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An Improved Model for Calculating Heats of Dilution and Equilibrium Constants for High Temperature Aqueous Electrolyte Solutions

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

by

Xiaoyun Lin

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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

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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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Department of Chemical Engineering
Master of Science

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[1, 2, 3] have designed a correlation model based on the excess Gibbs energy which can correlate log K and ΔH 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[4] and Archer and Wang's correlation of the dielectric constant of water[5] into the excess Gibbs engergy 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 $\Delta_{\mathrm{dil}}H$ 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[1, 2, 23]. 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 $\Delta_{\mathrm{dil}}H$ experiments[1, 2, 23] were 0.25, 0.5 and 1.0 m. Equilibrium constants K for Na_2SO_4 (aq), H_2SO_4 (aq), NaAc (aq), and HCl (aq) association were taken from conductivity values measured by Wood and co-workers[6, 7, 8] 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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	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

α	(1) Debye-Hückel parameter
	(2) parameters of the IAPWS-95 equation
β	(1) parameters of short-range interactions
	(2) parameters of the IAPWS-95 equation
γ	(1) activity coefficients
	(2) the angle between dipole moment
	(3) parameters of the IAPWS-95 equation
δ	reduced density
ε_0	permittivity of vacuum
ε	water dielectric constant
τ	reduced temperature
ρ	density of pure water
μ	molecular dipole moment of an arbitrary molecule
Δ	auxiliary function of the IAPWS-95 equation
Ψ	auxiliary function of the IAPWS-95 equation

Φ	reduced Helmoholtz 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
^{0}	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[9], i.e. (1) models that consider electrolytes as un-dissociated 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[10, 11, 12, 13].

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[14]. (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[9, 14]. According to Anderko[9] and Loehe and Donohue[14], 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[15] et al. and discussed in detail by Zemaitis[16] 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[17], and Liu, Harvey and Prausnitz[18] (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[19]. In 1990, Ghosh and Patwardhan[20] proposed the excess Gibbs energy as a combination of Pitzer's[21] 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 complexion reactions. To treat mixed-electrolyte systems effectively, a careful choice of existing species is required.

Patwardhan and Kumar[22] 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 - 350ºC have been conducted by Oscarson and co-workers[1, 2, 3, 23] . Their studies cover various aqueous solutions containing chemical species such as Na^+, K^+, Cs^+, Cl^-, SO_4^{-2} and $C_2H_3O^-$. 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[24] together with the mathematical procedure used to reduce the raw data.

For use in their study, Oscarson and co-workers[1, 2, 3, 23] 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 ΔH values for each reaction at different temperatures and zero ionic strength. Activity coefficients, γ_i, based on the Lindsay modification of the Meissner model[25] 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 ΔH values which give the best agreement between the predicted and measured heats. For all systems studied[1, 2, 3, 23], 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[26]. 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_2 in the NaCl system. The authors suggested that the poor agreement may due to the Lennard-Jones term which does not explicitly define species formed in equilibria between CO_2 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[12].

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

$$\frac{G^{ex}}{RT} = \frac{G^{ex}_{LR}}{RT} + \frac{G^{ex}_{MR}}{RT} + \frac{G^{ex}_{SR}}{RT} \tag{1.1}$$

where $G^{\mathrm{ex}}{}_{\mathrm{LR}}$ designates the contribution of long-range electrostatic interaction calculated from the Pitzer-Debye-Hückel formula, $G^{\mathrm{ex}}{}_{\mathrm{SR}}$ is the short range contribution resulting from intermolecular interactions by using a UNIQUAC model, and an additional (middle range) term $G^{\mathrm{ex}}{}_{\mathrm{MR}}$ 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, ρ, 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 Pizter (AP) [27] is considered one of the best models for correlation of the densities and phase equilibrium of the NaCl-H_2O system in the near-critical and supercritical region. This comprehensive equation of state includes a reference part and a perturbation contribution:

$$f^{res} = f^{ref} + f^{per} \tag{1.2}$$

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_2O 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[10, 11]. In 2001, Oscarson and Palmer[8] proposed a modified model (RI model) based on a Helmholtz expression developed by Anderko and Pitzer[27] (AP model) and the equilibrium constant equation for NaCl from conductivity measurements of Wood and co-workers[28, 29]. 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[11] as an extension of the

RI model shows its usefulness in correlating the thermodynamics of NaCl solutions as a function of solution ρ, 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 Na^+, Ac^-, SO_4^{2-} and 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 equlibria 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[1, 2, 3] 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 ΔH^0 valid at infinite dilution ($I \rightarrow 0$), (3) using the value of log K and ΔH^0 at zero ionic strength and the γ values determined from the modified Meissner's activity coefficient model[25] to calculate the concentrations and heats of dilution at experimental ionic strengths, and (4) determining the log K and ΔH 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[25], IAPWS-95 water equation of state[4] and the dielectric constant model[5] 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[6, 7, 8]. 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[25], the best water equation of state[4] and water dielectric constant model[5] 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:

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

In Eq.(2.1), subccript i represents each solute specie in the system, γ are the activity coefficients based on the 1 molal standard state, and φ 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[30] 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[31] 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),

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

$$B = 0.75 - 0.065q \tag{2.3}$$

$$\log \Gamma^* = -\frac{0.5107 I^{1/2}}{1 + C I^{1/2}} \tag{2.4}$$

$$C = 1 + 0.055 q e^{-0.023 I^3} \tag{2.5}$$

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[25] 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 (º C):

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

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

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

In Eq. (2.7), t is the temperature in º 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 ºC 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:

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

in which z is the ion charge (±2, ±3), $\gamma_{|z|}$ is a single ion activity coefficient for a multiple-charged ion, and $\gamma_{\pm(\mathrm{NaCl})}$ is the mean molal activity coefficient for NaCl. Lindsay[25] 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

$$A_\gamma = e^3 \cdot (2 \cdot \pi \cdot N_A \cdot \rho)^{\frac{1}{2}} \cdot (4 \cdot \pi \cdot \varepsilon \cdot \varepsilon_0 \cdot k \cdot T)^{\frac{-3}{2}} \tag{2.9}$$

where $e = 1.6021773\times10^{-19}$ C is the charge of an electron, $\varepsilon_0 = 8.8541878\times10^{-12}$ C^{2}J^{-1}m^{-1} is the permittivity of vacuum, ε is the dielectric constant of water, ρ is the density of water with unit g/cm^3, and N_A, π, 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[5]. For the limiting law slope calculated using Lindsay's fitting equation, differences from reported data[5] 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[5] 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 Δ that represents the effect of pressure/density:

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

With Δ falling in a range of values between -0.75 to 0.75, Eq. (2.10) was used to calculate the mean activity coefficients γ for NaAc + H_2O system. The mean activity coefficients γ for NaAc + H2O system vs. different Δ are plotted in Figure 2.1. for 1m NaAc at temperatures of 275 ºC and 300 ºC,

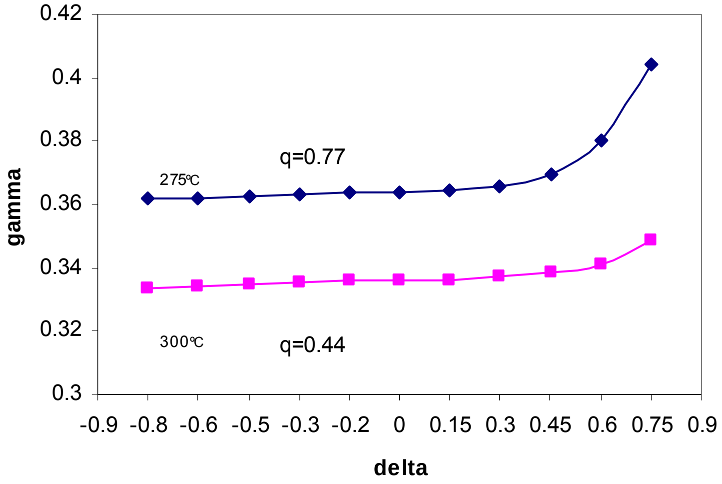


Figure 2.1. Plot of activity coefficients γ of 1m NaAc + H_2O system at 275ºC and 300ºC vs. different Δ values.

Figure 2.1 shows that when the range of Δ is between -0.75 to 0.45, γ changes relatively little; however, at 275°C, γ increases about 1.6% and 10.9% when Δ 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 γ. 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 ρ 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[4] 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 ρ 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 ρ and a part A^{r} that takes into account the residual fluid behavior. The Helmholtz free energy takes the form of:

$$A(\rho,T)=A^{0}(\rho,T)+A^{r}(\rho,T) \tag{2.11}$$

By using the dimensionless form $\Phi = A$ / ($\mathrm{R_g T}$), the reduced Helmoholtz energy, as a function of temperature T and density ρ, becomes

$$\phi(\delta,\tau)=\phi^{0}(\delta,\tau)+\phi^{r}(\delta,\tau) \tag{2.12}$$

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

The ideal gas part of the equation is:

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

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

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

in which n_i, d_i, t_i, α_i, and β_i are parameters, Δ and ψ are auxiliary function applicable to the critical region. The complete formulation is presented and discussed in detail in the original article[2]. 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[5] 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[5] is based on the Kirkwood[32] equation which relates the effect of intermolecular interactions on the dielectric constant of a fluid. The equation given by Kirkwood is:

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

Where

$$\mu \cdot \overline{\mu} = \mu^2\left[1 + (N_A/V_m)\int^{V_0} \cos\gamma \cdot e^{-W/kT} dW dV\right] \qquad (2.15b)$$

In Eq. (2.15b), ε is the dielectric constant, α is the molecular polarizability, V_m is the molar volume, N_A is Avogadro's constant, μ is the molecular dipole moment of an arbitrary molecule in the fluid, $\overline{\mu}$ 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 μ is the dipole moment of the molecule in the absence of all electric fields. Within the integral, γ 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 π have their usual meanings.

The difficulties inherent in the calculation of ε 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[5] calculated $(g\text{-}1)/\rho$ from the data of Heger et al. at various *T* and *P* and *T* and ρ values, respectively. Then the value of $(g\text{-}1)/\rho$ was fitted by means of a nonlinear least-squares fitting procedure to the following equation:

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

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

$$f(p,T,\rho) = N_A \cdot \frac{\left(\alpha + \dfrac{g(p,T,\rho)\mu^2}{3\varepsilon_0 kT}\right)}{3V_W} \tag{2.17}$$

where

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

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

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

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

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

$V_W = M_w / \rho$ and $M_W = 0.0180153 \quad kg/mol$

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

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

In this work, the dielectric constant equation from Archer and Wang[5] 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[34] 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[35] et al. measured enthalpies of dilution of aqueous $CaCl_2$ using a flow microcalorimeter over the temperature range 150 to 400°C. Archer[36] 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[6, 7, 8] determined accurate equilibrium constants for the formulation of Na_2SO_4 (aq), H_2SO_4 (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[1, 2, 23] 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 increased 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 ρ. 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[37], electrical conductivity[38, 39], calorimetry[3, 23], and potentionmetry[40, 41] have resulted in precise measurements of thermodynamic properties of electrolyte aqueous solutions at high temperatures. Among them, Wood and co-workers[6, 7, 8] were able to provide accurate equilibrium constants for the dissociation of Na_2SO_4 (aq), H_2SO_4 (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[39, 42]. Equilibrium constants determined from these experiments, together with some other values reported in the literature [1, 2, 23, 43, 44]for the association of electrolytes HCl (aq), H_2SO_4 (aq), Na_2SO_4 (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_2SO_4 (aq), Na_2SO4 (aq), HAc(aq), NaAc(aq), and NaOH(aq) in Aqueous Solutions.

T (K)	P (MPa)	logK	Method[a]	ref	density ρ(g/cm^3)
		$H^+ + Cl^- = HCl$			
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[a]	ref	density ρ(g/cm^3)
623.16	20	2.01	con	8	0.60059
623.16	28	1.82	con	8	0.63704
		$Na^+ + HSO_4^{-1} = Na_2SO_4$			
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
		$H^+ + Ac^- = HAc$			
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
		$Na^+ + Ac^- = NaAc$			
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
		$Na^+ + OH^- = NaOH$			
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

[a] 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 ρ.

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

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

where ρ is the density of water and T is temperature in K. It has been shown that ρ 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:

$$A^{+}\cdot \alpha H_2O + B^{-}\cdot \beta H_2O = C\ (aq)\cdot \gamma H_2O + (\alpha + \beta - \gamma)\cdot H_2O \tag{3.3}$$

The term $(\alpha + \beta - \gamma)$ in reaction (3.3) can be roughly represented by the $(c+d/T)$ term in eq. (3.2) since ρ is the concentration of water. However, when the temperature is above 350 ºC, 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_2SO_4 (aq), Na_2SO_4 (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 $gm\cdot cm^{-3}$ 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
$NaSO_4$	3.5888	-1267.999	-3.5326	-45.0004
HSO_4	13.4104	-4323.316	-2.5225	219.2622
H_2SO_4	7.6962	-3998.989	-14.3785	8898.995
Na_2SO_4	1.0333	9.9359	-2.7905	63.0129
HAc	-0.4558	-79.9671	-4.042	120.0167

Wood[28] 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 ΔG, the change in the standard state Gibbs energy ΔG^0, and the association constant K can be expressed as:

$$\Delta G = \Delta G^0 + RT \ln K \tag{3.4}$$

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

$$\Delta G^0 = -RT \ln K_m \tag{3.5}$$

From the thermodynamic identity:

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

the enthalpy change at zero ionic strength ΔH^0 can be determined as following:

$$\Delta H^0 = RT^2 (\frac{\partial \ln K_m}{\partial T})_P \tag{3.7}$$

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

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

The log K value for the ionization of water was obtained from the equation of Marshall and Franck[45]:

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

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

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

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

CHAPTER 4

CALCULATION PROCEDURE

In the preceeding chapter, the details of the modified Meissner's activity coefficient model[25], the equation of state for water[4], Archer and Wang's dielectric constant model[5] 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.[1, 2, 23], the reactions occurring in the systems NaAc (aq) + H_2O, HCl (aq)+ H_2O, and Na_2SO_4 (aq) + H_2O were studied. For example, in the process of dilution of NaAc, , aqueous NaAc solution with molalities $m_{\mathrm{Na}^+,\mathrm{initial}}$, and $m_{\mathrm{Ac}^-,\mathrm{initial}}$ 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:

$$H^+ + Ac^- = HAc \qquad (4.1)$$

$$Na^+ + OH^- = NaOH \tag{4.2}$$

$$Na^+ + Ac^- = NaAc \tag{4.3}$$

$$H^+ + OH^- = H_2O \tag{4.4}$$

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

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

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

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

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 $H^+ + OH^- = H_2O$,

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

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:

$$m_{H^+} + m_{Na^+} = m_{Ac^-} + m_{OH^-} \tag{4.9}$$

$$m_{Na^+,tot,final} = m_{Na^+} + m_{NaOH} + m_{NaAc} \tag{4.10}$$

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

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:

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

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 determined. Therefore, in terms of known or solvable quantities, the overall heat of dilution can be calculated.

A solution of Na_2SO_4 is usually treated as a mixed electrolyte solution. The correct selection of species present in the diluted Na_2SO_4 solution is critical for the success of the calculation procedure. There are seven species present in solution: Na^+, SO_4^{-2}, $NaSO_4^-$, $HSO4^-$, Na_2SO_4, H^+ and OH^-. In this study, we neglected $NaHSO_4$ and H_2SO_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 ΔH 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.[1, 2, 23]. Tables 5.1-5.3 contain total mass flow rates of solution and experimental heats obtained by mixing NaAc solution with H_2O, HCl solution with H_2O, and Na_2SO_4 solution with H_2O, 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. [1, 2, 23] with values calculated from this work and from the model of Oscarson et al.[1, 2, 23] .

Table5.1 Comparison of Measured and Calculated Heats of Dilution for NaAc + H_2O^a

T = 275 ºC					P = 10.3 Mpa						
1.0661m				0.5175m				0.2574m			
flow rate	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**flow rate**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**flow rate**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**
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 ºC					P = 10.3MPa						
1.0711m				0.4982m				0.2625m			
flow rate	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**flow rate**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**flow rate**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**
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 = 320ºC					P = 12.8 Mpa						
flow rate	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**flow rate**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**				
0.5115m				0.2530m							
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				

[a] Flow rate is the total flow rate of stream *a* and stream *b* with units of g H_2O-min^{-1}; $\Delta dilH^1$ and $\Delta dilH^2$ are heats of dilution calculated with modified model and model of Oscarson et al.[2], respectively, with units of J-min^{-1}.

Table 5.2 Comparison of Measured and Calculated Heats of Dilution for HCl + H_2O[a]

T = 275 ºC						P = 10.3 Mpa					
1.0164m				0.4999m				0.2502m			
flow rate	**meas ΔH**	**ΔdilH^1**	**ΔdilH^2**	**flow rate**	**meas ΔH**	**ΔdilH^1**	**ΔdilH^2**	**flow rate**	**meas ΔH**	**ΔdilH^1**	**ΔdilH^2**
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 ºC						P = 10.3MPa					
1.0210m				0.4677m				0.2715m			
flow rate	**meas ΔH**	**ΔdilH^1**	**ΔdilH^2**	**flow rate**	**meas ΔH**	**ΔdilH^1**	**ΔdilH^2**	**flow rate**	**meas ΔH**	**ΔdilH^1**	**ΔdilH^2**
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 = 320ºC						P = 12.8 Mpa	
0.4824m				0.2370m			
flow rate	**meas ΔH**	**ΔdilH^1**	**ΔdilH^2**	**flow rate**	**meas ΔH**	**ΔdilH^1**	**ΔdilH^2**
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

[a] Flow rate is the total flow rate of stream *a* and stream *b* with units of g H_2O-min^{-1}; ΔdilH^1 and ΔdilH^2 are heats of dilution calculated with modified model and model of Oscarson et al.[2, 23], respectively, with units of J-min^{-1}.

Table 5.3 Comparison of Measured and Calculated Heats of Dilution for $NA_2SO_4 + H_2O^a$

T = 250 ºC				P = 10.34 Mpa							
1.0711m				0.533m				0.1437m			
flow rate	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**flow rate**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**flow rate**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**
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 ºC				P = 10.3MPa							
0.5724m				0.2796m							
flow rate	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**flow rate**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**				
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 = 320ºC				P = 12.8 Mpa							
0.3128m				0.1544m							
total flow	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**	**total flow**	**meas ΔH**	**ΔdilH¹**	**ΔdilH²**				
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				

[a] Flow rate is the total flow rate of stream *a* and stream *b* with units of g H_2O-min^{-1}; ΔdilH^1 and ΔdilH^2 are heats of dilution calculated with modified model and model of Oscarson et al.[1] , respectively, with units of J-min^{-1}.

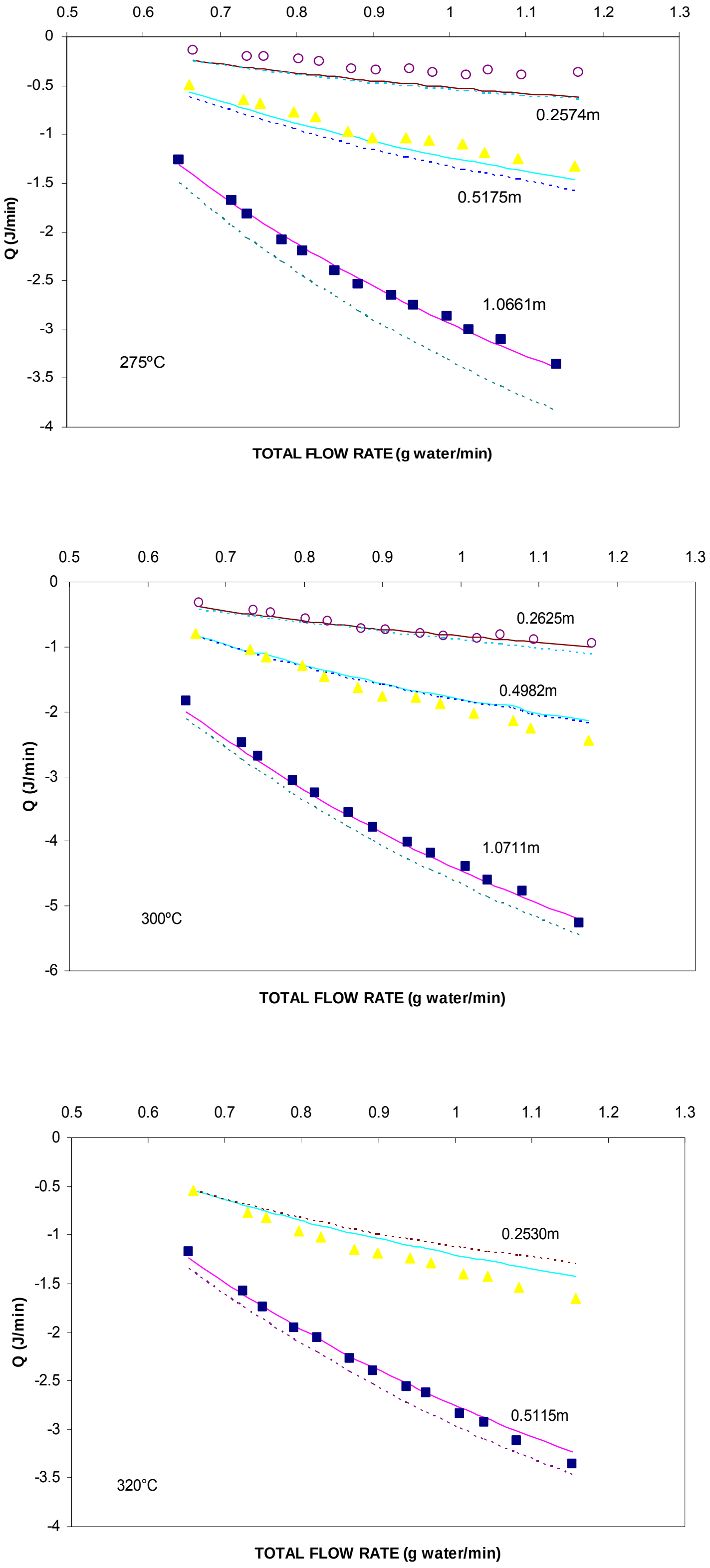


Figure 5. 1. Comparison of measured heat rates (symbols) and calculated heat rates from this work (solid lines) and the model of Oscarson et al.[2] (dotted line) vs. flow rate for NaAc + H_2O.

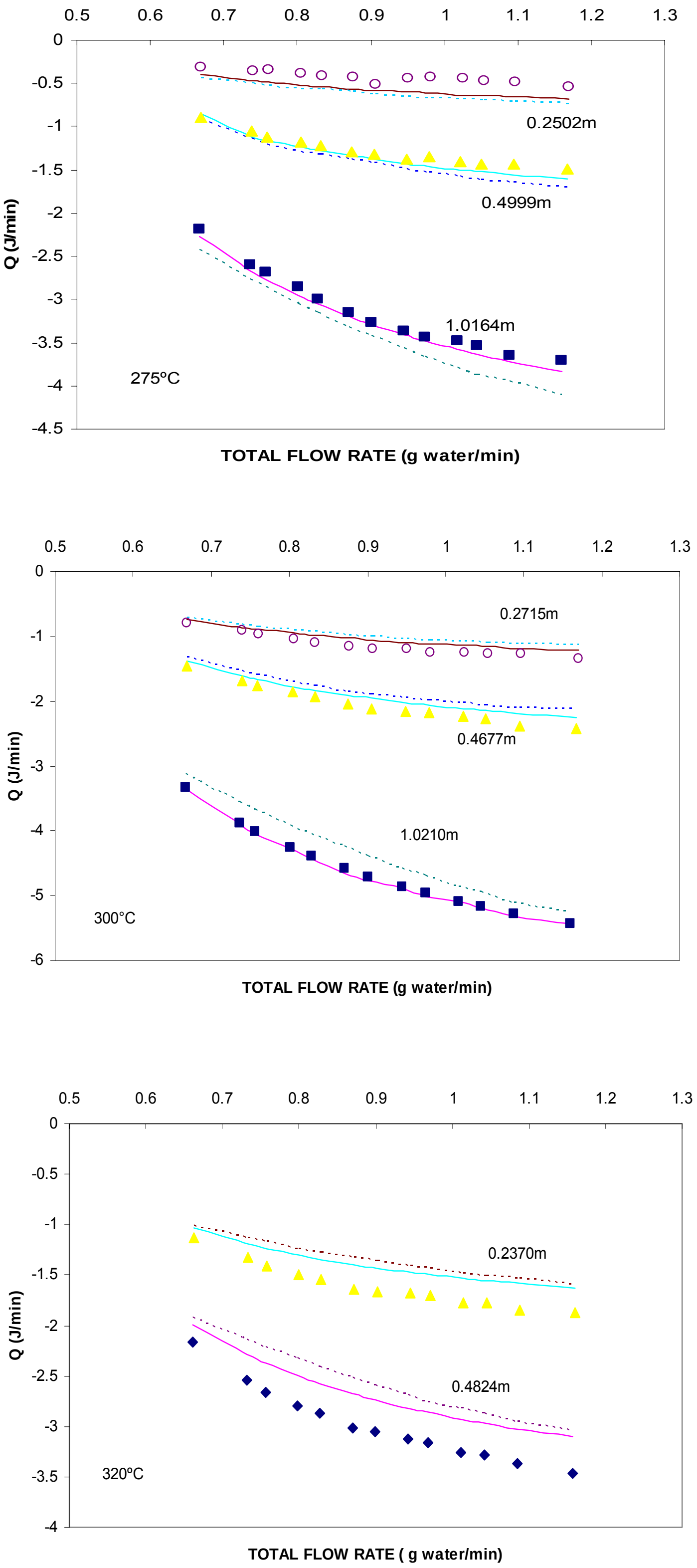


Figure 5.2. Comparison of measured heat rates (symbols) and calculated heat rates from this work (solid lines) and the model of Oscarson et al.[2, 23] (dotted line) vs. flow rate for HCl + H_2O.

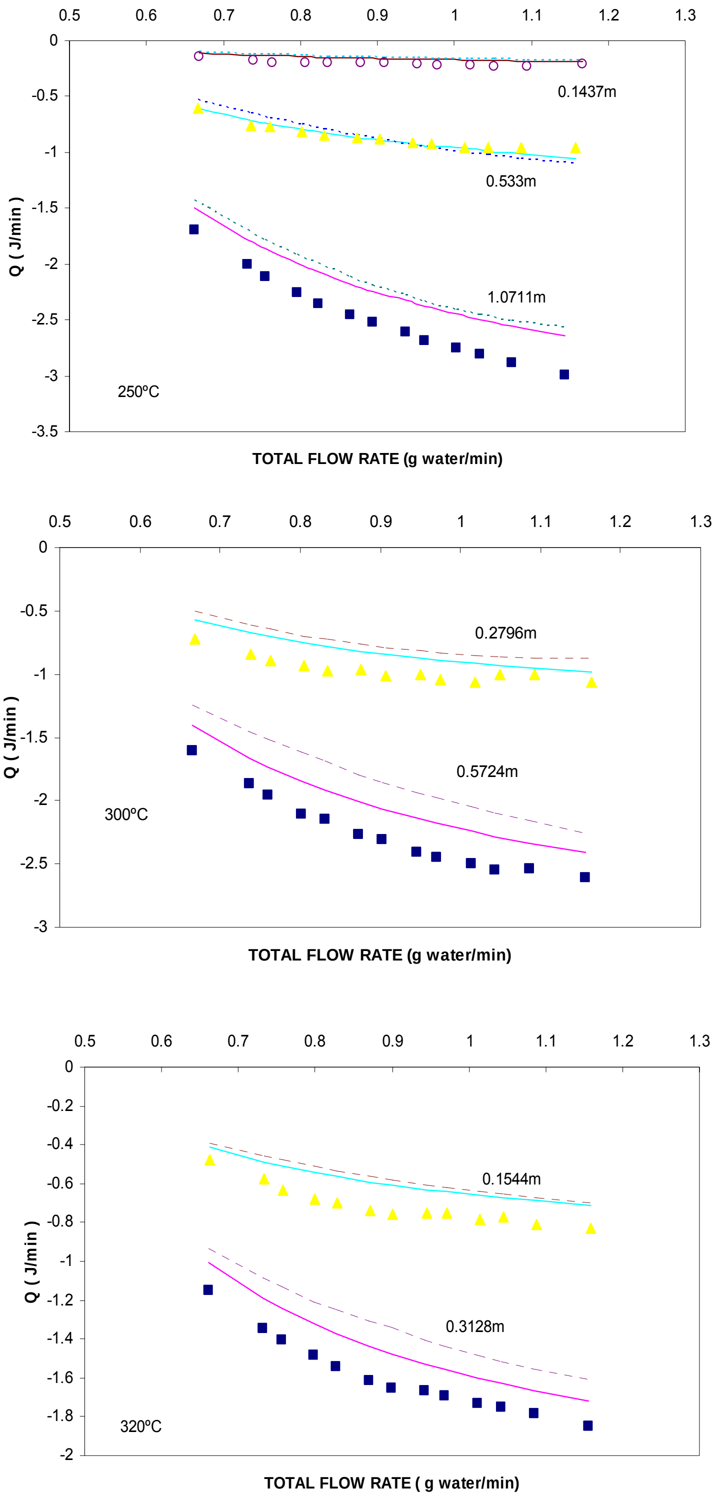


Figure 5. 3. Comparison of measured heat rates (symbols) and calculated heat rates from this work (solid lines) and the model of Oscarson et al.[1] (dotted line) vs. flow rate for $Na_2SO_4 + H_2O$.

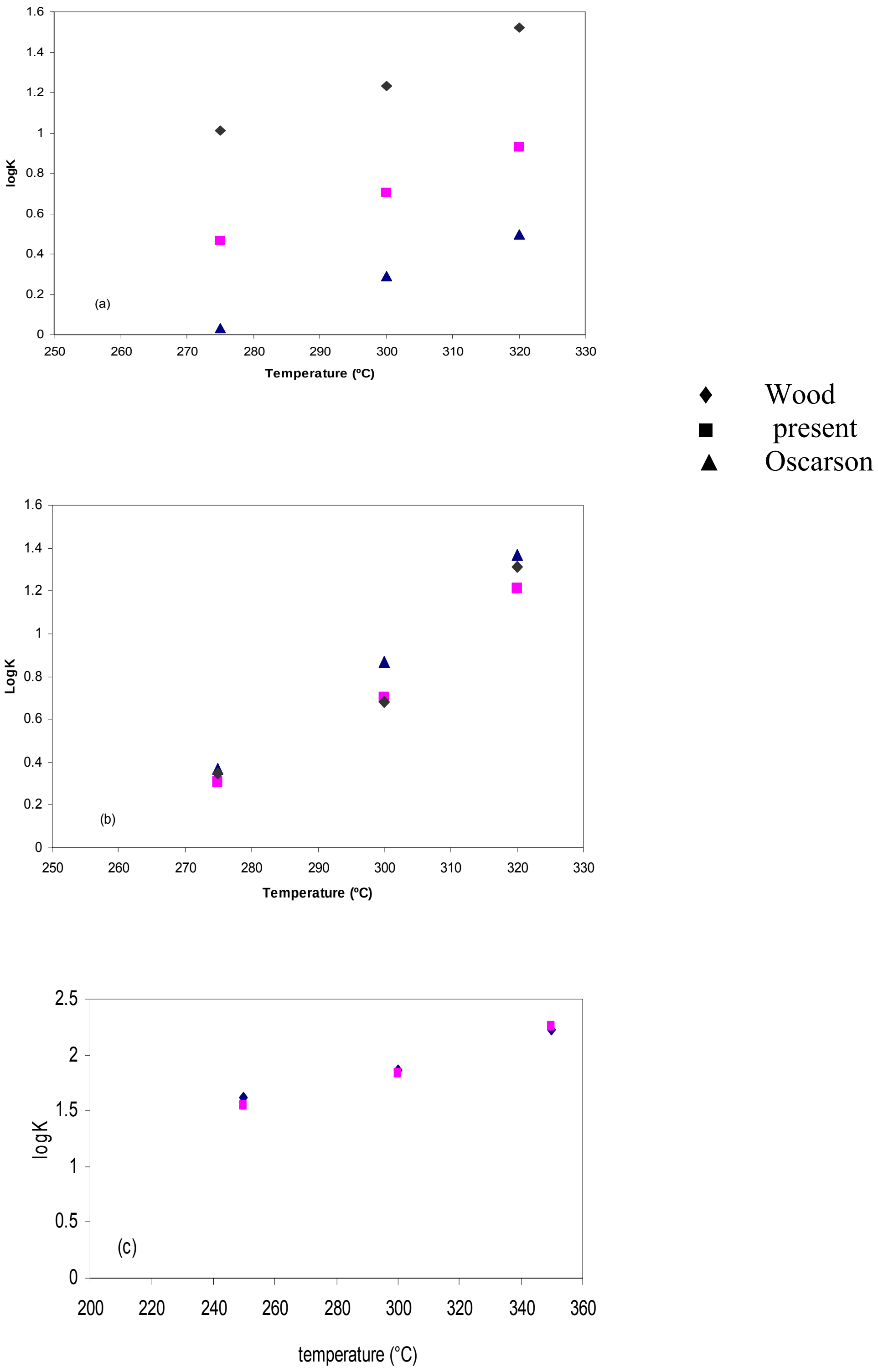


Figure 5.4. Plot of Log *K* for the ion association as a function of temperature for (a) NaAc (aq), (b) HCl (aq), and (c) Na_2SO_4 respectively. The solid triangles are taken from Oscarson et al.[1, 2, 23], the solid diamonds are taken from Wood et al.[6, 7, 8] , while the solid squares are the results obtained in the present study.

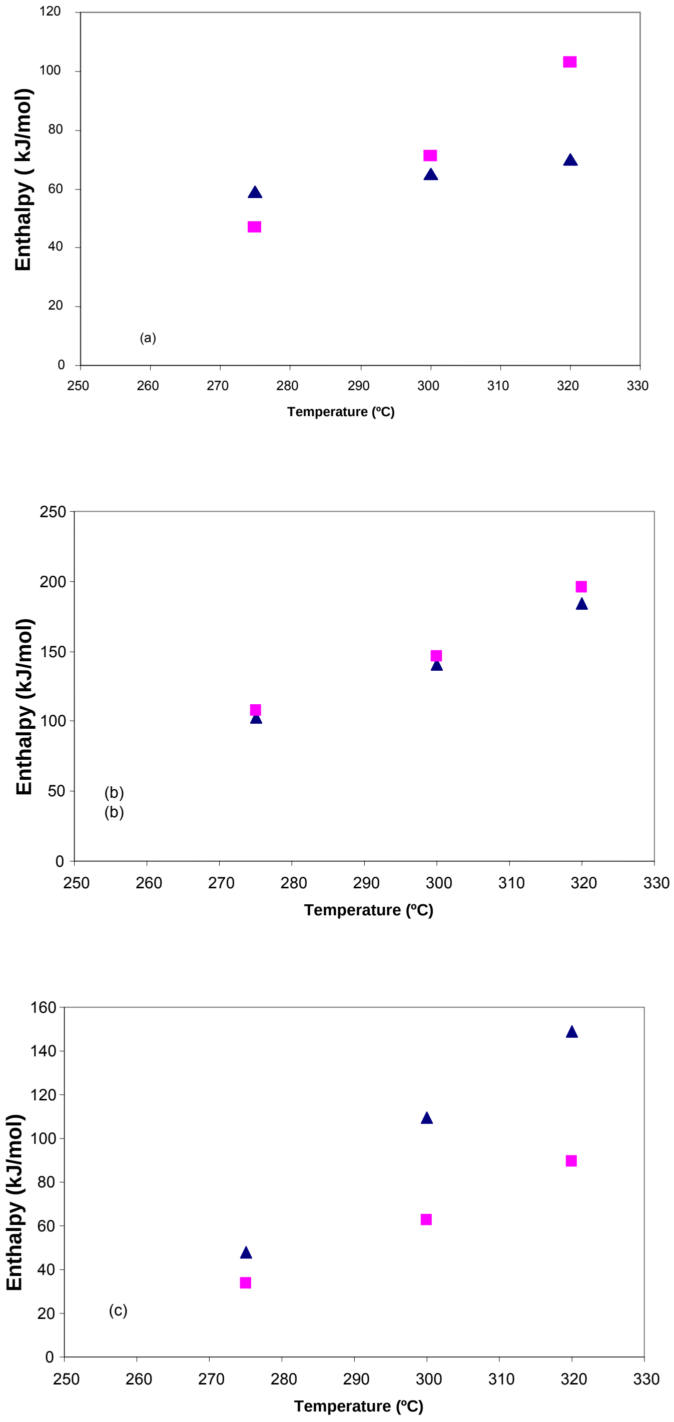


Figure 5.5. Plot of ΔH for the ion association as a function of temperature of (a) NaAc (aq), (b) HCl(aq), and (c) Na_2SO_4 (aq), respectively. The solid triangles are taken from Oscarson et al.[1, 2, 23], while the solid squares are the results obtained in the present study.

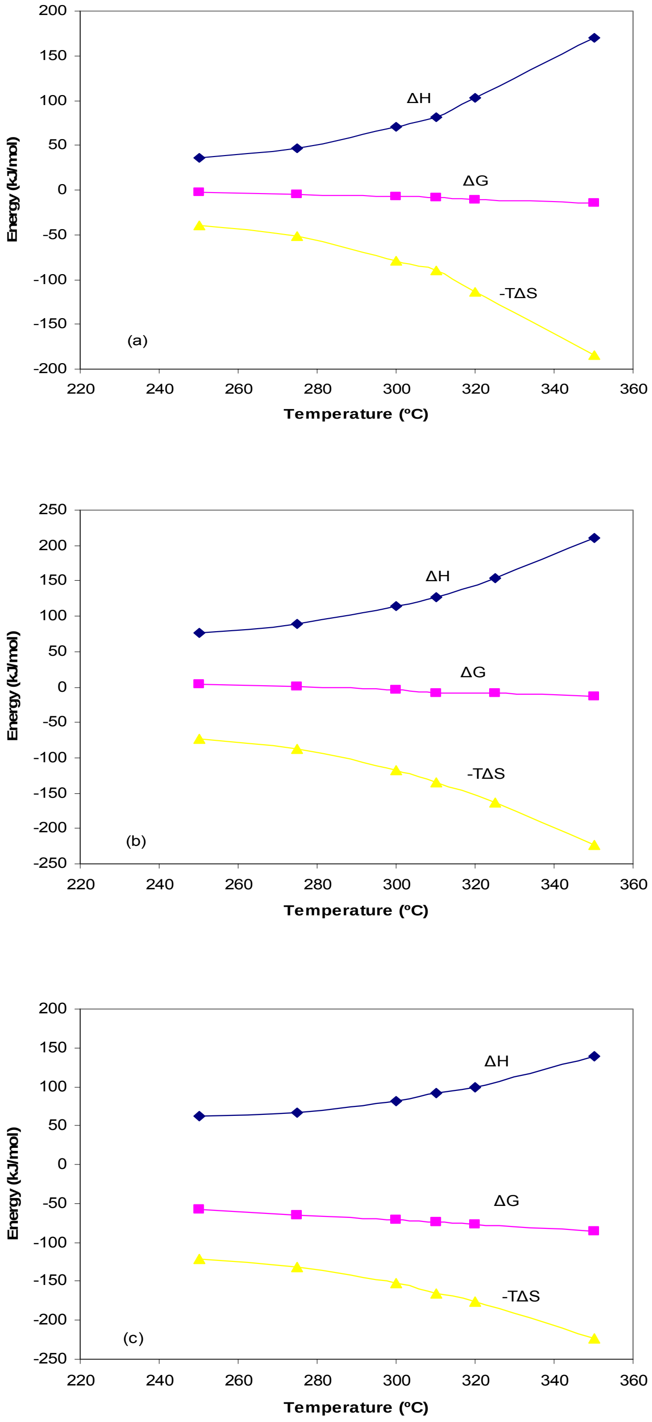
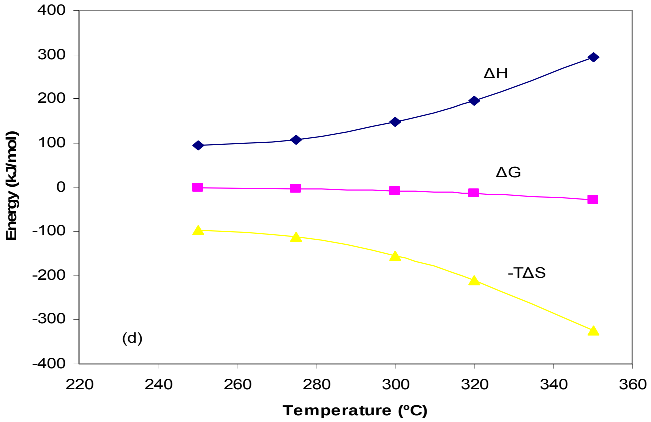
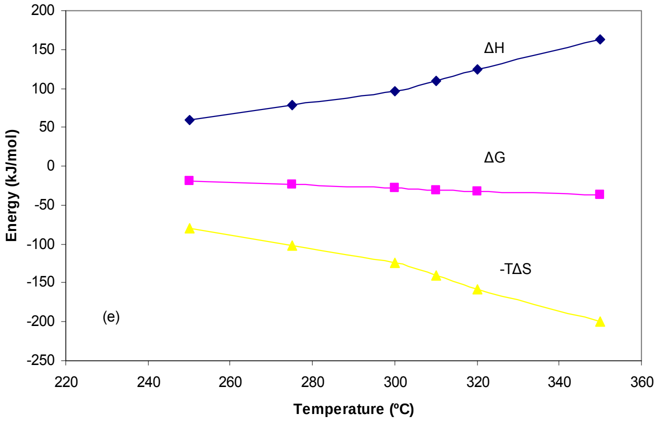


Figure 5.6. Plots of ΔG, ΔH, and –TΔS for the ion association as a function of temperature of (a) NaAc (aq), (b) NaOH(aq), and (c) HAc(aq), respectively.

Figure 5.6. (continued)





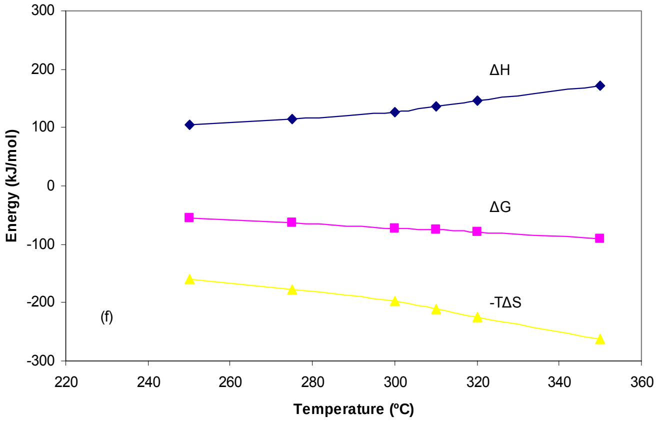
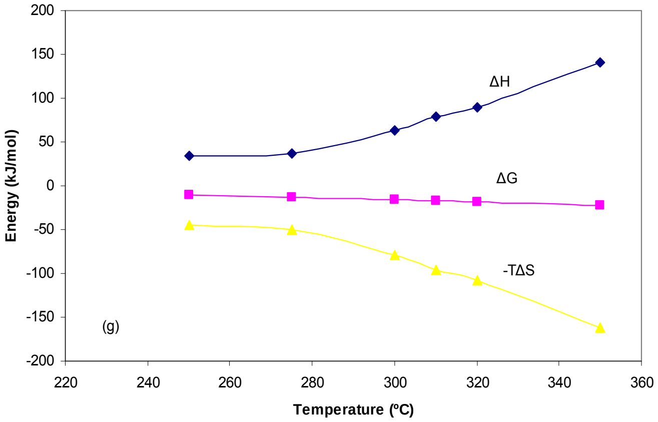


Figure 5.6. (continued)



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.[1, 2, 23]. 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.[1, 2, 23]. 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 ρ and the derivatives of ρ, 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 Meissmer'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 lager 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.[1, 2, 23] compared with those of Wood et al..[6, 7, 8] 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.[8] 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.[2] 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.[6, 7] reported data, which are considered to be the most accurate ion-pairing constants currently available. Oscarson et al.[1] did not derive log *K* values for Na_2SO_4, thus Figure 5.4 (d) contains log *K* values for Na_2SO_4 (aq) only from this work and from Wood et al.[8] 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, ΔH for the association of NaAc(aq), HCl(aq), and Na_2SO_4 (aq) are also changed, which is shown in Figure 5.5. The enthalpy changes in the systems NaAc(aq) + H_2O, HCl (aq)+ H_2O, and Na_2SO_4 (aq) + H_2O were plotted as a function of temperature, as is shown in Figure 5.6. In aqueous solution, the signs of ΔH and ΔS 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.[1, 2, 23] is valid for calculating heats of dilution as well as log K and $\Delta H°$ values for association reactions in aqueous solution over the temperature range from 250ºC to 350ºC. In the previous studies, the approach of Oscarson et al.[1, 2, 23] has been used to investigate various aqueous systems containing electrolytes such as NaAc, Na_2SO_4, 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[5] is used to determine the Debye-Hückel limiting law slope for the calculation of activity coefficent.

Over the temperature range from 250ºC to 350ºC, the average difference between the measured heats of dilution from Oscarson et al.[1, 2, 23] 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.[1, 2, 23] This work also provided log *K* and Δ*H* values for association reactions of NaAc, HCl, and Na_2SO_4 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[23] 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*, $\Delta_{\mathrm{dil}}H$ and Δ*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[30] and the mean spherical approximation[46] 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 = 'titlem',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
          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
          ca(1) = 1.0d - 06   ! concentration of H
          ca(2) = 1.0d - 06   ! concentration of OH
          ca(3) = 0.1d + 00
          if (nprispa .gt. 3) then
             do i = 4, nprispa
                ca(i) = 0.1d + 00    ! concentration of other primary species
             end do
          end if
c     then enter the initial guess for the concentrations of complexes formed in the stream
a
c
c          do i = 1, ncompa
               ca(nprispa + i) = 0.1d + 00   ! concentration of electrolyte
          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
        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,ersum)
        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+qwat-(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),qwat,
&            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 calcualted 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 residal 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. 00d+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
 rholiq = 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 subrountine integrates the integral (dlngam/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
```