Lappeenranta University of Technology
Faculty of Technology
LUT Chemistry
B.Sc. thesis
SPRING 2013

Thermodynamic properties of dilute HBr(aq) and HI(aq)

4.2.2013
Esko Makkonen
0296004

ABSTRACT

Author: Esko Makkonen

Supervisor: D. Sc. (Tech.), docent Jaakko Partanen

Title: Thermodynamic properties of dilute HBr(aq) and HI(aq)

Year: 2012

Academic seminar, Lappeenranta University of Technology

Keywords: Hydrobromic acid, hydriodic acid, electrolyte solution, Debye–Hückel model, Hückel model, activity coefficients, electrochemical measurements, isopiestic measurements.

The theory of electrolyte solutions was described by explaining Debye–Hückel theory and deriving the Debye–Hückel equation for the mean activity coefficient. Simple two-parameter Hückel equation was used for the calculation of the activity coefficients of aqueous hydrobromic and hydriodic acids up to 0.5 $\mathrm{mol\cdot kg^{-1}}$ at temperatures from (0 to 60) °C and from (0 to 50) °C, respectively. The parameters were observed to be independent of the temperature. The Hückel equation for the osmotic coefficients of water in the studied solutions was compared to that of Pitzer model by predicting the vapor pressures up to 1 $\mathrm{mol\cdot kg^{-1}}$ at 25 °C. The experimental vapor pressures over the reference electrolyte solutions were calculated with the Pitzer equation for the osmotic coefficients for isopiestic data in this comparison. The simple Hückel model was found to be equally good as the Pitzer model for both hydrobromic and hydriodic acids up to 0.5 $\mathrm{mol\cdot kg^{-1}}$ at 25 °C but applies also to other temperatures studied.

SYMBOLS

A	Helmholtz free energy
ΔA	change of free Helmholtz energy
A^{ϕ}	Pitzer parameter
a^{*}	distance of closest approach
a_{w}	activity of water
B	Hückel parameter describing the size of solvated ions, $\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}$
b_1	Hückel parameter
C^{ϕ}	Pitzer parameter
c	concentration, $\dfrac{\mathrm{mol}}{\mathrm{dm}^3}$
E	electromotive force of a cell, mV, V
E^0	standard electromotive force, mV, V
ΔE	cell potential error, mV
e	electronic charge, $1.6021773\cdot10^{-19}$ C
F	Faraday constant, $96485.3\ \dfrac{\mathrm{As}}{\mathrm{mol}}$
G	Gibbs free energy
I_{c}	ionic strength on concentration scale, $\dfrac{\mathrm{mol}}{\mathrm{dm}^3}$
I_{m}	ionic strength on molality scale, $\dfrac{\mathrm{mol}}{\mathrm{kg}}$
$k_{\mathbf{B}}$	Boltzmann constant, $1.380658\cdot10^{-23}\ \dfrac{\mathrm{J}}{\mathrm{K}}$
M	cation
M_{w}	molar mass of water
N_{A}	Avogadro number, $6.022\cdot10^{23}\ \dfrac{1}{\mathrm{mol}}$
m	molality of electrolyte, $\dfrac{\mathrm{mol}}{\mathrm{kg}}$
n	number of transferred electrons
n_i	amount of substance i, mol
p	vapor pressure over electrolyte solution, mmHg
p^{*}	vapor pressure of pure water above elecrolyte solution, mmHg

p^0	standard pressure, 101.325 kPa = 760 mmHg
Δp	vapor pressure difference, mmHg
R	molar gas constant, 8.31451 $\frac{\mathrm{J}}{\mathrm{Kmol}}$
r	radius of an ion
S	standard error
T	temperature, K
V	volume
v	number of ions (cations or anions)
X	anion
x	general, independant variable
y	quantity in linear-regression analysis
z	charge number

α	Debye–Hückel parameter, $\left[\mathrm{mol}\cdot\mathrm{kg}^{-1}\right]^{-1/2}$
β	constant in Debye–Hückel model, $\mathrm{m}^{-1}\left[\mathrm{mol}\cdot\mathrm{kg}^{-1}\right]^{-1/2}$
β^0	electrolyte specific parameter in Pitzer model
β^1	electrolyte specific parameter in Pitzer model
$\gamma_{i,\mathrm{c}}$	concentration based activity coefficient of ion *i*
$\gamma_{i,\mathrm{m}}$	molality based activity coefficient of ion *i*
$\gamma_{\pm}$	molality based mean activity coefficient
ε_0	relative permittivity in vacuum, $8.8542\cdot10^{-12}\ \frac{\mathrm{C}}{\mathrm{Vm}}$
ε_r	relative permittivity of solvent, $\frac{\mathrm{C}}{\mathrm{Vm}}$
ζ	bounded parameter
κ	Debye–Hückel inverse screening length
λ	Debye–Hückel screening length
μ_i	chemical potential of species *i*
ρ	density, $\frac{\mathrm{kg}}{\mathrm{dm}^3}$
ϕ	osmotic coefficient
ψ_i	time averaged electrical potential around ion *i*

CONTENTS

1 INTRODUCTION

Thermodynamic models for electrolyte solutions are developed for describing mathematically the properties of solutions. Electrolyte solutions are used in various chemical processes and it is therefore important to have reliable models for the electrolytes. In addition, it is good to mention that physical chemists are faced with the need to predict thermodynamic properties of complex or hazardous electrolyte systems for which experimental data may not exist. In order to model electrolyte systems with high precision, all different types of interactions, such as ion-ion, ion-dipole, dipole-dipole, molecule-molecule, should be taken into account. In this bachelor’s thesis, the Hückel model was observed to apply to the activity coefficients of hydrobromic acid in aqueous solutions at least up to $0.5\,\mathrm{mol}\cdot\mathrm{kg}^{-1}$ at temperatures from (0 to 60) °C and of hydriodic acid at least up to $0.5\ \mathrm{mol}\cdot\mathrm{kg}^{-1}$ at temperatures from (0 to 50) °C. The main results of this thesis are published in an article of Partanen, Makkonen, and Vahteristo (2013). The data for the models are obtained from results of various electrochemical measurements.

Both HBr(aq) and HI(aq) are strong uni-univalent electrolytes and thus only the ion-ion interactions need to be considered. The resulting Hückel model is also used to predict the vapor pressure and osmotic coefficient of electrolyte solutions, which are then compared to the vapour pressure and osmotic coefficient obtained from isopiestic data measured for these electrolyte solutions. The details of the Hückel model and Debye–Hückel theory, on which the Hückel model is based, are also described.

2 ELECTROSTATIC INTERACTIONS

2.1 The Debye–Hückel model

In 1923, physical chemists Peter Debye and Erich Hückel developed the first significant model for the electrostatic interactions between ions in aqueous electrolyte system (Debye and Hückel, 1923). Debye and Hückel postulated a local composition model that describes the thermodynamics of ideal solutions with charged ions. The model considers ions as infinitely small hard spheres, *i.e.*, points in solution space. Thus the ions have no volumes of exclusion. Electrostatic interactions between charged ions are long range interactions. The Debye–Hückel model does not describe the interactions between ions and water. In this model, the solvent (namely water) influences only through its relative permittivity and density. Thus, the space of interactions is called “dielectric continuum”.

The reasons explained above give answer to the question why the Debye–Hückel model can not be used to describe completely complex and concentrated electrolyte solutions. However, the Debye–Hückel model describes accurately the activity coefficients in dilute and simple electrolyte solutions. The Debye–Hückel model itself is not used here to study the activity coefficients, but the models which are used in this study (such as the Hückel model), have a strong theoretical connection to the Debye–Hückel model. Currently, the advanced models for electrolyte solutions use a modified Debye–Hückel term for describing long-range interactions in systems of electrolyte solutions (see Thomsen, 2005 and the recent COSMO (conductor-like screening molecule) adapted models, where contribution from short range interactions is calculated using quantum mechanics (Hsieh and Lin, 2010; Wang, Song and Chen, 2011; Ingram, Gerlach, Mehling and Smirnova, 2012)). Recently, a quantum mechanical polarizable continuum model purely for electrolytes called DESMO (Debye–Hückel-like screening molecule) with build-in Poisson–Boltzmann equation (theoretical backbone of Debye–Hückel equation, discussed later on) describing electrostatic interactions, has been published (Lange and Herbert, 2011). Next the derivation of Debye–Hückel equation is shown based mostly on the description presented by Robinson and Stokes (1965).

In the Debye–Hückel model, the electrostatic force (in vector form) that positive ion 1 exerts to an ion 2, is represented by Coulomb’s law of electrostatic interactions:

$$\vec{F}_{12} = \frac{1}{4\pi\varepsilon_0\varepsilon_\mathrm{r}} \frac{z_1 z_2 e^2}{\left\|\vec{r}_{21}\right\|^2} \hat{r}_{21} \tag{2.1.1}$$

e electronic charge = $1.6021773 \cdot 10^{-19}$ C
z_1 charge number of an ion 1 (cation) at position $\vec{r}_1$
z_2 charge number of an ion 2 at position $\vec{r}_2$
$\hat{r}_{21}$ unit vector in direction $\vec{r}_{21} = \vec{r}_1 - \vec{r}_2$
ε_0 permittivity in vacuum = $8.8542 \cdot 10^{-12}\ \frac{\mathrm{C}}{\mathrm{Vm}}$
ε_r relative permittivity of the solvent
$\left\|\vec{r}_{21}\right\|^2$ squared norm of vector $\vec{r}_{21}$

Let as consider that the charge distribution around ion *i* (central ion) has spherical symmetry. The relation between charge density ρ_e around ion *i*, and the electrical potential $\psi_i = \psi_i(r)$ for a sphere with radius *r* around ion *i* is given by Poisson's equation:

$$\nabla^2 \psi_i = -\frac{\rho_\mathrm{e}}{\varepsilon_0 \varepsilon_\mathrm{r}} \tag{2.1.2}$$

By applying the properties of sphere symmetry, ∇^2 operator reduces to form shown in equation (2.1.3), which is easier to handle.

$$\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{d\psi_i}{dr} \right) = -\frac{\rho_\mathrm{e}}{\varepsilon_0 \varepsilon_\mathrm{r}} \tag{2.1.3}$$

Due to the charges near to a cation, anions tend to be in excess and near to an anion cations tend to be in excess. The electrical potential energy of ions *j*, with the distance *r* from the ion *i*, is $z_j e \psi_i$. Debye and Hückel assumed that the ions in the solution obey Boltzmann statistics. The distribution of the other ions *j* around the ion *i* in origin can be described as follows:

$$c_j\left(\psi_i\right) = c_j \exp\left[-\frac{z_j e \psi_i}{k_\mathbf{B} T} \right] \tag{2.1.4}$$

$c_j(\psi_i)$ concentration of ions j at the point where potential is ψ_i

c_j concentration in the bulk solution ($r \to \infty$)

z_j charge number of ion j

k_B $\text{Boltzmann constant} = 1.380658 \cdot 10^{-23}\ \dfrac{\mathrm{J}}{\mathrm{K}}$

T temperature in Kelvin

$\exp\left[-\dfrac{z_j e \psi_i}{k_\mathbf{B} T}\right]$ the Boltzmann factor (radial distribution function)

Thus the charge density becomes:

$$\rho_\mathrm{e} = e\sum_j z_j c_j(\psi_i) = e\sum_j z_j c_j \exp\left[-\frac{z_j e \psi_i}{k_\mathbf{B} T}\right] \tag{2.1.5}$$

Substitution in equation (2.1.3) the Poisson–Boltzmann equation results in the following:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi_i}{dr}\right) = -e\sum_j \frac{z_j c_j}{\varepsilon_0 \varepsilon_\mathrm{r}} \exp\left[-\frac{z_j e \psi_i}{k_\mathbf{B} T}\right] \tag{2.1.6}$$

The Poisson–Boltzmann equation can not be solved analytically because it does not follow the principle of linear superposition for the relationship between the number of charges and the strength of the potential field. However, this equation can be linearized using Taylor expansion for the Boltzmann factor. Taylor expansion for the exponential function is

$$\exp[-x] \approx 1 - x,\ \ 0 \le x << 1 \tag{2.1.7}$$

Applying this to equation (2.1.6) we get:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi_i}{dr}\right) \approx -e\sum_j \frac{z_j c_j}{\varepsilon_0 \varepsilon_\mathrm{r}} \left(1 - \frac{z_j e \psi_i}{k_\mathbf{B} T}\right) \tag{2.1.8}$$

Due to the electrostatic neutrality of solution, the first summation is zero, and equation (2.1.8) simplifies:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right)\approx\sum_j\frac{z_j^2e^2c_j\psi_i}{\varepsilon_0\varepsilon_\mathrm{r}k_\mathbf{B}T} \qquad (2.1.9)$$

Taking the constants as one term in equation (2.1.9) and denoting it as κ^2 we get:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right)=\frac{e^2\sum_j z_j^2c_j}{\varepsilon_0\varepsilon_\mathrm{r}k_\mathbf{B}T}\psi_i=\kappa^2\psi_i \qquad (2.1.10)$$

The constant κ^2, which is square of the Debye–Hückel inverse screening length, can be defined with the concentration scale ionic strength of the solution (= I_c) by:

$$\kappa^2=\frac{e^2\sum_j z_j^2c_j}{\varepsilon_0\varepsilon_\mathrm{r}k_\mathbf{B}T}=\frac{2e^2I_\mathrm{c}}{\varepsilon_0\varepsilon_\mathrm{r}k_\mathbf{B}T}=\frac{2F^2I_\mathrm{c}}{\varepsilon_0\varepsilon_\mathrm{r}RT} \qquad (2.1.11)$$

where $F=96485.3\ \frac{\mathrm{As}}{\mathrm{mol}}$ is the Faraday constant, $R=8.31451\ \frac{\mathrm{J}}{\mathrm{Kmol}}$ is the molar gas constant, and I_c is defined the by:

$$I_\mathrm{c}=\frac{1}{2}\sum_j z_j^2c_j \qquad (2.1.12)$$

By using the product rule for differentiation, the equation (2.1.10) can be written in the form:

$$\frac{1}{r^2}\left(2r\frac{d\psi_i}{dr}+\frac{d^2\psi_i}{dr^2}r^2\right)=\kappa^2\psi_i \qquad (2.1.13)$$

The equation (2.1.13) can be simplified further to see that it is a linear second order homogenous differential equation:

$$\frac{d^2\psi_i}{dr^2}+\frac{2}{r}\frac{d\psi_i}{dr}-\kappa^2\psi_i=0 \tag{2.1.14}$$

Equation (2.1.14) can be easily solved by eliminating the first order derivative $\frac{d\psi_i}{dr}$ using a substitution method shown below:

$$\begin{aligned}
&P(r)=\frac{2}{r},\ r>0,\ z=z(r) \text{ arbitrary, twice differentiable function}\\
&\ln\psi_i=\ln z-\frac{1}{2}\int P(r)dr\\
&\Rightarrow \ln\psi_i=\ln\frac{z}{r}\\
&\Leftrightarrow \psi_i=\frac{z}{r}\\
&\Rightarrow \frac{d\psi_i}{dr}=\frac{z'r-z}{r^2}\\
&\Rightarrow \frac{d^2\psi_i}{dr^2}=\frac{z''r^2-2z'r+2z}{r^3}
\end{aligned}$$

Thus after substitution the equation (2.1.14) becomes:

$$\begin{aligned}
&\frac{z''r^2-2z'r+2z}{r^3}+\frac{2}{r}\frac{z'r-z}{r^2}-\kappa^2\frac{z}{r}=0\\
&\Leftrightarrow z''-\kappa^2 z=0\\
&\Rightarrow \text{characteristic equation: } \theta^2-\kappa^2=0\\
&\Leftrightarrow \theta=\pm\kappa\\
&\Rightarrow z=A\exp(-\kappa r)+B\exp(\kappa r)
\end{aligned} \tag{2.1.15}$$

Since physical reality dictates that the potential must remain finite when r approaches to infinity. Remembering $\psi_i=\frac{z}{r}$, the solution to equation (2.1.14) can be written from the last line of equation bundle (2.1.15) in the following way:

$$\psi_i=\frac{A}{r}\exp\left[-\kappa r\right] \tag{2.1.16}$$

The integration constant A depends on physical conditions of the electrolyte solutions. From equations (2.1.16), (2.1.11) and (2.1.5), the following equation can be obtained for the charge density:

$$\rho_{\mathrm{e}} = -A\frac{\kappa^2\varepsilon}{r}\exp\left[-\kappa r\right] \tag{2.1.17}$$

where $\varepsilon = \varepsilon_0\varepsilon_{\mathrm{r}}$.

Let say that the central ion i has the charge number z_i. The electrical neutrality condition dictates that net charge in the whole solution outside the central ion i is $z_i e$, and the charge at space outside the singled out ion has opposite to sign compared with the central ion. Assuming that there is a certain radius a^* around the central ion i inside which no ion can not exist (see Figure 1 for schematic presentation). This means that the charges outside the central ion are distributed on shells having radius gradually larger than a^* and the number of these cells infinite. Summing the charge densities of these shells throughout the solution space gives exactly the same charge as the central ion, but opposite in sign. This can be expressed by the following integral:

$$\int_{a^*}^{\infty} 4\pi r^2 \rho_{\mathrm{e}} dr = -z_i e \tag{2.1.18}$$

where $4\pi r^2 dr$ is the volume of a shell with radius r and thickness dr. Substituting the charge density ρ_{e} from equation (2.1.17), we get:

$$A\kappa^2\varepsilon\int_{a^*}^{\infty} 4\pi r \exp\left[-\kappa r\right] dr = z_i e \tag{2.1.19}$$

Integrating by parts or using the integral formula

$$\int x \exp[ax]dx = \frac{\exp[ax]}{a^2}(ax-1) \tag{2.1.20}$$

we get the following result to constant *A*:

$$A = \frac{z_i e}{4\pi\varepsilon} \frac{\exp\left[\kappa a^*\right]}{1+\kappa a^*} \tag{2.1.21}$$

Substituting (2.1.21) in to (2.1.16) we get the following equation for the potential:

$$\psi_i = \frac{z_i e}{4\pi\varepsilon} \frac{\exp\left[\kappa a^*\right]}{1+\kappa a^*} \frac{\exp[-\kappa r]}{r} \tag{2.1.22}$$

This Debye screened potential is the expression for the time average potential at point with a distance r from the ion *i*. The closest distance between ion pairs in the solution space is a^*. Because ions are assumed to be charged dots (spheres with zero radius) a^* is not the actual radius of an ion, but is an extended distance caused by the electrostatic interactions and water molecules surrounding the ion. Thus the ions in the solution space can be described as hard spheres with radius a^*, assuming that spherical symmetry holds. Experimental studies show that a^* is usually larger than actual radius of an ion, because of the attached water molecules. The schematic view of ions in solution described the Debye–Hückel model is presented in Figure 1.

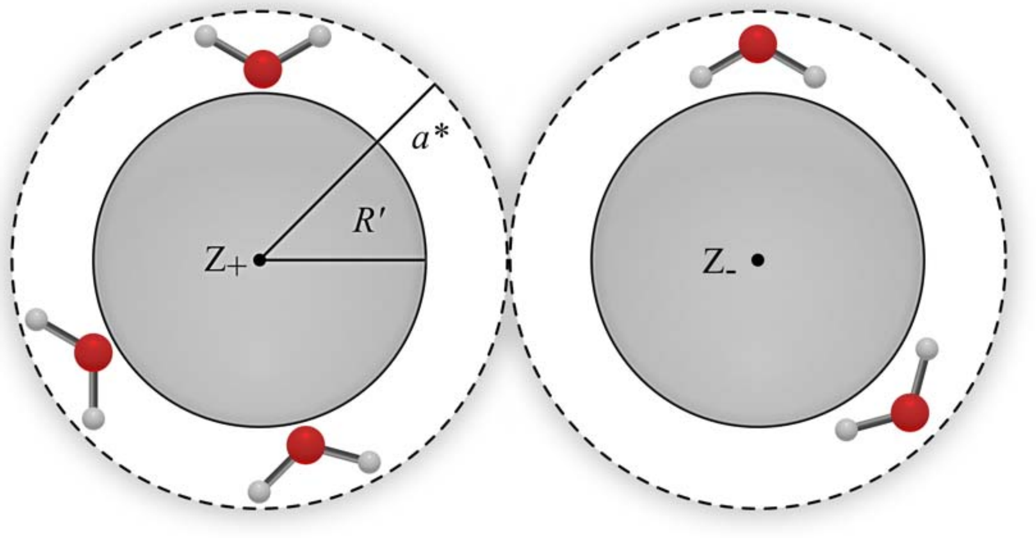

Figure 1. Schematic view of two ions in solution space described by the Debye–Hückel model, where a^* is the distance of closest approach and *R'* is the actual radius of an ion. The sizes of ions are over emphasized for clarity.

Let us then study how the electrostatic interactions between ions contribute to the Gibbs free energy of the electrolyte solution by imagining a large volume of extremely dilute electrolyte solution. Let us remove the charges of ions, and the energy required to do this being equivalent to work w_1. Next the discharged "ions" are transferred reversibly at a constant temperature to a new, actual volume of the solution. This is the non-electric contribution to the change of Helmholtz free energy noted as $\Delta A_{\text{nonelectrical}}$. In this new solution, the average concentration of the discharged ion species is c. In the third part of this Debye charging process (ions treated as classical capacitors) we recharge the ions simultaneously to their previous (real) charge levels. The energy of this part of the process is set to be equal to work w_3. Now we can write the following equation for the change of Helmholtz free energy

$$\Delta A = \Delta A_{\text{electrical}} + \Delta A_{\text{nonelectrical}} \tag{2.1.23}$$

where the term $\Delta A_{\text{electrical}}$ non-ideality describing can be written as follows:

$$\Delta A_{\text{electrical}} = w_1 + w_3 \tag{2.1.24}$$

For the work w_3, the central ion *i* is influenced by the potential given in a equation (2.1.22). For calculating the work w_3 for ion *i*, we must omit from (2.1.22) the potential due to ion *i* . The potential for ion *i* without interactions is

$$\psi_i^{\text{own}} = \frac{z_i e}{4\pi\varepsilon}\frac{1}{r} \tag{2.1.25}$$

Thus, the potential associated with the work w_3 is

$$\psi = \psi_i - \psi_i^{\text{own}} = \frac{z_i e}{4\pi\varepsilon r}\left[\frac{\exp\left[\kappa\left(a^* - r\right)\right]}{1+\kappa a^*} - 1\right] \tag{2.1.26}$$

Since a^* is the closest distance between the central ion *i* and any other ion in the solution and due to the sphere symmetry, the potential caused by the other ions inside a sphere with the radius a^* must be constant. This can be calculated by setting $r = a^*$ to equation (2.1.26). This leads to equation

$$\psi_i^{\text{other ions}} = -\frac{z_i e}{4\pi\varepsilon\lambda}\left[\frac{1}{1+a^*\lambda^{-1}}\right] \tag{2.1.27}$$

where additionally is denoted that $\kappa = \lambda^{-1}$, which is the Debye–Hückel inverse screening length. In this calculation, we need the potential difference between the shield where r is a^*, and the potential associated with the ion *i* itself. This work is given by

$$w_{3,i} = \int_0^{z_i e} \left(\psi_i^{\text{other ions}} + \psi_i^{\text{own}}\right) dq_i \tag{2.1.28}$$

and for the work w_1 for ion *i* can be expressed as

$$w_{1,i} = \int_{z_i e}^{0} \left(\psi_i^{\text{own}}\right) dq_i \tag{2.1.29}$$

In equations (2.1.28) and (2.1.29), dq_i is the charge differential during removing and restoring the charges. Summing (2.1.28) and (2.1.29) and using some calculus, we get for the total work equation

$$w_{3,i} + w_{1,i} = \int_{0}^{z_i e} \left(\psi_i^{\text{other ions}}\right) dq_i \tag{2.1.30}$$

At any time during the process for the equation (2.1.30), the fraction of the final charge possessed any ion *j* in the solution can be defined in the following way. Let us set the charge for ion *j* to be $q_j = z_j e\zeta$, where ζ is a bounded parameter varying from 0 to 1. From this definition results for the charge differential that $dq_j = z_j ed\zeta$. Additionally during the charging process, we must replace κ in equation (2.1.11) by $\zeta\lambda^{-1}$. Substituting these results into (2.1.30) and summing over all the ions j we get:

$$w_3 + w_1 = -\sum_j N_{\text{A}} n_j \frac{z_j^2 e^2}{4\pi\varepsilon\lambda} \int_0^1 \frac{\zeta^2}{1+\zeta a^* \lambda^{-1}} d\zeta \tag{2.1.31}$$

where N_{A} is the Avogadro number and n_j the amount of ion *j*. Applying the partial fraction method in the integration, we get the final form for the change in Helmholtz free energy concerning electrostatic interactions:

$$\Delta A_{\text{electrical}} = \frac{-Fe}{12\pi\varepsilon\lambda} \chi\left(\frac{a^*}{\lambda}\right) \sum_j z_j^2 n_j \tag{2.1.32}$$

where the function χ is defined by equation

$$\chi(x) = \frac{3}{(x)^3}\left[\ln(1+x) - x + \frac{(x)^2}{2}\right] \tag{2.1.33}$$

$\Delta A_{\text{electrical}}$ in equation (2.1.32) is also called the molar excess Helmholtz free energy for solution of charged ions. It considers the non-ideality of long-range electrostatic forces, but it does take into account the non-ideality caused by short-range forces such as molecule-molecule interactions.

From Helmholtz free energy, we get the chemical potential of species *i* at constant temperature and constant volume:

$$\mu_i \equiv \frac{\partial}{\partial c_i}\left(\frac{A}{V}\right)_{T,V,n_{i\neq j}} \tag{2.1.34}$$

Substituting equation (2.1.31) to equation (2.1.33) leads to the following equation:

$$\mu_{i,\text{electrical}} = \frac{\partial}{\partial c_i}\left(\frac{-Fe}{12\pi\varepsilon\lambda}\chi\left(\frac{a^*}{\lambda}\right)\sum_j z_j^2 c_j\right)_{T,V,n_{i\neq j}} \tag{2.1.35}$$

Remembering equation (2.1.12) and after long differentiation procedure, we get the final equation for electrical interactions contributing to the chemical potential:

$$\mu_{i,\text{electrical}} = -\frac{z_i^2 Fe}{8\pi\varepsilon\lambda}\left[\frac{1}{1+a^*\lambda^{-1}}\right] \tag{2.1.36}$$

For ideally dilute electrolyte solution, the chemical potential of ion *i* on a concentration scale is the following:

$$\mu_i^{\text{ideally dilute}} = \mu_i^0 + RT\ln\left(\frac{c_i}{c^0}\right) \tag{2.1.37}$$

Considering the chemical potential in a real solution, it is necessary to take into account term, which describes the non-ideality. The term is called the excess chemical potential. For ion species *i*, the excess chemical potential is denoted as μ_i^{excess} . The chemical potential of ion *i* in a real solution can then simply be written as a sum of ideal and non-ideal terms:

$$\mu_i = \mu_i^{\text{ideally dilute}} + \mu_i^{\text{excess}} \tag{2.1.38}$$

The activity coefficient of ion *i* on the concentration scale is defined by using excess chemical potential in the following way

$$\mu_i^{\text{excess}} \equiv RT \ln\left(\gamma_{i,c}\right) \tag{2.1.39}$$

Since the non-ideality is caused by electrostatic interactions, equation (2.1.38) can be written as follows:

$$\mu_i = \mu_i^{\text{ideally dilute}} + \mu_{i,\text{electrical}} \tag{2.1.40}$$

From equations (2.1.36), (2.1.39) and (2.1.40), it is easy to discover the connection between the activity coefficient and electrostatic interactions:

$$\ln\left(\gamma_{i,\text{c}}\right) = -\frac{z_i^2 Fe}{8\pi\varepsilon\lambda RT}\left[\frac{1}{1+a^*\lambda^{-1}}\right] \tag{2.1.41}$$

Obtaining κ^{-1} from equation (2.1.11) and replacing $\lambda = \kappa^{-1}$, we get the Debye–Hückel model for the activity coefficient of ion *i* :

$$\ln\left(\gamma_{i,\text{c}}\right) = -\frac{z_i^2 \alpha_\text{c} \sqrt{I_\text{c}}}{1+\beta_\text{c} a^* \sqrt{I_\text{c}}} \tag{2.1.42}$$

where $\alpha_\mathrm{c} \equiv \dfrac{\sqrt{2}F^2 e}{8\pi\left(\varepsilon RT\right)^{3/2}}$ and $\beta_\mathrm{c} \equiv \dfrac{\sqrt{2}F}{\left(\varepsilon RT\right)^{1/2}}$. For further use, it is preferable to change the ionic strength I_c to a more useful quantity that is the ionic strength on the molality scale (I_m). I_m is more reliable, because the volume of solution can vary when temperature changes, but the mass of the solvent remains the same. The equation for I_m is analogous to that of equation (2.1.12), and the concentration is simply replaced by the molality. The concentrations of ion *i* in dilute solutions can be expressed as

$$c_i \cong \frac{n_i \rho_\mathrm{A}^*}{w_\mathrm{A}} = m_i \rho_\mathrm{A}^* \tag{2.1.43}$$

where ρ_A^* is the density of solvent, w_A is the mass of the solvent, and m_i is the molality of the ion i. Substituting these results to (2.1.42) gives

$$\ln\left(\gamma_{i,\mathrm{m}}\right) = -\frac{z_i^2 \alpha \sqrt{I_\mathrm{m}}}{1 + \beta a^* \sqrt{I_\mathrm{m}}} \tag{2.1.44}$$

where $\alpha \equiv \dfrac{\sqrt{2\rho_\mathrm{A}^*}F^2 e}{8\pi\left(\varepsilon RT\right)^{3/2}}$ and $\beta \equiv \dfrac{\sqrt{2\rho_\mathrm{A}^*}F}{\left(\varepsilon RT\right)^{1/2}}$.

After derivation of the Debye–Hückel model for ion *i*, it is good to derive also the equation for a strong electrolyte. It dissociates in the following way:

$$M_{v_\mathrm{M}} X_{v_\mathrm{X}} \rightarrow v_\mathrm{M} M^{z_\mathrm{M}} + v_\mathrm{X} M^{z_\mathrm{X}} \tag{2.1.45}$$

M cation
v_M number of cations in the electrolyte
z_M charge number of the cation (positive)
X anion
v_X number of anions in the electrolyte
z_X charge number of the anion (negative)

For this electrolyte:

$$\gamma_{\pm}^{v_{\mathrm{M}}+v_{\mathrm{X}}}=\left(\gamma_{\mathrm{M}}\right)^{v_{\mathrm{M}}}\left(\gamma_{\mathrm{X}}\right)^{v_{\mathrm{X}}} \tag{2.1.46}$$

After taking the natural logarithm from both sides of the equation (2.1.46), we get:

$$\left(v_{\mathrm{M}}+v_{\mathrm{X}}\right)\ln\left(\gamma_{\pm}\right)=v_{\mathrm{M}}\ln\left(\gamma_{\mathrm{M}}\right)+v_{\mathrm{X}}\ln\left(\gamma_{\mathrm{X}}\right) \tag{2.1.47}$$

Substituting equation (2.1.44) into equation (2.1.47), the result is:

$$\left(v_{\mathrm{M}}+v_{\mathrm{X}}\right)\ln\left(\gamma_{\pm}\right)=-\frac{\alpha\sqrt{I_{\mathrm{m}}}}{1+\beta a^{*}\sqrt{I_{\mathrm{m}}}}\left[v_{\mathrm{M}}z_{\mathrm{M}}^{2}+v_{\mathrm{X}}z_{\mathrm{X}}^{2}\right] \tag{2.1.48}$$

Simplifying equation (2.1.48) and taking into account electrical neutrality condition

$$v_{\mathrm{M}}z_{\mathrm{M}}+v_{\mathrm{X}}z_{\mathrm{X}}=0 \tag{2.1.49}$$

we get the final form of the Debye–Hückel equation for mean molal activity coefficient of the electrolyte considered:

$$\ln\left(\gamma_{\pm}\right)=-\frac{\left|z_{\mathrm{M}}z_{\mathrm{X}}\right|\alpha\sqrt{I_{\mathrm{m}}}}{1+\beta a^{*}\sqrt{I_{\mathrm{m}}}} \tag{2.1.50}$$

2.2 The Debye screened potential from Statistical Mechanics

The Debye screened potential in Chapter 2.1 was derived classically by introducing Boltzmann distribution for charge density and plugging it into Poisson equation and then solving the screened potential with given boundaries. The result is presented in equation (2.1.22). This (and the entire Debye–Hückel model) can be derived using purely statistical mechanics, namely solving the integral equations of ion interactions in dielectric continuum media (Kirkwood and Poirier, 1954; Lee, 2008; Xiao and Song, 2011). This is presented by the Ornstein–Zernike integral equation:

$$h_{\mathrm{MX}}\left(r\right)=c_{\mathrm{MX}}\left(r\right)+\sum_{l}\rho_{l}\int c_{l\mathrm{X}}\left(\vec{\mathrm{r}}\,'\right)h_{\mathrm{M}l}\left(\left|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'\right|\right)\mathrm{d}\vec{\mathrm{r}}' \tag{2.2.51}$$

$h_{\mathrm{MX}}\left(r\right)$ total correlation function between cation M and anion X
$c_{\mathrm{MX}}\left(r\right)$ direct correlation function between cation M and anion X
l ion in solution space, can be cation or anion
ρ_{l} density of species l
$c_{l\mathrm{X}}\left(\vec{\mathrm{r}}\,'\right)$ indirect correlation function between anion and l
$h_{\mathrm{M}l}\left(\left|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'\right|\right)$ indirect correlation function between cation and l

The equation (2.2.51) is exact, if correlation functions are known. Generally, this is not the case and even if they are known, however, the integrals are too complicated to be solved analytically. For deriving Debye screened potential, low concentration conditions and Boltzmann distribution have to be assumed. From equation (2.1.1), we can find the Coulombic potential:

$$u(r)=\varepsilon_{\upsilon}\frac{z_{1}z_{2}e^{2}}{r} \tag{2.2.52}$$

where for simplicity $\varepsilon_{\upsilon}=\dfrac{1}{4\pi\varepsilon_{0}\varepsilon_{\mathrm{r}}}$. Thus, the direct correlation function between cation and anion can be approximated to be

$$c_{\mathrm{MX}}\left(r\right)\cong-\frac{u(r)}{k_{\mathrm{B}}T}=-\frac{\varepsilon_{\upsilon}}{k_{\mathrm{B}}T}\frac{z_{\mathrm{M}}z_{\mathrm{X}}e^{2}}{r} \tag{2.2.53}$$

and the corresponding indirect correlation function is

$$c_{l\mathrm{X}}\left(\vec{r}\,'\right) \cong -\frac{u(r)}{k_{\mathrm{B}}T} = -\frac{\varepsilon_{\upsilon}}{k_{\mathrm{B}}T}\frac{z_l z_{\mathrm{X}} e^2}{r'} \tag{2.2.54}$$

The total correlation function between cation and anion (or generally the total correlation function for any particles) is defined via radial distribution function $g\left(r\right)$ as follows:

$$h_{\mathrm{MX}}\left(r\right) \equiv g\left(r\right) - 1 \tag{2.2.55}$$

Now using the radial distribution function, namely the Boltzmann factor in equation (2.1.4) and Taylor expansion (2.1.7), we can approximate equation (2.2.55):

$$h_{\mathrm{MX}}\left(r\right) \cong \exp\left[-\frac{z_{\mathrm{M}}e}{k_{\mathbf{B}}T}\psi_{\mathrm{X}}(r)\right] - 1 \approx -\frac{z_{\mathrm{M}}e}{k_{\mathbf{B}}T}\psi_{\mathrm{X}}(r)$$

(2.2.56)

and for the indirect correlation:

$$h_{\mathrm{M}l}\left(\left|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'\right|\right) \approx -\frac{z_{\mathrm{M}}e}{k_{\mathbf{B}}T}\psi_l\left(\left|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'\right|\right) \tag{2.2.57}$$

Plugging these into (2.2.51) gives:

$$-\frac{z_{\mathrm{M}}e}{k_{\mathbf{B}}T}\psi_{\mathrm{X}}(r) = -\frac{\varepsilon_{\upsilon}}{k_{\mathrm{B}}T}\frac{z_{\mathrm{M}}z_{\mathrm{X}}e^2}{r} + \sum_l \rho_l \int \frac{\varepsilon_{\upsilon}}{k_{\mathrm{B}}T}\frac{z_l z_{\mathrm{X}}e^2}{r'}\frac{z_{\mathrm{M}}e}{k_{\mathbf{B}}T}\psi_l\left(\left|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'\right|\right)\mathrm{d}\vec{\mathrm{r}}'$$

$$\Leftrightarrow -z_{\mathrm{M}}e\psi_{\mathrm{X}}(r) = -\frac{\varepsilon_{\upsilon}z_{\mathrm{M}}z_{\mathrm{X}}e^2}{r} + \sum_l \rho_l \int \frac{\varepsilon_{\upsilon}z_l z_{\mathrm{X}}e^2}{r'}\frac{z_{\mathrm{M}}e}{k_{\mathbf{B}}T}\psi_l\left(\left|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'\right|\right)\mathrm{d}\vec{\mathrm{r}}'$$

Now let us try to guess the solution with a help of charge free radial term f :

$$\psi_l(r) = \varepsilon_{\nu}z_l e f(r) \text{ and } \psi_l\left(\left|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'\right|\right) = \varepsilon_{\nu}z_l e f\left(\left|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'\right|\right) \tag{2.2.58}$$

Substituting these into equation (2.2.58) and simplifying:

$$-f(r) = -\frac{1}{r} + \sum_l \rho_l \frac{\varepsilon_\upsilon \left(z_l e\right)^2}{k_\mathbf{B} T} \int \frac{f\left(\left|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'\right|\right) \mathrm{d}\vec{\mathrm{r}}'}{r'} \tag{2.2.59}$$

Remembering the equation for the Debye-inverse screening length, the equation above becomes:

$$-f(r) = -\frac{1}{r} + \frac{\kappa^2}{4\pi} \int \frac{f\left(\left|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'\right|\right) \mathrm{d}\vec{\mathrm{r}}'}{r'} \tag{2.2.60}$$

The integral can be written as convolution of two functions $f = f(r)$ and $f_o = f_o(r) = \frac{1}{r}$:

$$-f(r) = -\frac{1}{r} + \frac{\kappa^2}{4\pi} \left(f * f_o\right)(r) \tag{2.2.61}$$

Taking three dimensional Fourier transform of (2.2.61), we get:

$$-F(\mathrm{k}) = -F_o(\mathrm{k}) + \frac{\kappa^2}{4\pi} F(\mathrm{k}) F_o(\mathrm{k}) \tag{2.2.62}$$

where k is the inverse space of *r*. Now it is easy to solve $F(\mathrm{k})$:

$$F(\mathrm{k}) = \frac{F_o(\mathrm{k})}{1 + \dfrac{\kappa^2}{4\pi} F_o(\mathrm{k})} \tag{2.2.63}$$

One can do the transforms by integrating; using the following formulae (Hankel transforms), which are Fourier transforms in sphere symmetrical space:

$$\tilde{\mathcal{F}}(\mathrm{k}) = \frac{4\pi}{\mathrm{k}} \int_0^\infty \mathcal{F}(r)\, r \sin(\mathrm{k}r) dr \tag{2.2.64}$$

$$\mathcal{F}(r) = \frac{4\pi}{(2\pi)^3 r} \int_0^\infty \tilde{\mathcal{F}}(\mathrm{k})\, \mathrm{k} \sin(\mathrm{k}r) d\mathrm{k} \tag{2.2.65}$$

Thus using equation (2.2.64) for $f_o = \frac{1}{r} = \mathcal{F}(r)$ yields:

$$\begin{aligned} \tilde{\mathcal{F}}(\mathrm{k}) &= F_o(\mathrm{k}) \\ &= \frac{4\pi}{\mathrm{k}} \int_0^\infty \frac{1}{r} r \sin(\mathrm{k}r) dr \\ &= \frac{4\pi}{\mathrm{k}} \lim_{s \to 0} \int_0^\infty \exp\left[-sr\right] \sin(\mathrm{k}r) dr \end{aligned}$$

where $\exp\left[-sr\right]$ is introduced so that $F_o(\mathrm{k})$ converges when $r \to \infty$, and enabling to calculate the integral with Laplace transform. Taking Laplace transform of the integral gives:

$$F_o(\mathrm{k}) = \frac{4\pi}{\mathrm{k}} \lim_{s \to 0} \left[\frac{\mathrm{k}}{s^2 + \mathrm{k}^2} \right] = \frac{4\pi}{\mathrm{k}^2}$$

Plugging this into (2.2.63) gives:

$$F(\mathrm{k}) = \frac{4\pi}{\mathrm{k}^2 + \kappa^2} \tag{2.2.66}$$

The inverse transform can be calculated plugging (2.2.66) into (2.2.65):

$$
\begin{aligned}
f(r) &= \frac{4\pi}{(2\pi)^3 r}\int_0^\infty \left(\frac{4\pi}{\left[\mathrm{k}^2+\kappa^2\right]}\mathrm{k}\sin\mathrm{k} \right) d\mathrm{k} \\
&= \frac{2}{\pi r}\int_0^\infty \frac{\mathrm{k}\sin\mathrm{k}}{\mathrm{k}^2+\kappa^2} d\mathrm{k} \\
&= \frac{\exp\left[-\kappa r\right]}{r}
\end{aligned}
$$

Thus for the potential

$$\psi_l(r) = \varepsilon_v z_l e \frac{\exp\left[-\kappa r\right]}{r} \tag{2.2.67}$$

and furthermore

$$\psi_i(r) = \frac{z_i e}{4\pi\varepsilon}\frac{\exp\left[-\kappa r\right]}{r} \tag{2.2.68}$$

This is exactly the Debye screened potential in equation (2.1.22) when a^* is zero. The distance of closest approach can be easily introduced into (2.2.68), by multiplying (2.2.68) with a constant, let say *A’* and doing the same rumbling as in chapter 2.1 starting with the charge density integral (2.1.18). Ultimately the final outcome is the same as equation (2.1.22). From this point on thermodynamics would be introduced, which also can be done with statistical mechanics.

This chapter was included to show that there is a concrete background behind Debye–Hückel theory, which stands still in critics. The theory is studied even currently and different derivation methods have been presented. Recently an elegant derivation of Debye–Hückel theory was presented by Xiao and Song (2011), by building a connection between Maxwell’s equations and dispersion relation, which is familiar equation in the field of modern optics. Mathematically the most correct derivation, according to author’s knowledge, is the one presented by Li (2009).

2.3 The Hückel model

The Hückel model is an adaptation of the Debye–Hückel model. It contains one additional term, i.e, $b_1 \frac{m}{m^0}$ where b_1 depends on the electrolyte. Hückel (1925) added this term because he believed that the permittivity of the electrolyte solution is a linear function of the ionic strength. Although this has been proven to be incorrect (Helgeson, Kirkham and Flowers, 1981), the Hückel model is a major improvement to the Debye–Hückel model and it gives good values for activity coefficients even in medium high molalities. This equation can be presented in the form

$$\ln\left(\gamma_{\pm}\right) = -\frac{\left|z_{\mathrm{M}} z_{\mathrm{X}}\right| \alpha \sqrt{I_{\mathrm{m}}}}{1 + \beta a^{*} \sqrt{I_{\mathrm{m}}}} + b_1 \left(\frac{I_{\mathrm{m}}}{m^0}\right) \qquad (2.3.69)$$

The equation was also discovered by Helgeson, Kirkham, and Flowers (1981), but from different reasoning. They started with the Debye–Hückel model (2.1.50) and replaced the Helmholtz free energy used by Debye and Hückel with the one discovered by Born (1920). The Born term in equation (2.3.70) describes the electrostatic interactions contributing to the Helmholtz free energy of ion *i*.

$$\Delta A = \frac{Z_i^{2} e^{2}}{8\pi \varepsilon_0 \varepsilon_r r_i} \qquad (2.3.70)$$

The detailed derivation of the Hückel model using the Debye-Hückel model, and the Born term can be found in the article of Helgeson, Kirkham, and Flowers (1981).

In this work, the thermodynamic properties of aqueous hydrobromic and hydriodic acids were studied. HBr and HI are uni-univalent electrolytes, which means that hydrogen ion has the charge number +1 and bromide and iodide ions have the same charge number, but opposite in sign. Taking this into account and replacing term βa^* with a parameter B that is related to the size of the solvated ions, equation (2.3.69) reduces to:

$$\ln\left(\gamma_\pm\right) = -\frac{\alpha\sqrt{m}}{1+B\sqrt{m}} + b_1\left(\frac{m}{m^0}\right) \tag{2.3.71}$$

This is the final form of the Hückel model used in this study. The parameters B and b_1 proved to be independent of temperature and were obtained using linear regression analysis from galvanic cell data via Nernst equation, see below. Thus the only temperature dependent parameter needed is the Debye–Hückel parameter α.

2.4 The Pitzer model

One of the most often used models for electrolyte solutions is nowadays the Pitzer model (Pitzer, 1973). The model is intended to work over a wide range of electrolytes, temperatures, pressures and over of wide range of molalities by introducing empirically obtainable virial coefficients. In this study, the Pitzer model is used in comparison with the Hückel model. The basic equation of the Pitzer model is the definition of excess Gibbs free energy by means of virial coefficients. This is explained in more details later. Here the activity coefficient equations are first introduced.

For activity coefficient of a uni-univalent electrolyte, the Pitzer equation has the following form (Pitzer, 1973):

$$\ln\left(\gamma_\pm\right) = f^\gamma + B^\gamma\left(m/m^0\right) + \frac{3}{2}C^\phi\left(m/m^0\right)^2 \tag{2.4.72}$$

$$f^\gamma = -\frac{\alpha}{3}\left[\frac{\sqrt{m}}{1+1.2\sqrt{m/m^0}} + \frac{2\sqrt{m^0}}{1.2}\ln\left(1+1.2\sqrt{\frac{m}{m^0}}\right)\right] \tag{2.4.73}$$

$$B^\gamma = 2\beta^0 + \frac{\beta^1 m^0}{2m}\left[1-\exp\left\{-2\sqrt{\frac{m}{m^0}}\right\}\left(1+2\sqrt{\frac{m}{m^0}} - \frac{2m}{m^0}\right)\right] \tag{2.4.74}$$

where f^{γ} is the Debye–Hückel term, see equation (2.1.50). It sometimes mentioned as the Pitzer–Debye–Hückel term and it is general. B^{γ} is a function that depends on the electrolyte. Parameters β^{0}, β^{1} and C^{ϕ} are specific for each electrolyte.

3 PROPERTIES OF REVERSIBLE CELLS

In order to understand the electromotive-force measurements, one must understand the thermodynamics of the galvanic cells without liquid junctions. These electrochemical measurements are widely used and most precise methods but not without problems. For instance the materials of the electrodes have to be of top quality and the solubility of the electrode material into the electrolyte solution has to be taken into account.

3.1 Harned cell

The Harned cell introduced by Harned and Ehlers (1932; 1933) is a cell used very often in high quality studies of hydrochloric acid in aqueous solutions. It is a hydrogen–silver silver chloride cell:

$$^{(-)}\mathrm{H_2,Pt}\left|\mathrm{HCl(aq)}\,|\,\mathrm{AgCl}\right|\mathrm{Ag}^{(+)} \tag{A}$$

where platinum–hydrogen electrode is the anode. The platinum–hydrogen electrode is also called standard hydrogen electrode, when the partial pressure of hydrogen inside the electrode equals to $p^{0} = 101.325\ \mathrm{kPa}$. This condition is most often used in practical studies. The half cell reaction for the standard hydrogen electrode is the following:

$$\frac{1}{2}\mathrm{H_2(g)} \rightarrow \mathrm{H^{+}(aq)} + \mathrm{e^{-}} \tag{3.1.75}$$

The cathode in the Harned cell is the silver–silver chloride electrode for which the half cell reaction can be presented as

$$\mathrm{AgCl(s)} + \mathrm{e}^- \rightarrow \mathrm{Ag(s)} + \mathrm{Cl}^-\mathrm{(aq)} \tag{3.1.76}$$

The full cell reaction is sum of reactions (3.1.75) and (3.1.76) in the way that electrons cancel each other:

$$\frac{1}{2}\mathrm{H}_2\mathrm{(g)} + \mathrm{AgCl(s)} \rightarrow \mathrm{H}^+\mathrm{(aq)} + \mathrm{Ag(s)} + \mathrm{Cl}^-\mathrm{(aq)} \tag{3.1.77}$$

In order to study the electromotive force of the cell, we have to use the Nernst equation:

$$E = E^0 - \frac{RT}{nF}\ln\left[\frac{\prod \text{(molal activities of the products)}}{\prod \text{(molal activities of the reactants)}}\right] \tag{3.1.78}$$

where E^0 is the standard electromotive force and n is the number of cancelled electrons in moles. The molal activity of substance i is $a(i)$. For reaction (3.1.77), the Nernst equation has the form

$$E = E^0 - \frac{RT}{F}\ln\left[\frac{a(\mathrm{H}^+)\,a(\mathrm{Cl}^-)\,a(\mathrm{Ag})}{a(\mathrm{AgCl})\,a(\mathrm{H}_2)^{1/2}}\right] \tag{3.1.79}$$

Taking into account that activity for each pure solid phase is 1 and also changing the notations:

$$a(\mathrm{H}^+) \equiv \gamma_\mathrm{M}\left(m_\mathrm{M} / m^0\right)$$
$$a(\mathrm{Cl}^-) \equiv \gamma_\mathrm{X}\left(m_\mathrm{X} / m^0\right)$$
$$a(\mathrm{H}_2) \equiv \left(p_{\mathrm{H}_2} / p^0\right)^{1/2} = 1 \text{ for standard hydrogen electrode}$$

we get the Nernst equation into the following form:

$$E = E^0 - \frac{RT}{F}\ln\left[\frac{\gamma_{\mathrm{M}}\gamma_{\mathrm{X}}m_{\mathrm{M}}m_{\mathrm{X}}}{\left(m^0\right)^2}\right] \tag{3.1.80}$$

Remembering equation (2.1.46) and noting that $m = m_{\mathrm{M}} = m_{\mathrm{X}}$, the Nernst equation simplifies after some logarithmic operations to the following, final equation:

$$E = E^0 - \frac{2RT}{F}\ln\left[\frac{\gamma_{\pm}m}{m^0}\right] \tag{3.1.81}$$

This equation is valid for galvanic cells used to measure aqueous hydrobromic and hydriodic acids, since both of these electrolytes are uni-univalent, like hydrochloric acid.

3.2 Hydrogen–silver bromide cell

The main cell which is used to study thermodynamics of hydrobromic acid is the hydrogen–silver bromide cell:

$$^{(-)}\mathrm{H_2,Pt}\left|\mathrm{HBr(aq)}\,|\,\mathrm{AgBr}\right|\mathrm{Ag}^{(+)} \tag{B}$$

where the standard hydrogen electrode is the anode and the silver–silver bromide electrode is the cathode. In this study, the electromotive force data obtained for hydrogen–silver bromide cells by Harned, Keston and Donelson (1936); Hetzer, Robinson and Bates (1962); and Macaskill and Bates (1983). Biermann and Yamasaki (1955) stated that the solubility of silver bromide in concentrated hydrobromic acid is significant, and in the three molal solution the equilibrium was achieved not earlier than after three days. Thus their data used in this study are limited to a molality of 2.017 $\mathrm{mol \cdot kg^{-1}}$. The cell reaction is analogous to that presented in chapter 3.1. The silver chloride is only replaced by silver bromide and the chloride ion by bromide ion.

3.3 Hydrogen–silver iodide cell

Hetzer, Robinson, and Bates (1964) studied the thermodynamics of hydrogen – silver iodide cell:

$$^{(-)}\mathrm{H_2,Pt}\left|\mathrm{HI(aq)}\,|\,\mathrm{AgI}\right|\mathrm{Ag}^{(+)} \qquad \text{(C)}$$

where the standard hydrogen electrode is the anode and the silver-silver iodide electrode is the cathode. In these data, it is good note that the absolute value of electromotive force is relatively small through the used temperature range from (0 to 55) ºC. When the hydriodic acid molality is close to 0.06 $\mathrm{mol \cdot kg^{-1}}$, the electromotive force changes from positive to negative, meaning that at this point the solution is not conductive. This is problematic since the value of electromotive force closes to the precision of the measurement. However, this is not commented in the article. According to Hetzer, Robinson and Bates (1964), the solubility of silver iodide into the HI solution was significant when the quantity of this electrolyte was higher than 0.2 $\mathrm{mol \cdot kg^{-1}}$. The data were used for studying the thermodynamic properties of hydriodic acid. Also for this cell the reactions are analogous to those presented in chapter 3.1 for HCl.

3.4 Hydrogen–mercurous bromide cell

Gupta, Hills, and Ives (1962) studied the thermodynamic properties of HBr solutions by measuring the electromotive forces of hydrogen–mercurous bromide cell:

$$^{(-)}\mathrm{H_2,Pt}\left|\mathrm{HBr(aq)}\,|\,\mathrm{Hg_2Br_2}\right|\mathrm{Hg}^{(+)} \qquad \text{(D)}$$

where the standard hydrogen electrode is the anode and the mercury–mercurous bromide electrode is the cathode. The half cell reaction for the anode is same as in the cells mentioned above, but that the half cell reaction for cathode differs and has the form

$$\frac{1}{2}\mathrm{Hg_2Br_2(s)} + \mathrm{e^-} \rightarrow \mathrm{Hg(s)} + \mathrm{Br^-(aq)} \qquad (3.4.82)$$

However, the full cell reaction gives the same Nernst equation as that presented in (3.1.81), since the activity of $\mathrm{Hg_2Br_2(s)}$ is 1. One of the characteristics of this cell is short operational range. According to Gupta, Hills and Ives (1962) mercury in the mercurous form takes part in anionic complexes with bromide ions. This was problematic and has disturbed the electromotive-force measurements. The short operational range of this cell is due to the fact that if hydrobromic acid concentration is increased, there will be more bromide anions in the form of complex anions. This group stated that 0.2 $\mathrm{mol \cdot kg^{-1}}$ is the upper limit for the HBr molality. Measurements in higher molalities would not be reliable. The data were used for studying the thermodynamic properties of aqueous hydrobromic acid.

4 REGRESSION ANALYSIS WITH THE GALVANIC CELL DATA

In order to perform linear regression with the cell data, the equation for the mean activity coefficient has to be introduced into the Nernst equation. The procedure used in this study is the same as that presented by Partanen and Covington (2002a; b) and by Partanen, Juusola, Vahteristo and de Mendonça (2007) for hydrochloric acid. Substituting the Hückel equation (2.3.71) into equation (3.1.81) gives

$$E = E^0 - \frac{2RT}{F}\left(\left[-\frac{\alpha\sqrt{m}}{1+B\sqrt{m}} + b_1\left(\frac{m}{m^0}\right)\right] + \ln\left[\frac{m}{m^0}\right]\right) \qquad (4.83)$$

Rearranging terms we get:

$$E^0 - \frac{2RT}{F} b_1 \left(\frac{m}{m^0} \right) = E + \frac{2RT}{F} \left(\ln\left[\frac{m}{m^0} \right] - \frac{\alpha\sqrt{m}}{1+B\sqrt{m}} \right) \tag{4.84}$$

Generally, it is known that the parameter B is often lying between 1.2 and $1.7\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}$. Let the left-hand side of equation (4.84) to be defined as quantity y as follows:

$$y = E + \frac{2RT}{F} \left(\ln\left[\frac{m}{m^0} \right] - \frac{\alpha\sqrt{m}}{1+B\sqrt{m}} \right) \tag{4.85}$$

where α is the parameter depending on temperature. Listed values of α at various temperatures are presented in Appendix IV. Linear regression of y with a fixed value of B against the molality of the electrolyte enables us to calculate the error of each experimental point. From these values, the standard error for the set under consideration can be obtained and it is denoted as $S(y)$. Parameter B was chosen so that $S(y)$ is minimized, and also some aspects associated with the actual sizes of cation M and anion X of the electrolyte were taken into account in this choosing (Bates and Bower, 1954). The values of parameter B seems to be reasonable to report with two significant digits.

4.1 Aqueous hydrobromic acid

The method mentioned in the previous chapter is first applied to aqueous hydrobromic acid data. For these data the lowest standard error 0.148 mV was obtained with B value 1.5 $\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}$ from the data of Macaskill and Bates (1983) at 25 ºC. The B values and corresponding standard errors used in determination are presented in Table 1.

Table 1. Values of parameter *B* and the corresponding standard error *S*(*y*) obtained from the data measured by Macaskill and Bates (1983) on cell (B) for aqueous hydrobromic acid at 25 ºC.

$B\left[\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}\right]$	$S(y)$ [mV]
1.2	0. 582
1.3	0. 360
1.4	0. 173
1.5	0. 148
1.6	0. 301
1.7	0. 473

The values presented in Table 1 are also plotted in Figure 2.

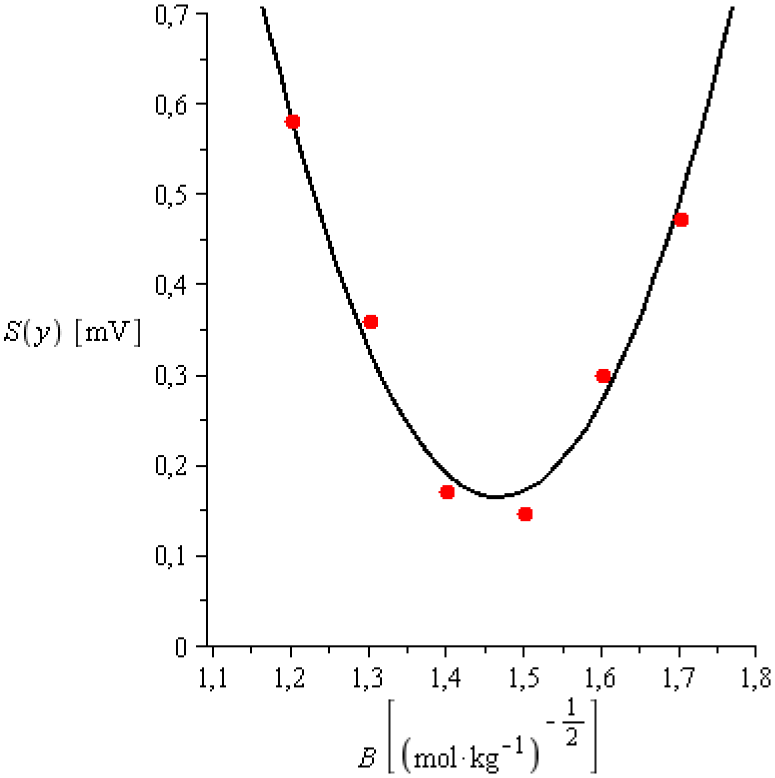

Figure 2. The standard error *S*(*y*) as a function of *B* (red dots) obtained from data of Macaskill and Bates (1983) on cell (B) for aqueous hydrobromic acid at 25 ºC. It can be seen that *B* value 1.5 $\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}$ gives the lowest value for standard error. The drawn parabola describes how the calculated points are situated on *B*,*S*(*y*) plane.

From equations (4.84) and (4.85), it can obtained the following for a straight line

$$y \equiv E^0 - \frac{2RT}{F} b_1 \left(\frac{m}{m^0} \right) \tag{4.1.86}$$

From the performed linear regression data, the value of parameter b_1 is given by equation

$$b_1 = \left(-\frac{F}{2RT} \right) \cdot \text{slope} \tag{4.1.87}$$

The standard error of parameter b_1 is

$$S\left(b_1\right) = \left(\frac{F}{2RT} \right) \cdot S\left(\text{slope}\right) \tag{4.1.88}$$

From equations (4.1.87) and (4.1.88), it was determined from data of Macaskill and Bates (1983) at 25 ºC that $b_1 = 0.348 \pm 0.002$. Preliminary calculations revealed that these parameter values apply to all HBr data. To show this, the E^0 values for each data set must be determined to be the best values. The standard electrode potential E^0 by linear optimization using equation (4.83) and setting the sum of all errors of cell equal to zero, i.e.

$$\sum \underbrace{\left[E_{\text{measured}} - E_{\text{calculated}} \right]}_{\text{cell potential error } \Delta E} = 0 \tag{4.1.89}$$

where the sum goes through all data points, $E_{\text{calculated}}$ is the right-hand side of (4.83), and the cell potential error is denoted as ΔE. Using parameters $B = 1.5\left(\text{mol} \cdot \text{kg}^{-1}\right)^{-1/2}$ and $b_1 = 0.384$ the cell potential errors ΔE were determined from the data of Gupta, Hills, and Ives (1963), Harned, Keston, and Donelson (1936), Hetzer, Robinson, and Bates (1962), and Macaskill and Bates (1983), and these errors are presented in Figures 3–6, respectively.

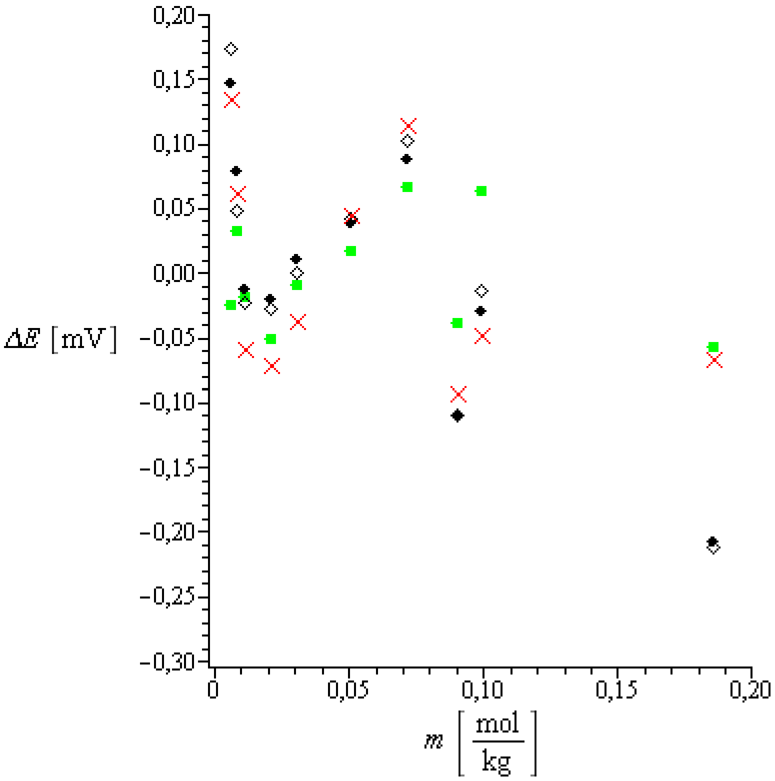

Figure 3. The cell potential errors in millivolts as a function of the molality for aqueous hydrobromic acid at temperatures (5 to 20) ºC from the data of Gupta, Hills and Ives (1963). Green solid circle, 5 ºC; diamond, 10 ºC; solid diamond, 15 ºC; red diagonal cross, 20 ºC. It can be seen that the absolute potential errors are lower than 0.25 mV and that there are no trends.

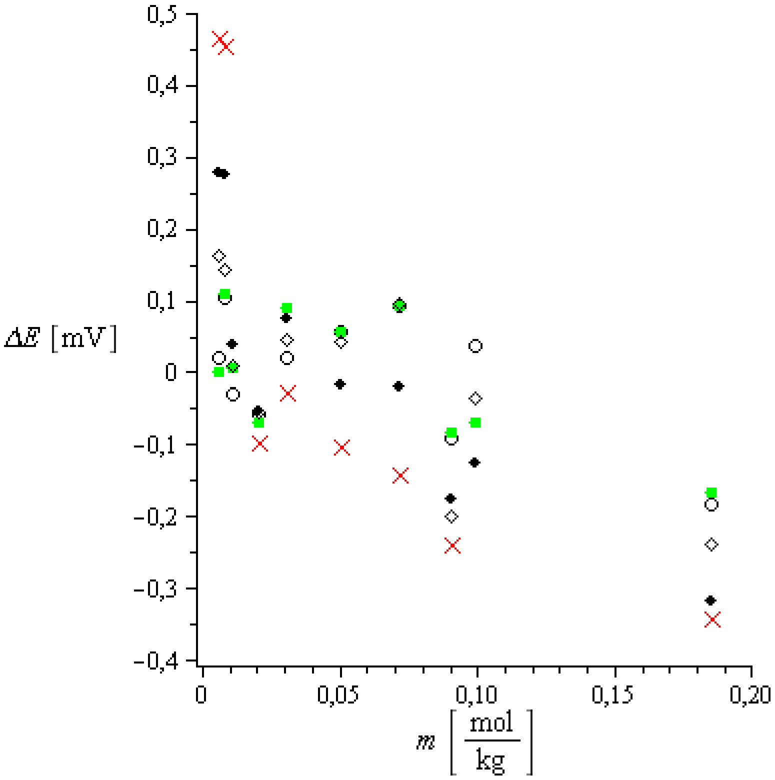

Figure 4. The cell pontential errors in millivolts calculated as a function of molality for aqueous hydrobromic acid at temperatures (25 to 45) ºC from the data of Gupta, Hills and Ives (1963). Circle, 25 ºC; green solid circle, 30 ºC; diamond, 35 ºC; solid diamond, 40 ºC; red diagonal cross, 45 ºC. It can be seen that the absolute potential errors are lower than 0.5 mV and that there are no trends.

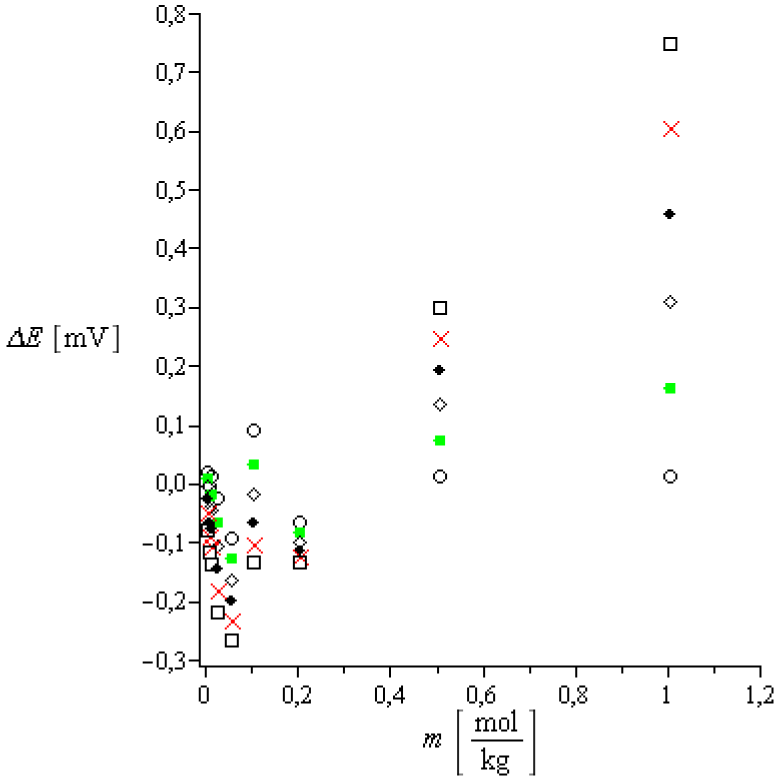

Figure 5. The cell potential errors in millivolts calculated as a function of molality for aqueous hydrobromic acid at temperatures (0 to 25) °C from the data of Harned, Keston and Donelson (1936). Circle, 0 °C; green solid circle, 5 °C; diamond, 10 °C; solid diamond, 15 °C; red diagonal cross, 20 °C; box, 25 °C. It is noticeable that there are trends in all temperatures on molality range [0.5, 1.0] $\mathrm{mol \cdot kg^{-1}}$. Also the cell potential error exceeds 0.5 mV at temperatures 20 and 25 °C at molality 1 $\mathrm{mol \cdot kg^{-1}}$. These results suggest that the data of Harned, Keston and Donelson (1936) are described only up to 0.5 $\mathrm{mol \cdot kg^{-1}}$ with the chosen parameters for the Hückel equation.

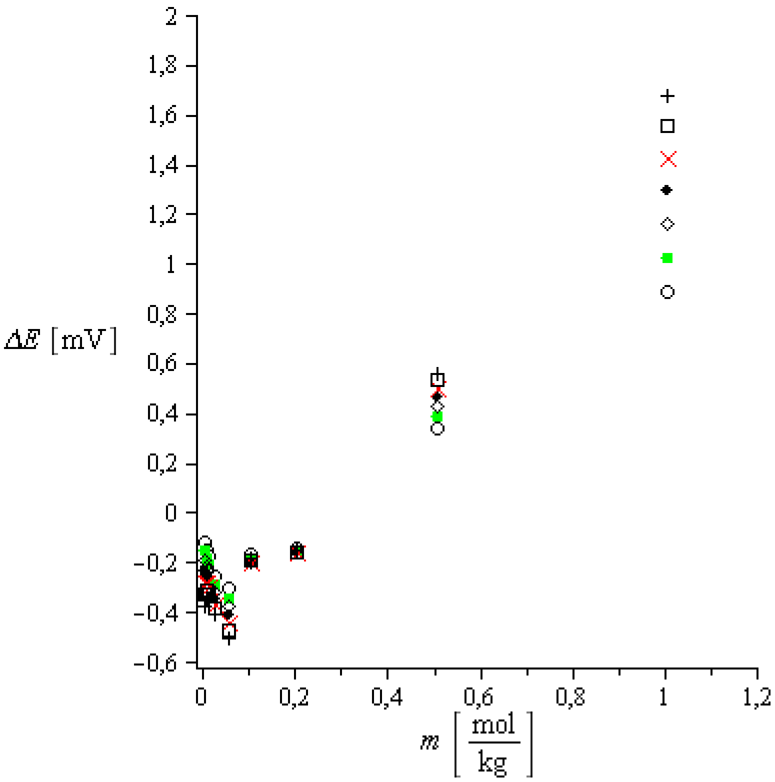

Figure 6. The cell potential differences in millivolts calculated as a function of molality for aqueous hydrobromic acid at temperatures (30 to 60) ºC from the data of Harned, Keston and Donelson (1936). Circle, 30 ºC; green solid circle, 35 ºC; diamond, 40 ºC; solid diamond, 45 ºC; red diagonal cross, 50 ºC; box, 55 ºC; cross, 60 ºC. Again trends are noticeable at all temperatures in the molality range $[0.5,\ 1.0]\ \mathrm{mol \cdot kg^{-1}}$. The cell potential error exceeds 0.75 mV at all temperatures at the molality $1\ \mathrm{mol \cdot kg^{-1}}$. In the same way as in Figure 5, the results obtained here suggest that with the chosen parameters the Hückel equation describes the data of Harned, Keston and Donelson (1936) only up to $0.5\ \mathrm{mol \cdot kg^{-1}}$. This can result from systematic measurement error in the data of Harned, Keston and Donelson (1936) between molalities 0.5 and $1\ \mathrm{mol \cdot kg^{-1}}$. Thus, in further studies above $0.5\ \mathrm{mol \cdot kg^{-1}}$ it is necessary to determine the upper limit of the new model.

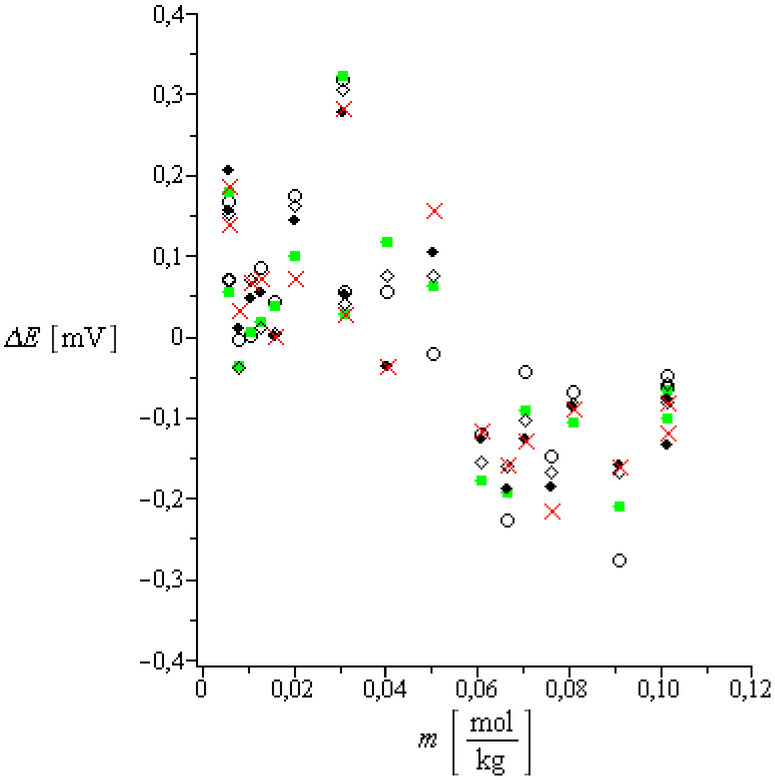

Figure 7. The cell potential errors in millivolts calculated as a function of molality for aqueous hydrobromic acid at temperatures (0 to 20) ºC from the data of Hetzer, Robinson and Bates (1963). Circle, 0 ºC; green solid circle, 5 ºC; diamond, 10 ºC; solid diamond, 15 ºC, red diagonal cross, 20 ºC. No trends are observed and absolute values of cell potential errors are below 0.35 mV.

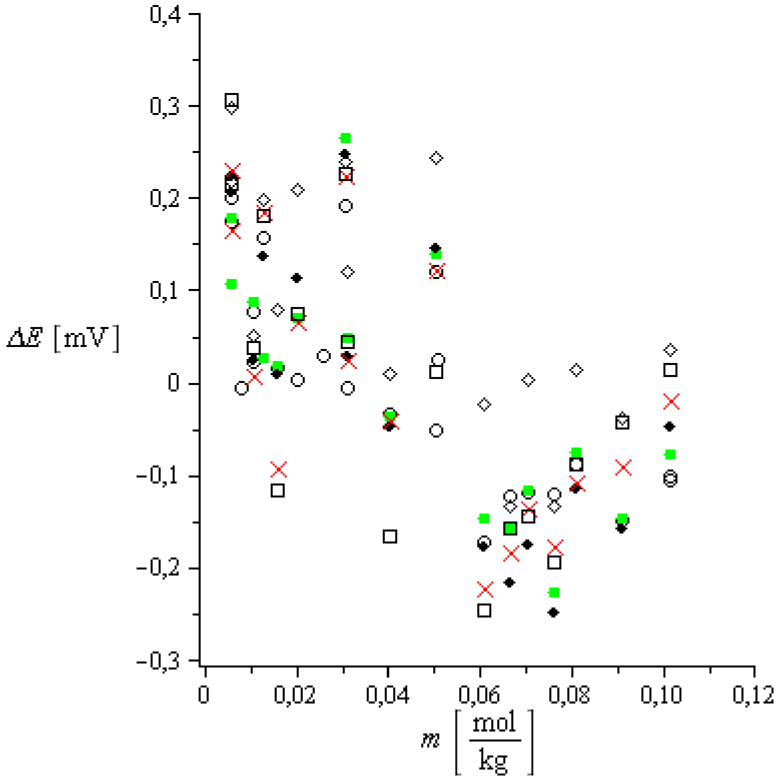

Figure 8. The cell potential errors in millivolts calculated as a function of molality for aqueous hydrobromic acid at temperatures (25 to 50) ºC from the data of Hetzer, Robinson and Bates (1963). Circle, 25 ºC; green solid circle, 30 ºC; diamond, 35 ºC; solid diamond, 40 ºC; red diagonal cross, 45 ºC; box, 50 ºC. No trends are observed and absolute values of cell potential errors are below 0.35 mV.

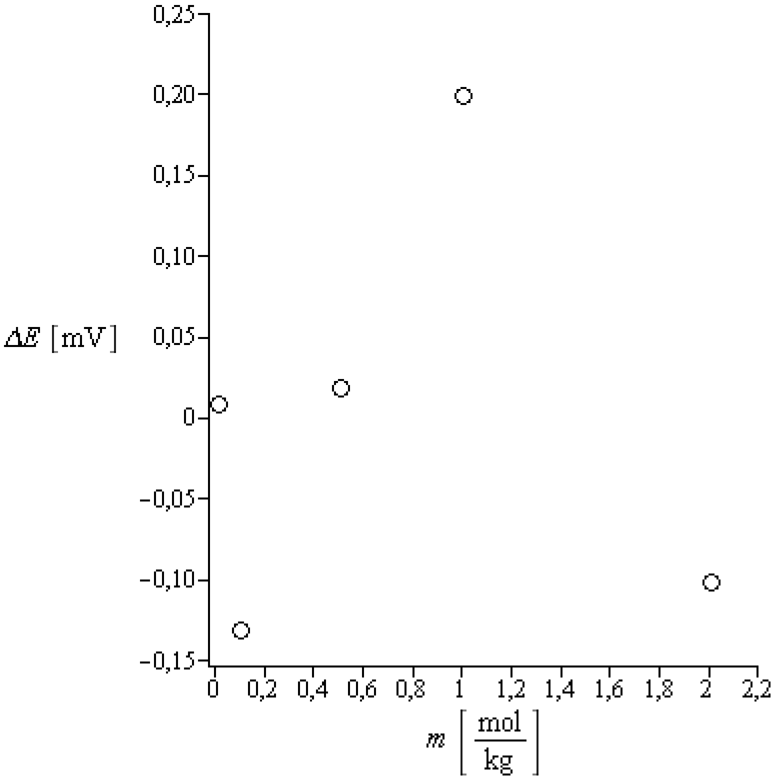

Figure 9. The cell potential differences in millivolts calculated as a function of molality for aqueous hydrobromic acid at temperature 25 ºC from data Macaskill and Bates (1983). Absolute values of cell potential differences are below 0.20 mV.

4.2 Aqueous hydriodic acid

The same procedure as that used above for the data of aqueous hydrobromic acid was done to the data of aqueous hydriodic acid. For hydriodic acid at 35 ºC, the standard error of 0.0494mV was obtained with *B* value $1.6\left(\text{mol}\cdot\text{kg}^{-1}\right)^{-1/2}$ from data of Hetzer, Robinson and Bates (1964). However, the *B* value of $1.5\left(\text{mol}\cdot\text{kg}^{-1}\right)^{-1/2}$ gave a smaller standard error of 0.0488 mV. The former value was chosen because parameter *B* is associated with the size of ions in aqueous solutions (it is related to the distance of closest approach a^*, see above) and the Shannon effective radius of iodide ion is larger than bromide ion. These radii are 2.2 Å and 1.96 Å, respectively (Shannon, 1976). Thus, the a^* for iodide ion can be assumed to be bigger and therefore larger *B* was chosen. However, it is important that the Shannon effective radii for ions have been determined using xray crystallography from solid materials. Thus they are not equal to the radii of dissolved ions in water. The *B* value 1.6 $\left(\mathrm{mol \cdot kg^{-1}}\right)^{-1/2}$ is also strongly supported analysis made at temperature 40 ºC, with smaller standard error (0.0709 mV) than that of *B* value 1.5 $\left(\mathrm{mol \cdot kg^{-1}}\right)^{-1/2}$ (0.0762 mV). Since there was 26 data points at temperature 40 ºC (18 points at 35 ºC), and the molality range goes up to 1 $\mathrm{mol \cdot kg^{-1}}$ (only up to 0.15 $\mathrm{mol \cdot kg^{-1}}$ at 35 ºC), the results obtained at temperature 40 ºC are emphasized. Different *B* values and corresponding standard errors are resented in Table 2.

Table 2. Values of parameter *B* and the corresponding standard error *S*(*y*) obtained from the data of Hetzer, Robinson and Bates (1964) on cell (C) for hydriodic acid at 35 ºC and at 40 ºC.

$B\left[\left(\mathrm{mol \cdot kg^{-1}}\right)^{-1/2}\right]$	*S*(*y*) [mV] at 35 ºC	*S*(*y*) [mV] at 40 ºC
1.2	0.0591	0.2545
1.3	0.0539	0.1856
1.4	0.0503	0.1234
1.5	0.0488	0.0762
1.6	0.0494	0.0709
1.7	0.0520	0.1087

The values presented in Table 2 are also plotted in Figure 10.

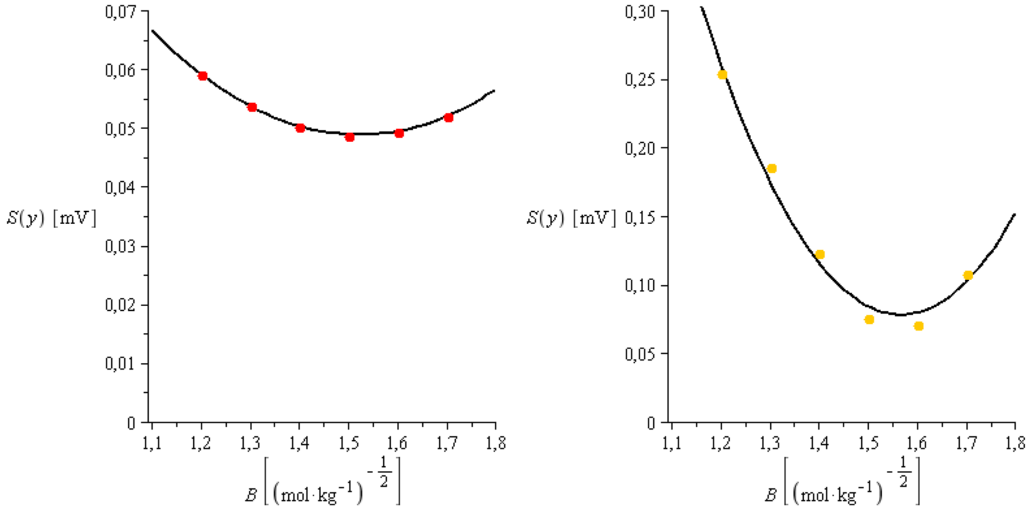

Figure 10. The standard error *S*(*y*) plotted as a function of *B* (red dots) obtained from data of Hetzer, Robinson and Bates (1964) for aqueous hydriodic acid at 35 ºC on the left and those obtained at 40 ºC (orange dots) on the right. It can be seen that *B* value 1.5 gives the lowest value for standard error at temperature 35 ºC, but not at 40 ºC. As mentioned above, *B* value 1.6 was chosen, since iodide is known to be larger than bromide from crystallographic data of solids (Shannon, 1976), and because at 40 ºC value 1.6 $\left(\mathrm{mol\cdot kg^{-1}}\right)^{-1/2}$ works better. The drawn parabolas describe how the calculated points are situated on *B*,*S*(*y*) planes.

For parameter b_1 three good candidates were obtained: $b_1(1) = 0.3897 \pm 0.0013$, $b_1(2) = 0.3886 \pm 0.0014$ and $b_1(3) = 0.3919 \pm 0.0009$ at temperatures 10, 25 and 40 ºC, respectively (Hetzer, Robinson and Bates, 1964). Only these three data sets contain points up to $1\,\mathrm{mol\cdot kg^{-1}}$. Thus the mean value with corresponding error was chosen to be the best candidate. The result is $b_1 = 0.390 \pm 0.0010$.

Using the determined parameter $B = 1.6\left(\mathrm{mol\cdot kg^{-1}}\right)^{-1/2}$ and $b_1 = 0.390$, the cell potential error ΔE and the standard electrode potential E^0 were determined from data of Hetzer, Robinson and Bates (1964) as above for the HBr data.

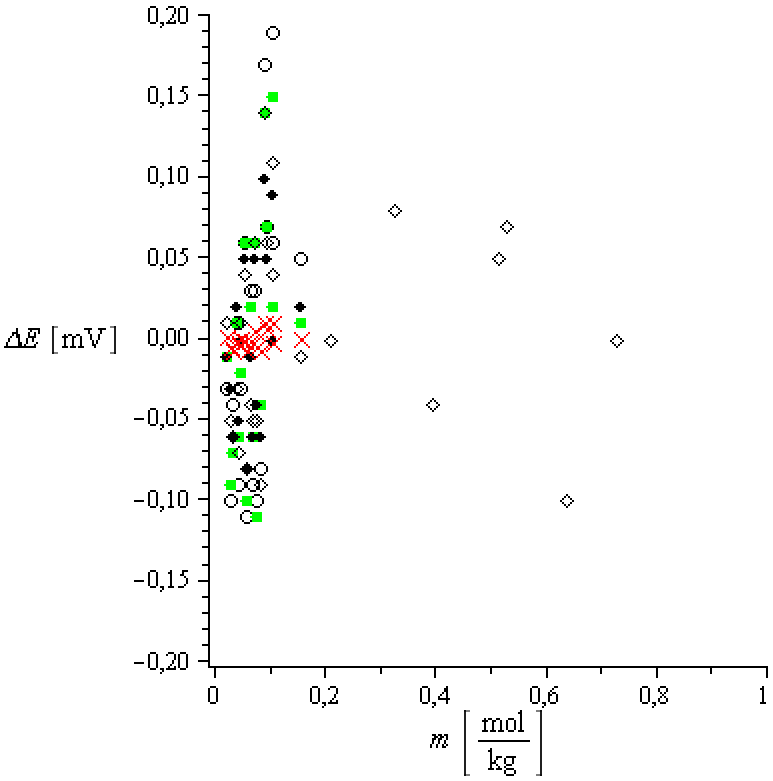

Figure 11. The cell potential errors in millivolts calculated as a function of molality for aqueous hydriodic acid at temperatures (0 to 20) ºC from data of Hetzer, Robinson and Bates (1964). Circle, 0 ºC; green solid circle, 5 ºC; diamond, 10 ºC; solid diamond, 15 ºC; red diagonal cross, 20 ºC. It can be seen that the absolute potential errors are lower than 0.2 mV and that there are no trends.

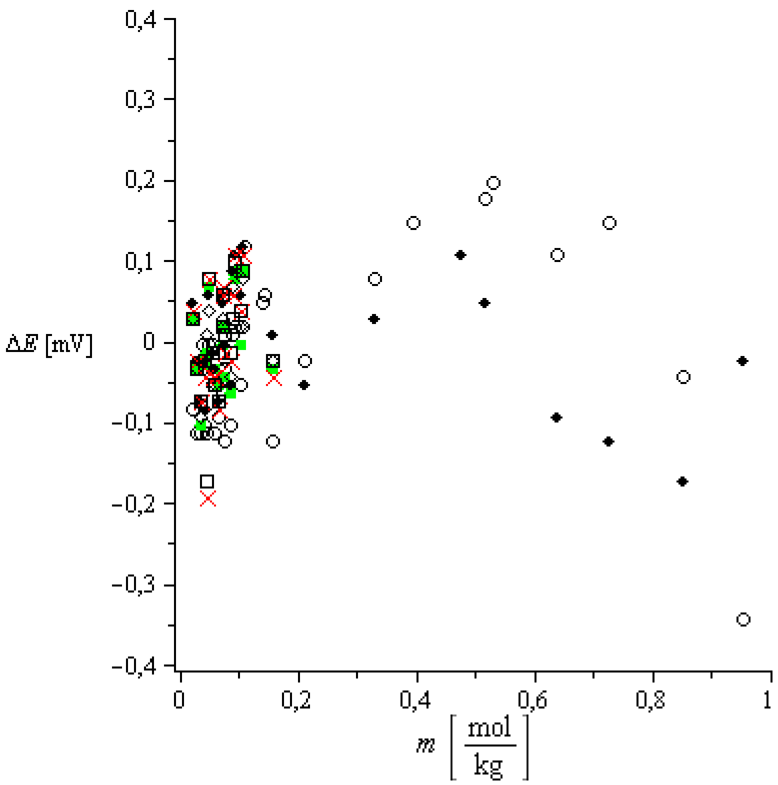

Figure 12. The cell potential errors in millivolts calculated as a function of molality for aqueous hydriodic acid at temperatures (25 to 50) ºC from data of Hetzer, Robinson and Bates (1964). Circle, 25 ºC; green solid circle, 30 ºC; diamond, 35 ºC; solid diamond, 40 ºC; red diagonal cross, 45 ºC; box, 50 ºC. It can be seen that the absolute potential errors are lower than 0.2 mV except at point (0.9507 $\mathrm{mol \cdot kg^{-1}}$, -0.340 mV). No trends are observed. The results here together with the results in Figure 11 suggest that the Hückel model for aqueous hydriodic acid works very well at least up to 0.5 $\mathrm{mol \cdot kg^{-1}}$ at all temperatures studied.

5 ISOPIESTIC MEASUREMENTS

The isopiestic measurement for solvent activity was introduced by Bousfield in 1918 and since has been widely used. In the method, the sample is brought to thermodynamic equilibrium (isopiestic means equal pressures) in vapour phase with a reference solution of known water activity. This means that the water activity will be the same for the sample and reference solutions. The known amount of the tested salt and the reference salt (usually sodium or potassium chloride) are put in separate dishes, which are placed in a container, usually a desiccator. The method allows studying several samples of different salts at the same time and thus the container is usually fully loaded. Then water is added to each dish and the container is closed. The dishes are made of material with high thermal conductivity as silver. If the electrolyte is extremely corroding like hydriodic acid, platinum is used (Harned and Robinson, 1941). Underneath the dishes there is a block of metal also with high thermal conductivity, usually of copper or silver. The isopiestic condition is achieved since the water will distill from solutions with higher water activity and condense in solutions with lower water activity. The measurement may take even weeks in very dilute solutions. After the equilibrium is achieved, the amount of water is determined from each dish.

The isopiestic measurement does not work well at molalities lower than 0.1 $\mathrm{mol \cdot kg^{-1}}$ since the water activity in dilute solutions is close to unity. This also means that the time to achieve the equilibrium is increased in dilute solutions. Another disadvantage is that the water activity in the sample solution is determined relative to the water activity of the reference solution, which has to be determined with great precision using direct vapor pressure or electrochemical measurements.

Properties of the salt under consideration have to be taken into account. For instance, if the substance is highly volatile, it will distill off instead of the water. For example, the vapor pressure of HCl in aqueous solution at 25 ºC and at a molality of $6\,\mathrm{mol \cdot kg^{-1}}$ is 0.140 mmHg (Bates and Kirschmann, 1919). This kind of magnitude in the vapor pressure would lead to unreliable results, since the substance is participating in the vapour pressure. In the article of Bates and Kirschmann ar given that the vapor pressure values of HBr(aq) and HI(aq) in the same conditions are 0.00151 mmHg and 0.00057 mmHg, respectively. Thus, the isopiestic method can be used for these solutions. The isopiestic data obtained by Harned and Robinson (1941) was used here for hydriodic acid and those by Macaskill and Bates (1983) for hydrobromic acid.

6 OSMOTIC COEFFICIENTS

6.1 The Hückel equation for Osmotic Coefficients

In order to study isopiestic data and relate it to cell data, the relationship between the mean activity coefficient $\gamma_{\pm}$ and osmotic coefficient ϕ, which is defined in terms of the solvent (water) activity, has to be derived. The idea is to obtain the necessary parameter values B and b_1 for the Hückel model from the cell data and then using the Hückel model with the same parameters for predicting osmotic coefficients and vapor pressures and then comparing the latter values to those obtained from isopiestic data.

The definition of osmotic coefficient was formulated by Bjerrum (1918) and later a more practical definition for the osmotic coefficient suggested by Guggenheim (1935) has been often accepted in the literature. In the present study where water is solvent, the following definition is used:

$$\phi = \frac{-\ln\left(a_{\mathrm{w}}\right)}{M_{\mathrm{w}} v m} \tag{6.1.90}$$

where $a_{\mathrm{w}} = x_{\mathrm{w}}\gamma_{\mathrm{w}}$ is activity of water, and it is the product of mole fraction of water x_{w} and the activity coefficient of water γ_{w}. M_{w} is the molar mass of water, $v = v_{\mathrm{M}} + v_{\mathrm{X}}$, and m is the molality of the electrolyte. Equation (6.1.90) can be used in Gibbs–Duhem equation:

$$\sum_i n_i \, d\mu_i = 0 \tag{6.1.91}$$

where n_i is the amount of substance *i* in solution and $d\mu_i$ is the differential of chemical potential of species *i*. This equation is valid at the constant temperature and pressure. For water containing only a single electrolyte this equation becomes:

$$n_{\mathrm{w}}\, d\mu_{\mathrm{w}} + n_{\mathrm{s}}\, d\mu_{\mathrm{s}} = 0 \qquad (6.1.92)$$

Now writing the chemical potentials in full extension yields:

$$n_{\mathrm{w}} d\left[\mu_{\mathrm{w}}^{0} + RT\ln(a_{\mathrm{w}})\right] + n_{\mathrm{s}} d\left[\mu_{\mathrm{s}}^{0} + vRT\ln\left(m_{\pm}\gamma_{\pm}\right)\right] = 0 \qquad (6.1.93)$$

Since the standard state chemical potentials are constant and the mean molality is defined by $m_{\pm} \equiv \left(m_{\mathrm{M}}^{v_{\mathrm{M}}} m_{\mathrm{X}}^{v_{\mathrm{X}}}\right)^{1/v} \equiv m_{\mathrm{s}}\left(v_{\mathrm{M}}^{v_{\mathrm{M}}} v_{\mathrm{X}}^{v_{\mathrm{X}}}\right)^{1/v}$, equation (6.1.93) after some simplifications gives:

$$d\left[-\phi M_{\mathrm{w}} v m_{\mathrm{s}}\right] + M_{\mathrm{w}} v m_{\mathrm{s}} d\left[\ln\left(m_{\mathrm{s}}\gamma_{\pm}\right)\right] = 0 \qquad (6.1.94)$$

Evaluation of the integrals in the integral form of equation (6.1.94) yields:

$$-\phi M_{\mathrm{w}} v m_{\mathrm{s}} + M_{\mathrm{w}} v m_{\mathrm{s}} + M_{\mathrm{w}} v \int m_{\mathrm{s}} d\ln\left(\gamma_{\pm}\right) = 0 \qquad (6.1.95)$$

After some simplifications and setting the integral limits to be 0 and m, replacing m_{s} by m, and taking the mean activity coefficient as expressed in equation (2.3.52), we get:

$$\phi = 1 + \frac{1}{m}\int_{0}^{m} m d\ln\left(-\frac{\alpha\sqrt{m}}{1+B\sqrt{m}} + b_{1}\left(\frac{m}{m^{0}}\right)\right) \qquad (6.1.96)$$

The integral can be computed by change of variable and then using the method of partial fractions. Ultimately the final outcome is

$$\phi = 1 - \frac{\alpha}{B^{3}m}\left[\left(1+B\sqrt{m}\right) - \ln\left(1+B\sqrt{m}\right)^{2} - \frac{1}{1+B\sqrt{m}}\right] + \frac{b_{1}m}{2m^{0}} \qquad (6.1.97)$$

6.2 The Pitzer equation for Osmotic Coefficients

The Pitzer (1973) model for activity coefficients was introduced in Chapter 2.4. Now the equation for the osmotic coefficients is derived. As earlier, the molality scale is used for the solute. First the general expression for Gibbs free energy is given in an ideal solution where all activity coefficients are unity:

$$G^{\mathrm{ideal}} = \underbrace{n_{\mathrm{w}}\left(\mu_{\mathrm{w}}^{0} + RT\ln x_{\mathrm{w}}\right)}_{\mathrm{water}} + \underbrace{n_{\mathrm{s}}\sum v_i\left(\mu_i^0 + RT\ln m_i\right)}_{\mathrm{ions}} \qquad (6.2.98)$$

The osmotic coefficient of water in an ideal solution is unity (as also the activity coefficient of water). This result substituted in the definition presented in equation (6.1.90) and plugging the outcome in equation (6.2.98) leads to:

$$G^{\mathrm{ideal}} = n_{\mathrm{w}}\left(\mu_{\mathrm{w}}^{0} - RTM_{\mathrm{w}}vm_{\mathrm{s}}\right) + n_{\mathrm{s}}\sum v_i\left(\mu_i^0 + RT\ln m_i\right) \qquad (6.2.99)$$

Gibbs free energy in a non-ideal solution is the following:

$$G = \underbrace{n_{\mathrm{w}}\left(\mu_{\mathrm{w}}^{0} + RT\ln\left(a_{\mathrm{w}}\right)\right)}_{\mathrm{water}} + \underbrace{n_{\mathrm{s}}\sum v_i\left(\mu_i^0 + RT\ln\left(m_i\gamma_i\right)\right)}_{\mathrm{ions}} \qquad (6.2.100)$$

Next the water activity is replaced with the one in the definition of osmotic coefficient (6.1.90):

$$G = n_{\mathrm{w}}\left(\mu_{\mathrm{w}}^{0} - RT\phi M_{\mathrm{w}}vm_{\mathrm{s}}\right) + n_{\mathrm{s}}\sum v_i\left(\mu_i^0 + RT\ln\left(m_i\gamma_i\right)\right) \qquad (6.2.101)$$

Thus the famous equation for excess Gibbs free energy can be created just by subtracting the ideal Gibbs free energy from non-ideal Gibbs free energy:

$$G^{\mathrm{excess}} = RTn_{\mathrm{s}}\sum v_i\left(1 - \phi + \ln\left(\gamma_i\right)\right) \qquad (6.2.102)$$

This was a short introductory to the background of Pitzer model for osmotic coefficients, and complete derivation is given in the original papers (Pitzer, 1973; Pitzer and Mayorga, 1973). The equation has the form

$$\phi = 1 - \frac{\alpha}{3} \frac{\sqrt{m}}{1 + 1.2\sqrt{m/m^0}} + \left(\beta^0 + \beta^1 e(m)\right)\left(\frac{m}{m^0}\right) + C^\phi \left(\frac{m}{m^0}\right)^2 \quad (6.2.103)$$

where $e(m) \equiv \exp\left[-2\sqrt{m/m^0}\right]$ and β^0, β^1, and C^ϕ are electrolyte specific parameters as above.

7 PREDICTING THE VAPOR PRESSURE OF WATER

Using the parameters B and b_1 obtained from the cell data, the Hückel model (6.1.97) is used to predict the vapor pressures for the isopiestic data of HBr(aq) and HI(aq). From equation (6.1.90), we see:

$$\ln\left(a_{\mathrm{w}}\right) = -M_{\mathrm{w}} v m \phi \quad (7.104)$$

Using $a_{\mathrm{w}} = \frac{p}{p^*}$, where p is the vapor pressure water over the reference electrolyte solution and p^* is the vapor pressure that of pure water (at 25ºC , it is 23.766 mmHg), and using the fact that the electrolytes are here uni-univalent, we obtain:

$$\ln\left(\frac{p}{p^*}\right) = -2M_{\mathrm{w}} m_{\mathrm{s}} \phi \quad (7.105)$$

Getting rid of the natural logarithm gives

$$p = p^* \exp\left[-2M_{\mathrm{w}} m_{\mathrm{s}} \phi\right] \quad (7.106)$$

Then we compare the predicted pressures of HBr and HI solutions to those obtained from isopiestic measurements using the Pitzer equation (6.2.103) for the reference electrolyte. Thus the following deviation quantity is calculated:

$$\Delta p = p_{\mathrm{Pitzer}}^{\mathrm{ref}} - p_{\mathrm{predicted}} \tag{7.107}$$

where $p_{\mathrm{predicted}}$ is the vapor pressure of water above the tested electrolyte solutions given by equation (7.106). Since both solutions are in isopiestic equilibrium, the vapor pressure of water over reference solutions and over the tested electrolyte solution must be equal. So for a good osmotic coefficient model, Δp should be as close to zero as possible.

For aqueous hydrobromic acid, the data of Macaskill and Bates (1983) up to 1.0 $\mathrm{mol \cdot kg^{-1}}$ were used to calculate vapor pressure over the reference solutions (NaCl) using Pitzer model in equation (6.2.103). Calculated vapor pressures of water over the reference electrolyte solutions were compared to those predicted by the Hückel model (6.1.97) and the Pitzer model (6.2.103) for tested HBr solutions. The results are presented in Figure 13.

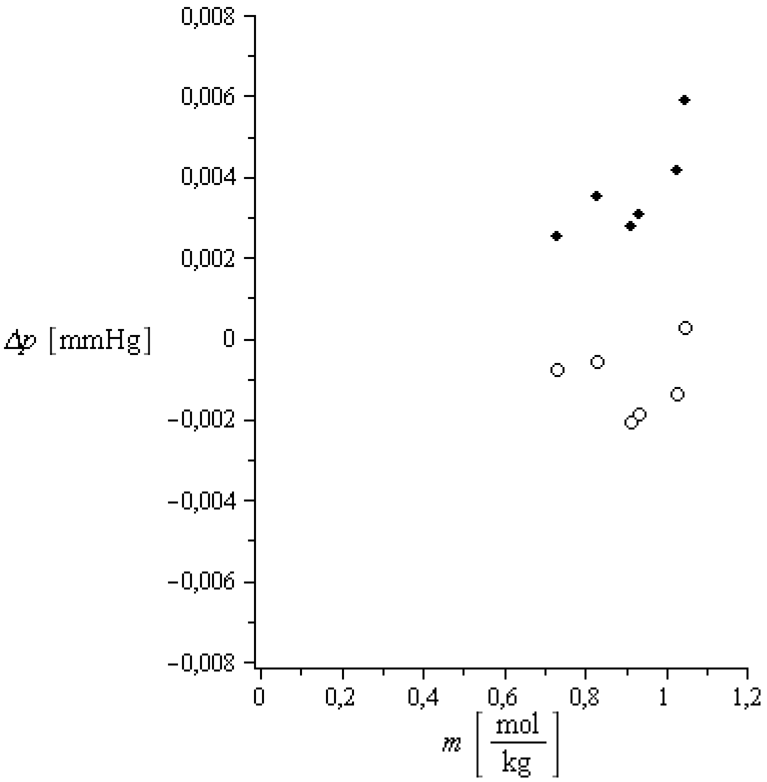

Figure 13. The difference between measured and predicted vapor pressures of water as a function of the molality of hydrobromic acid at 25 ºC. The vapor pressures over the reference solution (NaCl) have calculated from the isopiestic data of Macaskill and Bates (1983) using the Pitzer model. Solid diamonds, Δp values for the Hückel model; circles, delta Δp values for the Pitzer model. It can be seen in the case of Hückel model that vapor pressure differences are all positive, while they are all negative for the Pitzer model, except for one point.

For aqueous hydriodic acid the data of Harned and Robinson (1941) up to 1.0 $\mathrm{mol \cdot kg^{-1}}$ were used to calculate vapor pressure over the reference solutions (KCl) using Pitzer model in equation (6.2.103). Calculated vapor pressures of water over the reference electrolyte solutions were compared to those predicted by the Hückel model (6.1.97) and the Pitzer model (6.2.103) for tested HI solutions. The results are presented in Figure 14.

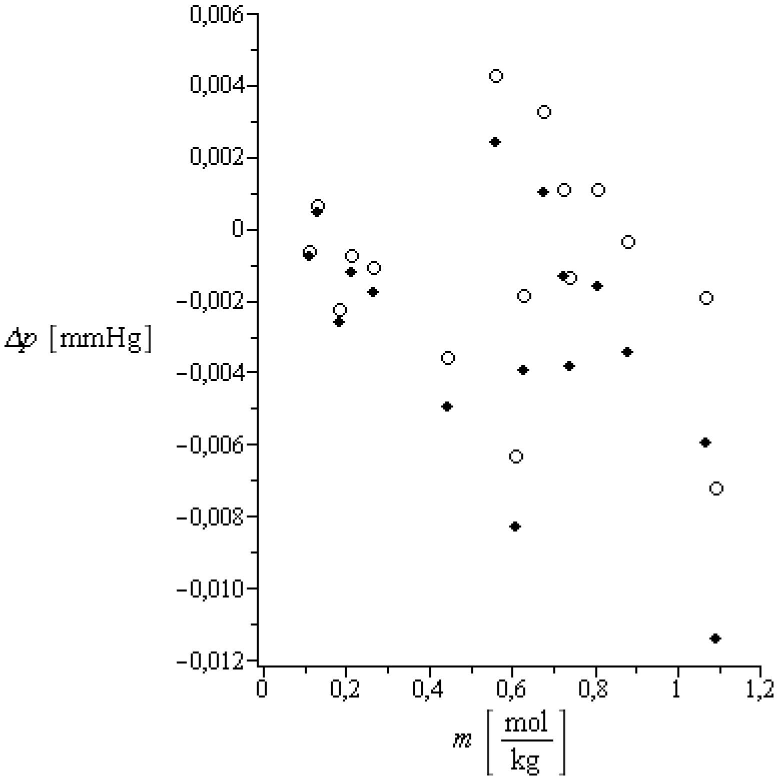

Figure 14. The difference between measured and predicted vapor pressures of water as a function of the molality of hydriodic acid at 25 ºC. The vapor pressures of water above reference electrolyte solution (KCl) are calculated from the isopiestic data of Harned and Robinson (1941) using the Pitzer model. Solid diamonds, Δp values for the Hückel model; circles, Δp values for the Pitzer model. It can be seen that the Hückel model gives good predictions when compared to the Pitzer model since there are no trends and all except two points are within $|\Delta p| = 0.007$ mmHg. No trends are observed. However, these results support that our model for hydriodic acid works very well up to $1.0\,\mathrm{mol \cdot kg^{-1}}$.

8 RECOMMENDED THERMODYNAMIC ACTIVITIES

In the previous chapters, it was established that a two-parameter Hückel, see equation (2.3.71), works for both aqueous hydrobromic and hydriodic acids at least up to $0.5\,\mathrm{mol \cdot kg^{-1}}$ at all temperatures studied. In Figures 15 and 16 the mean activity coefficients of HBr and HI are presented as a function of temperature at some rounded molalities, respectively.

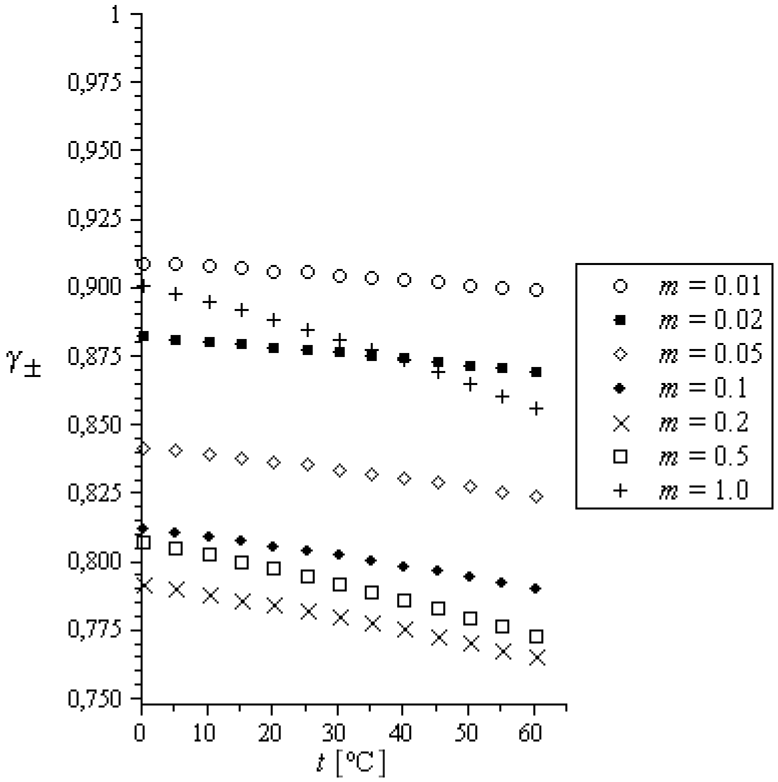

Figure 15. Mean activity coefficients for aqueous hydrobromic acid as a function of temperature on the basis of the new Hückel equation. The parameters used are $B = 1.5\left(\text{mol}\cdot\text{kg}^{-1}\right)^{-1/2}$ and $b_1 = 0.348$. Legend informs how the symbols correspond to the molalities in $\text{mol}\cdot\text{kg}^{-1}$. Recommended mean activity coefficients are valid at least up to $0.5\,\text{mol}\cdot\text{kg}^{-1}$. It can be seen that all values are between 0.760 and 0.920 and that they are linearly decreasing with temperature.

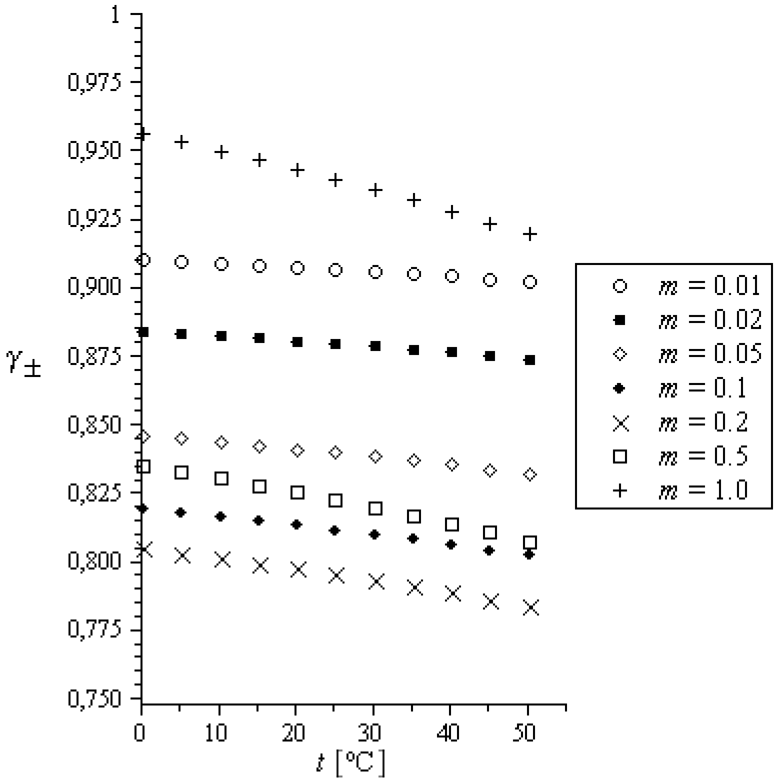

Figure 16. Mean activity coefficients for aqueous hydroiodic acid as a function of temperature on the basis of the new Hückel equation. The parameters used are $B = 1.6\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}$ and $b_1 = 0.390$. Legend informs how the symbols correspond to the molalities in $\mathrm{mol}\cdot\mathrm{kg}^{-1}$. Recommended mean activity coefficients are valid at least up to $0.5\,\mathrm{mol}\cdot\mathrm{kg}^{-1}$. It can be seen that all mean activity coefficient values are between 0.775 and 0.960 and that they are linearly decreasing with temperature.

In Tables 3 and 4, the recommended mean activity coefficients of the electrolyte, osmotic coefficients, and vapor pressures of water as functions of the molality are presented at some rounded molalities at 25 ºC.

Table 3. Recommended mean activity coefficients $\gamma_{\pm}$, osmotic coefficients ϕ and vapor pressures p for aqueous hydrobromic acid at 25 °C as functions of molality m.

$m\left[\mathrm{mol\cdot kg^{-1}}\right]$	$\gamma_{\pm}$	ϕ	$p\ [\mathrm{mmHg}]$
0.1	0.805	0.949	23.6849
0.2	0.783	0.955	23.6030
0.3	0.780	0.967	23.5188
0.4	0.785	0.982	23.4322
0.5	0.795	0.997	23.3430

Table 4. Recommended mean activity coefficients $\gamma_{\pm}$, osmotic coefficients ϕ and vapor pressures p for aqueous hydriodic acid at 25 °C as functions of molality m.

$m\left[\mathrm{mol\cdot kg^{-1}}\right]$	$\gamma_{\pm}$	ϕ	$p\ [\mathrm{mmHg}]$
0.1	0.813	0.953	23.6845
0.2	0.796	0.963	23.6017
0.3	0.798	0.978	23.5162
0.4	0.823	0.994	23.4278
0.5	0.823	1.012	23.3365

9 CONCLUSION

In this bachelor’s thesis, the Debye–Hückel model was derived in detail. Also the Hückel model, which was here, was thoroughly explained and a short introduction to the Pitzer model was given. As the main result of this investigation, the simple Hückel model with two temperature independent parameters can describe the thermodynamic properties of aqueous hydrobromic and hydriodic acids at least up to $0.5\,\mathrm{mol\cdot kg^{-1}}$ at temperatures from (0 to 50) and (0 to 60) ºC, respectively.

For future aspects the Hückel model could be introduced to more concentrated solutions and mixtures of electrolyte solutions. For instance in the recent studies involving such solutions, the Pitzer–Debye–Hückel term is used to describe long-range electrostatic interactions (Hsieh and Lin, 2010; Wang, Song, Chen, 2011; and latest Ingram, Gerlach, Mehling and Smirnova (2012)). This term could be possibly replaced with two-parameter Hückel equation. Another possibility for electrolyte system might be a model for mean activity coefficient that is composed of Hückel equations for single ions in solutions studied.

REFERENCES

Bates, R.G. and Bower, V.E., 1954. Standard potential of silver-silver-chloride electrode from 0º to 95ºC and the thermodynamic properties of dilute hydrochloric acid solutions. *Journal of research of the National Bureau of Standards*, 53, pp.283–290.

Bates, S.J. and Kirschman, H.D., 1919. The vapor pressures and free energies of hydrogen halides; the free energy formation of hydrogen chloride. *Journal of the American Chemical Society,* 41, pp.1991–2001.

Biermann, W.J. and Yamasaki, R.S., 1955. Activity Coefficients of Aqueous Hydrobromic Acid Solutions to Four Molal. *Journal of the American Chemical Society*, 77(1), p.241.

Bjerrum, N., 1918. Die Dissoziation der Starken Elektrolyte. *Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, 24 (19-20), pp.321–328.

Born, M., 1920. Volumen und Hydratationswärme der Ionen. *Zeitschrift für Physik*, 1, pp.45–49.

Bousfield, W.R., 1918. Iso–piestic solutions. *Transactions of the Faraday Society*, 13, pp.401–410.

Debye, P. and Hückel, E., 1923. Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen. *Physikalische Zeitschrift*, 24, pp.185–206.

Guggenheim, E.A., 1935. The specific thermodynamic properties of aqueous solutions of strong electrolytes. *Philosophical Magazine Series 7*, 19(127), pp. 588–643.

Gupta, S.R., Hills, G.J. and Ives, D.J.G., 1963. Standard E.m.f. of the Hydrogen–Mercurous Bromide Cell from 5 to 45°C. *Transactions of the Faraday Society*, 59, pp. 1886–1891.

Harned, H.S. and Ehlers R.W., 1932. The Dissociation Constant of Acetic Acid from 0 to 35 º Centigrade. *Journal of the American Chemical Society*, 54(4), pp.1350–1357.

Harned, H.S. and Ehlers R.W., 1933. The Thermodynamics od Aqueous Hydrochloric Acid Solutions from Electromotive Force Measurements. *Journal of the American Chemical Society*, 55(6), pp.2179–2193.

Harned, H.S., Keston, A.S. and Donelson J.G., 1936. The Thermodynamics of Hydrobromic Acid in Aqueous Solution from Electromotive Force Measurements. *Journal of the American Chemical Society*, 58(6), pp.989–994.

Harned, H.S. and Robinson R.A., 1941. The activity coefficient of hydriodic acid at 25º. From isopiestic vapour pressure measurements. *Transactions of the Faraday Society*, 37, pp.302–307.

Helgeson, H.C., Kirkham, D.H. and Flowers, G.C., 1981. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures: IV. Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600 °C and 5kb. *American Journal of Science*, 281, pp.1249–1516.

Hetzer, H.B., Robinson, R.A. and Bates R.G., 1962. Standard Electromotive Force of the Cell H_2; HBr(m), AgBr; Ag from 0 to 50°. *The Journal of Physical Chemistry*, 66(8), pp.1423–1426.

Hetzer, H.B., Robinson, R.A. and Bates, R.G., 1964. Thermodynamics of Aqueous Solutions of Hydriodic Acid from Electromotive force Measurements of Hydrogen-Silver Iodide Cells. *The Journal of Physical Chemistry*, 68(7), pp.1929–1933.

Hsieh, M–T. and Lin, S–T., 2011. A predictive model for the excess Gibbs free energy of fully dissociated electrolyte solutions. *American Institute of Chemical Engineers Journal*, 57(4), pp.1061–1074.

Hückel, E., 1925. Zur Theorie konzentrierterer wässeriger Lösungen starker Elektrolyte. *Physikalische Zeitschrift*, 26, pp.93–147.

Ingram, T., Gerlach, T., Mehling. T. and Smirnova, I., 2012. Extension of COSMO–RS for monoatomic electrolytes: Modeling of liquid–liquid equilibria in presence of salts. *Fluid Phase Equilibria*, 314, pp.29–37.

Kirkwood, J.G. and Poirier, J.C., 1954. The Statistical Mechanical Basis of the Debye–Hückel Theory of Strong Electrolytes. *Journal of Physical Chemistry*, 58(8), pp.591–596.

Lange, A.W. and Herbert, J.M., 2011. A simple polarizable continuum solvation model for electrolyte solutions. *The Journal of Chemical Physics*, 134(20/204110), pp.1–15.

Lee, L.L., 2008. *Molecular Thermodynamics of Electrolyte Solutions*. Singapore: World Scientific Publishing Co.Pte.Ltd.

Li, B., 2009. Continuum electrostatics for ionic solutions with non-uniform ionic sizes. *Nonlinearity*, 22(4), pp.811–833.

Macaskill, J.B. and Bates, B.G., 1983. Osmotic Coefficients and Activity Coefficients of Aqueous Hydrobromic Acid Solutions at 25 °C. *Journal of Solution Chemistry*, 12(9), pp.607–619.

Partanen, J.I., Covington, A.K., 2002a. Re-Evaluation of the Activity Coefficients of Aqueous Hydrochloric Acid Solutions up to a Molality of 2.0 Using Two-Parameter Hückel and Pitzer Equations. Part I Results at 25 °C. *Journal of Solution Chemistry*, 31(3), pp.187–196.

Partanen, J.I., Covington, A.K., 2002b. Re-Evaluation of the Activity Coefficients of Aqueous Hydrochloric Acid Solutions up to a Molality of 2.0 Using Two-Parameter Hückel and Pitzer Equations. Part II. Results from 0 to 95 °C. *Journal of Solution Chemistry,* 31(3), pp.197–210.

Partanen, J.I., Juusola, P.M., Vahteristo, K.P. and de Mendonça, J.G., 2007. Re-Evaluation of the Activity Coefficients of Aqueous Hydrochloric Acid Solutions up to a Molality of 16.0 $\mathrm{mol \cdot kg^{-1}}$ Using the Hückel and Pitzer Equations Temperatures from 0 to 50 °C. *Journal of Solution Chemistry*, 36(1), pp.39–59.

Partanen, J.I., Makkonen E.K. and Vahteristo, K.P., 2013. Re–evaluation of Activity Coefficients in Dilute Aqueous Hydrobromic and Hydriodic Acid Solutions at Temperatures from 0 to 60 ºC. *Journal of Solution Chemistry*, 42(1), pp.190–210.

Pitzer, K.S., 1973. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *The Journal of Physical Chemistry*, 77(2), pp.268–277.

Pitzer, K.S. and Mayorga G., 1973. Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent. *The Journal of Physical Chemistry*, 77(19), pp.2300–2308.

Robinson, R.A. and Stokes, R.H., 1959. *Electrolyte solutions*. 2nd revised ed. London: Butterworths.

Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, 32(5), pp.751–767.

Thomsen, K., 2005. Modeling electrolyte solutions with the extended universal quasichemical (UNIQUAC) model. *Pure and Applied Chemistry*, 77(3), pp.531–542.

Wang, S., Song, Y. and Chen, C–C., 2011. Extension of COSMO–SAC Solvation Model for Electrolytes. *Industrial & Engineering Chemistry Research*, 50(1), pp.176–187.

Xiao, T. and Song, X., 2011. A molecular Debye–Hückel theory and its applications to electrolyte solutions. *The Journal of Chemical Physics*, 135(10/104104), pp.1–14.

Appendix I

Cell data for aqueous hydrobromic acid.

Table 5. Electromotive force measurements in Volts by Gupta, Hills and Ives (1963) for aqueous hydrobromic acid at at temperatures (5 to 45) ºC. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$.

m_{HBr}	5 ºC	10 ºC	15 ºC	20 ºC	25 ºC	30 ºC	35 ºC	40 ºC	45 ºC
0.005064	0.39782	0.40244	0.40669	0.41082	0.41464	0.41842	0.42222	0.42589	0.42956
0.007546	0.37940	0.38351	0.38749	0.39129	0.39494	0.39842	0.40177	0.40513	0.40847
0.010140	0.36572	0.36957	0.37329	0.37682	0.38022	0.38349	0.38657	0.38959	0.35687
0.020010	0.33453	0.33786	0.34103	0.34401	0.34685	0.34953	0.35208	0.35453	0.33581
0.030070	0.31602	0.31901	0.32186	0.32452	0.32708	0.32952	0.33169	0.33385	0.30986
0.049620	0.29331	0.29592	0.29836	0.30068	0.30280	0.30478	0.30659	0.30827	0.29142
0.070880	0.27718	0.27952	0.28167	0.28373	0.28554	0.28734	0.28879	0.29014	0.27932
0.089400	0.26652	0.26857	0.27055	0.27242	0.27407	0.27560	0.27685	0.27816	0.24128
0.098290	0.26203	0.26427	0.26616	0.26792	0.26958	0.27092	0.27225	0.27337	0.42956
0.184700	0.23312	0.23451	0.23592	0.23734	0.23830	0.23927	0.24000	0.24064	0.40847

Table 6a. Electromotive force measurements in international Volts by Harned, Keston and Donelson (1936) for aqueous hydrobromic acid at temperatures (0 to 30) ºC. Data is calculated using function given in the original article. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$. (1 int Volt =1.00034 V)

m_{HBr}	0 ºC	5 ºC	10 ºC	15 ºC	20 ºC	25 ºC	30 ºC
0.001	0.40822	0.41244	0.41651	0.42043	0.42421	0.42784	0.43133
0.005	0.33416	0.33703	0.33975	0.34233	0.34477	0.34707	0.34922
0.01	0.30269	0.30498	0.30713	0.30913	0.31100	0.31273	0.31432
0.02	0.27144	0.27315	0.27473	0.27617	0.27748	0.27864	0.27968
0.05	0.23044	0.23143	0.23229	0.23301	0.23359	0.23404	0.23435
0.1	0.19967	0.20010	0.20039	0.20055	0.20059	0.20050	0.20028
0.2	0.16807	0.16798	0.16776	0.16740	0.16692	0.16630	0.16556
0.5	0.12411	0.12333	0.12240	0.12135	0.12016	0.11884	0.11739
1.0	0.08631	0.08494	0.08344	0.08181	0.08005	0.07817	0.07615

Table 6b. Electromotive force measurements in international Volts by Harned, Keston and Donelson (1936) for aqueous hydrobromic acid at temperatures (35 to 60) ºC. Data is calculated using function given in the original article. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$. (1 int Volt =1.00034 V).

m_{HBr}	35 ºC	40 ºC	45 ºC	50 ºC	55 ºC	60 ºC
0.001	0.43786	0.44090	0.44380	0.44655	0.44916	0.43786
0.005	0.35309	0.35482	0.35640	0.35783	0.35913	0.35309
0.01	0.31707	0.31823	0.31926	0.32014	0.32088	0.31707
0.02	0.28132	0.28194	0.28243	0.28277	0.28298	0.28132
0.05	0.23456	0.23446	0.23422	0.23384	0.23333	0.23456
0.1	0.19945	0.19884	0.19811	0.19725	0.19625	0.19945
0.2	0.16367	0.16253	0.16126	0.15985	0.15832	0.16367
0.5	0.11408	0.11223	0.11024	0.10813	0.10587	0.11408
1.0	0.07172	0.06931	0.06677	0.06410	0.06130	0.07172

Table 7a. Electromotive force measurements in Volts by Hetzer, Robinson and Bates (1962) for aqueous hydrobromic acid at temperatures (0 to 25) ºC. Data point shaded with red is omitted as an erroneous point. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$.

m_{HBr}	0 ºC	5 ºC	10 ºC	15 ºC	20 ºC	25 ºC
0.005125	0.33291	0.33592	0.33865	0.34129	0.34368	0.34594
0.005140	0.33268	0.33566	0.33843	0.34110	0.34349	0.34582
0.007617	0.31471	0.31735	0.31978	0.32209	0.32420	0.32611
0.010021						0.31265
0.010065	0.30209	0.30454	0.30681	0.30882	0.31070	0.31238
0.012389	0.29279	0.29500	0.29703	0.29894	0.30065	0.30229
0.015158	0.28366	0.28577	0.28761	0.28931	0.29084	0.29225
0.019876	0.27162	0.27344	0.27516	0.27663	0.27787	0.27898
0.02533						0.26718
0.03006	0.25325	0.25482	0.25613	0.25726	0.25825	0.25901
0.03041	0.25247	0.25400	0.25533	0.25649	0.25744	0.25825
0.03999	0.24025	0.24165	0.24271	0.24353	0.24429	0.24492
0.04974	0.23045	0.23170	0.23264	0.23343	0.23407	0.23449
0.04980						0.23426
0.05030						0.23385
0.06015	0.22188	0.22284	0.22364	0.22428	0.22473	0.22498
0.06586	0.21773	0.21871	0.21945	0.21996	0.22036	0.22063
0.06985	0.21529	0.21614	0.21679	0.21726	0.21758	0.21778
0.07578	0.21155	0.21325	0.21296	0.21337	0.21360	0.21382
0.08048	0.20894	0.20969	0.21026	0.21064	0.21085	0.21093
0.09035	0.20356	0.20432	0.20482	0.20512	0.20524	0.20524
0.10082	0.19886	0.19943	0.19982	0.20003	0.20006	0.19994
0.10085	0.19886	0.19945	0.19983	0.19996	0.20001	0.19993

Table 7b. Electromotive force measurements in Volts by Hetzer, Robinson and Bates (1962) for aqueous hydrobromic acid at temperatures (30 to 50) ºC. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$.

m_{HBr}	30 ºC	35 ºC	40 ºC	45 ºC	50 ºC
0.005125	0.34804	0.35004	0.35189	0.35359	0.35521
0.005140	0.34782	0.34981	0.35172	0.35337	0.35496
0.007617					
0.010021					
0.010065	0.31399	0.31529	0.31664	0.31777	0.31880
0.012389	0.30354	0.30488	0.30603	0.30706	0.30789
0.015158	0.29347	0.29454	0.29552	0.29624	0.29689
0.019876	0.28005	0.28098	0.28172	0.28228	0.28275
0.02533					
0.03006	0.25976	0.26020	0.26072	0.26098	0.26112
0.03041	0.25897	0.25950	0.25991	0.26018	0.26033
0.03999	0.24537	0.24566	0.24589	0.24596	0.24575
0.04974	0.23479	0.23497	0.23499	0.23486	0.23450
0.04980					
0.05030					
0.06015	0.22514	0.22519	0.22501	0.22471	0.22429
0.06586	0.22066	0.22054	0.22036	0.22007	0.21963
0.06985	0.21780	0.21773	0.21741	0.21708	0.21656
0.07578	0.21367	0.21351	0.21319	0.21283	0.21224
0.08048	0.21085	0.21064	0.21026	0.20979	0.20919
0.09035	0.20506	0.20478	0.20432	0.20382	0.20316
0.10082	0.19970	0.19934	0.19833	0.19821	0.19745
0.10085					

Table 8. Electromotive force measurements in Volts by Macaskill and Bates (1983) for aqueous hydrobromic acid at temperature 25 ºC. Data point shaded with yellow is omitted, since its molality is too high for this study. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$.

m_{HBr}	25 ºC
0.01	0.31290
0.1	0.20053
0.5	0.11859
1	0.07764
2	0.02705
3	-0.01113

Appendix II

Cell data for aqueous hydriodic acid.

Table 9a. Electromotive force measurements in Volts by Hetzer, Robinson and Bates (1964) for aqueous hydriodic acid at temperatures (0 to 25) ºC. Data points shaded with red are omitted as erroneous points. Molalities are in units $\mathrm{mol\cdot kg^{-1}}$.

m_{HI}	0 ºC	5 ºC	10 ºC	15 ºC	20 ºC	25 ºC
0.01746	0.04977	0.05258	0.05520	0.05759	0.05987	0.06184
0.02502	0.03354	0.03605	0.03839	0.04054	0.04249	0.04421
0.02932	0.02649	0.02883	0.03102	0.03302	0.03484	0.03646
0.03556						0.02716
0.03612	0.01720	0.01940	0.02138	0.02326	0.02490	0.02630
0.03997	0.01256	0.01472	0.01664	0.01841	0.02002	0.02136
0.04509	0.00723	0.00927	0.01113	0.01278	0.01429	0.01560
0.04960						0.01095
0.05072	0.00205	0.00399	0.00571	0.00728	0.00863	0.00981
0.05526	-0.00196	-0.00008	0.00162	0.00311	0.00445	0.00557
0.06065	-0.00599	-0.00420	-0.00266	-0.00121	0.00005	0.00106
0.06628	-0.01009	-0.00833	-0.00679	-0.00545	-0.00422	-0.00325
0.06725						-0.00383
0.06782	-0.01100	-0.00926	-0.00775	-0.00643	-0.00525	-0.00432
0.06982						-0.00576
0.07282	-0.01432	-0.01268	-0.01117	-0.00988	-0.00876	-0.00790
0.08077	-0.01896	-0.01735	-0.01603	-0.01481	-0.01378	-0.01295
0.08560	-0.02132	-0.01983	-0.01851	-0.01740	-0.01640	-0.01568
0.08980	-0.02358	-0.02210	-0.02082	-0.01972	-0.01875	-0.01802
0.09989	-0.02840	-0.02704	-0.02582	-0.02483	-0.02399	-0.02332
0.10106	-0.02880	-0.02745	-0.02629	-0.02530	-0.02442	-0.02383
0.10341						-0.02486
0.13463						-0.03797
0.13749						-0.03901
0.15177	-0.04746	-0.04644	-0.04559	-0.04487	-0.04434	-0.04411
0.2061			-0.06026			-0.05944
0.3238			-0.08251			-0.08280
0.3897			-0.09212			-0.09270
0.4697						
0.5122			-0.10651			-0.10789
0.5256			-0.10789			-0.10934
0.6327			-0.11835			-0.12024
0.7229			-0.12589			-0.12824
0.8463			-0.13576			-0.13828
0.9507			-0.14298			-0.14612

Table 9b. Electromotive force measurements in Volts by Hetzer, Robinson and Bates (1964) for aqueous hydriodic acid at temperatures (30 to 50) ºC. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$.

m_{HI}	30 ºC	35 ºC	40 ºC	45 ºC	50 ºC
0.01746	0.06392	0.06573	0.06742	0.06898	0.07043
0.02502	0.04597	0.04750	0.0489	0.05018	0.05134
0.02932	0.03804	0.03944	0.04073	0.04189	0.04294
0.03556					
0.03612	0.02778	0.02900	0.03012	0.03110	0.03200
0.03997	0.02278	0.02395	0.02488	0.02569	0.02652
0.04509	0.01689	0.01792	0.01887	0.01971	0.02043
0.04960					
0.05072	0.01096	0.01192	0.01279	0.01349	0.01415
0.05526	0.00672	0.00760	0.00839	0.00905	0.00959
0.06065	0.00209	0.00291	0.00359	0.00418	0.00467
0.06628	-0.00226	-0.00149	-0.00083	-0.00028	0.00009
0.06725					
0.06782	-0.00338	-0.00263	-0.00199	-0.00148	-0.00108
0.06982					
0.07282	-0.00697	-0.00627	-0.00569	-0.00525	-0.00489
0.08077	-0.01214	-0.01152	-0.01106	-0.01065	-0.01038
0.08560	-0.01488	-0.01435	-0.0139	-0.01360	-0.01341
0.08980	-0.01728	-0.01675	-0.01634	-0.01604	-0.01587
0.09989	-0.02267	-0.02222	-0.02187	-0.02168	-0.02158
0.10106	-0.02317	-0.02275	-0.02241	-0.02222	-0.02215
0.10341					
0.13463					
0.13749					
0.15177	-0.04375	-0.04364	-0.04363	-0.04379	-0.04400
0.2061			-0.05985		
0.3238			-0.08435		
0.3897					
0.4697			-0.10553		
0.5122			-0.11072		
0.5256					
0.6327			-0.12373		
0.7229			-0.13219		
0.8463			-0.14257		
0.9507			-0.15032		

Appendix III

Isopiestic data for aqueous hydrobromic and hydriodic acids.

Table 10. The isopiestic data of Macaskill and Bates (1983) for aqueous hydrobromic acid and sodium chloride solutions. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$. Only the green shaded values were used.

m_{HBr}	m_{NaCl}
0.7239	0.8025
0.8214	0.9203
0.9071	1.0276
0.9241	1.0485
1.0188	1.1666
1.0383	1.1893
1.1183	1.2937
1.2320	1.4415
1.3306	1.5677
1.3805	1.6333
1.5574	1.8708
1.6081	1.9398
1.8246	2.2408
2.0037	2.4846
2.0790	2.5965
2.3156	2.9264
2.6402	3.3978
2.7819	3.6089
2.9325	3.8283
3.1563	4.1557
3.3653	4.4697
3.6502	4.8896
3.7964	5.1143
3.9439	5.3283
4.1459	5.6405
4.3889	6.0105
4.4731	6.1452

Table 11. The isopiestic data of Harned and Robinson (1941) for aqueous hydriodic acid and potassium chloride solutions. Molalities are in units $\mathrm{mol \cdot kg^{-1}}$. Only the green shaded values were used.

m_{HI}	m_{KCl}
0.1072	0.1115
0.1238	0.1276
0.1787	0.191
0.2062	0.2195
0.2617	0.2825
0.4378	0.4934
0.554	0.6272
0.6013	0.7016
0.6233	0.724
0.6734	0.7824
0.7178	0.844
0.7326	0.867
0.8002	0.9548
0.876	1.061
1.063	1.329
1.087	1.371
1.127	1.419
1.239	1.595
1.479	1.963
1.592	2.14
1.788	2.443
1.878	2.63
2.003	2.813
2.083	2.973
2.135	3.092
2.252	3.275
2.434	3.596
2.503	3.715
2.711	4.124
2.882	4.452
2.893	4.469
3.002	4.676

Appendix IV

Results of least-squares fitting

Table 12. Results of least-squares fitting for data of Macaskill and Bates (1983) for aqueous hydrobromic acid. $S\left(E^0\right)$ and $S\left(b_1\right)$ are the standard deviations of E^0 and b_1, respectively. E^0_{re} is the recalculated and recommended standard electrode potential using parameter values $B = 1.5\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}$ and $b_1 = 0.348$.

$t\left[{}^{\mathrm{o}}\mathrm{C}\right]$	$\alpha\left[\mathrm{mol}\cdot\mathrm{kg}^{-1}\right]^{-1/2}$	$E^0\left[\mathrm{mV}\right]$	$S\left(E^0\right)\left[\mathrm{mV}\right]$	b_1	$\mathrm{S}\left(b_1\right)$	$E^0_{\mathrm{re}}\left[\mathrm{mV}\right]$
25	1.1744	71.18	0.09	0.348	0.002	71.19

Table 13. Results of least-squares fitting for data of Gupta, Hills and Ives (1963), Harned, Keston and Donelson (1936) and Hetzer, Robinson and Bates (1962) for aqueous hydrobromic acid. $E^0_{\mathrm{re\,GHI}}$, $E^0_{\mathrm{re\,HKD}}$ and $E^0_{\mathrm{re\,HRB}}$ are the recalculated and recommended standard electrode potential using parameter values $B = 1.5\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}$ and $b_1 = 0.348$. Sub indeces GHI, HKD and HRB correspond to Gupta, Hills and Ives (1963), Harned, Keston and Donelson (1936) and Hetzer, Robinson and Bates (1962), respectively.

$t\left[{}^{\mathrm{o}}\mathrm{C}\right]$	$\alpha\left[\mathrm{mol}\cdot\mathrm{kg}^{-1}\right]^{-1/2}$	$E^0_{\mathrm{re\,GHI}}\left[\mathrm{mV}\right]$	$E^0_{\mathrm{re\,HKD}}\left[\mathrm{mV}\right]$	$E^0_{\mathrm{re\,HRB}}\left[\mathrm{mV}\right]$
0	1.1293		81.41	81.12
5	1.1376	141.04	79.65	79.49
10	1.1462	140.82	77.70	77.61
15	1.1552	140.45	75.63	75.56
20	1.1646	139.94	73.42	73.33
25	1.1744	139.22	71.06	70.97
30	1.1848	138.37	68.49	68.42
35	1.1956	137.35	64.84	65.74
40	1.2068	136.25	63.04	62.93
45	1.2186	135.07	60.10	59.97
50	1.2308		57.02	56.86
55	1.2436		53.79	
60	1.2568		50.41	

Table 14. Results of least-squares fitting for data of Hetzer, Robinson and Stokes (1964) for aqueous hydroiodic acid. $S\left(E^0\right)$ and $S\left(b_1\right)$ are the standard deviations of E^0 and b_1, respectively. E^0_{re} is the recalculated and recommended standard electrode potential using parameter values $B = 1.6\left(\mathrm{mol}\cdot\mathrm{kg}^{-1}\right)^{-1/2}$ and $b_1 = 0.390$. Temperatures 10, 25 and 40 are emphasized in studies, by taking more digits to deviation values, since there are more data points at these temperatures.

$t\left[{}^{\mathrm{o}}\mathrm{C}\right]$	$\alpha\left[\mathrm{mol}\cdot\mathrm{kg}^{-1}\right]^{-1/2}$	$E^0\left[\mathrm{mV}\right]$	$S\left(E^0\right)\left[\mathrm{mV}\right]$	b_1	$S\left(b_1\right)$	$E^0_{\mathrm{re}}\left[\mathrm{mV}\right]$
0	1.1293	-146.33	0.04	0.361	0.013	-146.24
5	1.1376	-147.14	0.04	0.370	0.011	-147.08
10	1.1462	-148.122	0.018	0.3897	0.0013	-148.12
15	1.1552	-149.39	0.03	0.378	0.007	-149.35
20	1.1646	-150.78	0.03	0.378	0.008	-150.74
25	1.1744	-152.34	0.024	0.3886	0.0014	-152.33
30	1.1848	-154.02	0.03	0.382	0.007	-153.99
35	1.1956	-155.87	0.03	0.382	0.007	-155.84
40	1.2068	-157.805	0.018	0.3919	0.0009	-157.83
45	1.2186	-159.97	0.04	0.377	0.010	-159.92
50	1.2308	-162.18	0.03	0.378	0.009	-162.14

Appendix V

Pitzer parameters.

Table 15. Pitzer parameters used in this study obtained from Pitzer and Mayorga (1973).

electrolyte	β^0	β^1	C^ϕ	A^ϕ
HBr	0.196	0.3564	0.00827	0.392
HI	0.2362	0.392	0.0011	0.392
KCl	0.04835	0.2122	-0.00084	0.392
NaCl	0.0765	0.2664	0.00127	0.392