function  $q_1$  was

defined as the sum of the fitting equation of  $q$  and a perturbation term  $\Delta$  that represents the effect of pressure/density:

$$q_1 = 2.95869 - 0.321502(t/100) - 0.17233(t/100)^2 + \Delta \quad (2.10)$$

With  $\Delta$  falling in a range of values between -0.75 to 0.75, Eq. (2.10) was used to calculate the mean activity coefficients  $\gamma$  for NaAc + H<sub>2</sub>O system. The mean activity coefficients  $\gamma$  for NaAc + H<sub>2</sub>O system vs. different  $\Delta$  are plotted in Figure 2.1. for 1m NaAc at temperatures of 275 °C and 300 °C,



**Figure 2.1.** Plot of activity coefficients  $\gamma$  of 1m NaAc + H<sub>2</sub>O system at 275°C and 300°C vs. different  $\Delta$  values.

Figure 2.1 shows that when the range of  $\Delta$  is between -0.75 to 0.45,  $\gamma$  changes relatively little; however, at 275°C,  $\gamma$  increases about 1.6% and 10.9% when  $\Delta$  is 0.6 and 0.75, respectively. In this work, pronounced improvement in the performance of

Lindsay's modified activity coefficient model is achieved by changes of up to 25% in  $A$  values; on the other hand, a change of about 100% in the values of  $q$  is required to make a significant change in  $\gamma$ . That means Lindsay's modified activity coefficient model depends more on  $A$  than on  $q$ . Therefore, in this work, we chose to include all the  $P$  or  $\rho$  dependence in the equation for  $A$  and use Eq.(2.7) for parameter  $q$ .

### **Equation of State for Water**

Of all pure fluid substances, water, including liquid water and steam, is undoubtedly the most important substance. Numerous equations of state that describe the thermodynamic properties of water has been developed over decades. The IAPWS-95 formulation<sup>4</sup> proposed by Wagner and Pruß is the best water equation of state currently available for general and scientific use. By applying modern strategies for optimizing the functional form of the equation of state and for the simultaneous nonlinear fitting to the data of all measured properties, the IAPWS-95 formulation covers a validity range for temperatures from the melting line (lowest temperature 251.2K at 209.9Mpa) to 1273K and pressures up to 1000MPa. The significant advantages of the IAPWS-95 formulation are that it correlates accurate updated data within their experimental uncertainty in the whole range, and it has improved performance in the critical region and metastable regions. Moreover, IAPWS-95 can be extrapolated to high pressures and temperatures.

The IAPWS-95 formulation is based on an empirical description of the Helmholtz energy  $A$  with the independent variables density  $\rho$  and temperature  $T$ . This model defines the function  $A(\rho, T)$  as the sum of a part  $A^0$  that represents the properties of the ideal gas



at a given  $T$  and  $\rho$  and a part  $A^r$  that takes into account the residual fluid behavior. The Helmholtz free energy takes the form of:

$$A(\rho, T) = A^0(\rho, T) + A^r(\rho, T) \quad (2.11)$$

By using the dimensionless form  $\Phi = A / (R_g T)$ , the reduced Helmholtz energy, as a function of temperature  $T$  and density  $\rho$ , becomes

$$\phi(\delta, \tau) = \phi^0(\delta, \tau) + \phi^r(\delta, \tau) \quad (2.12)$$

where  $\delta = \rho/\rho_c$  is the reduced density and  $\tau = T_c/T$  is the inverse reduced temperature with  $\rho_c$  and  $T_c$  being the critical density and the critical temperature, respectively.

The ideal gas part of the equation is:

$$\begin{aligned} \phi^0(T, \rho) = & \ln(\delta(\rho)) + n_{01} + n_{02} \cdot \tau(T) + n_{03} \cdot \ln(\tau(T)) \\ & + \sum_{i=4}^8 n_{0i} \cdot \ln[1 - \exp(-\gamma_{0i} \cdot \tau(T))] \end{aligned} \quad (2.13)$$

in which  $n_{0i}$  and  $\gamma_i$  are the parameters. The residual part of the equation is:

$$\begin{aligned}
\phi^r(T, \rho) = & \sum_{i=1}^7 n_i \cdot \delta(\rho)^{d_i} \cdot \tau(T)^{t_i} + \sum_{i=8}^{51} n_i \cdot \delta(\rho)^{d_i} \cdot \tau(T)^{t_i} \cdot \exp(-\delta(\rho)^{c_i}) \\
& + \sum_{i=52}^{54} n_i \cdot \delta(\rho)^{d_i} \cdot \tau(T)^{t_i} \cdot \exp[-\alpha_i \cdot (\delta(\rho) - \varepsilon_i)^2 - \beta_i \cdot (\tau(T) - \gamma_i)^2] \quad (2.14) \\
& + \sum_{i=55}^{56} n_i \cdot \Delta(T, \rho)^{b_i} \cdot \delta(\rho) \cdot \psi(i, T, \rho)
\end{aligned}$$

in which  $n_i$ ,  $d_i$ ,  $t_i$ ,  $\alpha_i$ , and  $\beta_i$  are parameters,  $\Delta$  and  $\psi$  are auxiliary function applicable to the critical region. The complete formulation is presented and discussed in detail in the original article<sup>2</sup>. In order to find the density of water, the equation from DIPPR 801 Database was used to get a good initial estimate of the liquid water density.

### The Dielectric Constant of Water

In order to quantitatively describe the interaction between charged particles in the electrolyte solutions, the electrostatic permittivity of the solvent in which the particles are immersed should be expressed accurately. The dielectric constant of water or relative permittivity is a key property that strongly impacts the behavior of ions in water and is an important parameter in calculating the Debye-Hückel law limiting slope. In most cases, the solvent is considered a dielectric continuum. Previous models of the dielectric constant for water have been described either as a function of temperature and pressure or as a function of temperature and water density. Both of these two forms have advantages. However, differences in Debye-Hückel law limiting slope are found when they are calculated using the water dielectric constants from these two forms, which indicates these models have limitations for predicting accurate dielectric constants. Archer and Wang<sup>5</sup> proposed a more reliable equation for the dielectric constant of water that gives

not only a good representation of the experimentally observed dielectric constant, but also gives reliable values of the first and second derivatives of the dielectric constant with respect to temperature and pressure. This equation can be applied effectively over wider regions of independent variables (for temperature from 238.15 to 823.15 K) than the previous models mentioned above.

Archer and Wang's model<sup>5</sup> is based on the Kirkwood<sup>32</sup> equation which relates the effect of intermolecular interactions on the dielectric constant of a fluid. The equation given by Kirkwood is:

$$(\varepsilon - 1)(2\varepsilon - 1)/9\varepsilon = N_A (\alpha + \mu \cdot \bar{\mu}/3\varepsilon_0 kT)/3V_m \quad (2.15a)$$

Where

$$\mu \cdot \bar{\mu} = \mu^2 \left[ 1 + (N_A/V_m) \int \cos \gamma \cdot e^{-W/kT} dW dV \right] \quad (2.15b)$$

In Eq. (2.15b),  $\varepsilon$  is the dielectric constant,  $\alpha$  is the molecular polarizability,  $V_m$  is the molar volume,  $N_A$  is Avogadro's constant,  $\mu$  is the molecular dipole moment of an arbitrary molecule in the fluid,  $\bar{\mu}$  is a local dipole moment in a small region of fluid about the arbitrary molecule and from which reactive field contributions have been moved, and  $\mu$  is the dipole moment of the molecule in the absence of all electric fields. Within the integral,  $\gamma$  is the angle between dipole moments of an arbitrary pair of dipoles, and  $W$  is the potential of average force acting on the arbitrary pair of molecules. The symbols  $T$ ,  $k$  and  $\pi$  have their usual meanings.

The difficulties inherent in the calculation of  $\varepsilon$  using Eq. (2.15a) arise from the integral part of Eq. (2.15b). For simplicity, a suitable function  $g$  was employed to replace the quantity in the square bracket in Eq. (2.15b). Archer and Wang<sup>5</sup> calculated  $(g-1)/\rho$  from the data of Heger et al. at various  $T$  and  $P$  and  $T$  and  $\rho$  values, respectively. Then the value of  $(g-1)/\rho$  was fitted by means of a nonlinear least-squares fitting procedure to the following equation:

$$\begin{aligned} \rho^\circ (g-1)/\rho = & b_1 p T^{-1} + b_2 T^{-1/2} + b_3 (T-215K)^{-1} + b_4 (T-215K)^{-1/2} \\ & + b_5 (T-215K)^{-1/4} + \exp(b_6 T^{-1} + b_7 T^{-2} + b_8 p T^{-1} + b_9 p T^{-2}) \end{aligned} \quad (2.16)$$

In Eq. (2.16),  $b_i$  are the fitting parameters with  $b_1 = -0.04044525 \text{ KMPa}^{-1}$ ,  $b_2 = 103.6180 \text{ K}^{1/2}$ ,  $b_3 = 75.32165 \text{ K}$ ,  $b_4 = -23.23778 \text{ K}^{1/2}$ ,  $b_5 = -3.548184 \text{ K}^{1/4}$ ,  $b_6 = -1246.311 \text{ K}$ ,  $b_7 = 263307.7 \text{ K}^2$ ,  $b_8 = -0.6928953 \text{ KMPa}^{-1}$ , and  $b_9 = -204.4473 \text{ K}^2 \text{MPa}^{-1}$ . Using these values, one can obtain  $g$  as a function of  $P$ ,  $T$  and  $\rho$  by rearranging Eq. (2.16) and setting the right part of Eq. (2.15a) as a function  $f$ :

$$f(p, T, \rho) = N_A \cdot \frac{\left( \alpha + \frac{g(p, T, \rho) \mu^2}{3 \varepsilon_0 k T} \right)}{3V_w} \quad (2.17)$$

where

$$N_A = 6.0221367 \times 10^{23} \text{ mol}^{-1}$$

$$\alpha = 18.1458392 \times 10^{-30} \text{ m}^3$$

$$\mu = 6.1375776 \times 10^{-30} \quad C \cdot m$$

$$\varepsilon_0 = 8.8541878 \times 10^{-12} \quad C^2 \cdot J^{-1} \cdot m^{-1}$$

$$k = 1.380658 \times 10^{-23} \quad J / K$$

$$V_w = M_w / \rho \quad \text{and} \quad M_w = 0.0180153 \quad kg / mol$$

By substituting Eq. (2.17) into Eq. (2.15a), one may expand Eq. (2.15a) into a quadratic and solve for  $\varepsilon$ :

$$2\varepsilon^2 - [9f(p, \rho, T) + 1]\varepsilon - 1 = 0 \quad (2.18)$$

In this work, the dielectric constant equation from Archer and Wang<sup>5</sup> is used to determine the Debye-Hückel limiting law slope for the calculation of activity coefficients.

Once the best equation of state and dielectric constant for water were incorporated into the modified Meissner activity coefficients model, then model results were compared with experimental data for verification. In the next section of this chapter a review of some of the experimental work found in the literature is given. The experimental work contains measurements of thermodynamic values of various aqueous electrolyte solutions at high temperatures. Some of these measurements were selected for comparison in this work.

## **Experimental Data**

Various experimental techniques have been used to measure the properties of aqueous electrolyte solutions. Frantz and Marshall<sup>34</sup> made electrical conductance studies

of HCl solutions from 100 to 700 °C and reported log  $K$  values for HCl formation from 400 to 700°C. Simonson<sup>35</sup> et al. measured enthalpies of dilution of aqueous CaCl<sub>2</sub> using a flow microcalorimeter over the temperature range 150 to 400°C. Archer<sup>36</sup> has presented the thermodynamic properties of the aqueous NaCl system from 250 K to 600 K, and pressures ranging from the vapor pressure of the solution up to 100 MPa. Because the purpose of this work is to develop a method to better predict heats of dilution as well as log  $K$  for electrolyte solutions, it was desired to have measurements for these specific properties. Wood and co-workers<sup>6, 7, 8</sup> determined accurate equilibrium constants for the formulation of Na<sub>2</sub>SO<sub>4</sub> (aq), H<sub>2</sub>SO<sub>4</sub> (aq), NaAc (aq), and HCl (aq) from their constituent ions using a flow conductance apparatus that demonstrated unprecedented speed, precision and sensitivity. These measurements were found to be the most applicable to the condition of this work, and therefore were used to compare the results of Oscarson's model<sup>1, 2, 23</sup> to the results of the modified model.



### CHAPTER 3

## CORRELATION OF EQUILIBRIUM CONSTANTS FOR ASSOCIATION REACTIONS

At high temperatures, the properties of aqueous electrolyte systems differ markedly from those at low temperatures. Above 250°C, the rapid decrease of the dielectric constant for water with increasing temperature results in an increase in ion association. This increase necessitates the use of equilibrium constants in the calculation of thermodynamic properties of the solution. This is in contrast to other cases, such as aqueous HCl below 250°C where the amount of association is so small that it can be neglected. Models that assume complete solute dissociation fail to represent quantitatively the observed thermodynamic properties of strongly associated electrolytes at high temperatures. In order to account for association effects, models for aqueous electrolytes must include an association equilibrium expression as a function of  $T$  and  $P$  or  $T$  and  $\rho$ . In this chapter the equilibrium correlation that was used in this work to calculate the enthalpy of dilution of aqueous electrolytes is discussed.

New flow-through techniques, such as in-situ UV-vis spectroscopy<sup>37</sup>, electrical conductivity<sup>38, 39</sup>, calorimetry<sup>3, 23</sup>, and potentiometry<sup>40, 41</sup> have resulted in precise measurements of thermodynamic properties of electrolyte aqueous solutions at high temperatures. Among them, Wood and co-workers<sup>6, 7, 8</sup> were able to provide accurate equilibrium constants for the dissociation of Na<sub>2</sub>SO<sub>4</sub> (aq), H<sub>2</sub>SO<sub>4</sub> (aq), NaAc (aq), and



HCl (aq) into their constituent ions from conductivity measurements on various aqueous solutions. The flow instrument and the associated operating procedure have been described in detail<sup>39, 42</sup>. Equilibrium constants determined from these experiments, together with some other values reported in the literature<sup>1, 2, 23, 43, 44</sup> for the association of electrolytes HCl (aq), H<sub>2</sub>SO<sub>4</sub> (aq), Na<sub>2</sub>SO<sub>4</sub> (aq), HAc (aq), NaAc (aq), and NaOH (aq), are listed in Table 3.1.

Table 3.1 Equilibrium Constant Data for the Ion Association to Form HCl (aq), H<sub>2</sub>SO<sub>4</sub> (aq), Na<sub>2</sub>SO<sub>4</sub> (aq), HAc(aq), NaAc(aq), and NaOH(aq) in Aqueous Solutions.

T ( K )	P (MPa)	logK	Method <sup>a</sup>	ref	density ρ(g/cm <sup>3</sup> )
$H^+ + Cl^- = HCl$					
548.15	10.3	0.37	cal	23	0.7174
573.15	11	0.62	cal	23	0.7174
573.15	10.17	0.97	con	43	0.7157
573.15	10.26	0.68	con	43	0.7159
598.15	13.2	1.31	cal	23	0.6586
623.15	17.6	2.12	cal	23	0.5841
623.15	27.8	1.68	con	43	0.6363
623.15	26.16	1.83	con	43	0.6302
$H^+ + SO_4^{2-} = HSO_4^{-1}$					
523.15	10.3	5.34	cal	1	0.80603
523.15	12.45	5.543	con	8	0.80835
573.15	11	6.44	cal	1	0.71745
573.15	12.62	6.63	con	8	0.72067
573.15	28.08	6.53	con	8	0.748
593.15	12.8	6.94	cal	1	0.67209
623.16	20	7.63	con	8	0.60059
623.16	28	7.34	con	8	0.63704
$Na^+ + SO_4^{2-} = NaSO_4^{-1}$					
523.15	12.45	1.956	con	8	0.80835
573.15	12.62	2.61	con	8	0.72067
573.15	28.08	2.52	con	8	0.748
623.16	20	3.396	con	8	0.60059
623.16	28	3.11	con	8	0.63704
$H^+ + HSO_4^{-1} = H_2SO_4$					
523.15	12.45	1.04	con	8	0.80835
573.15	12.62	1.44	con	8	0.72067
573.15	28.08	1.32	con	8	0.748

Table 3.1 (continued)

T ( K )	P (MPa)	logK	Method <sup>a</sup>	ref	density $\rho$ (g/cm <sup>3</sup> )
623.16	20	2.01	con	8	0.60059
623.16	28	1.82	con	8	0.63704
$\text{Na}^+ + \text{HSO}_4^{-1} = \text{Na}_2\text{SO}_4$					
523.15	12.45	1.62	con	8	0.80835
573.15	12.62	1.98	con	8	0.72067
573.15	28.08	1.87	con	8	0.748
623.16	20	2.51	con	8	0.60059
623.16	28	2.23	con	8	0.63704
$\text{H}^+ + \text{Ac}^- = \text{HAc}$					
548.25	23.4	6.07±0.02	con	44	0.7828
548.15	10.3	6.18	cal	2	0.7657
572.95	23.1	6.54±0.01	con	44	0.7423
573.15	10.3	6.52	cal	2	0.7159
593.15	12.8	6.86	cal	2	0.6721
623.35	23.3	7.17±0.08	con	44	0.6173
$\text{Na}^+ + \text{Ac}^- = \text{NaAc}$					
548.15	10.3	0.033	cal	2	0.7656
573.15	10.3	0.29	cal	2	0.7159
593.15	12.8	0.498	cal	2	0.6721
$\text{Na}^+ + \text{OH}^- = \text{NaOH}$					
573.15	11	0.82	cal	23	0.7174
573.15	9.69	0.89	con	6	0.7146
598.15	14.8	1.24	cal	23	0.6642
623.15	17.6	1.76	cal	23	0.5841
623.15	23.93	1.65	con	6	0.6208

<sup>a</sup>The method is designated by cal (calorimetric) or con (conductance method).

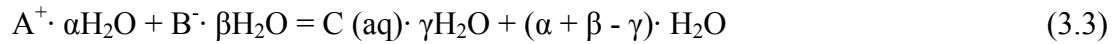
The data listed in Table 3.1 are reported from calorimetric and conductance measurements. These results are not done at the same pressures, but the agreement of data from different methods is not bad given the difficulties of making the measurements.

The following simple empirical equations have proved reliable and are widely used to give equilibrium constants as a function of  $T$  and  $\rho$ .

$$\log K = a + \frac{b}{T} + c \ln T + d \ln \rho \quad (3.1)$$

$$\log K = a + \frac{b}{T} + \left(c + \frac{d}{T}\right) \ln \rho \quad (3.2)$$

where  $\rho$  is the density of water and  $T$  is temperature in K. It has been shown that  $\rho$  is a better correlation parameter than  $P$ . The parameters  $a$ ,  $b$ ,  $c$ , and  $d$  are fitted using experimental data. The values of  $a$ ,  $b$ ,  $c$  and  $d$  will be different for each reaction. The argument for using these equations is that the water is a reactant as shown by:



The term  $(\alpha + \beta - \gamma)$  in reaction (3.3) can be roughly represented by the  $(c+d/T)$  term in eq. (3.2) since  $\rho$  is the concentration of water. However, when the temperature is above 350 °C, both equations can cause large errors in the value of  $\log K$ .

In this work, the equilibrium constants,  $K$ , for the association reactions of electrolytes HCl (aq), H<sub>2</sub>SO<sub>4</sub> (aq), Na<sub>2</sub>SO<sub>4</sub> (aq), HAc(aq), NaAc(aq), and NaOH(aq), were correlated using Eq. (3.2). When using Eq. (3.2) to fit the experimental data, the density of water that in units of gm·cm<sup>-3</sup> was calculated from the IAPWS-95 equation. Values of parameters  $a$ ,  $b$ ,  $c$ , and  $d$  were found using a least-squares fit and are listed in Table 3.2. The fitting parameters in table 3.2 are capable of sufficient accuracy to provide values of  $\log K$  which are in good agreement with experimental results. The minimum R-squared value is 0.9886 when regressed with a second-order polynomial.

Table 3.2 Parameters for Eq. ( 3.2)

	a	b(K)	c	d(K)
NaOH	0.9222	-1262.11	-4.3136	-75.2634
NaAc	-0.4558	79.96713	-4.0419	120.0167
HCl	1.0451	-800.001	-13.695	5818.004
NaSO <sub>4</sub>	3.5888	-1267.999	-3.5326	-45.0004
HSO <sub>4</sub>	13.4104	-4323.316	-2.5225	219.2622
H <sub>2</sub> SO <sub>4</sub>	7.6962	-3998.989	-14.3785	8898.995
Na <sub>2</sub> SO <sub>4</sub>	1.0333	9.9359	-2.7905	63.0129
HAc	-0.4558	-79.9671	-4.042	120.0167

Wood<sup>28</sup> et al. have stated in their equilibrium correlation that the density of pure water can be used instead of the density of electrolyte solution in a similar correlation because the density of the dilute solutions used in their study was so close to that of water that using the density of water led only to negligible errors. The same treatment was employed in this work.

The relationship between the change in Gibbs energy  $\Delta G$ , the change in the standard state Gibbs energy  $\Delta G^0$ , and the association constant  $K$  can be expressed as:

$$\Delta G = \Delta G^0 + RT \ln K \quad (3.4)$$

When the system reaches equilibrium, the change in Gibbs energy is equal to zero, and Eq. (3.4) becomes

$$\Delta G^0 = -RT \ln K_m \quad (3.5)$$

From the thermodynamic identity:

$$-\frac{\Delta H}{T^2} = \left( \frac{\partial(\Delta G/T)}{\partial T} \right)_p \quad (3.6)$$

the enthalpy change at zero ionic strength  $\Delta H^0$  can be determined as following:

$$\Delta H^0 = RT^2 \left( \frac{\partial \ln K_m}{\partial T} \right)_p \quad (3.7)$$

Substituting Eq. (3.2) into Eq. (3.7), one obtains the enthalpy change for ion association:

$$\Delta H^0 = RT^2 \ln(10) \left[ -\frac{b}{T^2} + \left( c + \frac{d}{T} \right) \frac{\partial \ln \rho}{\partial T} - \frac{d}{T^2} \ln \rho \right] \quad (3.8)$$

The log  $K$  value for the ionization of water was obtained from the equation of Marshall and Franck<sup>45</sup>:

$$\log K = a + b/T + c/T^2 + d/T^3 + (e + f/T + g/T^2) \times \log \rho \quad (3.9)$$

where  $a = -4.098$ ,  $b = -3.2452 \times 10^3$  K,  $c = 2.2362 \times 10^5$  K<sup>2</sup>,  $d = -3.984 \times 10^7$  K<sup>3</sup>,  $e = 13.957$ ,  $f = -1.12623 \times 10^3$  K,  $g = 8.5641 \times 10^5$  K<sup>2</sup>, and  $\rho$  is the density of pure water with unit g/cm<sup>3</sup>.

Substitution of Eq. (3.9) to Eq. (3.7) results in the enthalpy change for the formation of water from its constituent ions:

$$\Delta H = -RT^2 \ln(10) \left[ \frac{b}{T^2} - \frac{2c}{T^3} - \frac{3d}{T^4} - \left( \frac{f}{T^2} + \frac{2g}{T^3} \right) \times \log \rho \right. \\ \left. + \left( e + \frac{f}{T} + \frac{g}{T^2} \right) \times \frac{\partial \ln \rho}{\partial T} \right] \quad (3.10)$$



## CHAPTER 4

### CALCULATION PROCEDURE

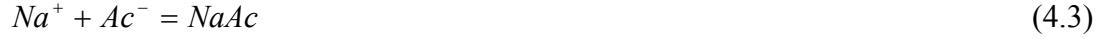
In the preceding chapter, the details of the modified Meissner's activity coefficient model<sup>25</sup>, the equation of state for water<sup>4</sup>, Archer and Wang's dielectric constant model<sup>5</sup> and the correlated empirical equation for the equilibrium constants of ion-pairing reactions in high temperature aqueous solutions were presented. In this chapter, a description of how these equations were combined to calculate heats of dilution of high temperature aqueous electrolyte systems is given.

In the previous work of Oscarson et al.<sup>1, 2, 23</sup>, the reactions occurring in the systems NaAc (aq) + H<sub>2</sub>O, HCl (aq) + H<sub>2</sub>O, and Na<sub>2</sub>SO<sub>4</sub> (aq) + H<sub>2</sub>O were studied. For example, in the process of dilution of NaAc, aqueous NaAc solution with molalities  $m_{\text{Na}^+}$ ,<sub>initial</sub> and  $m_{\text{Ac}^-}$ ,<sub>initial</sub> were mixed with a given amount of pure water to yield a final solution with smaller species molalities. During the dilution, all the solutions were at the same temperature and pressure.

For the process of dilution of NaAc (aq), a flow stream of water is combined with the initial solution to change the overall concentrations of the species. The solution containing sodium acetate as well as pure water involves seven species, according to the following association reactions:







The association constants for the first three reactions were expressed as:

$$K_{HAc} = \frac{\gamma_{HAc} m_{HAc}}{(\gamma_{\pm} m_{H^+})(\gamma_{\pm} m_{Ac^-})} \quad (4.5)$$

$$K_{NaOH} = \frac{\gamma_{NaOH} m_{NaOH}}{(\gamma_{\pm} m_{Na^+})(\gamma_{\pm} m_{OH^-})} \quad (4.6)$$

$$K_{NaAc} = \frac{\gamma_{NaAc} m_{NaAc}}{(\gamma_{\pm} m_{Na^+})(\gamma_{\pm} m_{Ac^-})} \quad (4.7)$$

Where  $\gamma_{\pm}$  is the mean activity coefficient of ions in the solution, and the activity coefficients of the neutral aqueous species are assumed to be unity at the conditions of the experiment. The association constants for HAc, NaOH, and NaAc can be calculated using the empirical equation for  $\log K$  (Eq. (3.2)).

For the association reaction  $H^+ + OH^- = H_2O$ ,

$$K_{H_2O} = (m_{H^+} \gamma_{\pm})(m_{OH^-} \gamma_{\pm}) \quad (4.8)$$

with the activity coefficient of water assumed to be unity.

After the solution reaches equilibrium, charge and mass balances for this system may be expressed as:

$$m_{H^+} + m_{Na^+} = m_{Ac^-} + m_{OH^-} \quad (4.9)$$

$$m_{Na^+,tot,final} = m_{Na^+} + m_{NaOH} + m_{NaAc} \quad (4.10)$$

$$m_{Ac^-,tot,final} = m_{Ac^-} + m_{NaAc} + m_{HAc} \quad (4.11)$$

where the final concentrations of species  $m_i$  are molal-based, and  $m_{i,tot,final}$  is the total amount of primary species in the diluted solution. The total amount of primary species in solution  $m_{i,tot,final}$ , which decreased by dilution, is calculated as:

$$m_{i,tot,final} = m_{i,tot,initial} \cdot \frac{flowa}{flowa + flowb} \quad (4.12)$$

where  $m_{i,tot,initial}$  is the total amount of primary species entering into the reservoir per unit mass of water,  $flowa$  and  $flowb$  are the mass flow rates of specific solution and water, respectively. These mass flow rates were determined using volumetric flow rates and fluid densities at the reservoir conditions.

In Eqs. (4.5) - (4.11), there are seven unknowns, i.e., molalities of the seven species  $C_i$  in diluted aqueous solution. In order to calculate heats of dilution, the basic approach is to solve the set of simultaneous equations that apply to all of the chemical equilibria that are being considered, along with mass balance equations for each of the components, and the charge balance equation for the system. First, the equations were reformulated in terms of the natural logarithm of the concentration. By applying the Newton-Raphson procedure, iteration was performed, and then the solution is found. In the procedure described above, the quantities of the final concentrations after dilution, the activity

coefficients and the ionic strength at the experimental condition can be determined. Therefore, in terms of known or solvable quantities, the overall heat of dilution can be calculated.

A solution of  $\text{Na}_2\text{SO}_4$  is usually treated as a mixed electrolyte solution. The correct selection of species present in the diluted  $\text{Na}_2\text{SO}_4$  solution is critical for the success of the calculation procedure. There are seven species present in solution:  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NaSO}_4^-$ ,  $\text{HSO}_4^-$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{H}^+$  and  $\text{OH}^-$ . In this study, we neglected  $\text{NaHSO}_4$  and  $\text{H}_2\text{SO}_4$  because they are only important at very low water densities and caused a poor fit when included in this calculation.

## CHAPTER 5

### RESULTS

The content of this chapter is a brief introduction of the computer program written for this work and the results of this modified model.

#### **Computer Program**

The set of equations discussed in this work were coded into a FORTRAN computer program. The program was written to accept two user input files: one is the system file, which provides system temperature, pressure, number of experimental runs, number of primary species in the solution and their concentrations, flow rates of stream *a* (electrolyte solution) and stream *b* (pure water), and the measured heats of dilution. The other input file is the chemistry file, which contains the species and complexes presenting in stream *a*. The program provides three outputs: (1) the initial and final molalities of species and complexes in stream *a*; (2) the heats of dilution from the prediction of the modified model and the experimental measurements; and (3)  $\log K$  and  $\Delta H$  values at experimental conditions. The program code is constructed such that the IAPWS-95 equations and dielectric constant are broken out into subroutines and functions, while solving for concentrations and heats of dilution in stream *a* comprises the main body of the program. The reader is referred to Appendix A for a complete FORTRAN computer code.

## Results of This Work

The computer program was run to generate heats of dilution for the modified model at the same experimental conditions as those used by Oscarson et al.<sup>1,2,23</sup>. Tables 5.1-5.3 contain total mass flow rates of solution and experimental heats obtained by mixing NaAc solution with H<sub>2</sub>O, HCl solution with H<sub>2</sub>O, and Na<sub>2</sub>SO<sub>4</sub> solution with H<sub>2</sub>O, respectively. Tables 5.1-5.3 also include the heats of dilution calculated by the correlation model of this work and Oscarson's previous work; Figures 5.1-5.4 graphically show the comparison of experimental measurements of heats of dilution from Oscarson et al.<sup>1,2,23</sup> with values calculated from this work and from the model of Oscarson et al.<sup>1,2,23</sup>.

Table5.1 Comparison of Measured and Calculated Heats of Dilution for NaAc + H<sub>2</sub>O<sup>a</sup>

T = 275 °C											
1.0661m				0.5175m				0.2574m			
flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>
0.6465	-1.2674	-1.306	-1.5033	0.6604	-0.4919	-0.5683	-0.6185	0.6656	-0.138	-0.2424	-0.2563
0.7159	-1.68	-1.698	-1.9461	0.7312	-0.6435	-0.7276	-0.8009	0.7363	-0.1971	-0.3134	-0.3312
0.7364	-1.8199	-1.805	-2.0668	0.752	-0.6785	-0.7837	-0.8512	0.7572	-0.1974	-0.3333	-0.3516
0.7809	-2.0765	-2.026	-2.3149	0.7972	-0.7689	-0.8784	-0.9521	0.8024	-0.2266	-0.3732	-0.3933
0.8085	-2.2	-2.156	-2.4601	0.8254	-0.8248	-0.9343	-1.0117	0.8305	-0.2582	-0.3966	-0.4177
0.8501	-2.3984	-2.342	-2.6676	0.8678	-0.9661	-1.014	-1.097	0.873	-0.3234	-0.4301	-0.4526
0.8807	-2.5305	-2.473	-2.8123	0.8988	-1.0316	-1.069	-1.1561	0.9041	-0.336	-0.4533	-0.4767
0.9244	-2.6495	-2.65	-3.0084	0.9434	-1.0306	-1.145	-1.2366	0.9485	-0.3239	-0.4848	-0.5094
0.9538	-2.7502	-2.763	-3.1339	0.9732	-1.061	-1.193	-1.2878	0.9784	-0.3659	-0.5049	-0.5303
0.9968	-2.8688	-2.922	-3.309	1.0171	-1.1024	-1.261	-1.3596	1.0223	-0.3869	-0.533	-0.5594
1.0255	-2.9989	-3.023	-3.4207	1.0462	-1.1916	-1.304	-1.4051	1.0515	-0.3469	-0.5508	-0.5779
1.0681	-3.1036	-3.168	-3.5795	1.0896	-1.2465	-1.365	-1.4699	1.0948	-0.388	-0.5762	-0.6041
1.1402	-3.3573	-3.398	-3.8308	1.1631	-1.3272	-1.462	-1.5725	1.1682	-0.3612	-0.6162	-0.6454
T = 300 °C											
1.0711m				0.4982m				0.2625m			
flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>
0.6496	-1.8392	-2	-2.1181	0.6608	-0.8036	-0.8279	-0.8502	0.6655	-0.3157	-0.3873	-0.4288
0.7203	-2.4865	-2.601	-2.7489	0.7315	-1.0462	-1.076	-1.1025	0.7362	-0.4334	-0.5026	-0.533
0.7412	-2.6931	-2.766	-2.9209	0.7524	-1.16	-1.1144	-1.1712	0.7571	-0.4765	-0.5341	-0.5633
0.7864	-3.0577	-3.104	-3.2744	0.7976	-1.2838	-1.283	-1.3125	0.8023	-0.5745	-0.599	-0.6394
0.8145	-3.251	-3.303	-3.4822	0.8257	-1.4499	-1.365	-1.3954	0.8305	-0.5992	-0.637	-0.6676
0.8569	-3.566	-3.59	-3.7802	0.8682	-1.6314	-1.483	-1.5142	0.8727	-0.7138	-0.6915	-0.7261
0.888	-3.7906	-3.789	-3.9872	0.8993	-1.7651	-1.565	-1.5968	0.9039	-0.7473	-0.7294	-0.7686
0.9326	-4.0194	-4.061	-4.2697	0.9437	-1.7847	-1.676	-1.7088	0.9484	-0.7855	-0.781	-0.8284
0.9624	-4.1753	-4.235	-4.4497	0.9736	-1.8674	-1.748	-1.7806	0.9783	-0.8281	-0.814	-0.8679
1.0063	-4.3999	-4.479	-4.7026	1.0175	-2.03	-1.848	-1.8809	1.0222	-0.8784	-0.8602	-0.9349
1.0353	-4.5929	-4.635	-4.8632	1.067	-2.1377	-1.912	-1.9449	1.0513	-0.822	-0.8895	-0.9621
1.0787	-4.776	-4.857	-5.0925	1.09	-2.2549	-2.003	-2.0357	1.0947	-0.8922	-0.9314	-1.0166
1.1522	-5.2677	-5.211	-5.4567	1.1635	-2.4372	-2.148	-2.1798	1.1682	-0.9424	-0.9979	-1.1109
T = 320°C											
0.5115m				0.2530m							
flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>				
0.6533	-1.1732	-1.233	-1.3477	0.6584	-0.5412	-0.5425	-0.5375				
0.7244	-1.5811	-1.611	-1.7397	0.7295	-0.7688	-0.7093	-0.6981				
0.7489	-1.7355	-1.732	-1.8651	0.754	-0.8245	-0.7622	-0.7462				
0.7911	-1.9568	-1.929	-2.0824	0.7962	-0.9606	-0.849	-0.825				
0.8206	-2.0597	-2.06	-2.2134	0.8257	-1.0176	-0.9065	-0.8671				
0.8635	-2.275	-2.241	-2.4087	0.8686	-1.1491	-0.9857	-0.9472				
0.8937	-2.4004	-2.362	-2.5402	0.8988	-1.1839	-1.039	-0.9955				
0.9371	-2.5594	-2.528	-2.7207	0.9422	-1.2406	-1.112	-1.0437				
0.9631	-2.6308	-2.623	-2.824	0.9683	-1.2823	-1.153	-1.0841				
1.0068	-2.8399	-2.776	-2.9964	1.0119	-1.3976	-1.22	-1.1391				
1.0377	-2.929	-2.88	-3.1001	1.0429	-1.4266	-1.266	-1.1792				
1.0809	-3.1204	-3.018	-3.2464	1.0842	-1.5385	-1.324	-1.2083				
1.1526	-3.3522	-3.235	-3.4682	1.1576	-1.6552	-1.421	-1.2995				

<sup>a</sup> Flow rate is the total flow rate of stream *a* and stream *b* with units of g H<sub>2</sub>O·min<sup>-1</sup>; ΔdilH<sup>1</sup> and ΔdilH<sup>2</sup> are heats of dilution calculated with modified model and model of Oscarson et al.<sup>2</sup>, respectively, with units of J·min<sup>-1</sup>.

Table 5.2 Comparison of Measured and Calculated Heats of Dilution for HCl + H<sub>2</sub>O<sup>a</sup>

T = 275 °C											
1.0164m				0.4999m				0.2502m			
flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>
0.6668	-2.1869	-2.275	-2.4313	0.6685	-0.8887	-0.8503	-0.9252	0.6695	-0.3133	-0.3974	-0.4338
0.7362	-2.5973	-2.669	-2.76	0.7387	-1.05	-1.117	-1.1321	0.7399	-0.3504	-0.4688	-0.5008
0.7567	-2.6782	-2.766	-2.8542	0.7594	-1.1178	-1.158	-1.2024	0.7607	-0.3473	-0.4864	-0.5182
0.8012	-2.8479	-2.954	-3.0472	0.8042	-1.1741	-1.236	-1.2867	0.8058	-0.3792	-0.5203	-0.5638
0.8288	-2.996	-3.057	-3.1579	0.8321	-1.2155	-1.28	-1.3192	0.8338	-0.4117	-0.539	-0.5741
0.8704	-3.1459	-3.196	-3.3162	0.8742	-1.2952	-1.339	-1.3693	0.8761	-0.428	-0.5643	-0.6029
0.901	-3.2649	-3.288	-3.4257	0.905	-1.3168	-1.377	-1.4199	0.9071	-0.5113	-0.581	-0.6225
0.9447	-3.3618	-3.407	-3.5613	0.9492	-1.3723	-1.427	-1.4872	0.9514	-0.4383	-0.6024	-0.648
0.9741	-3.4364	-3.48	-3.6618	0.9788	-1.3551	-1.458	-1.5279	0.9812	-0.4327	-0.6155	-0.6635
1.0171	-3.4726	-3.577	-3.7963	1.0223	-1.4062	-1.498	-1.5812	1.0249	-0.4352	-0.6331	-0.6841
1.0458	-3.5382	-3.636	-3.8801	1.0512	-1.4385	-1.523	-1.6123	1.054	-0.4622	-0.6438	-0.6962
1.0884	-3.644	-3.717	-3.9512	1.0942	-1.4341	-1.557	-1.6524	1.0972	-0.4865	-0.6585	-0.712
1.1605	-3.7062	-3.839	-4.1052	1.1671	-1.4868	-1.608	-1.7033	1.1703	-0.5408	-0.6804	-0.7326
T = 300 °C											
1.0210m				0.4677m				0.2715m			
flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>
0.6667	-3.339	-3.3591	-3.129	0.6686	-1.4497	-1.386	-1.3173	0.6694	-0.794	-0.7417	-0.7148
0.7362	-3.875	-3.9009	-3.5656	0.7388	-1.6765	-1.611	-1.537	0.7398	-0.9154	-0.8648	-0.821
0.7567	-4.006	-4.0517	-3.6767	0.7595	-1.7557	-1.666	-1.5942	0.7606	-0.9682	-0.8948	-0.8484
0.8011	-4.258	-4.2766	-3.918	0.8044	-1.8597	-1.771	-1.7064	0.8057	-1.0452	-0.9525	-0.9119
0.8287	-4.396	-4.4356	-4.0462	0.8323	-1.9396	-1.828	-1.7679	0.8337	-1.0951	-0.9841	-0.9345
0.8704	-4.582	-4.6505	-4.2453	0.8744	-2.0535	-1.906	-1.8487	0.8759	-1.1594	-1.027	-0.977
0.9009	-4.704	-4.7764	-4.384	0.9053	-2.1206	-1.957	-1.899	0.9069	-1.1948	-1.054	-1.0048
0.9447	-4.862	-4.8918	-4.5729	0.9494	-2.1594	-2.022	-1.9573	0.9512	-1.201	-1.09	-1.032
0.974	-4.958	-5.0427	-4.6926	0.9791	-2.1804	-2.062	-1.9878	0.981	-1.2516	-1.112	-1.0598
1.0171	-5.087	-5.0948	-4.8587	1.0226	-2.2417	-2.115	-2.0305	1.0247	-1.2407	-1.141	-1.0846
1.0457	-5.165	-5.1902	-4.943	1.0516	-2.2766	-2.147	-2.0621	1.0537	-1.2634	-1.159	-1.098
1.0883	-5.272	-5.3161	-5.1077	1.0946	-2.388	-2.192	-2.0983	1.0969	-1.2745	-1.183	-1.1132
1.1605	-5.432	-5.436	-5.362	1.1675	-2.4208	-2.258	-2.121	1.1701	-1.3528	-1.219	-1.127
T = 320°C											
0.4824m				0.2370m							
flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>	flow rate	meas ΔH	ΔdilH <sup>1</sup>	ΔdilH <sup>2</sup>				
0.6613	-2.1696	-1.994	-1.921	0.6621	-1.1274	-1.036	-1.0038				
0.7318	-2.5374	-2.29	-2.138	0.733	-1.3304	-1.194	-1.1315				
0.7561	-2.6627	-2.372	-2.2121	0.7574	-1.4146	-1.238	-1.1705				
0.798	-2.795	-2.497	-2.3185	0.7995	-1.5008	-1.304	-1.2341				
0.8273	-2.8705	-2.574	-2.4073	0.8289	-1.5397	-1.345	-1.2758				
0.8698	-3.0157	-2.672	-2.5162	0.8716	-1.6396	-1.397	-1.3285				
0.8998	-3.0567	-2.735	-2.6122	0.9017	-1.6642	-1.43	-1.3596				
0.9429	-3.1219	-2.815	-2.717	0.945	-1.6778	-1.472	-1.409				
0.9687	-3.1605	-2.858	-2.7644	0.971	-1.7082	-1.496	-1.4363				
1.012	-3.2627	-2.925	-2.8209	1.0144	-1.7754	-1.531	-1.4781				
1.0427	-3.2831	-2.968	-2.872	1.0453	-1.7701	-1.554	-1.505				
1.0855	-3.3697	-3.023	-2.9584	1.0883	-1.8453	-1.583	-1.5282				
1.1567	-3.4626	-3.104	-3.042	1.1597	-1.8778	-1.625	-1.5931				

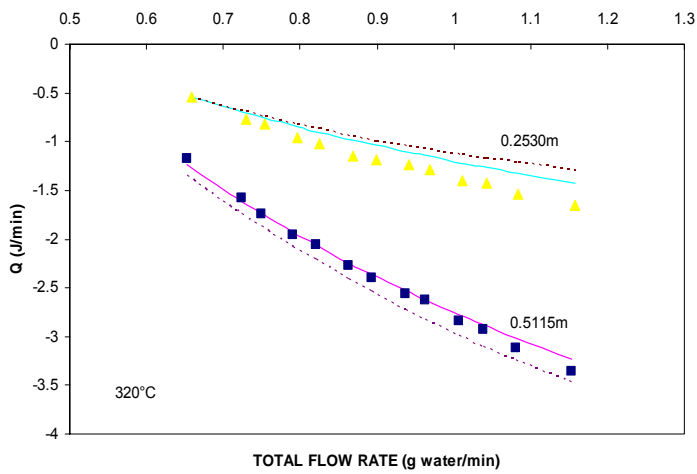
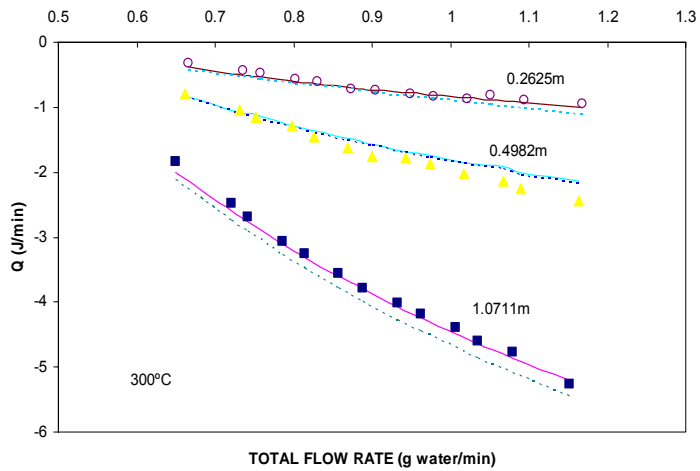
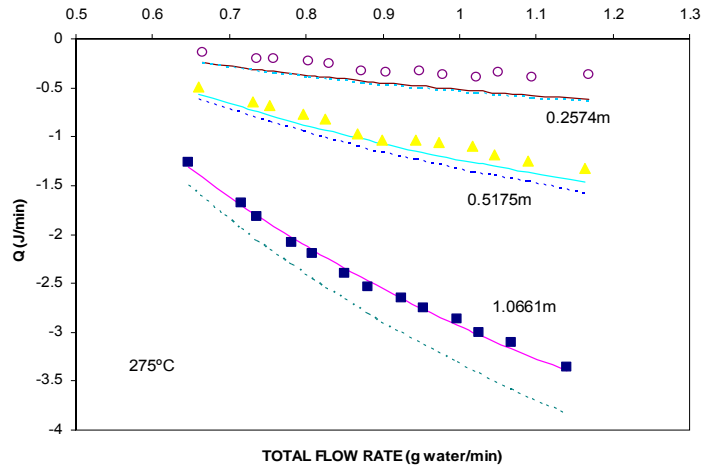
<sup>a</sup> Flow rate is the total flow rate of stream *a* and stream *b* with units of g H<sub>2</sub>O·min<sup>-1</sup>; ΔdilH<sup>1</sup> and ΔdilH<sup>2</sup> are heats of dilution calculated with modified model and model of Oscarson et al.<sup>2, 23</sup>, respectively, with units of J·min<sup>-1</sup>.

Table 5.3 Comparison of Measured and Calculated Heats of Dilution for  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}^a$

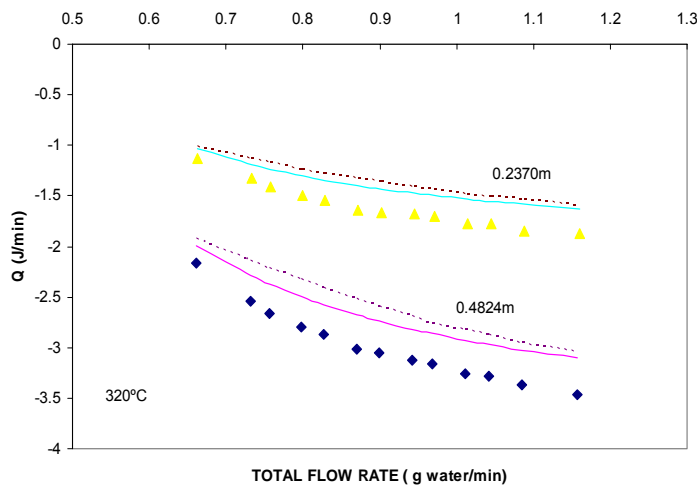
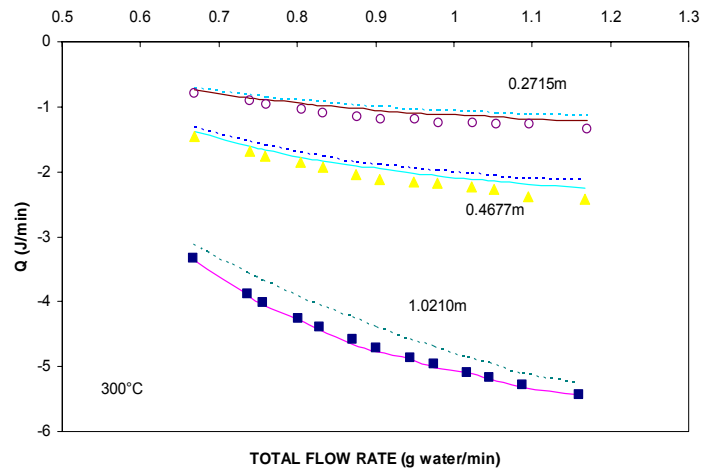
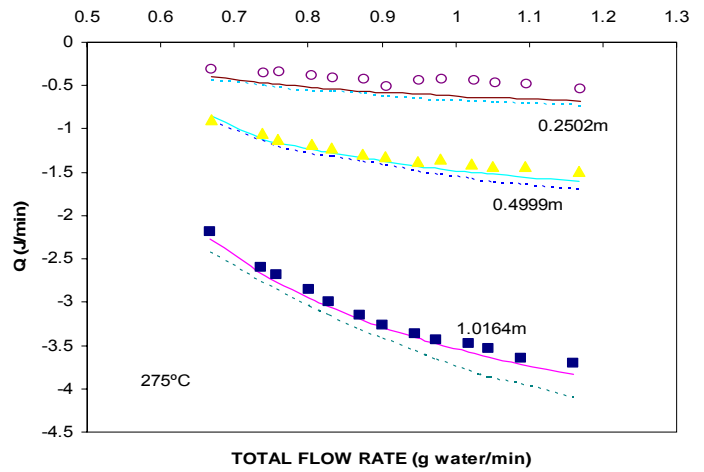
T = 250 °C				P = 10.34 Mpa							
1.0711m				0.533m				0.1437m			
flow rate	meas $\Delta\text{H}$	$\Delta\text{dilH}^1$	$\Delta\text{dilH}^2$	flow rate	meas $\Delta\text{H}$	$\Delta\text{dilH}^1$	$\Delta\text{dilH}^2$	flow rate	meas $\Delta\text{H}$	$\Delta\text{dilH}^1$	$\Delta\text{dilH}^2$
0.6626	-1.6952	-1.496	-1.4305	0.6666	-0.6067	-0.6014	-0.5325	0.669	-0.1459	-0.108	-0.0949
0.7311	-2.0001	-1.782	-1.6977	0.7364	-0.7573	-0.7143	-0.6534	0.7398	-0.1742	-0.1284	-0.1161
0.7548	-2.1107	-1.864	-1.7821	0.7605	-0.7745	-0.7469	-0.6915	0.7642	-0.1937	-0.1343	-0.1225
0.7955	-2.2548	-1.991	-1.9174	0.8021	-0.8191	-0.7971	-0.7536	0.8063	-0.1965	-0.1433	-0.1336
0.824	-2.3593	-2.071	-1.9948	0.8311	-0.843	-0.8282	-0.7942	0.8357	-0.1993	-0.1489	-0.139
0.8653	-2.4521	-2.175	-2.111	0.8732	-0.8747	-0.8689	-0.8492	0.8784	-0.1986	-0.1563	-0.1473
0.8944	-2.517	-2.241	-2.1853	0.9029	-0.8857	-0.8948	-0.8851	0.9085	-0.1979	-0.1609	-0.1534
0.9363	-2.6117	-2.327	-2.2813	0.9456	-0.9082	-0.9286	-0.9326	0.9518	-0.2072	-0.167	-0.1588
0.9614	-2.6812	-2.374	-2.3326	0.9712	-0.9283	-0.9472	-0.9587	0.9777	-0.2166	-0.1703	-0.162
1.0034	-2.7483	-2.447	-2.4081	1.014	-0.9557	-0.9557	-0.9985	1.0212	-0.2248	-0.1754	-0.1664
1.0333	-2.8087	-2.495	-2.454	1.0445	-0.9527	-0.9944	-1.0248	1.052	-0.233	-0.1787	-0.1688
1.0749	-2.8809	-2.556	-2.5068	1.0869	-0.9599	-1.018	-1.055	1.0951	-0.23	-0.183	-0.1711
1.1431	-2.997	-2.645	-2.5658	1.1574	-0.9566	-1.054	-1.0961	1.1665	-0.2121	-0.1893	-0.1722
T = 300 °C				P = 10.3MPa							
0.5724m				0.2796m							
flow rate	meas $\Delta\text{H}$	$\Delta\text{dilH}^1$	$\Delta\text{dilH}^2$	flow rate	meas $\Delta\text{H}$	$\Delta\text{dilH}^1$	$\Delta\text{dilH}^2$				
0.6663	-1.6071	-1.407	-1.2443	0.6681	-0.7258	-0.5717	-0.5033				
0.7361	-1.8629	-1.662	-1.4506	0.7386	-0.8403	-0.6768	-0.6084				
0.7602	-1.9573	-1.735	-1.5142	0.763	-0.8907	-0.707	-0.6393				
0.8016	-2.1116	-1.847	-1.6183	0.8048	-0.9335	-0.753	-0.6979				
0.8306	-2.1454	-1.917	-1.6874	0.8341	-0.9712	-0.7817	-0.7186				
0.8726	-2.2719	-2.007	-1.792	0.8766	-0.9657	-0.8189	-0.7583				
0.9023	-2.3072	-2.064	-1.8549	0.9066	-1.0162	-0.8425	-0.7929				
0.9449	-2.4043	-2.139	-1.9394	0.9497	-1.0048	-0.8732	-0.8131				
0.9705	-2.4518	-2.18	-1.9769	0.9755	-1.0416	-0.89	-0.8284				
1.0133	-2.4982	-2.242	-2.0509	1.0187	-1.0644	-0.9159	-0.8492				
1.0437	-2.5453	-2.283	-2.0992	1.0494	-1.0033	-0.9327	-0.8603				
1.0861	-2.543	-2.336	-2.161	1.0923	-1.0081	-0.9543	-0.8709				
1.1565	-2.6061	-2.413	-2.2587	1.1634	-1.068	-0.986	-0.8754				
T = 320°C				P = 12.8 Mpa							
0.3128m				0.1544m							
total flow	meas $\Delta\text{H}$	$\Delta\text{dilH}^1$	$\Delta\text{dilH}^2$	total flow	meas $\Delta\text{H}$	$\Delta\text{dilH}^1$	$\Delta\text{dilH}^2$				
0.661	-1.1471	-1.009	-0.9345	0.662	-0.4745	-0.413	-0.3953				
0.7315	-1.3457	-1.191	-1.0881	0.7328	-0.5754	-0.4892	-0.4578				
0.7558	-1.4036	-1.243	-1.1311	0.7572	-0.6365	-0.511	-0.4782				
0.7976	-1.4834	-1.322	-1.2111	0.7993	-0.679	-0.5444	-0.5114				
0.8268	-1.54	-1.371	-1.2472	0.8287	-0.6961	-0.5651	-0.5332				
0.8693	-1.6158	-1.435	-1.3101	0.8714	-0.738	-0.592	-0.5627				
0.8992	-1.6521	-1.475	-1.3415	0.9015	-0.7558	-0.609	-0.5832				
0.9423	-1.6692	-1.528	-1.4067	0.9447	-0.75	-0.6311	-0.6075				
0.9681	-1.6896	-1.556	-1.4373	0.9707	-0.7502	-0.6433	-0.6216				
1.0112	-1.7309	-1.6	-1.4845	1.0141	-0.7856	-0.6619	-0.6431				
1.0419	-1.754	-1.629	-1.5149	1.0449	-0.7723	-0.674	-0.6568				
1.0847	-1.7848	-1.666	-1.5531	1.0879	-0.8125	-0.6895	-0.6737				
1.1557	-1.85	-1.719	-1.6054	1.1593	-0.8306	-0.7123	-0.6961				

<sup>a</sup> Flow rate is the total flow rate of stream *a* and stream *b* with units of  $\text{g H}_2\text{O}\cdot\text{min}^{-1}$ ;  $\Delta\text{dilH}^1$  and  $\Delta\text{dilH}^2$  are heats of dilution calculated with modified model and model of Oscarson et al.<sup>1</sup>, respectively, with units of  $\text{J}\cdot\text{min}^{-1}$ .

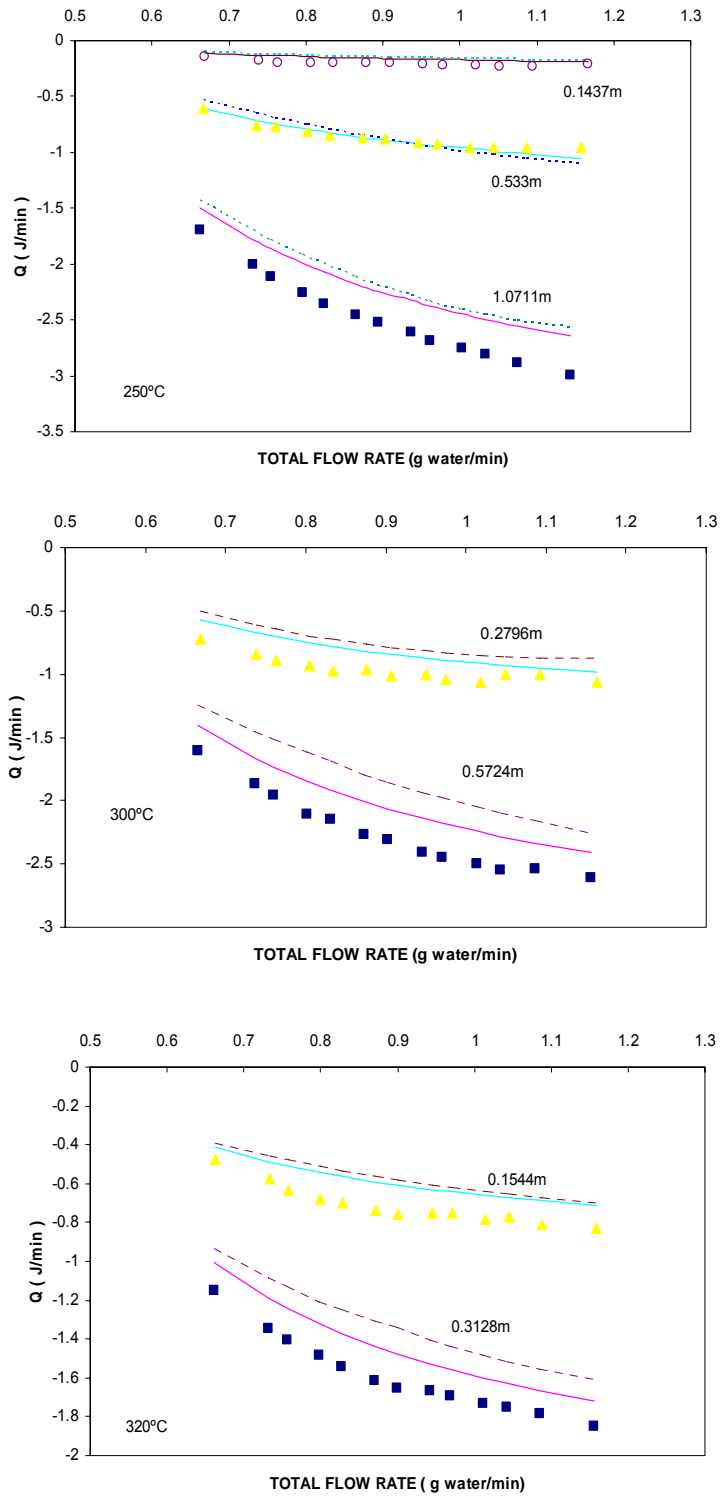




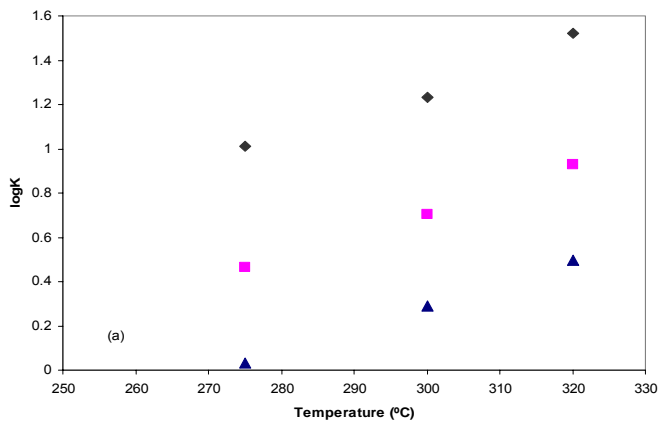
**Figure 5. 1.** Comparison of measured heat rates (symbols) and calculated heat rates from this work (solid lines) and the model of Oscarson et al.<sup>2</sup> (dotted line) vs. flow rate for NaAc + H<sub>2</sub>O.



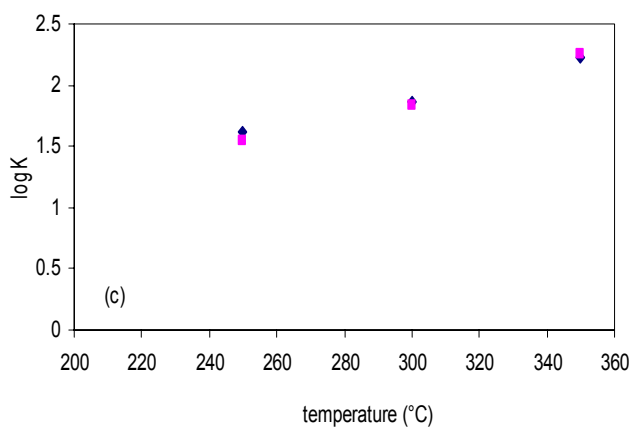
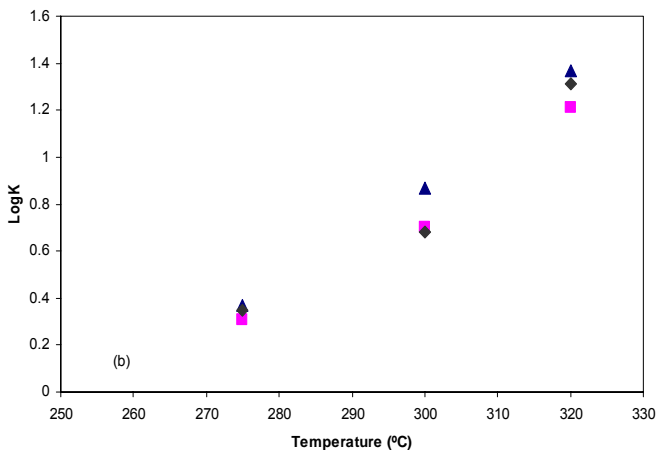
**Figure 5.2.** Comparison of measured heat rates (symbols) and calculated heat rates from this work (solid lines) and the model of Oscarson et al.<sup>2, 23</sup> (dotted line) vs. flow rate for HCl + H<sub>2</sub>O.



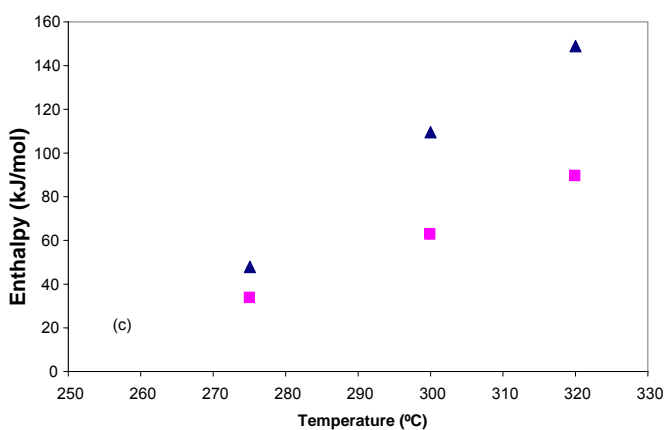
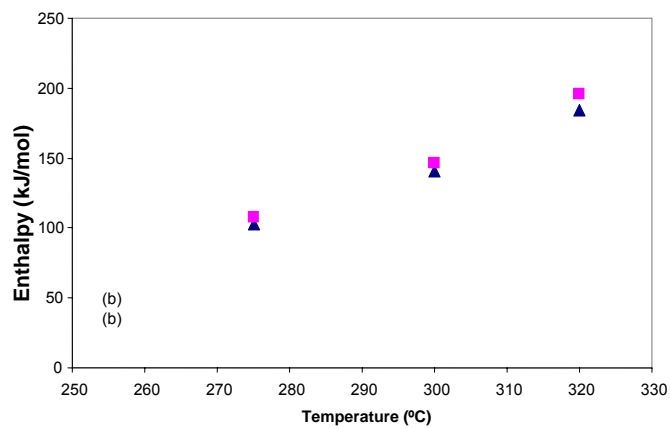
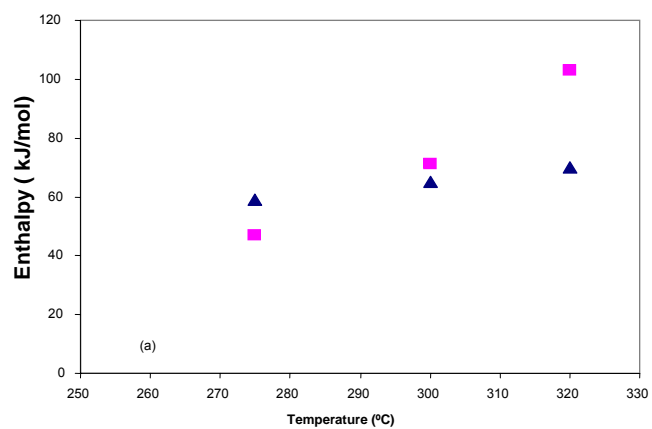
**Figure 5. 3.** Comparison of measured heat rates (symbols) and calculated heat rates from this work (solid lines) and the model of Oscarson et al.<sup>1</sup> (dotted line) vs. flow rate for  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ .



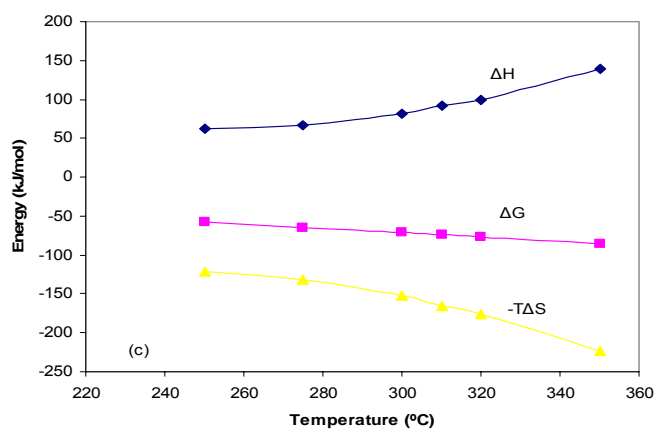
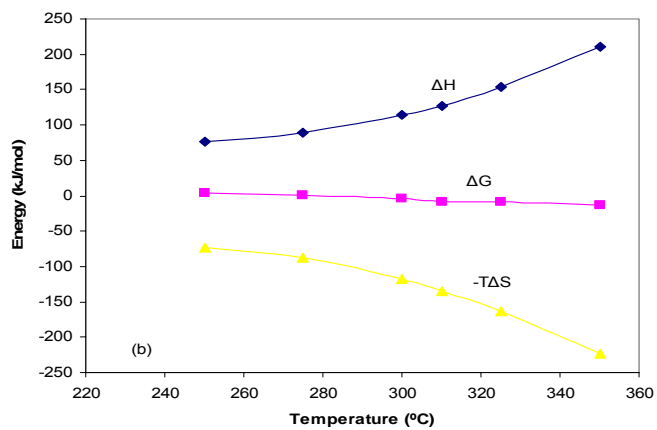
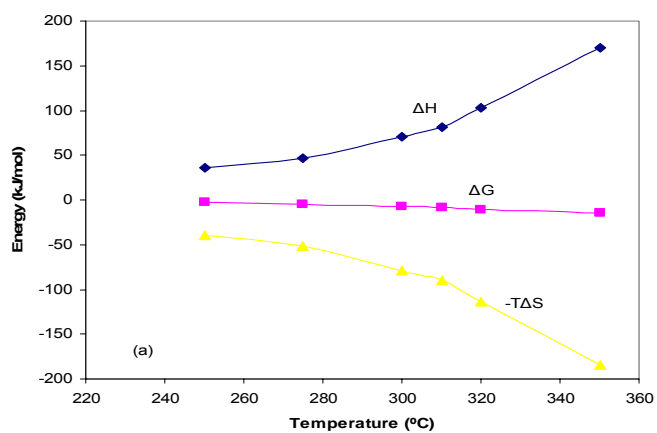
◆ Wood  
 ■ present  
 ▲ Oscarson



**Figure 5.4.** Plot of Log  $K$  for the ion association as a function of temperature for (a) NaAc (aq), (b) HCl (aq), and (c) Na<sub>2</sub>SO<sub>4</sub> respectively. The solid triangles are taken from Oscarson et al.<sup>1, 2, 23</sup>, the solid diamonds are taken from Wood et al.<sup>6, 7, 8</sup>, while the solid squares are the results obtained in the present study.



**Figure 5.5.** Plot of  $\Delta H$  for the ion association as a function of temperature of (a) NaAc (aq), (b) HCl(aq), and (c) Na<sub>2</sub>SO<sub>4</sub> (aq), respectively. The solid triangles are taken from Oscarson et al.<sup>1, 2, 23</sup>, while the solid squares are the results obtained in the present study.



**Figure 5.6.** Plots of  $\Delta G$ ,  $\Delta H$ , and  $-T\Delta S$  for the ion association as a function of temperature of (a) NaAc(aq), (b) NaOH(aq), and (c) HAc(aq), respectively.

Figure 5.6. (continued)

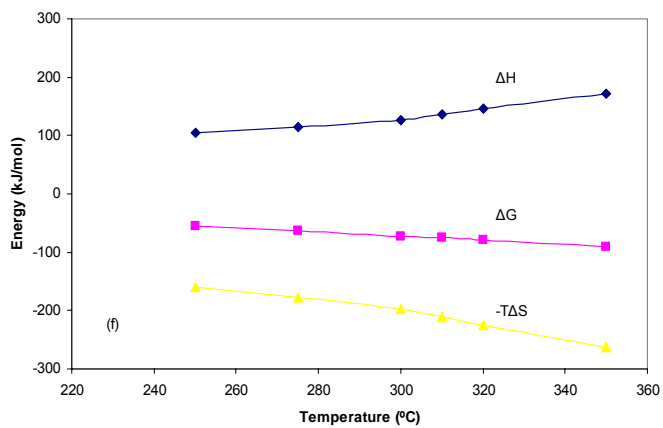
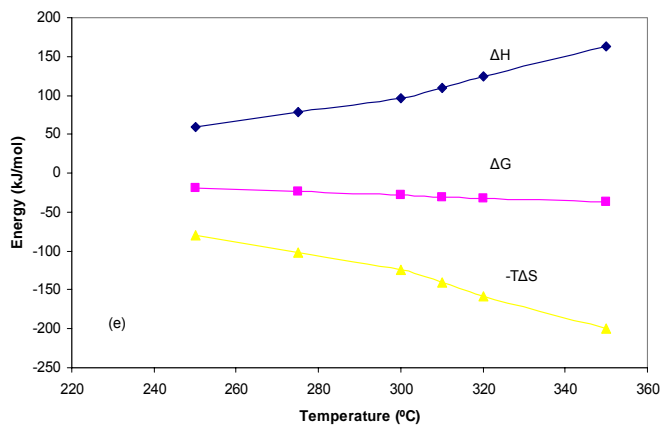
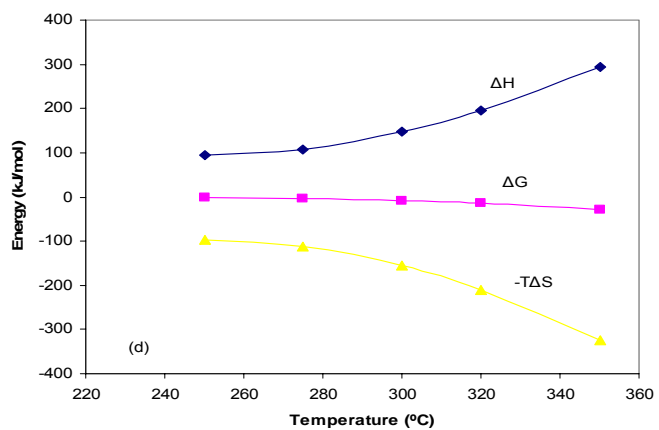
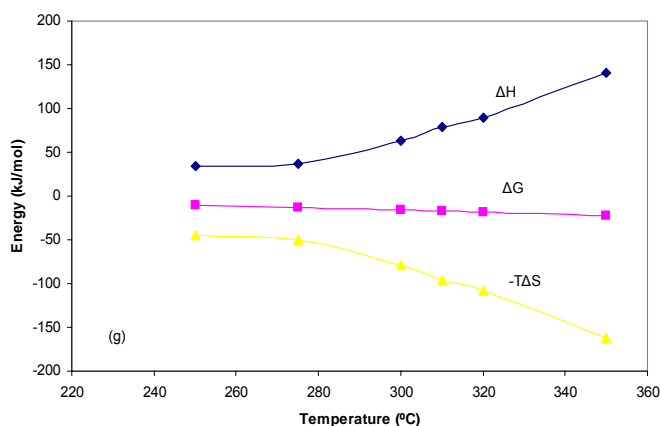


Figure 5.6. (continued)



In Figure 5.1-5.3, the heats of dilution relative to the initial concentration of the reactant solutions are plotted against the total flow rate. The first observation that may be made from Figures 5.1 -5.3 is that the heats of dilution generated from the modified model agree well with the measured data from Oscarson et al.<sup>1, 2, 23</sup>. Heat of dilution values determined by the modified model differ from the measured values by 0.1% to 56% and have an average variance with experimental data below 10%, which is within the range of experimental error. Also the figures show that the heats of dilution calculated from this work are more consistent with experimental data than those calculated using the model of Oscarson et al.<sup>1, 2, 23</sup>. Of the results examined in this section, the modified model is superior on calculating heats of dilution of electrolytes solutions at high temperature because the equations used in this work can provide values of the Debye-Hückel limiting law slopes which are as accurate as the experimental results allow. The Debye-Hückel limiting law slopes are directly related to the density of water  $\rho$  and the derivatives of  $\rho$ , therefore, errors in calculating Debye-Hückel limiting law slopes in Oscarson's model



can be expected to increase because less accurate equations of state for water were substituted. It appears that in the very dilute regions, large percentage errors occurred both on this modified model and Oscarson's model. The first thought of the reason is the fitting of parameter  $q$  in Eq. (2.4). In Lindsay's modification of Meissner's equations,  $q$  was determined for each temperature by using only one data point, which is the activity coefficient of sodium chloride at its solubility limit. The sodium chloride  $q$  values decrease monotonically for temperature of 100-350°C, thus, a more complicated equation for fitting values of  $q$  over more data points of activity coefficient may be needed. Therefore, a perturbation term was added to the equation of  $q$ , but this did not produce any significant difference in the dilute region results. Another possible reason for the large error in the very dilute regions is that measured heats were small. At small heats, the calorimetric measurements appear to have larger systematic error. Figure 5.3 shows larger discrepancy between the calculated heats and measured heats, this is because modified Meissner's activity coefficients model used in this work introduces significant errors when applied to multiple-charged species. For all the systems studied, Figure 5.1-5.3 show, as expected, that the heats of dilution become more negative as the temperature increases.

Figure 5.4 is a graph of  $\log K$  values for association reactions vs. temperature for the present results and for the results of Oscarson et al.<sup>1, 2, 23</sup> compared with those of Wood et al.<sup>6, 7, 8</sup> Wood's equilibrium constants are not at the same experimental condition as those of this study and of model of Oscarson et al., but Wood et al.<sup>8</sup> have stated that their equilibrium constants can be estimated at all the points by using extrapolations as a linear function of water density. As is seen in Figure 5.4 (a)- (c),  $\log K$  values for the ion

association of NaAc(aq) obtained from this work and from previous model of Oscarson et al.<sup>2</sup> are quite different, while the log  $K$  data for the association of HCl (aq) are very close. However, values from this work are more consistent with Wood et al.<sup>6, 7</sup> reported data, which are considered to be the most accurate ion-pairing constants currently available. Oscarson et al.<sup>1</sup> did not derive log  $K$  values for Na<sub>2</sub>SO<sub>4</sub>, thus Figure 5.4 (d) contains log  $K$  values for Na<sub>2</sub>SO<sub>4</sub> (aq) only from this work and from Wood et al.<sup>8</sup> Good agreement was obtained between these two results. The log  $K$  values for all the other reactions investigated in this work are in good agreement with previous results.

As a result of different  $K$  values,  $\Delta H$  for the association of NaAc(aq), HCl(aq), and Na<sub>2</sub>SO<sub>4</sub> (aq) are also changed, which is shown in Figure 5.5. The enthalpy changes in the systems NaAc(aq) + H<sub>2</sub>O, HCl (aq)+ H<sub>2</sub>O, and Na<sub>2</sub>SO<sub>4</sub> (aq) + H<sub>2</sub>O were plotted as a function of temperature, as is shown in Figure 5.6. In aqueous solution, the signs of  $\Delta H$  and  $\Delta S$  are positive and the magnitudes of both these quantities increase significantly as temperature increases. This is because as temperature increases, the extent of hydrogen bonding decreases, water has lower density and possibly to lower dipole moment, resulting in the decrease of the dielectric constant of water.



## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

A correlation approach developed by Oscarson et al.<sup>1, 2, 23</sup> is valid for calculating heats of dilution as well as  $\log K$  and  $\Delta H^\circ$  values for association reactions in aqueous solution over the temperature range from 250°C to 350°C. In the previous studies, the approach of Oscarson et al.<sup>1, 2, 23</sup> has been used to investigate various aqueous systems containing electrolytes such as NaAc, Na<sub>2</sub>SO<sub>4</sub>, NaOH, KOH and HCl. One shortcoming of the model used by these workers is that it uses approximately fitted equations for the density of water and the Debye-Hückel law limiting slopes, which leads to deviations of calculated heats of dilution as well as predicted  $\log K$  values from reported data.

The present study has improved the approach developed by Oscarson et al. by incorporating a more accurate water equation of state, a more accurate water dielectric constant, and the equilibrium correlation equation. In this work, the IAPWS-95 formulations were coded and used to calculate the density of water as well as the derivatives of density with respect to temperature. This code can also be used to obtain the quantities of engineering interest such as enthalpy, entropy, internal energy, and heat capacity of water. The dielectric constant equation for water from Archer and Wang<sup>5</sup> is used to determine the Debye-Hückel limiting law slope for the calculation of activity coefficient.

Over the temperature range from 250°C to 350°C, the average difference between the measured heats of dilution from Oscarson et al.<sup>1, 2, 23</sup> and those calculated from this work is below 10%, which is roughly within experimental error of the measurements and in better agreement than those calculated from the approach of Oscarson et al.<sup>1, 2, 23</sup> This work also provided  $\log K$  and  $\Delta H$  values for association reactions of NaAc, HCl, and Na<sub>2</sub>SO<sub>4</sub> from their constituent ions, which are in good agreement with the most accurate data currently available. This modified model is superior to that used in previous work in calculating heats of dilution of electrolytes solutions at high temperature because the equations used in this work can provide values of the Debye-Hückel limiting law slopes which are functions of pressure/density and are as accurate as the experimental results allow.

The inadequacies of this modified model and Oscarson's previous one at the lower concentrations (0.1-0.25m) may be due to: As observed by Fuangswasdi<sup>23</sup> et al., there is a systematic error in the data that causes up to 10% error when the heats measured are small (at high dilution) but causes only an error of 1-2% when the heats measured are large.

### **Recommendations for Future Work**

The work in this thesis demonstrates that incorporating a more accurate water equation of state and a more accurate water dielectric constant improves the performance of models for aqueous electrolyte systems at high temperature.

The modified model developed in this work correlates thermodynamic values such as  $\log K$ ,  $\Delta_{\text{dil}}H$  and  $\Delta S$  for high temperature electrolyte systems from calorimetric

measurements. The modified Meissner's activity coefficients model used in this work introduces significant errors when applied to multiply-charged species. The next step is to improve the accuracy of the correlation. This may involve using more accurate activity coefficients and/or trying a different equilibrium correlation model. Two kinds of activity coefficient models are recommended to replace the modified Meissner's model: Pitzer's ion-interaction model<sup>30</sup> and the mean spherical approximation<sup>46</sup> equation. For the molality range studied, only two parameters in the Pitzer ion-interactions model need to be found.



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## APPENDIX A

### MODIFIED CORRELATION FORTRAN COMPUTER CODE

c this code is to find the heat of dilution in a electrolyte aqueous solution

c

c

```
implicit real* 8 (a-h,o-z)
character * 8 complexa, prispna, pria
character * 14 titlem, titles, headila, condila
dimension x(20), flowa(100,50), flowb(100,50), ab(20,21), ca(100),
&          q(100,50), conda(100), cda(100), cdas(100,100), ta(50),
&          ps(50), nfl(50), totflow(100), alogkcor(15), bbb(20),
&          cone(50,50), cona(50), ncom(50)
common /atrixr/ a(20,20), b(20), alogka(15), delha(15),
&          alogw, complexcha(15), sta(15,4), prispcha(10)
common /atrixc/ pria(15,4), complexa(15), npa(15), prispna(10), titlem
common /atrixi/ nprispa, ncompa, na, maxa

conv = log(10.d0)
print *, 'Enter the name of file for heats of dilution of A.'
read *, headila
Print *, 'Enter the name of the file for the concentrations '
print*, ' of stream A and diluted A.'
read *, condila
Print *, 'Enter the name of the chemistry file to be read.'
read *, titlem
Print *, 'Enter the name of the system file to be read.'
read *, titles
open (unit = 10, status = 'old', file = 'titles')
read (10, *) nrun
do ii = 1, nrun
  read (10, *) ncom(ii)
  do jj = 1, ncom(ii)
    read (10, *) cone(ii, jj)! concentrations of primary species in solution
  end do
  read (10,*) ta(ii) ! here ta is the system temperature in centigrade
  read (10,*) ps(ii) ! p is the system pressure in KPa
  read (10,*) nfl(ii) ! the number of experimental points
```

```

do i = 1, nfl(ii)
  read (10,*) flowa(i,ii),flowb(i,ii),q(i,ii) ! q is the heat of measurement
end do
end do
close (unit = 10)
c
c
open (file = 'titeml',status = 'old', unit = 11 )
open (unit = 12, status = 'unknown', file = headila)
open (unit = 14, status = 'unknown', file = condila)
c
c
do ii = 1, nrun
  tt = ta(ii) + 273.15d + 00 ! tt is in Kelvin
  p = ps(ii)
  ncomp2 = ncom(ii) + 2
  do jj = 3, ncomp2
    jjm2 = jj - 2
    cona(jj) = cone(ii, jjm2)
  end do
c
  call water(tt,p,rho,ee,dlnrhodt,drhodt,deedt)
c
c the following equations were used to calcualte activity coefficents from the modified
c Meissner's model
c
  qm = 2.95869d0 - 0.321502d-02 * ta(ii) - 0 .17233d-04 * ta(ii) ** 2
  bm = 0.75d + 00 - 6.5d-02 * qm
  dqmdt = - 0.321502d-02 - 0.34466d-04 * ta(ii)
  dbmdt = - 6.5d-02 * dqmdt
c
c "ame" is the Debye-Huckel limiting law slope,which is a function
c of temperature and pressure.
c
  ame = (1.17202 * (rho/1.0d + 03) **0.5d + 00 * (2.33752d+
&      04 / (ee * tt) **1.5d+00)/conv
  damdt = (1.17202d+00 * 2.33752d+04 **1.5d+00 * 0.5d+00 *
&      (1.0d+03/rho) ** 0.5d+00 * (1.0d+00/(ee * tt) ** 2.5d+00
&      * (drhodt * ee * tt-3.0d+00 * rho * 1.0d-03 * ee-3.0d+00 * rho *
&      1.0d-03 * tt * deedt)) / conv
c
c
c Calculate the log K for formation of water from Marshall and Frank
c
  aw = - 4.098d + 00
  bw = - 3.2452d + 03

```

```

cw = 2.2362d + 05
dw = - 3.984d + 07
ew = 1.3957d + 01
fw = -1.2623d + 03
gw = 8.5641d + 05
alogw = aw + bw/tt + cw/tt**2 + dw/tt**3 + (ew + fw/tt + gw/tt**2)
&      *dlog10(rho*1.0d-03)
c
c Calculate the heat of ionization of waterc
c
c      delhw = - bw/tt**2 - 2.0d+00 * cw/tt**3 - 3.0d+00 * dw/tt**4 - (fw/tt**2 +
&      2.0d+00* gw/tt**3)*dlog10(rho*1.0d-03) + (ew + fw/tt +
&      gw/tt**2)/(conv*rho*1.0d-03)*drhodt
delhw = - delhw*8.3144d0*tt**2*conv
call atmak(tt,p,rho,dlnrhodt,drhodt)
c
c      complexa(ncompa+1) = 'H2O'
c
c Solve for initial concentrations in stream A
c
c first enter the initial guess for the concentrations of primary species in stream a
c
c      ca(1) = 1.0d - 06 ! concentration of H
c      ca(2) = 1.0d - 06 ! concentration of OH
c      ca(3) = 0.1d + 00
c      if (nprispa .gt. 3) then
c          do i = 4, nprispa
c              ca(i) = 0.1d + 00 ! concentration of other primary species
c          end do
c      end if
c then enter the initial guess for the concentrations of complexes formed in the stream
a
c
c      do i = 1, ncompa
c          ca(nprispa + i) = 0.1d + 00 ! concentration of electrolyte
c      end do
errsum = 10.d+00
ersum = 10.d+00
do while (ersum .gt. 1.d-06 .or. errsum .gt. 1.d-06)
ais = 0.0d+00 ! ais is the ionic strength
do i = 1, na
ais = ais + ca(i)*a(1,i)**2
end do
ais = ais/2.d0
cme = 1.d0 + 5.5d-02*qm*dexp(-2.3d-02*ais**3)
alngams = - conv*(ame*ais**.5/(1.d0 + cme*ais**.5))

```

```

alngam = log(1.d0 + bm*(1.d0 + 0.1d0*ais)**qm - bm)
gamma = dexp(alngams + alngam)
do i = 1, nprispa-1
  do j = 1, na
    ab(i,j) = a(i,j)*ca(j)
  end do
end do
do i = nprispa, na
  do j = 1, na
    ab(i,j) = a(i,j)
  end do
end do
bbb(1) = 0.d0
do j = 1, na
  bbb(1) = bbb(1) + ab(1,j)
end do
do i = 2, nprispa-1
  f = -cona(i+1)
  do j = 3, na
    f = f + ab(i,j)
  end do
  bbb(i) = f
end do
do i = nprispa, na
  alogkcor(i) = b(i)
  bbb(i) = -b(i)*conv
  do j = 1, na
    alogkcor(i) = alogkcor(i) - a(i,j)*a(1,j)**2*log10(gamma)
    bbb(i) = bbb(i) + a(i,j)*a(1,j)**2*log(gamma)
  end do
  do j = 1, na
    bbb(i) = bbb(i) + a(i,j)*log(ca(j))
  end do
end do
errsum = 0.d0
do i = 1, na
  errsum = errsum + dabs(bbb(i))
end do
call simq(na, ab, bbb, x, ersum)
do j = 1, na
  if (abs(x(j)) .gt. 2.0d0) x(j) = 2.0d0*x(j)/abs(x(j))
  if (dabs(x(j)) .lt. 1.d-10) then
    ca(j) = (1.d0 - x(j))*ca(j)
  else
    ca(j) = ca(j)*dexp(-x(j))
  end if
end do

```

```

        end do
    end do
    do j = 1, na
        cdas(1,j) = ca(j)
    end do
    write (12, '( " HEATS OF DILUTION FOR STREAM A" )')
    write (12,*)
    write (12,*)
    write (12, '( " Totflow   Qwater   Qother ",
&       " Qpred   Qmea   Qdif   %dif" )')
    write (12,*)
    write (12,*)
    write (12, '(f8.4,3d12.4,3f10.4)') flowa(1,ii),0.d0,0.d0,
&       0.0,0.0,0.0,0.0
    write (14,*)
    write (14,*)
    write (14, '( " gamma   vinta   vintb   dlngamdt " )')
    write (14,*)
    aisa = ais
c
c
c Calculate heats of dilution
c
    do jj = 1, nfl(ii)
        totflow(jj) = flowa(jj,ii) + flowb(jj,ii)
        do i = 1, na
            cda(i) = flowa(jj,ii)*ca(i)/totflow(jj)
        end do
        do i = 3, nprispa
            conda(i) = cona(i)*flowa(jj,ii)/totflow(jj)
        end do
        errsum = 10.d0
        ersum = 10.d0
        do while (ersum .gt. 1.d-06 .or. errsum .gt. 1.d-06)
            ais = 0.d0
            do i = 1, na
                ais = ais + cda(i)*a(1,i)**2
            end do
            ais = ais/2.d0
            cme = 1.d0 + 5.5d-02*qm*dexp(-2.3d-02*ais**3)
            alngams = -conv*(ame*ais**0.5d+00/(1.d0 + cme*ais**0.5d+00))
            alngam = log(1.d0 + bm*(1.d0 + 0.1d0*ais)**qm - bm)
            gamma = dexp(alngams + alngam)
            do i = 1, nprispa-1
                do j = 1, na
                    ab(i,j) = a(i,j)*cda(j)

```



```

        end do
    end do
    do i = nprispa, na
        do j = 1, na
            ab(i,j) = a(i,j)
        end do
    end do
    bbb(1) = 0.d0
    do j = 1, na
        bbb(1) = bbb(1) + ab(1,j)
    end do
    do i = 2, nprispa-1
        f = -conda(i+1)
        do j = 3, na
            f = f + ab(i,j)
        end do
        bbb(i) = f
    end do
    do i = nprispa, na
        alogkcor(i) = b(i)
        bbb(i) = -b(i)*conv
    do j = 1, na
        alogkcor(i) = alogkcor(i) - a(i,j)*a(1,j)**2*
&         log10(gamma)
        bbb(i) = bbb(i) + a(i,j)*a(1,j)**2*log(gamma)
    end do
    do j = 1, na
        bbb(i) = bbb(i) + a(i,j)*log(cda(j))
    end do
    end do
    errsum = 0.d0
    do i = 1, na
        errsum = errsum + dabs(bbb(i))
    end do
    call simq(na,ab,bbb,x,errsum)
    do j = 1, na
        if (dabs(x(j)) .gt. 2.d0) x(j) = 2.d0*x(j)/
&         (dabs(x(j)))
        if (dabs(x(j)) .lt. 1.d-10) then
            cda(j) = (1.d0 - x(j))*cda(j)
        else
            cda(j) = cda(j)*dexp(-x(j))
        end if
    end do
    end do
    do j = 1, na

```

```

        cdas(jj+1,j) = cda(j)
    end do
    qreact = 0.d0
    chnh = 0.d0
    do i = nprispa+1, na
        delcom = totflow(jj)*cda(i)-flowa(jj,ii)*ca(i)
        chnh = chnh + a(i-1,1)*delcom
        qreact = qreact + delcom*delha(i-nprispa)
    end do
    qreact = qreact/1.d+03
    aisda = ais
    qwat = (ca(1)*flowa(jj,ii)
&      -cda(1)*totflow(jj)+chnh)*delhw
    qwat = qwat/1.d+03
    call simp(aisda,aisa,qm,bm,dqmdt,dbmdt,ame,damdt,vinta,
&      dlngamdt)
    call simp(aisda,0.d0,qm,bm,dqmdt,dbmdt,ame,damdt,vintb,
&      dlngamdt)
    delhdila = qreact+qwata-(2.0d+00*8.3144d+00*tt**2*
&      (flowa(jj,ii)*vinta + flowb(jj,ii)*vintb))/1.0d+03
    qdif = q(jj,ii) - delhdila
    pcdif = 1.0d+02*qdif/q(jj,ii)
    write (12,'(f8.4,3d12.4,3f10.4)') totflow(jj),qwata,
&      qreact,delhdila, q(jj,ii), qdif, pcdif
    write (14,'(f8.4,4d12.4)') gamma,vinta,vintb,dlngamdt
    end do
    write (14, ' ("CONCENTRATIONS OF STREAM A INITIALLY AND
&DILUTED"'))
    write (14,*)
    write (14,(' Dilution #",20a11'))(prispna(i),i = 1,nprispa),
&      (complexa(i),i = 1, ncompa)
    write (14,*)
    write (14,*)
    do jj = 1, nfl(ii)+1
        k = jj-1
        write(14,'(i6," ",20d11.4)') k, (cdas(jj,i),i = 1, na)
    end do
    write (14, '(d12.4)') (alogka(i), i = 1,ncompa)
    write (14, '(d12.4)') (delha(i), i = 1,ncompa)
    end do
    write (12,*)
    write (12,*)
    write (12, ' ("THE SUMMARY OF SQUARED Qdif is"'))
    write (12, '(d12.4) ') sumqdif
    close (unit = 11)
    close (unit = 12)

```

```

close (unit =14)
print*, 'dilution done'
end
c
c
c this subroutine is to Calculate some properties of the water
c the density of water is calculated from IAPWS Formulation 1995, "ame" is the
c Debye- Hückel limiting law slopes (see Table 1. in Archer's paper. In the below
c equations, the 'ta' is the temperature in centigrade, 'tt' is the temperature in Kelvin
c
subroutine water(tt,p,rho,ee,dlnrhodt,drhodt,deedt)
implicit real*8(a-h,o-z)
dimension bn(56),d(56),t(56),c(56),alfa(54),beita(56),gama(56),
&      blamta(56),bigc(56),bigd(56),biga(56),bigb(56),a(56),
&      b(56)
c
tc = 647.096d+00      !critical temperature of water in K
rhoc = 3.22d+02      !critical density in Kg/m**3
rg = 0.46151805d+00  !gas constant in KJ/Kg*K
bMw = 18.0153d+00    !mole mass of water in gm
c
c
c bn(),d(),t(),c(),alfa(),beita(),gama(),blamta(),bigc(), bigd(),
c biga(),bigb(),a(),and b() are all parameters of "fresid" , which
c is the residual part of Helmholtz energy
c
c parameters bn,d,t,c:
do i = 1,7
  c(i) = 0.0d+00
end do
do i = 8,22
  c(i) = 1.0d+00
end do
do i = 23,42
  c(i) = 2.0d+00
end do
do i = 43,46
  c(i) = 3.0d+00
end do
  c(47) = 4.0d+00
do i = 48,51
  c(i) = 6.0d+00
end do
do i = 52,56
  c(i) = 0.0d+00
end do

```

c

```
do i = 1,3
  d(i) = 1.0d+00
end do
d(4) = 2.0d+00
d(5) = 2.0d+00
d(6) = 3.0d+00
d(7) = 4.0d+00
do i = 8,10
  d(i) = 1.0d+00
end do
d(11) = 2.0d+00
d(12) = 2.0d+00
d(13) = 3.0d+00
d(14) = 4.0d+00
d(15) = 4.0d+00
d(16) = 5.0d+00
d(17) = 7.0d+00
d(18) = 9.0d+00
d(19) = 10.0d+00
d(20) = 11.0d+00
d(21) = 13.0d+00
d(22) = 15.0d+00
d(23) = 1.0d+00
do i = 24,26
  d(i) = 2.0d+00
end do
d(27) = 3.0d+00
do i = 28,30
  d(i) = 4.0d+00
end do
d(31) = 5.0d+00
d(32) = 6.0d+00
d(33) = 6.0d+00
d(34) = 7.0d+00
do i = 35,39
  d(i) = 9.0d+00
end do
d(40) = 10.0d+00
d(41) = 10.0d+00
d(42) = 12.0d+00
d(43) = 3.0d+00
d(44) = 4.0d+00
d(45) = 4.0d+00
d(46) = 5.0d+00
d(47) = 14.0d+00
```

```
d(48) = 3.0d+00
do i = 49,51
  d(i) = 6.0d+00
end do
do i = 52,54
  d(i) = 3.0d+00
end do
d(55) = 0.0d+00
d(56) = 0.0d+00
```

c

```
t(1) = -0.5d+00
t(2) = 0.875d+00
t(3) = 1.0d+00
t(4) = 0.5d+00
t(5) = 0.75d+00
t(6) = 0.375d+00
t(7) = 1.0d+00
t(8) = 4.0d+00
t(9) = 6.0d+00
t(10) = 12.0d+00
t(11) = 1.0d+00
t(12) = 5.0d+00
t(13) = 4.0d+00
t(14) = 2.0d+00
t(15) = 13.0d+00
t(16) = 9.0d+00
t(17) = 3.0d+00
t(18) = 4.0d+00
t(19) = 11.0d+00
t(20) = 4.0d+00
t(21) = 13.0d+00
t(22) = 1.0d+00
t(23) = 7.0d+00
t(24) = 1.0d+00
t(25) = 9.0d+00
t(26) = 10.0d+00
t(27) = 10.0d+00
t(28) = 3.0d+00
t(29) = 7.0d+00
t(30) = 10.0d+00
t(31) = 10.0d+00
t(32) = 6.0d+00
t(33) = 10.0d+00
t(34) = 10.0d+00
t(35) = 1.0d+00
t(36) = 2.0d+00
```

t(37) = 3.0d+00  
t(38) = 4.0d+00  
t(39) = 8.0d+00  
t(40) = 6.0d+00  
t(41) = 9.0d+00  
t(42) = 8.0d+00  
t(43) = 16.0d+00  
t(44) = 22.0d+00  
t(45) = 23.0d+00  
t(46) = 23.0d+00  
t(47) = 10.0d+00  
t(48) = 50.0d+00  
t(49) = 44.0d+00  
t(50) = 46.0d+00  
t(51) = 50.0d+00  
t(52) = 0.0d+00  
t(53) = 1.0d+00  
t(54) = 4.0d+00  
t(55) = 0.0d+00  
t(56) = 0.0d+00

c

bn(1) = 0.12533547935523d-01  
bn(2) = 0.78957634722828d+01  
bn(3) = -0.87803203303561d+01  
bn(4) = 0.31802509345418d+00  
bn(5) = -0.26145533859358d+00  
bn(6) = -0.78199751687981d-02  
bn(7) = 0.88089493102134d-02  
bn(8) = -0.66856572307965d+00  
bn(9) = 0.20433810950965d+00  
bn(10) = -0.66212605039687d-04  
bn(11) = -0.19232721156002d+00  
bn(12) = -0.25709043003438d+00  
bn(13) = 0.16074868486251d+00  
bn(14) = -0.40092828925807d-01  
bn(15) = 0.39343422603254d-06  
bn(16) = -0.75941377088144d-05  
bn(17) = 0.56250979351888d-03  
bn(18) = -0.15608652257135d-04  
bn(19) = 0.11537996422951d-08  
bn(20) = 0.36582165144204d-06  
bn(21) = -0.13251180074668d-11  
bn(22) = -0.62639586912454d-09  
bn(23) = -0.10793600908932d+00  
bn(24) = 0.17611491008752d-01  
bn(25) = 0.22132295167546d+00

bn(26) = -0.40247669763528d+00  
bn(27) = 0.58083399985759d+00  
bn(28) = 0.49969146990806d-02  
bn(29) = -0.31358700712549d-01  
bn(30) = -0.74315929710341d+00  
bn(31) = 0.47807329915480d+00  
bn(32) = 0.20527940895948d-01  
bn(33) = -0.13636435110343d+00  
bn(34) = 0.14180634400617d-01  
bn(35) = 0.83326504880713d-02  
bn(36) = -0.29052336009585d-01  
bn(37) = 0.38615085574206d-01  
bn(38) = -0.20393486513704d-01  
bn(39) = -0.16554050063734d-02  
bn(40) = 0.19955571979541d-02  
bn(41) = 0.15870308324157d-03  
bn(42) = -0.16388568342530d-04  
bn(43) = 0.43613615723811d-01  
bn(44) = 0.34994005463765d-01  
bn(45) = -0.76788197844621d-01  
bn(46) = 0.22446277332006d-01  
bn(47) = -0.62689710414685d-04  
bn(48) = -0.55711118565645d-09  
bn(49) = -0.19905718354408d+00  
bn(50) = 0.31777497330738d+00  
bn(51) = -0.11841182425981d+00  
bn(52) = -0.31306260323435d+02  
bn(53) = 0.31546140237781d+02  
bn(54) = -0.25213154341695d+04  
bn(55) = -0.14874640856724d+00  
bn(56) = 0.31806110878444d+00

c

c parameters alfa,gama,blamta,beita:

```
do i = 52,54
  alfa(i) = 20.0d+00
end do
gama(52) = 1.21d+00
gama(53) = 1.21d+00
gama(54) = 1.25d+00
do i = 52,54
  blamta(i) = 1.0d+00
end do
beita(52) = 150.0d+00
beita(53) = 150.0d+00
beita(54) = 250.0d+00
beita(55) = 0.3d+00
```

```

beita(56) = 0.3d+00
c parameters bigc,bigd,biga,bigb,a,b:
bigc(55) = 28.0d+00
bigc(56) = 32.0d+00
bigd(55) = 7.0d+02
bigd(56) = 8.0d+02
biga(55) = 0.32d+00
biga(56) = 0.32d+00
bigb(55) = 0.2d+00
bigb(56) = 0.2d+00
a(55) = 3.5d+00
a(56) = 3.5d+00
b(55) = 0.85d+00
b(56) = 0.95d+00
c
c
c Now find the density of liquid water "rho" at temperature tt and pressure P:
c
rho = rholiq(tt,p,bn,d,t,c,alfa,blamta,beita,gama,
& bigc,bigd,biga,bigb,a,b) ! rho is in kg/m^3
c
c then find "drhodt" and "dln(rho)dt" at constant Pressure P
c
delt = 1.0d-05 ! kelvin
tp = tt+delt
tm = tt-delt
rhop = rholiq(tp,p,bn,d,t,c,alfa,blamta,beita,gama,
& bigc,bigd,biga,bigb,a,b) ! kg/m^3
rhom = rholiq(tm,p,bn,d,t,c,alfa,blamta,beita,gama,
& bigc,bigd,biga,bigb,a,b) ! kg/m^3
drhodt = (rhop-rhom)*1.0d-03/(2.0d+00*delt) ! g/cm^3
dlnrhodt = (1.0d+00/(rho*1.0d-03))*drhodt ! g/cm^3
c
c Now find the dielectric constant of water "ee" as a function of temperature and
density c and pressure and "deedt" at constant P. The dielectric constant "ee" was
solved by
c finding the root of a polynomial equation from "The Dielectric constant of water
c and Debye-Huckel limiting law slopes", J.Phys.Chem.Ref.Data, Vol.19,No.2, 1990,
c Archer and Wang.
fac = ff(p,tt,rho)
ee = (9.0d+00*fac+1.0d+00+((9.0d+00*fac+1.0d+00)**2 +
& 8.0d+00)**0.5d+00)/4.0d+00
deedt = (9.0d+00*dffdt(p,tt,rho,drhodt)+(0.5/((9.0d+00*fac+
& 1.0d+00)**2+8.0d+00)**(0.5d+00))*18.0d+00*(9.0d+00*
& fac+1.0d+00)*dffdt(p,tt,rho,drhodt))/4.0d+00
return

```



```

end
c
c by now we have found the density of water "rho" and the dielectric constant of water
c "ee"
c
c the followings are the functions and subroutines used for calculating the density and
c the dielectric constant of water
c
c functions for calculating the dielectric constant of water
c
c
function gar(p,tt,rho)
implicit real*8 (a-h, o-z)
b1 = -4.044525d-02
b2 = 103.6180d+00
b3 = 75.32165d+00
b4 = -23.23778d+00
b5 = -3.548184d+00
b6 = -1246.311d+00
b7 = 2.633077d+05
b8 = -6.928953d-01
b9 = -204.4473d+00
gar = rho/1.0d+03*(b1*p*1.0d-03/tt+b2/tt**0.5d+00+b3/(tt-215)
& +b4/(tt-215)**0.5d+00+b5/(tt-215)**0.25d+00+exp(b6/tt
& +b7/tt**2+b8*p*1.0d-03/tt+b9*p*1.0d-03/tt**2))+1.0d+00
return
end
c
c
function dgardt(tt,p,rho,drhodt)
implicit real*8 (a-h, o-z)
b1 = -4.044525d-02
b2 = 103.6180d+00
b3 = 75.32165d+00
b4 = -23.23778d+00
b5 = -3.548184d+00
b6 = -1246.311d+00
b7 = 2.633077d+05
b8 = -6.928953d-01
b9 = -204.4473d+00
dgardt = drhodt*(b1*p*1.0d-03/tt+b2/tt**0.5d+00
& +b3/(tt-215)+b4/(tt-215)**0.5d+00+b5/(tt-215)**
& 0.25d+00+exp(b6/tt+b7/tt**2+b8*p*1.0d-03/tt+b9*p*1.0d-03/
& tt**2))+rho*1.0d-03*(-b1*p*1.0d-03/tt**2-0.5d+00*b2/tt**
& 1.5d+00-b3/(tt-215)**2-0.5d+00*b4/(tt-215)**1.5d+00-
& 0.25d+00*b5/(tt-215)**1.25d+00+exp(b6/tt+b7/tt**2+b8*p*

```

```

& 1.0d-03/tt+b9*p*1.0d-03/tt**2)*(-b6/tt**2-2.0d+00*b7/tt**3
& -b8*p*1.0d-03/ tt**2-2.0d+00*b9*p*1.0d-03/tt**3))
return
end
c
c
function volume(rho)
implicit real*8 (a-h, o-z)
bMw = 18.0153d+00
volume = bMw*1.0d-03/rho
return
end
c
c
function ff(p,tt,rho)
implicit real*8 (a-h, o-z)
bNa = 6.0221367d+23          !mol^-1
dalfa = 18.1458392d-30
dmiu = 6.1375776d-30
dlamta0 = 8.8542d-12
dk = 1.380658d-23
ff = bNa*(dalfa+gar(p,tt,rho)*dmiu**2/(3.0d+00*dlamta0*dk*tt))
& /(3.0d+00*volume(rho))
return
end
c
c
function dffdt(p,tt,rho,drhodt)
implicit real*8 (a-h, o-z)
bNa = 6.0221367d+23          !mol^-1
dalfa = 18.1458392d-30
dmiu = 6.1375776d-30
dlamta0 = 8.8542d-12
dk = 1.380658d-23
bMw = 0.0180153d+00
dffdt = bNa/(3.0d + 00 * bMw) * (dalfa * drhodt * 1.0d +03 + dmiu**2
& /(3.0d + 00*dlamta0*dk)*(rho/tt*dgardt(tt,p,rho,
& drhodt)+gar(p,tt,rho)*drhodt*1.0d+03/tt-gar(p,tt,rho)
& *rho/tt**2))
return
end
c
c
c functions for calculating density of water
c
function rholiq(tt,p,bn,d,t,c,alfa,

```

```

&      blamta,beita,gama,bigc,bigd,biga,bigb,a,b)
implicit real*8 (a-h, o-z)
dimension bn(56),d(56),t(56),c(56),alfa(54),beita(56),gama(56),
&      blamta(56),bigc(56),bigd(56),biga(56),bigb(56),a(56),
&      b(56)
rg = 0.46151805d+00
tc = 647.096d+00
bMw = 18.0153d+00
rho1 = (17.863d+00+58.606d+00*(1.0d+00-(tt/tc))**0.35d+00-95.396d
& +00*(1.0d+00-(tt/tc))**(2.0d+00/3.0d+00)+2.1389d+02*(1.0d+00
& -(tt/tc))-1.4126d+02*(1.0d+00-(tt/tc))**(4.0d+00/3.0d+00))
& *bMw
delrho = 0.01d+00*rho1
p1 = pf(rg,tt,rho1,bn,d,t,c,alfa,
&      blamta,beita,gama,bigc,bigd,biga,bigb,a,b)
f1 = p-p1
rho2 = rho1+delrho
p2 = pf(rg,tt,rho2,bn,d,t,c,alfa,
&      blamta,beita,gama,bigc,bigd,biga,bigb,a,b)
f2 = p-p2
prod = f1*f2
if (prod .lt. 0.0d+00) then
  f1 = f1
  else if (abs(f2) .gt. abs(f1)) then
    delrho = -delrho
  end if
do while (prod .gt. 0.0d+00)
  rho2 = rho1+delrho
  p2 = pf(rg,tt,rho2,bn,d,t,c,alfa, blamta,beita,gama,
&      bigc,bigd,biga,bigb,a,b)
  f2 = p-p2
  prod = f1*f2
  If (prod .gt. 0.0d+00) then
    f1 = f2
    p1 = p2
    rho1 = rho2
  end if
end do
error = 1.0d+00
do while (error .gt. 1.0d-08)
  rho2 = (f1*rho2-f2*rho1)/(f1-f2)
  f2 = p- pf(rg,tt,rho2,bn,d,t,c,alfa,blamta,beita,gama,
&      bigc,bigd,biga,bigb,a,b)
  error = abs(f2)
end do
rho1iq = rho2

```

```

return
end
c
c
function pf(rg,x,y,bn,d,t,c,alfa,blamta,
&      beita,gama,bigc,bigd,biga,bigb,a,b)
implicit real*8 (a-h, o-z)
dimension bn(56),d(56),t(56),c(56),alfa(56),blamta(56),beita(56),
&      gama(56),bigc(56),bigd(56),biga(56),bigb(56),a(56),b(56)
pf = y*rg*x*(1.0d+00+delta(y)*dfresiddelta(x,y,bn,d,t,c,alfa,
&      blamta,beita,gama,bigc,bigd,biga,bigb,a,b))
return
end
c
c
c calculate function tao(tt) and delta(rho)
function tao(x)
implicit real*8 (a-h, o-z)
tc = 647.096d+00
tao = tc/x
return
end
c
c
function delta(y)
implicit real*8 (a-h, o-z)
rhoc = 3.22d+02
delta = y/rhoc
return
end
c
c
c calculate auxiallary functions
function zeta(tt,rho)
implicit real*8 (a-h, o-z)
dimension biga(56), beita(56)
do i = 1, 56
    biga(i) = 0.0d+00
    beita(i) = 0.0d+00
end do
biga(55)=0.32d+00
beita(55)=0.3d+00
zeta=(1.0d+00-tao(tt))+biga(55)*((delta(rho)-1.0d+00)**2)**(1.0d
& +00/(2.0d+00*beita(55)))
return
end

```

```

c
c
function deta(x,y)
implicit real*8 (a-h, o-z)
dimension bigb(56),a(56)
bigb(55) = 0.2d+00
a(55) = 3.5d+00
deta = zeta(x,y)**2+bigb(55)*((delta(y)-1.0d+00)**2)**a(55)
return
end

c
c
function pesai(x,y,bigc, bigd, i)
implicit real*8 (a-h, o-z)
dimension bigc(56),bigd(56)
pesai = exp(-bigc(i)*(delta(y)-1.0d+00)**2-bigd(i)*(tao(x)-
& 1.0d+00)**2)
return
end

c
c
c Partial derivative of fresid with respect of delta keep tao constant.
c
function dfresiddelta(tt,rho,bn,d,t,c,alfa,blamta,beita,
& gama,bigc,bigd,biga,bigb,a,b)
implicit real*8 (a-h, o-z)
dimension bn(56),d(56),t(56),c(56),alfa(56),blamta(56),beita(56),
& gama(56),bigc(56),bigd(56),biga(56),bigb(56),a(56),b(56)
call dfr(tt,rho,bn,d,t,c,alfa,blamta,beita,gama,bigc,
& bigd,biga,bigb,a,b,sum11,sum21,sum31,sum41)
dfresiddelta = sum11+sum21+sum31+sum41
return
end

c
c
subroutine dfr(tt,rho,bn,d,t,c,alfa,blamta,beita,gama,bigc,
& bigd,biga,bigb,a,b,sum11,sum21,sum31,sum41)
implicit real*8 (a-h, o-z)
dimension bn(56),d(56),t(56),c(56),alfa(56),blamta(56),beita(56),
& gama(56),bigc(56),bigd(56),biga(56),bigb(56),a(56),b(56)
sum11 = 0.0d+00
sum21 = 0.0d+00
sum31 = 0.0d+00
sum41 = 0.0d+00
do i=1,7
sum11 = sum11+bn(i)*d(i)*delta(rho)**(d(i)-1.0d+00)*tao(tt)**

```

```

&      t(i)
end do
do i=8,51
  sum21 = sum21+bn(i)*tao(tt)**t(i)*exp(-delta(rho)**c(i))*
&      delta(rho)**(d(i)-1.0d+00)*(d(i)-c(i)*delta(rho)**c(i))
end do
do i = 52,54
  sum31 = sum31+bn(i)*delta(rho)**d(i)*tao(tt)**t(i)*exp(-alfa(i)
&      *(delta(rho)-blamta(i))**2-beita(i)*(tao(tt)-gama(i))
&      **2)*(d(i)/delta(rho)-2.0d+00*alfa(i)*(delta(rho)-
&      blamta(i)))
end do
do i = 55,56
  sum41 = sum41+bn(i)*(deta(tt,rho)**b(i)*(pesai(tt,rho,bigc,
&      bigd,i)+delta(rho)*dpesaiddelta(tt,rho,i))+b(i)*
&      deta(tt,rho)**(b(i)-1.0d+00)*ddetaddelta(tt,rho)*
&      delta(rho)*pesai(tt,rho,bigc,bigd,i))
end do
return
end
c
c
c  calculate the derivative of anxiallary functions ddetaddelta
function ddetaddelta(x,y)
implicit real*8 (a-h, o-z)
dimension biga(56),beita(56),a(56),bigb(56)
biga(55) = 0.32d+00
beita(55) = 0.3d+00
a(55) = 3.5d+00
bigb(55) = 0.2d+00
ddetaddelta = 2.0d+00*(delta(y)-1.0d+00)*(biga(55)*zeta(x,y)/
&      beita(55)*((delta(y)-1.0d+00)**2)**((1.0d+00-2.0d
&      +00*beita(55))/(2.0d+00*beita(55)))+a(55)*bigb(55)
&      *((delta(y)-1.0d+00)**2)**(a(55)-1.0d+00))
return
end
c
c
function dpesaiddelta(x,y,i)
implicit real*8 (a-h, o-z)
dimension bigc(56)
bigc(55) = 2.8d+01
bigc(56) = 3.2d+01
dpesaiddelta = -2.0d+00*bigc(i)*(delta(y)-1.0d+00)*
&      pesai(x,y,bigc,bigd,i)
return

```

```

end
c
c
c
c
c This subroutine solves n linear equations using a maximum pivot strategy
c
subroutine simq(na, ab, bbb, x, ersum)
implicit real*8 (a-h,o-z)
dimension ab(20,21), bbb(20), x(20)
c Forward solution
tol = 1.d-12
do j = 1, na
  biga = 0.d0
c Search for maximum coefficient in column
  do i = j, na
    if (dabs(biga) .lt. dabs(ab(i,j))) then
      biga = ab(i,j)
      imax = i
    end if
  end do
c Interchange rows if necessary
  do k = j, na
    save = ab(j,k)
    ab(j,k) = ab(imax,k)
    ab(imax,k) = save
c Divide equations by leading coefficient
    ab(j,k) = ab(j,k)/biga
  end do
  save = bbb(imax)
  bbb(imax) = bbb(j)
  bbb(j) = save/biga
c Eliminate next variable
  do ix = j+1, na
    do jx = j + 1, na
      ab(ix,jx) = ab(ix,jx) - ab(ix,j)*ab(j,jx)
    end do
    bbb(ix) = bbb(ix) - bbb(j)*ab(ix,j)
  end do
end do
c Back solution
do i = na, 1, -1
  x(i) = bbb(i)
  do j = i + 1, na
    x(i) = x(i) - ab(i,j)*x(j)
  end do

```

```

end do
ersum = 0.d0
do i = 1, na
  ersum = ersum + dabs(x(i))
end do
return
end
c
c
c   The following subroutine creates the matrices a
c
subroutine atmak(tt,p,rho,dlnrhodt,drhodt)
implicit real*8(a-h,o-z)
character*8 prispna, complexa, pria
character*14 titlem
dimension aa(10),bb(10),cc(10),dd(10)
common /atrixr/ a(20,20),b(20),alogka(15),delha(15),
&      alogw,complexcha(15),sta(15,4),prispcha(10)
common /atrixc/ pria(15,4),complexa(15),npa(15),prispna(10),titlem
common /atrixi/ nprispa,ncompa,na,maxa
prispna(1) = 'H'
prispna(2) = 'OH'
conv = log(10.d0)
rg=8.3144d+00      !gas constant in J/mol*K
bMw=18.0153d+00
read (11,*) nprispa  ! number of primary species in solution
nprispa = nprispa + 2
do i = 3, nprispa
  read (11,*) prispna(i), prispcha(i)
end do
read (11,*) ncompa  ! number of complexes formed in solution
do i = 1, ncompa
  read (11,*) complexa(i),complexcha(i)
  read (11,*) aa(i), bb(i),cc(i),dd(i)
  read (11,*) npa(i)
  do j = 1, npa(i)
    read (11,*) pria(i,j), sta(i,j)
  end do
end do
c
c
c
c
c   Then make matrix aa to find logK and deltaH for each associate reaction
c
do i= 1, ncompa

```



```

    alogka(i)= aa(i)+bb(i)/tt +( cc(i) + dd(i)/tt)*log(rho*1.0d-03)
    delha(i)= rg*tt**2*log(10.0d+00)*(-bb(i)/tt**2+(cc(i)+dd(i)/tt)
&      *dlnrhodt-(dd(i)/tt**2)*log(rho*1.0d-03))  !J/mol
end do
na = nprispa + ncompa
maxa = na + 1
do i = 1, na
    do j = 1, maxa
        a(i,j) = 0.d0
    end do
end do
a(1,1) = 1.d0
a(1,2) = -1.d0
do j = 3, nprispa
    a(1,j) = prispcha(j)
end do
do j = nprispa + 1, na
    a(1,j) = complexcha(j-nprispa)
end do
do i = 2, nprispa - 1
    do j = 3, nprispa
        if (i .eq. j - 1) a(i,j) = 1.d0
    end do
    do j = nprispa + 1, na
        kk = j - nprispa
        do ii = 1, npa(kk)
            if (pria(kk,ii) .eq. prispna(i+1))
1                a(i,j) = dabs(sta(kk,ii))
            end do
        end do
    end do
do kk = 1, ncompa
    i = kk + nprispa -1
    a(i,i+1) = 1.d0
    do j = 1, na
        do ii = 1, npa(kk)
            if (pria(kk,ii) .eq. prispna(j))
1                a(i,j) = sta(kk,ii)
            end do
        end do
    end do
a(na,1) = 1.d0
a(na,2) = 1.d0
do i = nprispa, na -1
    b(i) = alogka(i-nprispa+1)
end do

```

```

b(na) = alogw
return
end
c
c
c
c
c This subroutine integrates the integral (dln gam/dt)dI from
c the Meissner equation fitted to nacl using Simpson's rule
c
subroutine simp(fmax,fmin,qm,bm,dqmdt,dbmdt,ame,damdt,vint,
&          dlngamdt)
implicit real*8 (a-h,o-z)
dimension u(81), f(81)
conv = log(10.d0)
delx = (fmax - fmin)/80.d0
ais = fmin
do i = 1, 81
  if (ais .lt. 1.d-12) then
    f(i) = 0.d0
  else
    cme = 1.0d+00 + 5.5d-02*qm*dexp(-2.3d-02*ais**3)
    dcmedt = 5.5d-02*dqmdt*dexp(-2.3d-02*ais**3)
    dlngamsdt = (-1.0d+00 + cme*ais**0.5)*damdt*ais**0.5
&          + ame*ais*dcmedt)/((1.0d+00 + cme*ais**0.5)**2)
    dlngamsdt = conv*dlngamsdt
    dlngamdt = (1.d0/(1.d0 + bm*(1.d0 + 0.1d0*ais)**qm - bm))
&          *(dbmdt*(1.d0 + 0.1d0*ais)**qm + bm*log(1.d0 +
&          0.1*ais)*dqmdt*(1.d0 + 0.1d0*ais)**qm - dbmdt)
    dlngamdt = dlngamdt + dlngamsdt
    f(i) = dlngamdt
  end if
  ais = ais + delx
end do
do i = 2, 80
  if (i .eq. i/2*2) then
    u(i) = 4.d0
  else
    u(i) = 2.d0
  end if
end do
u(1) = 1.d0
u(81) = 1.d0
vint = 0.d0
do i = 1, 81
vint = vint + u(i)*f(i)

```

```
end do
vint = vint*delx/3.d0
return
end
```