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## Thermodynamic Properties of Mixtures of Aqueous Solutions of Hydrochloric Acid and Cadmium Chloride, Copper Chloride, Manganese Chloride, and Zinc Chloride

Samia A. Kosa

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**THERMODYNAMIC PROPERTIES OF MIXTURES OF AQUEOUS SOLUTIONS  
OF HYDROCHLORIC ACID AND CADMIUM CHLORIDE, COPPER  
CHLORIDE, MANGANESE CHLORIDE, AND ZINC CHLORIDE**

by

**Samia A. Kosa**

**A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
Degree of Master of Arts  
Department of Chemistry**

**Western Michigan University  
Kalamazoo, Michigan  
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Samia A. Kosa

# THERMODYNAMIC PROPERTIES OF MIXTURES OF AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID AND CADMIUM CHLORIDE, COPPER CHLORIDE, MANGANESE CHLORIDE, AND ZINC CHLORIDE

Samia A. Kosa, M.A.

Western Michigan University, 1993

The densities of mixtures of aqueous solutions of hydrochloric acid and cadmium chloride, copper chloride, manganese chloride, and zinc chloride have been measured at constant ionic strengths of 1.0 and 3.0 molal at 25°C. In the case of HCl, CdCl<sub>2</sub>, and ZnCl<sub>2</sub> the literature data were refit using Pitzer's apparent molal volume equation and the binary solution parameters were determined. Density data were used to determine the volume of mixing ( $\Delta V_m$ ). Data from Török and Berecs were combined with our data for the mixtures with CuCl<sub>2</sub> and MnCl<sub>2</sub>. Pitzer's volume of mixing equation was fit to the volume of mixing data to obtain the parameters  $\theta^{v(0)}_{MN}$ ,  $\theta^{v(1)}_{MN}$ , and  $\psi^v_{MNX}$ . These parameters are the pressure derivatives of Pitzer's free energy equation parameters.

The heats of mixing ( $\Delta H_m$ ) of solutions of cadmium chloride, copper chloride, manganese chloride, and zinc chloride with solutions of hydrochloric acid were measured at constant ionic strengths of 1.0 and 3.0 molal at 25°C. The excess enthalpy equation of Pitzer was fit to the resulting  $\Delta H_m$  data to obtain the Pitzer mixing parameters  $\theta^{L(0)}_{MN}$ ,  $\theta^{L(1)}_{MN}$ , and  $\psi^L_{MNX}$ . These parameters are the temperature derivatives of the free energy equation parameters.

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## CHAPTER I

### INTRODUCTION

In recent years there has been increasing interest in the thermodynamic properties of aqueous mixed electrolyte solutions. This interest has been generated by areas outside traditional chemistry like industrial engineering,<sup>1,2</sup> oceanography,<sup>3</sup> and oil recovery.<sup>4</sup> Data available about the thermodynamic properties is currently insufficient. More data is needed at moderate as well as high temperatures, pressures, and concentrations.<sup>1,5</sup> Therefore it is essential to have accurate aqueous electrolyte data over wide ranges of temperature, pressure, and concentration.

The composition of natural waters such as rivers and seawater, for example, are quite different. Table 1 shows the composition of average river water and seawater.<sup>6,7</sup> From the table we see that the most abundant ions found in rivers are  $\text{Ca}^{+2}$  and  $\text{HCO}_3^-$  while the most abundant ions found in seawater are  $\text{Na}^+$  and  $\text{Cl}^-$ . Although the  $\text{Cl}^-$  ion is not the most abundant anion found in river water it is one of its major anionic constituents. In addition to variation in composition, the pressure and temperature of natural waters varies significantly.<sup>8,9</sup> The temperature of natural waters varies from about  $-2^\circ\text{C}$  to  $30^\circ\text{C}$  and in the summer months temperature may become as high as  $36^\circ\text{C}$ , while the pressure of natural waters increases one atmosphere for every 10 meters of depth.

Table 1  
The Composition of Average River Water and Seawater

Species	River water $\text{n}10^3^{\text{a}}$	Seawater $\text{n}^{\text{a}}$
$\text{Na}^+$	0.283	0.48534
$\text{Mg}^{2+}$	0.169	0.05519
$\text{Ca}^{2+}$	0.374	0.01065
$\text{K}^+$	0.059	0.01058
$\text{Cl}^-$	0.220	0.56579
$\text{Sr}^{2+}$	---	0.00010
$\text{SO}_4^{2-}$	0.117	0.02927
$\text{F}^-$	---	0.00007
$\text{HCO}_3^-$	0.950	0.00200
$\text{Br}^-$	---	0.00087
$\text{CO}_3^{2-}$	0.002	0.00021
$\text{NO}_3^-$	0.016	-----
$\text{Si}(\text{OH})_3\text{O}^-$	0.005	-----
$\text{Si}(\text{OH})_4$	0.213	-----
$\text{B}(\text{OH})_3$	---	0.00034
$\text{B}(\text{OH})_4^-$	---	0.00009

<sup>a</sup>Units:  $\text{mol}\cdot\text{l}^{-1}$

We are interested in transition metal salts because transition metals are important in biology,<sup>10</sup> geology,<sup>11</sup> water treatment,<sup>12,13</sup> engineering,<sup>1,2</sup> and steam power.<sup>14</sup> The importance of transition metals in these systems has developed a need for accurate thermodynamic data for these salts in aqueous solution. In biological systems, metals like copper, manganese, and zinc are used in enzymes to catalyze oxidation, while others like cadmium can poison enzymes by substituting for their

required metal.<sup>10</sup> Copper is one of the principle inorganic metals found in several proteins, metalloenzymes, and some naturally occurring pigments.<sup>15,16</sup> Zinc is essential for normal growth, reproduction, and life expectancy of animals and has a beneficial effect on the process of tissue repair and wound healing.<sup>15,16</sup> Manganese is a primary source of energy for many organisms.<sup>17</sup> In the soil some bacteria oxidize manganese compounds and accumulate manganese dioxide ( $\text{MnO}_2$ ) in their cells. This oxidation is a primary energy source for these organisms. The accumulation depletes the manganese available to plants until reducer organisms render  $\text{MnO}_2$  deposits soluble and available once more.<sup>17</sup> In the oceans both of these reactions have been noted.<sup>17</sup> Species of *Arthrobacter* have been found associated with ferromanganese nodules. These nodules contain as much as 63 percent  $\text{MnO}_2$  deposited by oxidative bacteria. A species of *Bacillus* isolated from nodules and deep-sea sediments can reduce  $\text{MnO}_2$  as a stage of its electron transport system. In geology,<sup>11</sup> the aqueous solution chemistry of transition metals are important in the deposition of various minerals.

Transition metals are also an important problem in water treatment.<sup>12,13</sup> Copper, iron, manganese, and zinc are frequently found in natural waters. Water containing large quantities of iron and manganese are undesirable because they cause brown colored deposits on vegetables during washing and cooking. An additional source of copper in drinking water is water pipes. In steam generators and other engineering systems, copper and zinc play roles in the corrosion processes. The presence of copper in water which comes into contact with any galvanized steel or

aluminum may accelerate corrosion.<sup>14</sup> Zinc is used to coat metals to protect them from corrosion.<sup>14</sup> An additional source of transition metals in the environment is the incineration of wastes containing them.<sup>18</sup>

Chloride ion is the most abundant anion found in natural waters. Hydrogen ions are important in aqueous acid solutions,<sup>19</sup> especially in acid lakes and acid rain due to acid pollution. Hydrochloric acid is important in biological systems because HCl is found in all human body fluids like blood and gastric juices.<sup>20</sup> An additional source of hydrochloric acid in the environment is the incineration of plastic.<sup>18</sup>

Since most natural waters are complicated, models have been developed to predict the thermodynamic properties of these more complex systems. These models require binary solution data which is becoming available over a wide range of temperatures for many of the components.<sup>21</sup> These models can be improved by the inclusion of ternary solution data. One widely used model is the Pitzer virial coefficient system.<sup>22-25</sup> There are various ways to obtain information about ion interactions including isopestic,<sup>26,27</sup> vapor pressure,<sup>28</sup> calorimetric,<sup>29-32</sup> and densimetry<sup>33-35</sup> measurements. The heat and volume of mixing are useful methods which give us information about the effect of temperature and pressure, respectively, on the interaction of ions.

A survey of the literature indicated a lack of experimental data on the heat and volume of mixing of transition metal salts with HCl. A few studies have been made on the osmotic and activity coefficient of transition metal salts with NaCl.<sup>26,27,28,36</sup> Due to growing interest in transition metals, some workers have started to measure

the heat of mixing of some transition metal salts with NaCl<sup>30,31</sup> and heat of dilution of some transition metal salts.<sup>29</sup> Few studies have been made on the volume of mixing of transition metal salts with HCl.<sup>37</sup>

In this study we measured the densities of aqueous solutions of CdCl<sub>2</sub>, CuCl<sub>2</sub>, MnCl<sub>2</sub>, and ZnCl<sub>2</sub> mixed with HCl at 25°C and at constant ionic strengths of 1.0 and 3.0 molal. From the density data the volumes of mixing were calculated. The volume of mixing equations of Pitzer were then fit to the volume of mixing data and the resulting parameters are given. We also measured the heat of mixing of these transition metals with HCl at the same temperature and ionic strengths. The heat of mixing equations of Pitzer were then fit to the heat of mixing data and the resulting parameters are given.

## CHAPTER II

### DEFINITIONS AND EQUATIONS

#### Volumetric Equations

Apparent molal volumes of the binary solutions were calculated using the equation

$$\phi_v(i) = (M_i/d) - [1000(d-d_0)/m_i d d_0] \quad (1)$$

where  $d_0$  is the density of pure water,  $m_i$  is the molality of electrolyte  $i$ ,  $d$  is the density of the solution, and  $M_i$  is the molar mass of electrolyte  $i$ . Millero<sup>6,7</sup> has shown it is better to use the equivalent molality of the electrolyte rather than the molality for calculations in natural waters especially at higher concentrations. The apparent molal volumes of the binary solutions can also be calculated from the densities using the equation

$$\phi_v(i) = (E_i/d) - [1000(d-d_0)/e_i d d_0] \quad (2)$$

where  $e_i$  is the equivalent molality and  $E_i$  is the equivalent weight of electrolyte  $i$ . The equivalent molality is defined as  $e_i = m_i x$ , where  $m_i$  is the molality of electrolyte  $i$  in mol/kg  $H_2O$ , and  $x$  is an equivalent factor equal to 1 for HCl and 2 for  $CdCl_2$ ,  $CuCl_2$ ,  $MnCl_2$ , and  $ZnCl_2$ . The equivalent weight is defined as  $E_i = M_i/x$ . The molar

masses used for each of the transition metal salts and HCl along with the equivalent and ionic strength factors are given in Appendix A.

The mean apparent molal volume,  $\phi_v(2,3)$ , for the ternary mixtures of electrolyte (2) of molality  $m_2$  and electrolyte (3) of molality  $m_3$  is calculated from the equation

$$\phi_v(2,3) = (E_T/d) - [1000(d-d_0)/e_T d d_0] \quad (3)$$

where  $d$  and  $d_0$  are, respectively, the density of the mixture and pure water,  $e_T$  is the total equivalent molality of the mixture ( $e_T = e_2 + e_3 = \sum e_i$ ), and  $E_T$  is the mean equivalent weight of the mixture ( $E_T = E_2 F_2 + E_3 F_3$ , where  $E_2$  and  $E_3$  are the equivalent weights, and  $F_2$  and  $F_3$  are the equivalent fractions of electrolytes (2) and (3), respectively, [ $F_i = e_i/e_T$ ]).

The mean apparent molal volumes,  $\phi_v(2,3)$ , of these ternary mixtures were calculated using the equation

$$\phi_v(2,3) = (M_T/d) - [1000(d-d_0)/m_T d d_0] \quad (4)$$

where  $d$  and  $d_0$  are, respectively, the density of the mixture and pure water,  $m_T$  is the total molality of the mixture ( $m_T = m_2 + m_3$ ), and  $M_T$  is the mean molar mass,  $M_T = (m_2 M_2 + m_3 M_3)/(m_2 + m_3)$  where  $M_2$  and  $M_3$  are the molar masses of electrolytes (2) and (3), respectively.

The volumes of mixing  $\Delta V_m$  of the ternary solutions were calculated from the experimental values of  $\phi_v(2)$ ,  $\phi_v(3)$ , and  $\phi_v(2,3)$  using the equation

$$\Delta V_m = e_T \phi_v(2,3) - e_2 \phi_v(2) - e_3 \phi_v(3) \quad (5)$$

where  $\Delta V_m$  is the volume of mixing,  $\phi_v(2)$  and  $\phi_v(3)$  are, respectively, the experimental apparent molal volumes of electrolyte 2 and 3 at the same ionic strength as the mixture,  $\phi_v(2,3)$  is the experimental mean apparent molal volume of the mixture,  $e_T$  is the total equivalent molality of the mixture, and  $e_2$  and  $e_3$  are, respectively, the equivalent molality of electrolyte 2 and 3.

Pitzer<sup>22,24,25</sup> has developed a general set of equations to describe the thermodynamic properties of pure and mixed electrolyte solutions based on a Debye-Hückel term together with virial coefficients. Appropriate derivatives of the excess Gibbs energy equation yield the thermodynamic properties of aqueous electrolyte solutions, such as activity or osmotic coefficient,<sup>26,27,28</sup> excess enthalpy,<sup>29-32</sup> heat capacity,<sup>32</sup> and excess volume.<sup>33-35</sup> Pitzer's equations have been used by workers to accurately predict properties of natural aquatic systems.<sup>3,23,25,38</sup>

A brief explanation of Pitzer's equations is given here. The Pitzer<sup>22,24</sup> derivation begins with the calculation of the excess Gibbs free energy,  $G^{\text{EX}}$ , of the system. The excess Gibbs free energy of the system is defined as the difference between the Gibbs free energy of the real system,  $G$ , and the Gibbs free energy of an ideal system under the same conditions

$$G = G^{\text{ex}} + n_1 \bar{G}_1^\circ + n_2 \bar{G}_2^\circ \quad (6)$$

where  $n_1$  and  $n_2$  are, respectively, the number of moles of solvent and solute, and  $\bar{G}_1^\circ$

and  $\bar{G}_2^\circ$  are, respectively, the partial molal Gibbs free energies of solvent and solute at standard condition.

The general form of a virial equation for the excess Gibbs energy of electrolytes is

$$G^{ex}/(n_w RT) = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} \quad (7)$$

where  $n_w$  is the number of kilograms of solvent,  $R$  is the gas constant,  $T$  is the temperature in Kelvin,  $m_i$ ,  $m_j$ , and  $m_k$  are, respectively, the molalities of the solute species  $i$ ,  $j$ , and  $k$ , and  $f(I)$  is an ionic strength dependent Debye-Hückel limiting term for electrolytes

$$f(I) = -A_\phi (4I/b) \ln (1 + bI^{1/2}) \quad (8)$$

where  $A_\phi$  is the Debye-Hückel parameter,  $I$  is the ionic strength and  $b$  is a parameter given the value  $1.2 \text{ Kg}^{1/2}\text{-mol}^{-1/2}$  for all solutions. The quantities  $\lambda_{ij}(I)$  are the second virial coefficients for interactions between ions  $i$  and  $j$  and are functions of ionic strength. The quantities  $\mu_{ijk}$  are the third virial coefficients for triple ion interactions which may be significant at high concentrations. These terms don't include ionic strength dependence.

Pitzer has rewritten the equation for use with experimental data which utilizes empirical parameters. For a pure electrolyte solution containing  $n_w$  kg of solvent, the excess Gibbs free energy equation becomes

$$G^{ex}/(n_w RT) = -A_\phi (4I/b) \ln (1 + bI^{1/2}) + m^2 (2\nu_M \nu_X) B_{MX} + m^3 [2\nu_M \nu_X (\nu_M z_M)] C_{MX} \quad (9)$$

where  $\nu_M$  and  $\nu_X$  are, respectively, the number of cations and anions in the formula,  $z_M$  is the charge on ion M, and  $A_\phi$ ,  $I$ ,  $b$ ,  $n_w$ ,  $R$ ,  $T$ , and  $m$  are as defined above.  $B$  and  $C$  are empirical parameters related to short range interaction of ions of the opposite sign and for indirect forces arising from the solvent. The empirical parameters are related to the virial coefficients by the following equations

$$B_{MX} = \lambda_{MX} + (\nu_M/2\nu_X) \lambda_{MM} + (\nu_X/2\nu_M) \lambda_{XX} \quad (10)$$

$$C_{MX} = [(3/\nu_M \nu_X)^{1/2}] [\nu_M \mu_{MMX} + \nu_X \mu_{MMX}] \quad (11)$$

where M and X are ions of the opposite sign.  $B$  is a function of ionic strength but  $C$  is not. These parameters are defined as

$$B_{MX} = \beta_{MX}^{(0)} + (2\beta_{MX}^{(1)}/\alpha^2 I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (12)$$

$$C_{MX} = C_{MX}^\phi / 2 |z_M z_X|^{1/2} \quad (13)$$

where  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$ , and  $C_{MX}^\phi$  account for the interaction of ions of opposite charge,  $\alpha$  is a parameter given the value  $2.0 \text{ Kg}^{1/2}\text{-mol}^{-1/2}$  for 1:1 and 2:1 electrolyte solutions, and  $z_M$  and  $z_X$  are, respectively, the charges of the cation and anion.

Pitzer's equation for the activity coefficients,  $\gamma$ , of binary electrolyte solutions obtained from the appropriate derivatives of the excess Gibbs free energy equation

is

$$\begin{aligned} \ln \gamma = \partial G^{ex}/RT \partial n = & - |z_M z_X| A \phi [I^{1/2}/(1 + bI^{1/2}) \\ & + (2/b) \ln(1 + bI^{1/2})] + m (2\nu_M \nu_X / \nu) B_{MX}^\gamma \\ & + m^2 [2(\nu_M \nu_X)^{3/2} / \nu] C_{MX}^\gamma \end{aligned} \quad (14)$$

where the terms are defined as before and  $B_{MX}^\gamma$  and  $C_{MX}^\gamma$  are Pitzer's activity coefficient parameters defined as

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + (2\beta_{MX}^{(1)}/\alpha^2 I) [1 - (1 + \alpha I^{1/2} - 1/2\alpha^2 I) \exp(-\alpha I^{1/2})] \quad (15)$$

$$C_{MX}^\gamma = 3/2 C_{MX}^\phi \quad (16)$$

where the terms are defined as before.

The effect of temperature and pressure on the parameters of this equation may be determined in either of two ways. Either experiments may be repeated as a function of temperature and pressure, or experiments may examine the derivatives of free energy, the volume and the enthalpy.

The partial derivatives of the total Gibbs free energy of the solution with respect to the pressure at constant temperature is equal to the total volume of the solution

$$V = (\partial G / \partial P)_{T,m} \quad (17)$$

By differentiating Eq. (6) with respect to pressure and substituting into Eq. (17), the total volume of the solution is given as

$$V = n_1 \bar{V}_1^\circ + n_2 \bar{V}_2^\circ + (\partial G^{\text{ex}}/\partial P)_{T,m} \quad (18)$$

where  $\bar{V}_1^\circ$  and  $\bar{V}_2^\circ$  are, respectively, the partial molal volumes of the solvent and solute.

The apparent molal volume of the solution,  $\phi_v$ , is defined as

$$\phi_v = (V - n_1 \bar{V}_1^\circ) / n_2 \quad (19)$$

where the terms are defined as before.

By substituting Eq. (18) into Eq. (19), the apparent molal volume can be defined in terms of the excess Gibbs free energy as

$$\phi_v = \bar{V}_2^\circ + (1/n_2) (\partial G^{\text{ex}}/\partial P)_{T,m} \quad (20)$$

where  $\bar{V}_2^\circ$  is the partial molal volume of the solute at infinite dilution. By differentiating the excess Gibbs free energy equation for a pure electrolyte solution, Eq. (9), with respect to the pressure and substituting into the apparent molal volume equation, Eq. (20), the final Pitzer equation for apparent molal volume is obtained

$$\begin{aligned} \phi_v = \bar{V}_2^\circ + \nu |z_M z_X| (A_v/2b) \ln(1 + bI^{1/2}) \\ + 2RT\nu_M\nu_X [m B_{MX}^v + m^2 (\nu_M z_M) C_{MX}^v] \end{aligned} \quad (21)$$

where  $\nu$  is the total number of ions formed from the dissociation of the salt ( $\nu = \nu_M + \nu_X$ ), and  $A_v$  is the Debye-Hückel slope for the volume [ $A_v = -4RT (\partial A_\phi/\partial P)_T = 1.874$ ].<sup>39</sup> The other terms are as defined before.  $B_{MX}^v$  and  $C_{MX}^v$  are the pressure

derivatives of the ion interaction parameters for Pitzer's free energy equation.

$$B_{MX}^v = (\partial B_{MX} / \partial P)_T \quad (22)$$

$$C_{MX}^v = (\partial C_{MX} / \partial P)_T \quad (23)$$

The excess Gibbs free energy equation for the mixture containing  $n_w$  kg of solvent is

$$\begin{aligned} G^{ex}/(n_w RT) = & - A_\phi (4I/b) \ln (1 + bI^{1/2}) \\ & + 2 \sum_c \sum_a m_c m_a [B_{ca} + (\sum m_z) C_{ca}] \\ & + \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'} + \sum_a m_a \psi_{cc'a}/2] \\ & + \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'} + \sum_c m_c \psi_{caa'}/2] \end{aligned} \quad (24)$$

where the sums are over the various cations  $c, c'$  and the anions  $a, a'$ , the quantity  $\sum m_z$  is the total electrical charge (positive or negative), and  $\theta$  and  $\psi$  are parameters related to the interaction of ions of the same sign.  $\theta$  depends on the ionic strength but  $\psi$  does not. The other terms are as defined before. This equation is not different from the original equation, Eq. (9), but is an extension where the  $\theta$  and  $\psi$  terms for mixtures were added. Differentiation of Eq. (24) with respect to pressure yields the excess volume of the mixture

$$\begin{aligned}
V^{ex}/(n_w RT) = & (A_v/RT) (I/b) \ln (1 + bI^{1/2}) \\
& + 2 \sum_c \sum_a m_c m_a [B_{ca}^v + (\sum m_z) C_{ca}^v] \\
& + \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'}^v + \sum_a m_a \psi_{cc'a}^v/2] \\
& + \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'}^v + \sum_c m_c \psi_{caa'}^v/2]
\end{aligned} \tag{25}$$

where  $B_{ca}^v$ ,  $C_{ca}^v$ ,  $\theta_{cc'}^v$ ,  $\theta_{aa'}^v$ ,  $\psi_{cc'a}^v$ , and  $\psi_{caa'}^v$  are the pressure derivatives of the ion interaction parameters for Pitzer's free energy equation.

$$\theta^v = (\partial \theta / \partial P)_T \tag{26}$$

$$\psi^v = (\partial \psi / \partial P)_T \tag{27}$$

Pitzer<sup>32,40</sup> has split the like-ion interaction parameter,  $\theta_{MN}$ , into two parts

$$\theta_{MN} = {}^s\theta_{MN} + {}^E\theta_{MN} \tag{28}$$

where  ${}^s\theta_{MN}$  accounts for the short range interactions and  ${}^E\theta_{MN}$  accounts for the electrostatic unsymmetric mixing effects. The  ${}^E\theta_{MN}$  term is only significant below an ionic strength of about 0.5 molal. Since our work was at ionic strengths higher than 0.5 molal,  ${}^E\theta_{MN}$  was not required.  ${}^s\theta_{MN}$ , which is related to the second virial coefficients, can be further separated in the same manner as  $B$  into a constant and an ionic strength dependent term

$$\theta = \theta^{(0)} + (2\theta^{(1)}/\alpha^2 I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \tag{29}$$

where the terms are defined as before.

The volume of mixing  $\Delta V_m$  is defined as the difference between the excess volume of the mixture and the excess volumes of the pure electrolyte solutions.

$$\Delta V_m = V^{\text{ex}}(\text{mix}) - y_2 V^{\text{ex}}(2) - y_3 V^{\text{ex}}(3) \quad (30)$$

where  $V^{\text{ex}}(\text{mix})$  is the excess volume of the mixture,  $V^{\text{ex}}(2)$  and  $V^{\text{ex}}(3)$  are the excess volumes of the two pure electrolytes,  $y_3$  is the ionic strength fraction of electrolyte 3 (electrolyte with the highest molecular weight), and  $y_2$  is the ionic strength fraction of electrolyte 2.

For a common anion mixture of electrolytes of charge type (1:1) MX salt and (2:1)  $\text{NX}_2$  salt, the volume of mixing equation is obtained by substituting Pitzer's excess volume equation, Eq. (25), into Eq. (30) yielding

$$\begin{aligned} \Delta V_m / (n_w R T I^2) = & y_3 y_2 \left[ -(2/3) B_{\text{MX}}^v - (2/9)(6-y_3) I C_{\text{MX}}^v \right. \\ & + (2/9) B_{\text{NX}}^v + (2/27)(5-y_3) I C_{\text{NX}}^v \\ & \left. + (2/3) \theta_{\text{MN}}^v + (1/9)(3-y_3) I \psi_{\text{MNX}}^v \right] \end{aligned} \quad (31)$$

where  $y_3$  is the ionic strength fraction of solution  $\text{NX}_2$  and  $y_2$  is the ionic strength fraction of solution MX.  $y_3$  is defined by the following equation

$$y_3 = w_3 m_3 / (w_2 m_2 + w_3 m_3) \quad (32)$$

where  $m_i$  is the molality of electrolyte  $i$  and  $w$  is a valence factor equal to 1, 3, and 4 for 1:1, 1:2, and 2:2 electrolytes, respectively.

The volume of mixing,  $\Delta V_m$ , has been traditionally fit using the equation<sup>33-35</sup>

$$\Delta V_m = y_2 y_3 n_w I^2 [RTv_0 + RTv_1 (1-2y_3)] \quad (33)$$

where  $\Delta V_m$  is the volume of mixing,  $v_0$  and  $v_1$  are mixing coefficients, and the remaining terms are as previously defined. When raw data is not available, Pitzer's mixing parameters can also be obtained from the traditional parameters ( $v_0$  and  $v_1$ ).<sup>33-</sup>

<sup>35</sup> The relationships of  $v_0$  and  $v_1$  to the corresponding in Pitzer parameters are

$$\begin{aligned} v_0 = & - (2/3) B_{MX}^v - (11/9)I C_{MX}^v + (2/9) B_{NX}^v \\ & + (1/3)I C_{NX}^v + (2/3) \theta_{MN}^v + (5/18)I \psi_{MNX}^v \end{aligned} \quad (34)$$

$$v_1 = -(1/9)I C_{MX}^v + (1/27)I C_{NX}^v + (1/18)I \psi_{MNX}^v \quad (35)$$

where the terms are defined as before.

### Enthalpic Equations

The relative apparent molal enthalpy is defined as

$$\phi_L = (L - n_1 L^\circ_1)/n_2 = L/n_2 \quad (36)$$

where  $L$  is the excess enthalpy of the solution,  $L^\circ_1$  is the excess enthalpy of the solvent, and  $n_1$  and  $n_2$  are the number of moles of the solvent and solute, respectively.

The excess enthalpy of the solution ( $L=H^{ex}$ ) is defined by the equation

$$L = H - H^\circ = -T^2 [\partial(G^{ex}/T) / \partial T]_{P,m} \quad (37)$$

where  $H^\circ$  is the enthalpy of the mixture at infinite dilution and  $H$  is the enthalpy of the mixture. By substitution of Eq. (37) into Eq. (36), the relative apparent molal enthalpy can be defined in terms of the excess Gibbs free energy as

$$\phi_L = -T^2/n_2 [\partial(G^{ex}/T) / \partial T]_{P,m} \quad (38)$$

By differentiating the excess Gibbs free energy equation for pure electrolyte solution, Eq. (9), with respect to the temperature and substituting into the relative apparent molal enthalpy equation, Eq. (38), the final Pitzer equation for the relative apparent molal enthalpy is obtained.

$$\begin{aligned} \phi_L = \nu \left| z_M z_X \right| (A_H/3b) \ln (1 + bI^{1/2}) \\ - 2RT^2 \nu_M \nu_X [m B_{MX}^L + m^2 (\nu_M z_M) C_{MX}^L] \end{aligned} \quad (39)$$

Differentiation of Eq. (24) with respect to temperature and substituting into Eq. (37), gives Pitzer's equation for the excess enthalpy of the mixture

$$\begin{aligned} L/(n_w RT^2) = (A_H I / RT^2 b) \ln (1 + bI^{1/2}) \\ - 2 \sum_c \sum_a m_c m_a [B_{ca}^L + (\sum m_z) C_{ca}^L] \\ - \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'}^L + \sum_a m_a \psi_{cc'a}^L / 2] \\ - \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'}^L + \sum_c m_c \psi_{caa'}^L / 2] \end{aligned} \quad (40)$$

where  $A_H$  is the Debye-Hückel parameter for enthalpy [ $A_H = 6RT^2 (\partial A_\phi / \partial T)_p =$

0.802]<sup>39</sup>,  $n_w$  is the number of kilograms of water,  $b$  is a parameter given the value 1.2 Kg<sup>1/2</sup>-mol<sup>-1/2</sup> for all solutions,  $I$  is the ionic strength,  $R$  is the gas constant (8.31441 J-mol<sup>-1</sup>-K<sup>-1</sup>),  $T$  is the temperature in kelvin, and  $m_i$  is the molality of ion  $i$ . The sums are over the various cations  $c$ ,  $c'$  and the various anions  $a$ ,  $a'$  while the quantity  $\sum mz$  is the total electrical positive (or negative) charge.  $B_{ca}^L$ ,  $C_{ca}^L$ ,  $\theta_{cc'}^L$ ,  $\theta_{aa'}^L$ ,  $\psi_{cc'a}^L$ , and  $\psi_{caa'}^L$  are the temperature derivatives of the ion interaction parameters for Pitzer's free energy equation.<sup>21,22,24,26,32,41</sup>

$$B_{ca}^L = (\partial B_{ca} / \partial T)_P \quad (41)$$

$$C_{ca}^L = (\partial C_{ca} / \partial T)_P \quad (42)$$

$$\theta_{ca}^L = (\partial \theta_{ca} / \partial T)_P \quad (43)$$

$$\psi_{ca}^L = (\partial \psi_{ca} / \partial T)_P \quad (44)$$

The enthalpy of mixing  $\Delta H_m$  is defined as the difference between the excess enthalpy ( $L=H^{ex}$ ) of the mixture and the excess enthalpies of the pure electrolyte solutions.

$$\Delta H_m = L_{mix} - y_2 L_2 - y_3 L_3 \quad (45)$$

where  $L_{mix}$  is the excess enthalpy of the mixture,  $L_2$  and  $L_3$  are the excess enthalpies of the pure electrolyte solutions, respectively,  $y_3$  is the ionic strength fraction of electrolyte 3 (electrolyte with the highest molecular weight), and  $y_2$  is the ionic

strength fraction of electrolyte 2.

For a common anion mixture of electrolytes of charge type (1:1) MX salt and (2:1) NX<sub>2</sub> salt the heat of mixing equation is obtained by substituting Pitzer's excess enthalpy equation, Eq. (40), into Eq. (45) yielding

$$\begin{aligned} \Delta H_m / (n_w R T^2 I^2) = & y_2 y_3 [(2/3) B_{MX}^L + (2/9)(6-y_3) I C_{MX}^L \\ & - (2/9) B_{NX}^L - (2/27)(5-y_3) I C_{NX}^L \\ & - (2/3) \theta_{MN}^L - (1/9)(3-y_3) I \psi_{MNX}^L] \end{aligned} \quad (46)$$

where  $y_3$  is the ionic strength fraction of solution NX<sub>2</sub> and  $y_2$  is the ionic strength fraction of solution MX.

Enthalpy of mixing data have been traditionally fit using the equation<sup>21,32,42</sup>

$$\Delta H_m = y_2 y_3 n_w I^2 [RTh_0 + RTh_1 (1-2y_3)] \quad (47)$$

where  $\Delta H_m$  is the heat of mixing,  $h_0$  and  $h_1$  are mixing coefficients, and the other terms are as previously defined. When raw data is not available, Pitzer's mixing parameters may also be obtained from the traditional parameters ( $h_0$  and  $h_1$ ).<sup>21,32,42</sup>

The relationships of  $h_0$  and  $h_1$  to the corresponding in Pitzer parameters are

$$\begin{aligned} h_0 = & T [(2/3) B_{MX}^L + (11/9) I C_{MX}^L - (2/9) B_{NX}^L \\ & - (1/3) I C_{NX}^L - (2/3) \theta_{MX}^L - (5/18) I \psi_{MNX}^L] \end{aligned} \quad (48)$$

$$h_1 = T [(1/9) I C_{MX}^L - (1/27) I C_{NX}^L - (1/18) I \psi_{MNX}^L] \quad (49)$$

where the terms are defined as before.

## CHAPTER III

### EXPERIMENTAL METHODS

This Chapter is divided into three sections: 3.1 deals with the preparation of solutions, 3.2 deals with the measurement of the density of solutions, and 3.3 deals with the measurement of the heat of mixing of transition metal chlorides with aqueous HCl.

#### Solution Preparation

The salts used were all A.C.S reagent grade without further purification. The stock concentrated solutions of HCl, CdCl<sub>2</sub>, CuCl<sub>2</sub>, MnCl<sub>2</sub>, and ZnCl<sub>2</sub> were prepared by mixing the salts with fresh ion-exchanged Millipore Milli-Q water, 18 MΩ. The prepared solutions were then filtered using Millipore 0.45 micrometer filters to remove any particulate contaminants. The molalities of these solutions were determined by measuring their densities using an Anton Paar DMA 602HT natural vibrating densimeter at 25°C and back calculating their concentration using the following equation<sup>43</sup>

$$d = d_0 + A_1m + A_2m^{3/2} + A_3m^2 + A_4m^{5/2} + A_5m^3 \quad (50)$$

where  $d$  is the density of solution (kg-m<sup>-3</sup>),  $d_0$  is the density of pure water,  $m$  is the

molality of the solution, and  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$ , and  $A_5$  are the coefficients of the polynomial in molality and are taken from the literature.<sup>29,31,44</sup> The coefficients for the density equation for each of the transition metal salts and for hydrochloric acid are given in Table (2). Weight dilutions were made from these stock solutions with fresh ion-exchanged Millipore Milli-Q water, 18 M $\Omega$ , to obtain the final solutions.

Mixtures were made by mixing known masses of hydrochloric acid solution with transition metal salt solution at the same ionic strength. The final molality,  $m_f$ , of hydrochloric acid in the mixture is given by the following equation

$$m_f = \frac{\frac{m_{\text{HCl}} g_{\text{HCl}}}{m_{\text{HCl}} M_{\text{HCl}} + 1000}}{\frac{g_{\text{HCl}}}{m_{\text{HCl}} M_{\text{HCl}} + 1000} + \frac{g_{\text{T.m}}}{m_{\text{T.m}} M_{\text{T.m}} + 1000}} \quad (51)$$

where  $m_{\text{HCl}}$  and  $m_{\text{T.m}}$  are, respectively, the initial molality of hydrochloric acid solution and transition metal solution,  $g_{\text{HCl}}$  and  $g_{\text{T.m}}$  are, respectively, the weight of hydrochloric acid and transition metal solution, and  $M_{\text{HCl}}$  and  $M_{\text{T.m}}$  are, respectively, the molar masses of hydrochloric acid and transition metal salt. By the same method we can calculate the final molality of transition metal salt in the mixture.

### Density Measurement

An Anton Paar DMA 602HT densimeter was used to measure the density of aqueous hydrochloric acid, transition metal solutions, and their mixtures. The

densimeter operates on the principle of measuring the natural vibration frequency of a tube containing a fluid [a diagram of a similar vibrating tube is given in Figure 1].<sup>45</sup>

The period ( $\tau$ ) is related to the mass ( $m$ ) of the tube by

$$\tau = 2\pi (m/k)^{1/2} \quad (52)$$

where  $k$  is an instrument constant. Since the volume of the tube is constant, the density ( $d$ ) of the fluid contained in the tube is directly related to the period ( $\tau$ ) by

$$d = A + B \tau^2 \quad (53)$$

where  $A$  and  $B$  are instrument constants. Relative densities were determined by measuring the period in a solution and a reference fluid

$$\Delta d = d - d_0 = B(\tau^2 - \tau_0^2) \quad (54)$$

where  $d$  and  $d_0$  are, respectively, the densities of the unknown solution and the reference fluid, and  $\tau$  and  $\tau_0$  are, respectively, the periods of the unknown solution and the reference fluid. The instrument constant  $B$  is calculated by measuring the period  $\tau$  for two fluids of known density, pure water (fresh ion-exchanged Millipore Milli-Q water, 18 M $\Omega$ ) and zero-grade nitrogen. The density of pure water is 997.045 kg-m<sup>-3</sup> at 25°C and is taken from Kell.<sup>46</sup> The density of nitrogen at 25°C was calculated as a function of barometric pressure from its equation of state.<sup>47</sup> The temperature of the densimeter was set to 25 $\pm$ 0.005°C using an N.B.S. certified mercury thermometer (Parr, serial NO.9D8669).

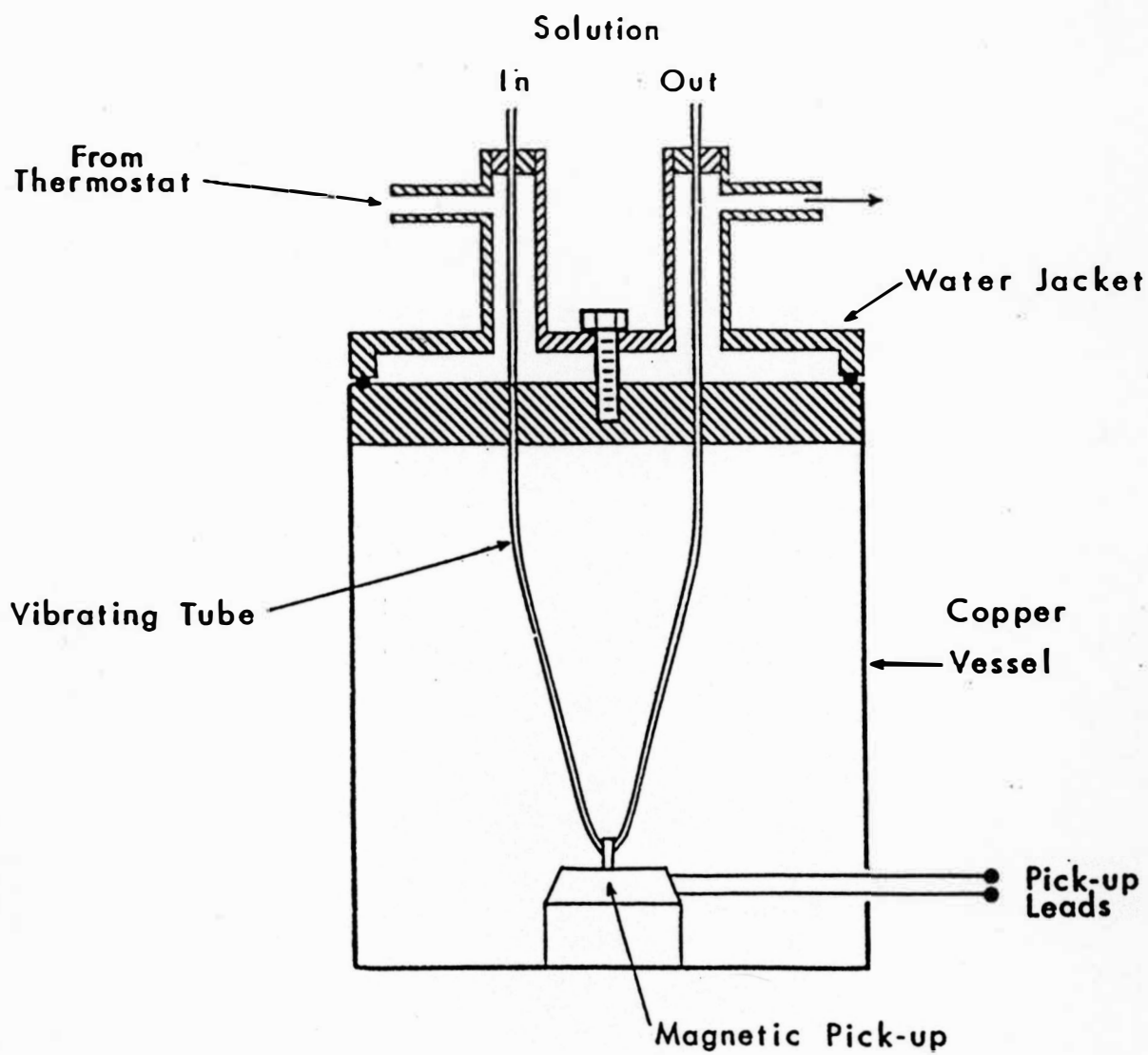


Figure 1. Vibrating Densimeter.

Table 2

The Coefficients for the Density Equation for Each of the  
Transition Metal Salts and for Hydrochloric Acid

Electrolyte	$A_1^a$	$A_2^a$	$A_3^a$	$A_4^a$	$A_5^a$	Ref.
HCl	18.54168	-1.32594	0.00699	0.05899	0.00764	44
CdCl <sub>2</sub>	159.8545	-5.91724	-4.40232	0.0	0.0	29
CuCl <sub>2</sub>	123.3914	-5.27145	-4.53473	0.51460	0.0	29
MnCl <sub>2</sub>	106.572	-3.94279	-3.60195	0.43277	0.0	29
ZnCl <sub>2</sub>	124.6518	2.09408	-20.6873	2.25840	1.77758	31

<sup>a</sup>Units: Kg-m<sup>-3</sup>.

The density was determined by the method described by Connaughton<sup>35</sup>, as follows: the densimeter was filled with solution through the use of a peristaltic pump set at a very slow flow rate (about 0.5 ml/min) to prevent entrapping air bubbles as the solution entered the cell. The entire flow system was flushed with an excess of the fluid about to be measured (approximately 10 mls compared to the total volume of about 1.5 ml for the densimeter cell) before the pump was turned off. After a period of at least 5 minutes for temperature equilibration, period of oscillation readings were taken. If the reading was stable, indicating temperature equilibration and no air bubbles, then a total of 10 readings were taken and averaged. For calibration of the densimeter, pure water was introduced into the cell and readings were taken. The cell was then dried using nitrogen, which was passed through a gas drying column (containing drierite) and a second drying column that contained molecular sieves for trapping any particulate contaminants. The flow rate of nitrogen was monitored by placing the exit tube from the densimeter into a flask of water. After the cell was completely dry, the flow rate of nitrogen was adjusted until a single bubble was suspended from the exit tube. This was done to ensure that the nitrogen was at atmospheric pressure and to prevent water from entering the system through this tubing. Period of oscillation readings were then taken and averaged. The flow rate was increased to again flush the cell with a fresh stream of nitrogen, and then decreased as before. The procedure was repeated to give three different period averages for nitrogen. The cell was then flushed again with water and new period values for water were taken. The pressure of nitrogen in the cell was

assumed to be equal to the atmospheric pressure. The atmospheric pressure was determined using a mercury barometer. The instrument constant B was then calculated using the period readings obtained for pure water and nitrogen. This procedure was repeated every alternate day prior to running the solution density. At 25°C, the instrument constant,  $10^3B$ , for the densimeter was equal to  $57.395 \pm 0.003$ .

The solutions were then run in the same manner, with one reading for water and one reading for the solution. All solutions were run three times with a reproducibility of 0.01 percent. After the third run for the solution was completed, the cell was flushed first with water then with dilute nitric acid, and then again with water before the water for the next set of readings was introduced. In this manner, water then solution, then water were run for all the solutions. From these period measurements, the relative densities,  $\Delta d$ , were determined.

### Heat Measurement

An L.K.B Batch Microcalorimeter (Model No. 10700) was used to measure the heats of mixing. The heat change due to mixing known masses of each transition metal solution and hydrochloric acid solution in the reaction cell caused a temperature difference and heat flow between the mixing cell and the heat sink. The heat sink, with its relatively high heat capacity, liberates or absorbs this heat flow. The thermopile which was located between the mixing cell and the heat sink measured the heat flow as a temperature difference, which is output as an electrical potential. The area under the potential versus time curve is proportional to the experimental heat and

is accurate to 0.5 percent. To cancel disturbances, the output of the thermopile of the sample cell is connected in opposition to the thermopile of the reference cell.

In our experiments the reference cell was left empty and mechanical heats of mixing were measured in a second mixing following the initial reaction. The output was measured and recorded by a Shimadzu Chromatopac (Model C-R3A) integrator.

The heat of mixing was determined by the following method: first the calorimeter is adjusted to 25°C and allowed to equilibrate before starting the calorimetric experiment. The solutions are added to the calorimeter with a syringe. The syringe is first flushed with the solution and discharged. This is to make certain that there is nothing else in the syringe but the proper solution. The syringe is then used to extract the desired volume of solution. The syringe is weighed to 0.01 mg using a balance with an accuracy of 0.02 mg. The solution is then injected into the proper cell. The syringe is weighed again for the precise determination of solution added. Repeat this procedure for the other reactant, which is added to the other side of the cell (see Figure 2).<sup>48</sup> The temperature was maintained at  $25 \pm 0.005^\circ\text{C}$  and monitored with a thermocouple using a multimeter. After two hours the internal components of the calorimeter will have reached thermal equilibrium.

Once the system has come to equilibrium it must be calibrated. The system can be electrically calibrated using a heater inside the cell (see figure (2)).<sup>48</sup> The calibration heat,  $Q_{\text{cal}}$ , can be calculated using the following equation

$$Q_{\text{cal}} = V^2/R \times t \quad (55)$$

### Batch Microcalorimeter

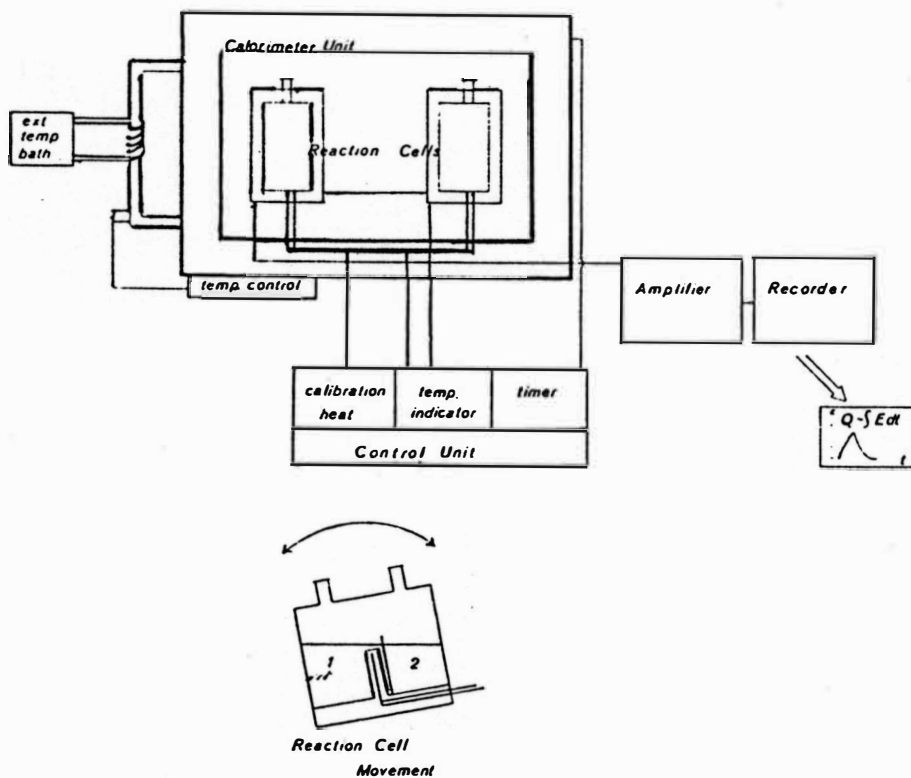


Figure 2. The LKB Batch Microcalorimeter.

where  $V$  is the voltage in volts,  $R$  is the resistance in ohms, and  $t$  is the second calibration time in sec.

Once the system has been calibrated the mixing experiment may be performed. After the first mix has been run a second mix needs to be run to account for any mechanical heats of mixing. To ensure the heat for second calibration is the same as the heat of the mixture, the time of the calibration run must be adjusted using the following equation

$$\text{new time} = (A_{\text{mix}} / A_{\text{cal}}) \times t \quad (56)$$

where  $A_{\text{mix}}$  is the area under the potential time curve for the mixing experiment,  $A_{\text{cal}}$  is the area under the potential time curve for the first calibration experiment, and  $t$  is the initial calibration time in sec.

Adjust the timer to the new time, then the second calibration may be run.

The heat of mixing,  $Q_{\text{mix}}$ , can be calculated using the equation

$$Q_{\text{mix}} = Q_{\text{cal}} \times (A_{\text{mix}} / A_{\text{cal}}) \quad (57)$$

where  $A_{\text{cal}}$  is the area under the potential time curve for the second calibration experiment

The heat of mixing,  $\Delta H_m$ , can be calculated using the equation

$$\Delta H_m = Q_{\text{mix}} / W_{\text{H}_2\text{O}} \quad (58)$$

where  $W_{\text{H}_2\text{O}}$  is the weight of water of the final mixture in kg.

To empty and clean the cell the liquid is removed using a syringe fitted with a teflon tube. Then the cell is cleaned by injecting Milli Q-water and pushing the mixing start button. The water is removed and these processes are repeated once using 10% nitric acid, then three times with Milli Q-water, and finally with acetone. Then the cell is dried by blowing air through both sides for at least 10 minutes.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### Calculation of the Volume of Mixing and Their Parameters

The densities of mixing of aqueous solutions of four transition metal chlorides,  $\text{CdCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{MnCl}_2$ , and  $\text{ZnCl}_2$  with aqueous solutions of hydrochloric acid at constant molal ionic strengths of 1.0 and 3.0 at 25°C were determined. The mixtures were made by mixing the transition metal chlorides with HCl in the proportion of 4:1, 3:2, 7:3, 1:1, 2:3, and 1:4 by volume at constant ionic strength. This was done with each transition metal at each ionic strength. Once the densities had been measured, the apparent equivalent volumes of the two binary solutions [ $\phi_v(2)$  and  $\phi_v(3)$ ] and the mean apparent equivalent volume of the resulting mixture [ $\phi_v(2, 3)$ ], were calculated using equations (2) and (3). The volumes of mixing ( $\Delta V_m$ ) were then calculated using these values of  $\phi_v$ 's and Equation (5).

The binary interaction parameters of  $\text{CuCl}_2$ <sup>49</sup> and  $\text{MnCl}_2$ <sup>50</sup> were taken from the literature. Since there was a variation in the literature in the binary interaction parameters of HCl,<sup>37,51,52</sup>  $\text{CdCl}_2$ ,<sup>53,54</sup> and  $\text{ZnCl}_2$ ,<sup>53-55</sup> we refit these data to the Pitzer apparent molal volume equation, Eq. (21). The new parameters, along with the parameters for the other salts previously determined and the standard deviation of the fit are given in Table 3.

Table 3  
The Parameters for Pitzer's Apparent Molal Volume Equation

Electrolyte	$\phi V^{\circ(a,d)}$	$\beta^{(0)v(b,d)}$	$\beta^{(1)v(c,d)}$	$C^{v(c,d)}$	Ref.
		$\times 10^5$	$\times 10^5$	$\times 10^6$	
HCl	17.48(0.049)	0.0	1.48(0.21)	0.097(0.0014)	e
CdCl <sub>2</sub>	22.36(0.18)	0.0	5.4(1.7)	10.1(1.2)	e
CuCl <sub>2</sub>	10.10	3.12	-1.59	-4.18	49
MnCl <sub>2</sub>	18.15	1.47	-7.23	-2.26	50
ZnCl <sub>2</sub>	10.71(0.94)	18.2(2.5)	-43.(17.)	-60.(14.)	e

<sup>a</sup>Units: cm<sup>3</sup>-mol<sup>-1</sup>. <sup>b</sup>Units: Kg-mol<sup>-1</sup>-atm<sup>-1</sup>. <sup>c</sup>Units: Kg<sup>2</sup>-mol<sup>-2</sup>-atm<sup>-1</sup>. <sup>d</sup>The numbers in the parentheses is the standard error in the parameter. <sup>e</sup>This work.

Appendix B lists the experimental densities for each of the mixtures and the calculated  $\phi_v(2)$ ,  $\phi_v(3)$ ,  $\phi_v(2,3)$ , and  $\Delta V_m$  at constant ionic strength of  $I=1.0$  and  $3.0$  at  $25^\circ\text{C}$ . The large value of  $\Delta V_m$  is due to cation-cation interactions between the  $\text{Zn}^{+2}$  and  $\text{H}^+$  ions. All of the values of  $\Delta V_m$  increased with increasing ionic strength, due to the closer proximity of the ions.

The volumes of mixing ( $\Delta V_m$ ) of the ternary solutions were then fit to the traditional equation, Eq. (33). The resulting interaction parameters  $v_0$  and  $v_1$  along with their standard deviations, and the standard deviation of the fits are reported in Table 4.

The parameter  $v_0$  is a measure of the magnitude of the ionic interactions occurring in the solution after mixing, and the parameter  $v_1$  is a measure of the skew or asymmetry of  $\Delta V_m$  when plotted versus the ionic strength fraction.<sup>56</sup> When two electrolytes with a common anion are mixed,  $v_0$  is related to cation-cation interaction. In this study the cations were  $\text{H}^+$  and transition metals. Using Table 4, the sign and change in magnitude of  $v_0$  can be used to understand the ionic interactions occurring in the solution. These interactions can be explained by utilizing the model for water structure proposed by Gurney.<sup>57</sup> Gurney described a cosphere model for water structure that states that water can exist in two different forms: a more structured form and a less structured form. When ion-ion or ion-water interactions lead to the more structured form, the volume is increased due to the formation of more hydrogen bonds. When the ionic interactions lead to the less structured form, the volume is decreased due to the breaking of hydrogen bonds. This can be seen in the sign of  $v_0$ .

Table 4  
The Parameters for the Traditional Equation, Eq.(33),  
For Each of the Mixtures at I=1.0 and I=3.0

Salt	I	$RTv_0^{a,c}$	$RTv_1^{a,c}$	$\sigma^{b,d}$
$CdCl_2$	1.0	0.614(0.013)	0.189(0.039)	0.012
	3.0	0.7016(0.0079)	0.644(0.024)	0.0071
$CuCl_2$	1.0	0.2825(0.0073)	0.049(0.022)	0.0065
	3.0	0.2659(0.0021)	0.0	0.0019
$MnCl_2$	1.0	0.1701(0.0036)	0.039(0.011)	0.0032
	3.0	0.06678(0.00092)	0.0066(0.0028)	0.00082
$ZnCl_2$	1.0	1.3701(0.0085)	0.532(0.026)	0.0076
	3.0	2.195(0.013)	0.675(0.040)	0.011

<sup>a</sup>Units:  $cm^3 \cdot Kg \cdot mol^{-2}$ . <sup>b</sup>Units:  $cm^3 \cdot Kg^{-1}$ , water. <sup>c</sup>The numbers in the parentheses are the standard errors in the parameters. <sup>d</sup>The standard error in the fit.

A positive  $v_0$  indicates that the volume change has created a more highly structured water, a negative  $v_0$  indicates that the change in volume has led to a less structured water. This theory was further expanded by Young et al<sup>58,59</sup> who stated that the mixing of two cations of the same size (two large or two small) causes heat to be absorbed and an increase in volume. The mixing of two cations of different sizes

causes heat to be evolved and a decrease in volume. From these studies the ions can be divided into two groups:<sup>60,61</sup> Structure-makers, which are characterized by increase in the order (decrease in the entropy) which is greatest for the smallest ions with larger charges. Structure-breakers, which are characterized by increase in the disorder (increase in the entropy) which is greatest for the largest ions with smaller charges.

In our case the two cations ( $H^+$  and the transition metal ion) are structure makers, therefore  $v_0$  and  $\Delta V_m$  for all mixtures will have a positive signs due to the formation of more structured water.

The magnitudes of the values of  $v_0$  and  $\Delta V_m$  will increase as the magnitude of the limiting partial molal volumes ( $\bar{V}^\circ$ ) of ions at zero molality increase.<sup>56,59</sup> Therefore in the case of a structure maker, with a structure maker as the partial molal volumes get more negative we get larger volumes of mixing. This is the trend we see with hydrochloric acid and transition metal salts with the exception of copper. This anomalous behavior of copper has been seen before.<sup>30,31</sup>

The volumes of mixing  $\Delta V_m$  for the four systems are plotted in Figures 3 through 6 as a function of ionic strength fraction  $y_3$  at constant ionic strengths of  $I=1.0$  and  $I=3.0$  at  $25^\circ C$ . These figures (3-6) show that in the case of  $CdCl_2$  and  $ZnCl_2$  the plots are skewed, however in the case of  $CuCl_2$  and  $MnCl_2$  the plots are fairly symmetrical about the  $y_3 = 0.5$  point, showing very little to no skew.

We can see from the data in Table 4 that the interaction parameter  $v_1$  for the systems  $HCl-CdCl_2$  and  $HCl-ZnCl_2$  is large, so we expect to see the skew. In the

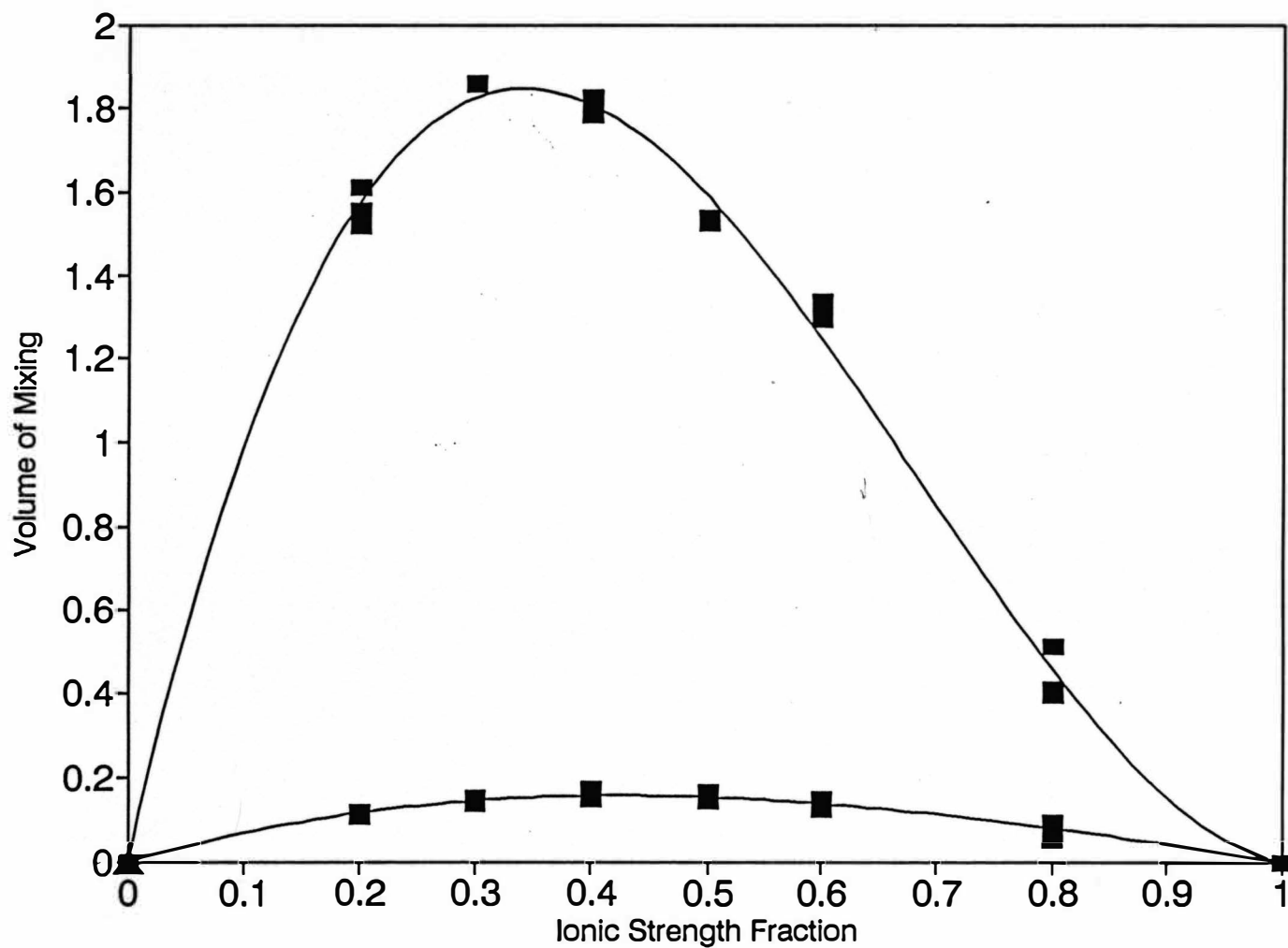


Figure 3. The Volume of Mixing in  $\text{cm}^3\text{-kg}^{-1}$  Plotted vs. The Ionic Strength Fraction,  $y_3$ , for  $\text{HCl-CdCl}_2$  Mixtures at Constant Ionic Strength of  $I=1.0$  and  $I=3.0$  at  $25^\circ\text{C}$ : At  $I=3.0$  Upper Set and at  $I=1.0$  Lower Set.

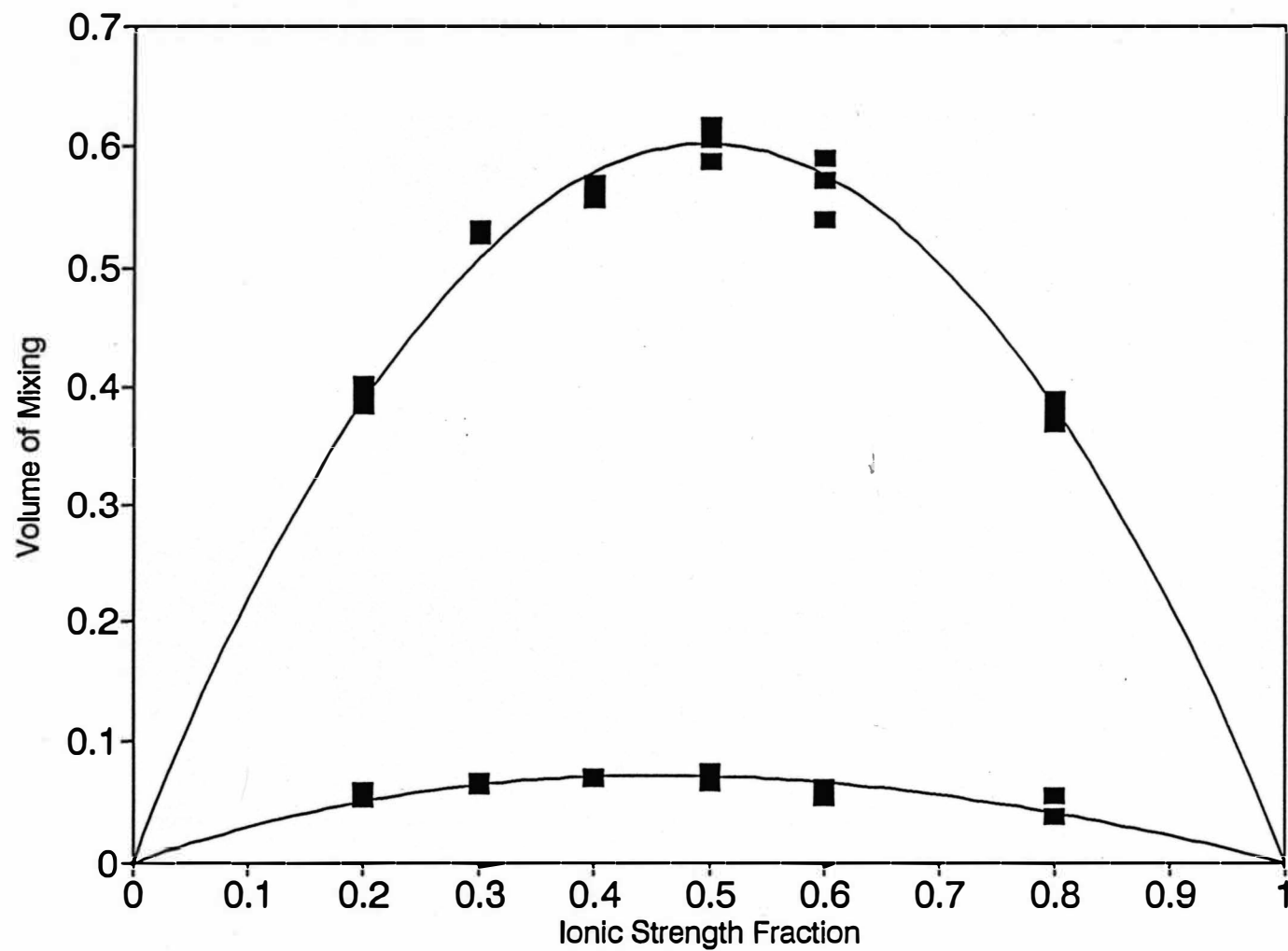


Figure 4. The Volume of Mixing in  $\text{cm}^3\text{-kg}^{-1}$  Plotted  $\nu s.$  The Ionic Strength Fraction,  $y_3$ , for HCl-CuCl<sub>2</sub> Mixtures at Constant Ionic Strength of  $I=1.0$  and  $I=3.0$  at  $25^\circ\text{C}$ : At  $I=3.0$  Upper Set and at  $I=1.0$  Lower Set.

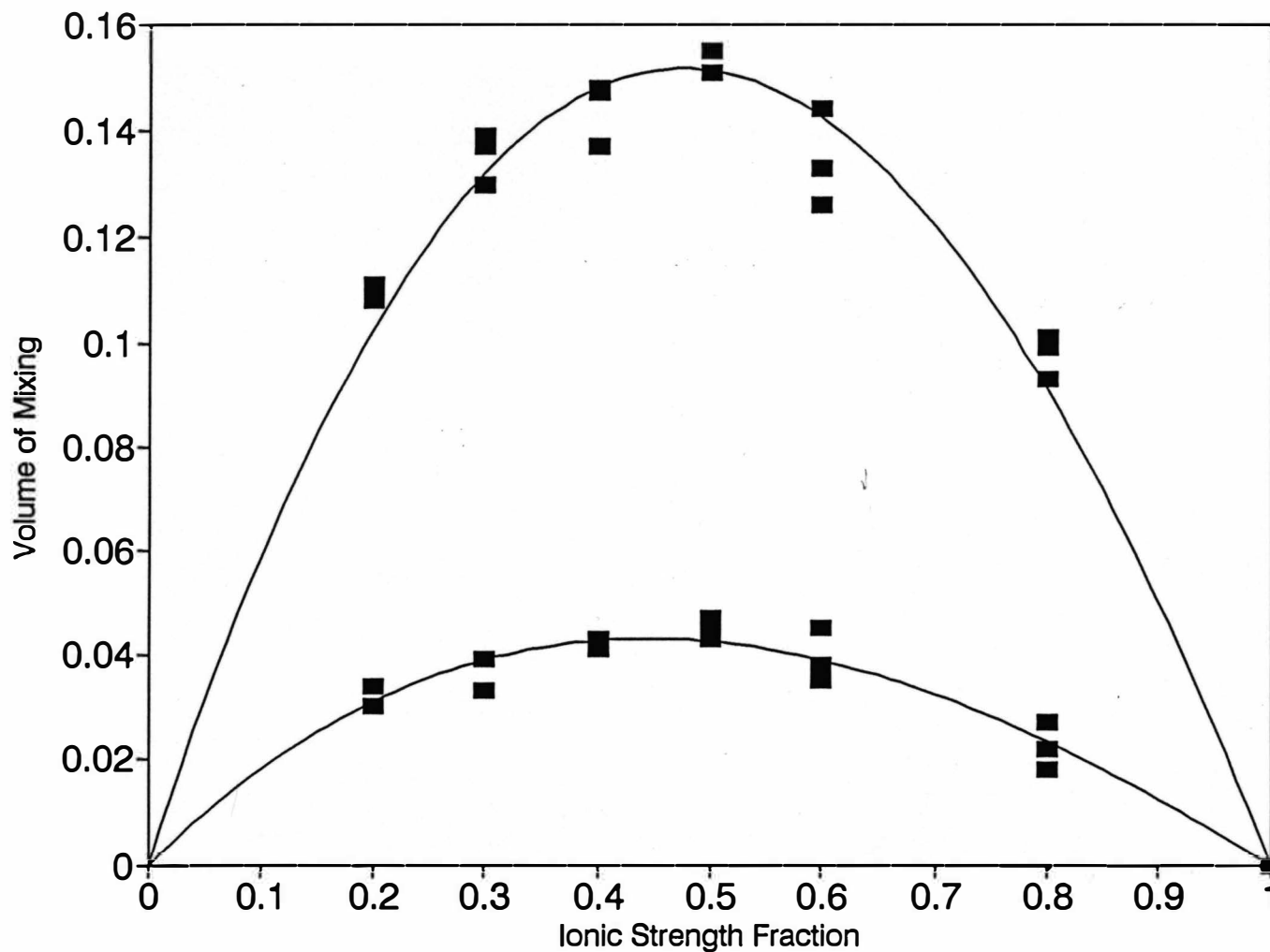


Figure 5. The Volume of Mixing in  $\text{cm}^3\text{-kg}^{-1}$  Plotted  $\nu s.$  The Ionic Strength Fraction,  $y_3$ , for  $\text{HCl-MnCl}_2$  Mixtures at Constant Ionic Strength of  $I=1.0$  and  $I=3.0$  at  $25^\circ\text{C}$ : At  $I=3.0$  Upper Set and at  $I=1.0$  Lower Set.

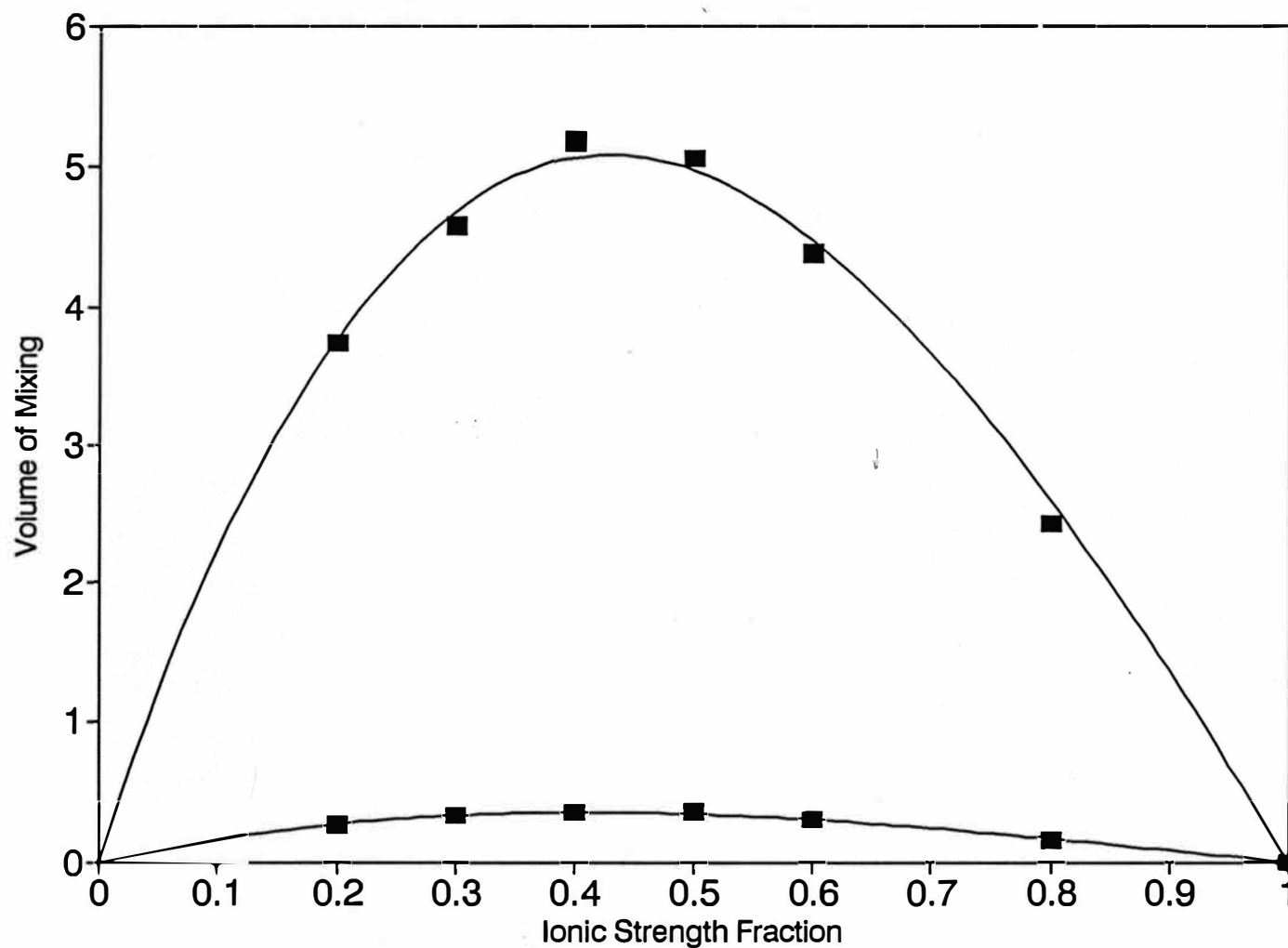


Figure 6. The Volume of Mixing in  $\text{cm}^3\text{-kg}^{-1}$  Plotted  $\nu s.$  The Ionic Strength Fraction,  $y_3$ , for HCl-ZnCl<sub>2</sub> Mixtures at Constant Ionic Strength of  $I=1.0$  and  $I=3.0$  at  $25^\circ\text{C}$ : At  $I=3.0$  Upper Set and at  $I=1.0$  Lower Set.

case of the systems HCl-CuCl<sub>2</sub> and HCl-MnCl<sub>2</sub> the magnitude of the  $v_1$  parameters is small. In addition, if we compare the  $v_1$  parameters for the systems HCl-CuCl<sub>2</sub> and HCl-MnCl<sub>2</sub> with their errors, they are of the same magnitude, therefore we don't expect to see the skew. For example in the case of the system HCl-CuCl<sub>2</sub> at ionic strength 3.0 we don't require a  $v_1$  parameter.

Pitzer's volume of mixing equation, Eq. (31), was also fit to the volume of mixing data. The resulting parameters along with their standard deviations, and the standard deviation in the fits are listed in Table 5.

In previous studies only two parameters [ $\theta^{(0)}$  and  $\psi$ ] have been required for unsymmetrical mixing. From Table 5 it can be seen that CdCl<sub>2</sub> and ZnCl<sub>2</sub> required three parameters [ $\theta^{(0)v}$ ,  $\theta^{(1)v}$ , and  $\psi^v$ ] to fit the data. The requirement of the ionic strength dependent term,  $\theta^{(1)v}$ , can be seen in Figure 7. This variation with ionic strength is not surprising considering these salts are significantly complexed even at low concentration.<sup>62,63</sup> The two remaining salts, CuCl<sub>2</sub> and MnCl<sub>2</sub>, required only two parameters,  $\theta^{(0)v}$  and  $\psi^v$  for CuCl<sub>2</sub> and  $\theta^{(1)v}$  and  $\psi^v$  for MnCl<sub>2</sub>. The magnitude of these parameters are smaller than the magnitude of the parameters in the case of CdCl<sub>2</sub> and ZnCl<sub>2</sub> due to smaller volumes of mixing. The smaller volume of mixing also does not allow us to determine all the three parameters. This means that in the case of MnCl<sub>2</sub> the value of  $\theta^{(0)v}$  is either equal to zero or smaller than the magnitude of the error in the parameter. In the case of CuCl<sub>2</sub> the data is insufficient to show any ionic strength dependence in  $\theta^v$ .

While little data is available on the volume of mixing of transition metal salts

Table 5  
Parameters Required for Pitzer's Volume of Mixing Equation

$10^5 \theta^{(0)v(a,c)}$	$10^5 \psi^{v(b,c)}$	$10^5 \theta^{(1)v(a,c)}$	$10^5 \sigma^d$
HCl-CdCl <sub>2</sub>			
-27.2(1.1)	15.12(0.54)	81.9(3.1)	0.030
1.84(0.89)	1.53(0.74)		0.167
HCl-ZnCl <sub>2</sub>			
-18.4(1.7)	18.46(0.80)	64.8(4.6)	0.054
4.57(0.75)	7.71(0.62)		0.140
HCl-CuCl <sub>2</sub>			
0.46(1.1)	0.27(0.54)	2.8(3.1)	0.012
1.45(0.19)	-0.19(0.16)		0.013
HCl-MnCl <sub>2</sub>			
-0.93(1.1)	0.28(0.54)	8.7(3.1)	0.0061
	-0.164(0.073)	6.2(0.54)	0.0079

<sup>a</sup>Units: Kg-mol<sup>-1</sup>-K<sup>-1</sup>. <sup>b</sup>Units: Kg<sup>2</sup>-mol<sup>-2</sup>-K<sup>-1</sup>. <sup>c</sup>The numbers in the parentheses are the standard errors in the parameters. <sup>d</sup>The standard errors in the fit.

with HCl, there was a previous study by Török and Berces.<sup>37</sup> They studied the volume of mixing of CuCl<sub>2</sub> and MnCl<sub>2</sub> with HCl at constant ionic strength of I=10

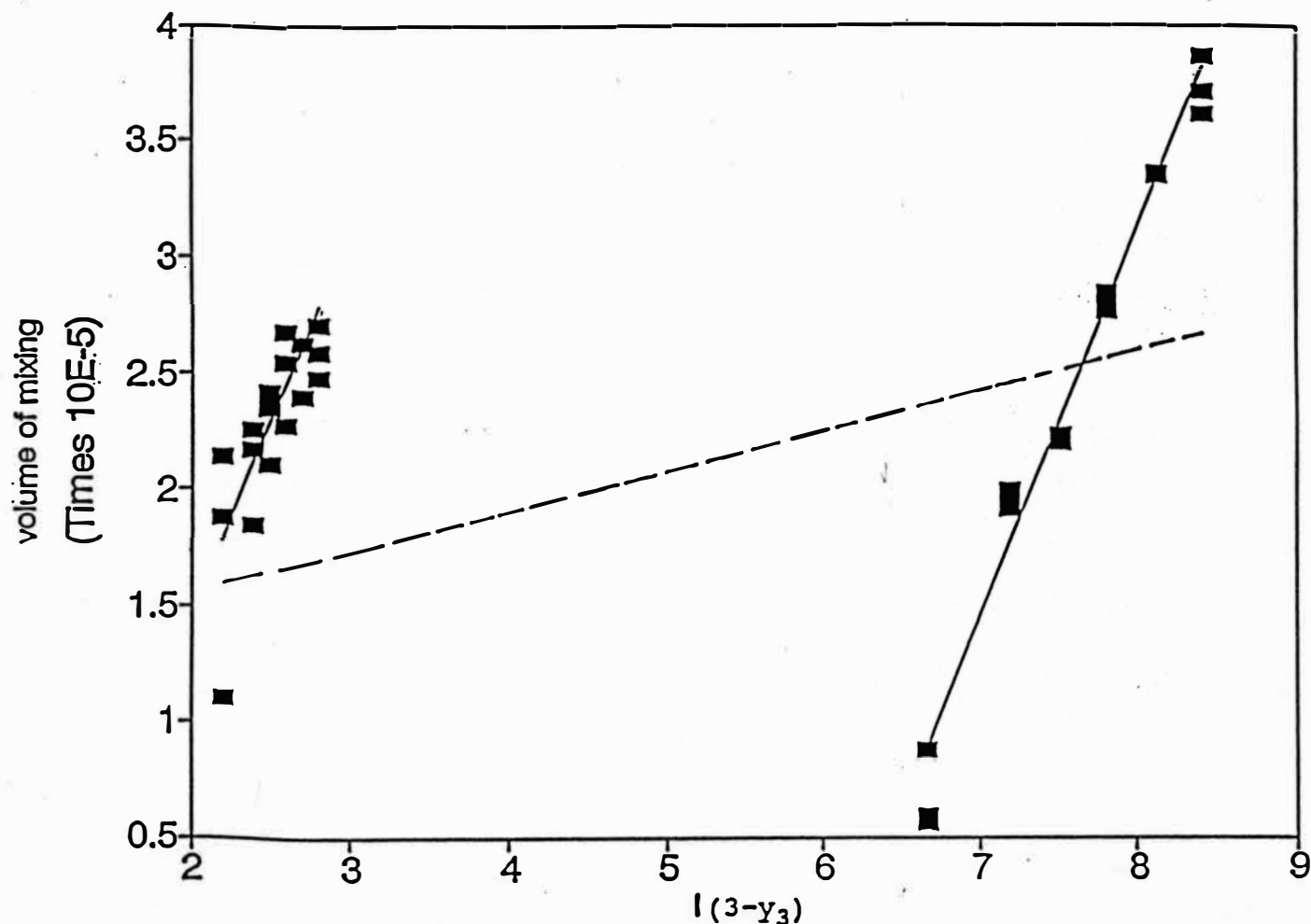


Figure 7. The Volume of Mixing in  $\text{cm}^3\text{-kg}^{-1}$  Divided by  $RTI^2$  of Aqueous Solutions of  $\text{CdCl}_2$  with Aqueous Solutions of Hydrochloric Acid as a Function of Ionic Strengths Times  $(3-y_3)$ .

The solid symbols represent our experimental data (■), the solid line represents the three parameter fit, and the dashed line represent the two parameter fit.

at 25°C. Since their data was at an ionic strength much higher than ours, we decided to combine their data with our data in a fit of Pitzer's volume of mixing equation, Eq. (31). The resulting parameters along with the final parameters for the mixtures of HCl-CdCl<sub>2</sub> and HCl-ZnCl<sub>2</sub> are shown in Table 6.

From Table 6 it can be seen that CuCl<sub>2</sub> again required the parameters  $\theta^{(0)v}$  and  $\psi^v$ , while MnCl<sub>2</sub> again required the parameters  $\theta^{(1)v}$  and  $\psi^v$ . This means that the number of parameters needed was the same as with our original fit but the magnitude of the parameters have changed. This change in the magnitude of the parameters is not surprising since the equation has been extended to an ionic strength of 10.0 molal.

Table 6  
The Parameters for Pitzer's Volume of Mixing Equation

System	$10^5 \theta^{(0)v}_{MN}{}^{a,c}$	$10^5 \psi^v_{MN}{}^{b,c}$	$10^5 \theta^{(1)v}_{MN}{}^{a,c}$
HCl-CdCl <sub>2</sub>	-27.2(1.1)	15.12(0.54)	81.9(3.1)
HCl-CuCl <sub>2</sub>	1.120(0.062)	0.026(0.016)	0.0
HCl-MnCl <sub>2</sub>	0.0	-0.0866(0.0056)	5.71(0.28)
HCl-ZnCl <sub>2</sub>	-18.4(1.7)	18.46(0.80)	64.8(4.6)

<sup>a</sup>Units: Kg-mol<sup>-1</sup>-K<sup>-1</sup>. <sup>b</sup>Units: Kg<sup>2</sup>-mol<sup>-2</sup>-K<sup>-1</sup>. <sup>c</sup>The numbers in the parentheses are the standard errors in the parameters.

### Calculation of the Heat of Mixing and Their Parameters

The heat of mixing of aqueous solutions of four transition metal chlorides,  $\text{CdCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{MnCl}_2$ , and  $\text{ZnCl}_2$ , with aqueous solutions of hydrochloric acid at constant molal ionic strengths at  $25^\circ\text{C}$ , were determined at molal ionic strength 1.0 and 3.0. The mixtures were made by mixing the transition metal chlorides with  $\text{HCl}$  in the proportion of 4:1, 3:2, 1:1, 2:3, and 1:4 by volume at constant ionic strength. Once the heat had been determined, the enthalpy of mixing was calculated using Equation (58).

Appendix C lists the experimental heat for each of the mixtures and the calculated  $\Delta H_m$  at constant ionic strength of  $I=1.0$  and  $3.0$  at  $25^\circ\text{C}$ . The largest value of  $\Delta H_m$  is due to cation-cation interactions between the  $\text{Zn}^{2+}$  and  $\text{H}^+$  ions. All of the values of  $\Delta H_m$  increased with increased ionic strength, due to the closer proximity of the ions.

The heats of mixing of the ternary solutions were then fit to the traditional equation, Eq. (47), in the same manner as the volumes of mixing data. The resulting interaction parameters  $h_0$  and  $h_1$  along with their standard deviations, and the standard deviation of the fits are listed in Table 7.

The parameter  $h_0$  like  $v_0$  is related to the magnitude of the ionic interactions occurring in the solution after mixing, and the parameter  $h_1$  is a measure of the skew or asymmetry of  $\Delta H_m$  when plotted versus the ionic strength fraction.<sup>56</sup> When two electrolytes with a common anion are mixed,  $h_0$  is related to cation-cation interaction,

in this study the cations were  $H^+$  and transition metals. Using Table 7, the sign and magnitude of  $h_0$  can be used to understand the ionic interactions occurring in the solution. These interactions can be explained by the theories of Desnoryes et al.<sup>64</sup> who stated that two solutes will attract each other if their structural influences, or their tendencies to orient water molecules are compatible with each other; conversely, an incompatibility in these structural influences or tendencies will result in repulsion forces. This theory was further developed by Wood and Anderson<sup>65</sup> who stated that the sign of the heats of mixing follows a simple rule. The mixing of two structure makers or structure breakers gave endothermic heats of mixing, while a structure maker with a structure breaker gave an exothermic heat of mixing.

It is evident from the positive sign of  $h_0$  ( $\Delta H_m$ ) for all mixtures that the heat change due to mixing has led to a more highly structured water. The positive sign is expected, the mixing of structure maker,  $H^+$ , and structure maker, transition metal, leads to more structured water and increases the enthalpy.

The magnitude of the value of  $h_0$  and  $\Delta H_m$  will increase as the magnitude of the limiting partial molal volumes ( $\bar{V}^\circ$ ) of ions at zero molality increase.<sup>56,59</sup> Therefore in the case of a structure maker with a structure maker as the partial molal volumes get more negative, the heats of mixing get larger. This is the trend we see with hydrochloric acid and transition metal salts with the exception of copper. This anomalous behavior of copper has been seen before.<sup>30,31</sup>

The heat of mixing  $\Delta H_m$  for the four systems are plotted in Figures 8 through 11 as a function of ionic strength fraction  $y_3$  at constant ionic strengths of  $I=1.0$  and

$I=3.0$  at  $25^{\circ}\text{C}$ . These figures show that in the case of  $\text{CdCl}_2$  and  $\text{ZnCl}_2$  the plots are skewed, however in the case of  $\text{CuCl}_2$  the plot is fairly symmetrical about  $y_3=0.5$  point, showing very little to no skew.

Table 7

The Parameters for the Traditional Equation, Eq.(47),  
for Each of the Mixtures at  $I=1.0$  and  $I=3.0$

Salt	I	$RTh_0^{a,c}$	$RTh_1^{a,c}$	$\sigma^{b,d}$
$\text{CdCl}_2$	1.0	610.7(1.8)	215.6(5.8)	1.5
	3.0	352.2(3.9)	353.(12.)	3.2
$\text{CuCl}_2$	1.0	383.5(3.9)	46.(12.)	3.2
	3.0	340.7(1.5)	17.9(4.8)	1.3
$\text{MnCl}_2$	1.0	98.8(2.4)	-23.2(7.8)	2.0
	3.0	70.40(0.28)	-16.39(0.88)	0.23
$\text{ZnCl}_2$	1.0	1308.8(6.4)	581.(20.)	5.3
	3.0	1866.(25.)	662.(80.)	21.

<sup>a</sup>Units:  $\text{J-Kg-mol}^{-2}$ . <sup>b</sup>Units:  $\text{J-Kg}^{-1}$ ,water. <sup>c</sup>The numbers in the parentheses are the standard errors in the parameters. <sup>d</sup>The standard error in the fit.

We can see from the data in Table 7 that the interaction parameter  $h_1$  for the

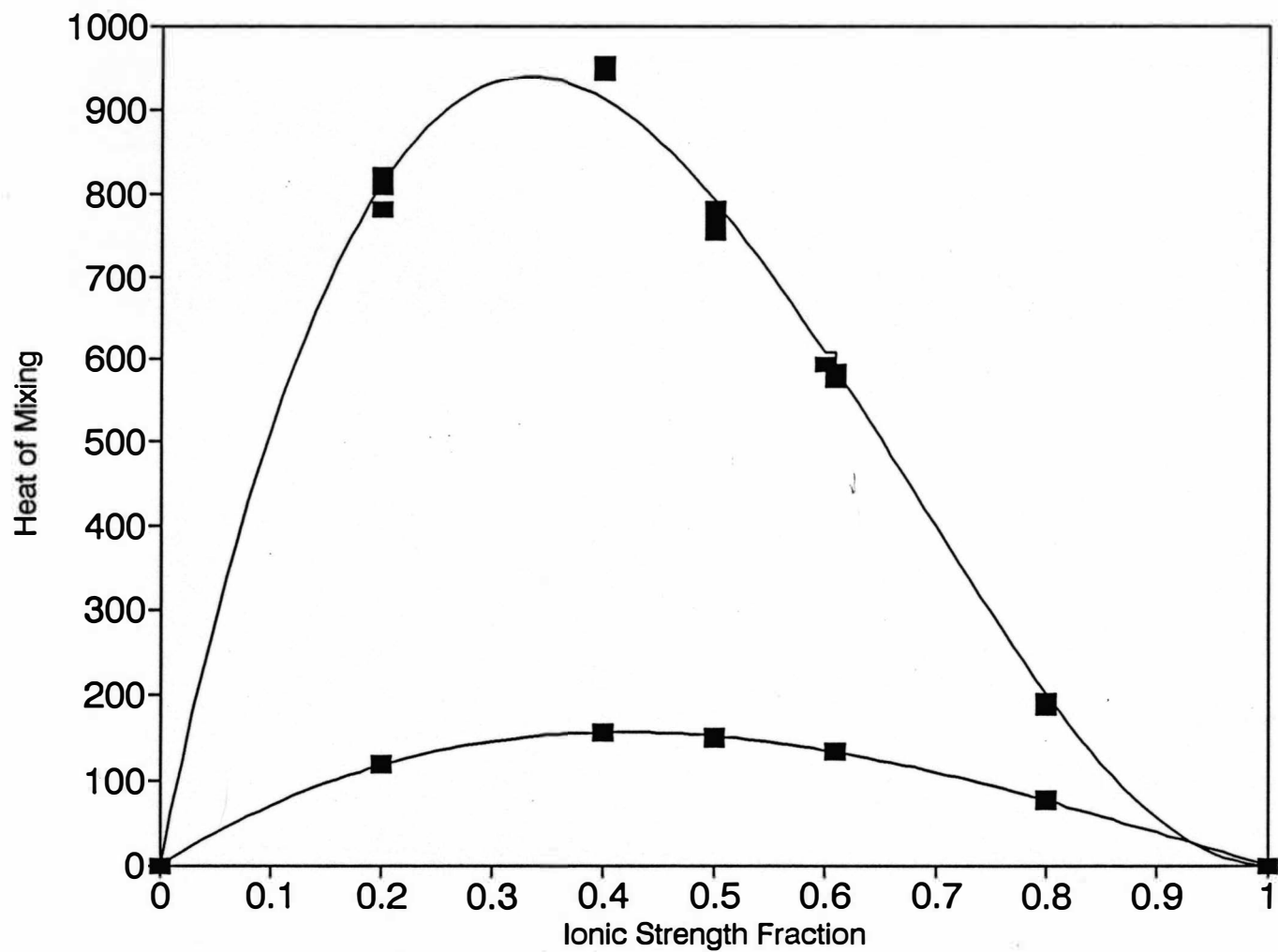


Figure 8. The Heat of Mixing in J/kg<sup>-1</sup> Plotted vs. The Ionic Strength Fraction,  $y_3$ , for HCl-CdCl<sub>2</sub> Mixtures at Constant Ionic Strength of  $I=1.0$  and  $I=3.0$  at 25°C: At  $I=3.0$  Upper Set and at  $I=1.0$  Lower Set.

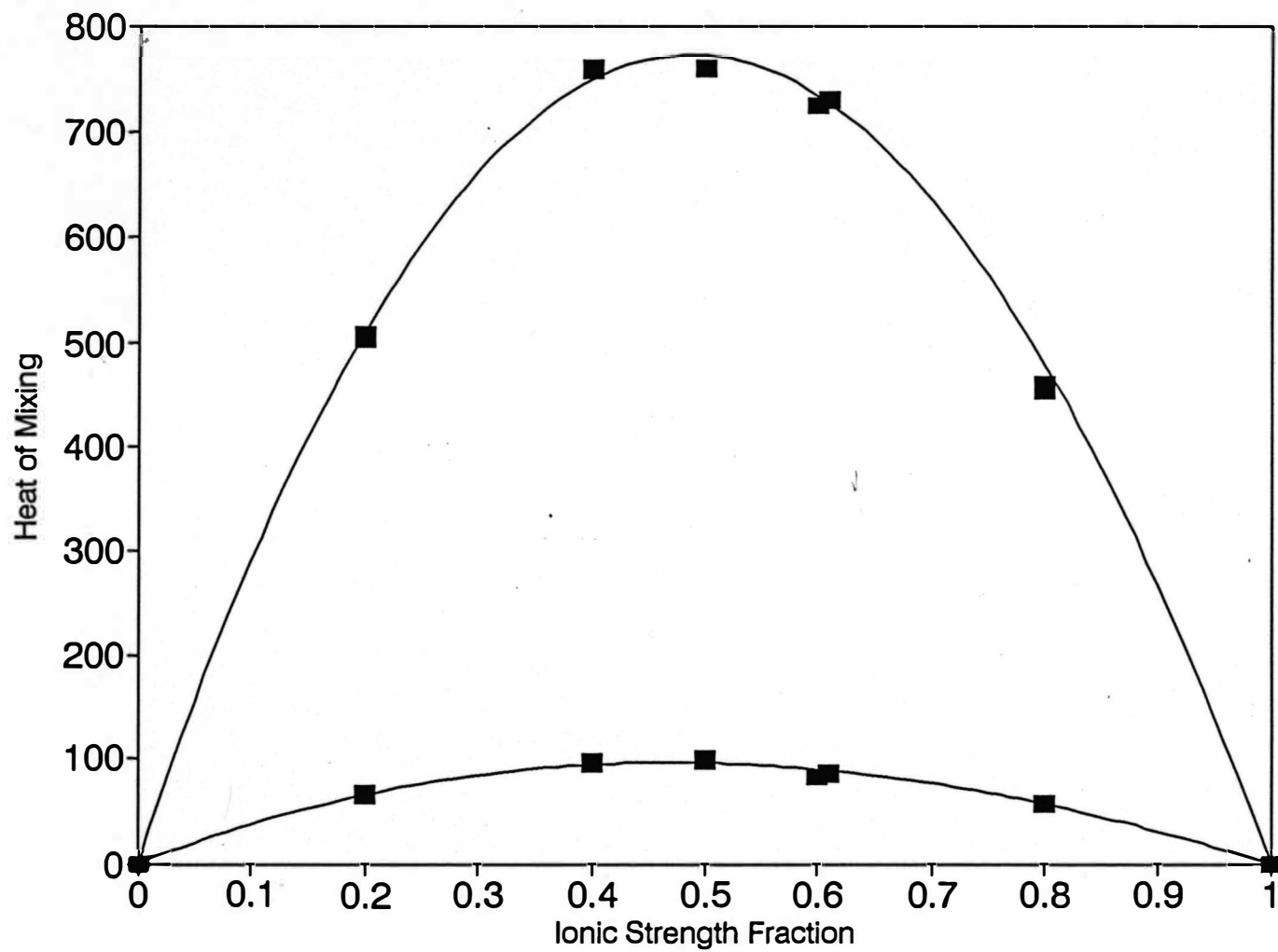


Figure 9. The Heat of Mixing in  $\text{J/kg}^{-1}$  Plotted  $\nu$ s. The Ionic Strength Fraction,  $y_3$ , for  $\text{HCl-CuCl}_2$  Mixtures at Constant Ionic Strength of  $I=1.0$  and  $I=3.0$  at  $25^\circ\text{C}$ : At  $I=3.0$  Upper Set and at  $I=1.0$  Lower Set.

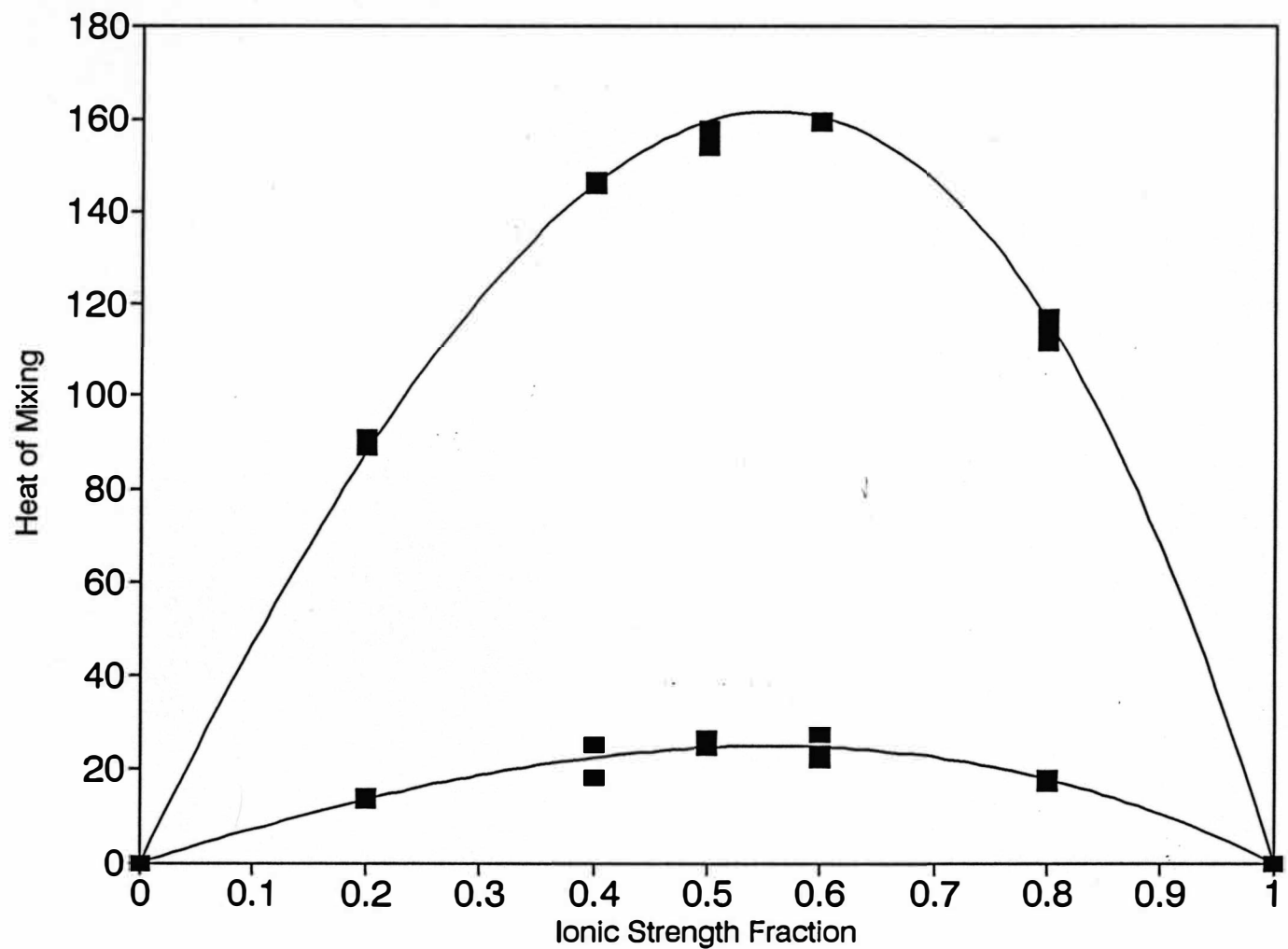


Figure 10. The Heat of Mixing in  $\text{J/kg}^{-1}$  Plotted  $\nu s.$  The Ionic Strength Fraction,  $y_3$ , for  $\text{HCl-MnCl}_2$  Mixtures at Constant Ionic Strength of  $I=1.0$  and  $I=3.0$  at  $25^\circ\text{C}$ : At  $I=3.0$  Upper Set and at  $I=1.0$  Lower Set.

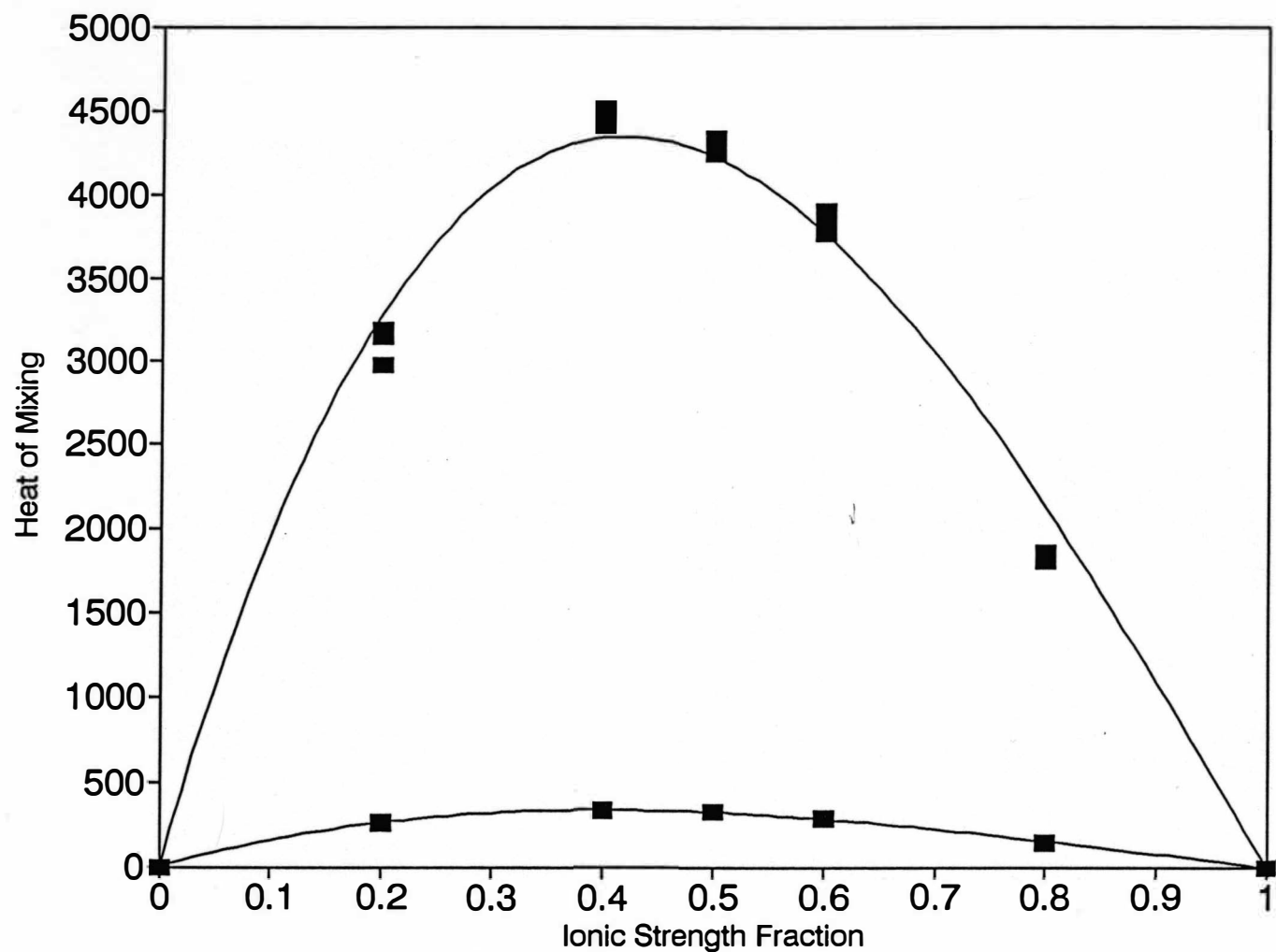


Figure 11. The Heat of Mixing in  $\text{J/kg}^{-1}$  Plotted vs. The Ionic Strength Fraction,  $y_3$ , for HCl- $\text{ZnCl}_2$  Mixtures at Constant Ionic Strength of  $I=1.0$  and  $I=3.0$  at  $25^\circ\text{C}$ : At  $I=3.0$  Upper Set and at  $I=1.0$  Lower Set.

mixtures,  $\text{HCl-CdCl}_2$  and  $\text{HCl-ZnCl}_2$  is large, so we expect to see the skew. However in the case of  $\text{HCl-CuCl}_2$  mixture the magnitude of  $h_1$  parameter is small, therefore we don't expect to see the skew.

Pitzer's heat of mixing equation, Eq. (46), was also fit to the heat of mixing data. The resulting parameters along with their standard deviations and the standard deviation in the fit are listed in Table 8. The binary interaction parameters used in the fit were taken from the literature<sup>21,29,31</sup> and are listed in Table 9.

From the data in Table 8 it can be seen that  $\text{CuCl}_2$  and  $\text{MnCl}_2$ , both required two parameters [ $\theta^{(0)L}$  and  $\psi^L$ ]. For  $\text{CdCl}_2$  and  $\text{ZnCl}_2$ , which are significantly complexed even at low concentration,<sup>61,62</sup> we required three parameters [ $\theta^{(0)L}$ ,  $\theta^{(1)L}$ , and  $\psi^L$ ] to fit the data as we did with the volume of mixing. In the case of  $\text{CuCl}_2$  and  $\text{MnCl}_2$  the data didn't show any ionic strength dependence. The magnitudes of these parameters are smaller than the magnitudes of the parameters in the case of  $\text{ZnCl}_2$ . The final parameters of Pitzer's heat of mixing equation are shown in Table 10.

From the table it can be seen that  $\theta^{(0)L}$  and  $\theta^{(1)L}$  have opposite signs in all cases where both are known and not zero. This behavior is also implied by the higher-order limiting law for symmetrical mixing.<sup>21</sup>

While little data is available on the heat of mixing of transition metal salts a few previous studies by Schreiber et al.<sup>30,31</sup> They studied the heats of mixing of these transition metal salts with  $\text{NaCl}$  at constant ionic strength 0.5, 1.0, and 3.0. When we compare our heats of mixing values with the values from the earlier studies

Table 8  
Parameters Required for Pitzer's Heat of Mixing Equation

$10^4 \theta^{(0)L(a,c)}$	$10^4 \psi^{L(b,c)}$	$10^2 \theta^{(1)L(a,c)}$	$10^5 \sigma^d$
HCl-CdCl <sub>2</sub>			
57.51(0.88)	-28.83(0.47)	-1.836(0.023)	0.21
-11.6(1.2)	8.48(1.2)		3.1
HCl-CuCl <sub>2</sub>			
6.13(4.14)	-4.1(2.1)	-0.201(0.11)	0.461
-1.35(0.11)	-0.38(0.14)		0.48
HCl-MnCl <sub>2</sub>			
-2.97(1.3)	0.77(0.66)	0.021(0.036)	0.0041
-2.203(0.035)	0.384(0.028)		0.0040
HCl-ZnCl <sub>2</sub>			
126.(16.)	-93.6(8.1)	-3.86(0.44)	1.34
-18.91(0.62)	-22.0(1.1)		2.60

<sup>a</sup>Units: Kg-mol<sup>-1</sup>-K<sup>-1</sup>. <sup>b</sup>Units: Kg<sup>2</sup>-mol<sup>-2</sup>-K<sup>-1</sup>. <sup>c</sup>The numbers in the parentheses are the standard errors in the parameters. <sup>d</sup>The standard errors in the fit.

we found that our values are of the same sign but the magnitudes are smaller. Also when we compare our interaction parameters ( $h_0$  and  $h_1$ ) with the parameters from

Table 9  
The Parameters for Pitzer's Apparent Molal Enthalpy Equation

Electrolyte	$(\partial\beta^{(0)}/\partial T)_p^a$ $\times 10^3$	$(\partial\beta^{(1)}/\partial T)_p^a$ $\times 10^3$	$(\partial C^\phi/\partial T)_p^b$ $\times 10^4$	Ref.
HCl	-0.308	0.141	0.310	21
CdCl <sub>2</sub>	-7.209	-3.179	-2.077	29
CuCl <sub>2</sub>	-1.675	-3.147	0.0	29
MnCl <sub>2</sub>	-1.677	2.340	3.661	29
ZnCl <sub>2</sub>	-9.27	21.5	35.92	31

<sup>a</sup>Units: Kg-mol<sup>-1</sup>-K<sup>-1</sup>. <sup>b</sup>Units: Kg<sup>2</sup>-mol<sup>-2</sup>-K<sup>-1</sup>.

the earlier studied we found that the parameters are of the same sign but the magnitudes are smaller. The magnitudes of the values of  $h_0$  and  $\Delta H_m$  will increase as the magnitude of the limiting partial molal volumes ( $\bar{V}^\circ$ ) of ions at zero molality increase.<sup>56,59</sup> In the case of a structure maker with a structure maker as the partial molal volumes get more negative, the heats of mixing get larger. The  $\bar{V}^\circ$  of a Na<sup>+</sup> ion is more negative than the  $\bar{V}^\circ$  of a H<sup>+</sup> ion, therefore the heats of mixing of transition metal salts with NaCl will be larger than the heats of mixing of transition metal salts with HCl.

Table 10  
The Parameters for Pitzer's Enthalpy of Mixing Equation

System	$10^4 \theta_{MN}^{(0)L}$ <sup>a,c</sup>	$10^4 \psi_{MN}^L$ <sup>b,c</sup>	$10^2 \theta_{MN}^{(1)L}$ <sup>a,c</sup>
HCl-CdCl <sub>2</sub>	57.51(0.88)	-27.83(0.47)	-1.836(0.023)
HCl-CuCl <sub>2</sub>	-1.350(0.11)	-0.38(0.14)	0.0
HCl-MnCl <sub>2</sub>	-2.203(0.035)	0.384(0.028)	0.0
HCl-ZnCl <sub>2</sub>	126.(16.)	-93.6(8.1)	-3.86(0.44)

<sup>a</sup>Units: Kg·mol<sup>-1</sup>·K<sup>-1</sup>. <sup>b</sup>Units: Kg<sup>2</sup>·mol<sup>-2</sup>·K<sup>-1</sup>. <sup>c</sup>The numbers in the parentheses are the standard errors in the parameters.

Earlier studies<sup>61</sup> of the enthalpies and volumes of mixing of the same electrolyte systems, have compared the values of  $v_0$  to the enthalpy interaction  $RTh_0$ . Millero et al<sup>61</sup> compared the values of  $v_0$  with the values of  $RTh_0$  and found a linear relationship. This is also the case when  $RTv_0$ 's ( $\Delta V_m$ ) from this study are compare to  $RTh_0$ 's ( $\Delta H_m$ ) from this study of the same mixture at the same ionic strength. This demonstrates that  $RTv_0$ 's correlate well with  $RTh_0$ 's. Table 11 shows the comparison of the volume of mixing parameter ( $RTv_0$ ) with the enthalpy of mixing parameter ( $RTh_0$ ) for all mixtures. When we compare the number of Pitzer's parameters we needed we found that we needed the same number of parameters in both heats and volumes of mixing.

Table 11

Comparison of the Volume of Mixing Parameter ( $RTv_0$ )  
With the Enthalpy of Mixing Parameter ( $RTh_0$ )

Salt	I	$RTv_0^a$	$RTh_0^b$
$CdCl_2$	1.0	0.614	610.7
	3.0	0.7016	352.2
$CuCl_2$	1.0	0.2825	383.5
	3.0	0.2659	340.7
$MnCl_2$	1.0	0.1701	98.8
	3.0	0.06678	70.40
$ZnCl_2$	1.0	1.3701	1308.8
	3.0	2.195	1866.

<sup>a</sup>Units:  $cm^3 \cdot Kg \cdot mol^{-2}$ . <sup>b</sup>Units:  $J \cdot Kg \cdot mol^{-2}$ .

## CHAPTER V

### CONCLUSIONS

The densities of mixing of aqueous solutions of four transition metal chlorides, cadmium chloride, copper chloride, manganese chloride, and zinc chloride with aqueous solutions of hydrochloric acid at constant ionic strengths of 1.0 and 3.0 molal at 25°C were determined. Density data were used to determine the volume of mixing ( $\Delta V_m$ ). The traditional equation was fit to the volume of mixing and the interaction parameters  $v_0$  and  $v_1$  were determined. The magnitudes of  $v_0$  parameter and  $\Delta V_m$  in the mixtures follow the structure breakers and structure makers theory.<sup>58,59,64</sup>

In the case of HCl, CdCl<sub>2</sub>, and ZnCl<sub>2</sub> there were variations in the literature data in the binary solution volume parameters, we refit the literature data to Pitzer's apparent molal volume equation and determined the volume parameters.

Pitzer's volume of mixing equation was also fit to the volume of mixing data and parameters were determined. In the case of CuCl<sub>2</sub> and MnCl<sub>2</sub>, data from Török and Berecs has been combined with our data, so that the parameters are valid to  $I=10$  molal. In the case of CuCl<sub>2</sub> and MnCl<sub>2</sub> only two parameters,  $\theta^v$  and  $\psi^v$ , are required, while in the case of CdCl<sub>2</sub> and ZnCl<sub>2</sub> all three parameters were needed  $\theta^{v(0)}$ ,  $\theta^{v(1)}$ , and  $\psi^v$ .

The heats of mixing ( $\Delta H_m$ ) of aqueous solutions of cadmium chloride, copper chloride, manganese chloride, and zinc chloride with solutions of hydrochloric acid were measured calorimetrically at constant ionic strengths of 1.0 and 3.0 molal at 25°C. The traditional equation was fit to the heat of mixing and the interaction parameters  $h_0$  and  $h_1$  were determined. The magnitudes of  $h_0$  parameter and  $\Delta H_m$  in the mixtures follow the structure breakers and structure makers theory.<sup>58,59,64</sup>

Pitzer's heat of mixing equation was also fit to the heat of mixing data and parameters were determined. In the case of  $\text{CuCl}_2$  and  $\text{MnCl}_2$  only two parameters,  $\theta^{L(0)}$  and  $\psi^L$ , were needed, while in the case of  $\text{CdCl}_2$  and  $\text{ZnCl}_2$  all three parameters were needed  $\theta^{L(0)}$ ,  $\theta^{L(1)}$ , and  $\psi^L$ .

Pitzer's parameters can be used to predict the effect of temperature and pressure on the activity coefficient, which can be used to predict the thermodynamic properties of electrolyte mixtures and the solubility of minerals in natural waters. The enthalpy parameters are valid for temperatures from 5°C to 45°C and the volume parameters are valid for pressures 0 bar to 10 bar. If we want to go to higher temperatures we will need to include the heat capacity terms and if we want to go to higher pressures we will need to do additional work under pressure.

**Appendix A**  
**Constants for the Four Transition Metal Salts**  
**and Hydrochloric Acid**

## APPENDIX A

Constants for the Four Transition Metal Salts  
and Hydrochloric Acid

Electrolyte	Molar Mass	Ionic Strength	Equivalent
		Factor(w)	Factor(x)
HCl	36.4609	1	1
CdCl <sub>2</sub>	183.316	3	2
CuCl <sub>2</sub>	134.452	3	2
MnCl <sub>2</sub>	125.844	3	2
ZnCl <sub>2</sub>	136.286	3	2

## **Appendix B**

**Experimental Density and Volume of Mixing Data for Each  
of the Mixtures at  $I=1.0$  and  $I=3.0$  at  $25^{\circ}\text{C}$**

## APPENDIX B

Experimental Density and Volume of mixing data for each  
of the Mixtures at  $I=1.0$  and  $I=3.0$  at  $25^{\circ}\text{C}$

Mixture:  $\text{HCl}(2)\text{-CdCl}_2(3)$ ,  $I=1.0$

$10_3\Delta d(2) = 17.163$   
 $m_2 = 1.0003$   
 $\text{Eq. Wt. (2)} = 36.4609$   
 $\phi_v(2) = 18.982$   
 $I(2) = 1.0003$   
 $\text{mean } I = 0.99905$

$10_3\Delta d(3) = 51.543$   
 $m_3 = 0.3326$   
 $\text{Eq. Wt. (3)} = 91.658$   
 $\phi_v(3) = 13.297$   
 $I(3) = 0.9978$

$10_3\Delta d(2) = 17.178$   
 $m_2 = 1.00124$   
 $\text{Eq. Wt. (2)} = 36.4609$   
 $\phi_v(2) = 18.984$   
 $I(2) = 1.0012$   
 $\text{mean } I = 0.99965$

$10_3\Delta d(3) = 51.560$   
 $m_3 = 0.3327$   
 $\text{Eq. Wt. (3)} = 91.658$   
 $\phi_v(3) = 13.295$   
 $I(3) = 0.9981$

$m(3)^a$	$m(2)^a$	$y_3$	$10^3\Delta d^b$	$\phi_v(2,3)^c$	$\Delta V_m^c$
0.3326	1.0003	0.20032	23.897	18.289	0.112
		0.20032	23.892	18.294	0.117
		0.20032	23.901	18.284	0.108
0.3327	1.0012	0.30213	27.378	17.863	0.138
		0.30213	27.366	17.876	0.150
		0.30213	27.378	17.863	0.138
0.3326	1.0003	0.40217	30.778	17.394	0.149
		0.40217	30.754	17.422	0.173
		0.40217	30.761	17.413	0.166
		0.50003	34.129	16.899	0.159
		0.50003	34.124	16.905	0.164
		0.50003	34.144	16.881	0.144
		0.60147	37.655	16.285	0.123
		0.60147	37.636	16.309	0.142
		0.60147	37.630	16.315	0.147
		0.80088	44.603	14.912	0.052
		0.80088	44.572	14.954	0.083
		0.80088	44.561	14.968	0.093

<sup>a</sup>Units: Initial molality,  $\text{mol}\cdot\text{kg}^{-1}$ . <sup>b</sup>Units:  $\text{gm}\cdot\text{cm}^{-3}$ . <sup>c</sup>Units:  $\text{cm}^3\cdot\text{kg}^{-1}$ .

## APPENDIX B-Continued

Mixture: HCl(2)-CdCl<sub>2</sub>(3), I=3.0

$10_3\Delta d(2) = 48.138$   
 $m_2 = 3.0123$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 19.550$   
 $I(2) = 3.0123$   
 mean I = 3.01005

$10_3\Delta d(3) = 149.899$   
 $m_3 = 1.0026$   
 Eq. Wt. (3) = 91.658  
 $\phi_v(3) = 14.544$   
 $I(3) = 3.0078$

$10_3\Delta d(2) = 48.272$   
 $m_2 = 3.0216$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 19.552$   
 $I(2) = 3.0216$   
 mean I = 3.0162

$10_3\Delta d(3) = 150.039$   
 $m_3 = 1.0036$   
 Eq. Wt. (3) = 91.658  
 $\phi_v(3) = 14.546$   
 $I(3) = 3.0108$

$m(3)^a$	$m(2)^a$	$y_3$	$10^3\Delta d^b$	$\phi_v(2,3)^c$	$\Delta V_m^c$
1.0026	3.0123	0.20389	66.824	19.393	1.610
		0.20389	66.879	19.374	1.558
		0.20389	66.917	19.360	1.517
1.0036	3.0216	0.30448	76.826	19.107	1.860
		0.30448	76.833	19.105	1.854
		0.30448	76.829	19.106	1.857
1.0026	3.0123	0.40655	86.966	18.682	1.825
		0.40655	86.994	18.672	1.799
		0.40655	87.011	18.665	1.782
		0.50368	97.100	18.145	1.540
		0.50368	97.104	18.143	1.536
		0.50368	97.116	18.138	1.524
		0.60724	107.909	17.548	1.293
		0.60724	107.893	17.554	1.308
		0.60724	107.862	17.566	1.338
		0.78657	128.691	16.133	0.512
		0.78657	128.815	16.081	0.397
		0.78657	128.802	16.087	0.409

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: gm·cm<sup>-3</sup>. <sup>c</sup>Units: cm<sup>3</sup>·kg<sup>-1</sup>.

## APPENDIX B-Continued

Mixture: HCl(2)-CuCl<sub>2</sub>(3), I=1.0

$10_3\Delta d(2) = 17.163$   
 $m_2 = 1.0003$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 18.982$   
 $I(2) = 1.0003$   
 mean I = 1.0016

$10_3\Delta d(3) = 39.753$   
 $m_3 = 0.3343$   
 Eq. Wt. (3) = 67.226  
 $\phi_v(3) = 7.323$   
 $I(3) = 1.0029$

$10_3\Delta d(2) = 17.178$   
 $m_2 = 1.00124$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 18.984$   
 $I(2) = 1.0012$   
 mean I = 1.0034

$10_3\Delta d(3) = 39.860$   
 $m_3 = 0.3352$   
 Eq. Wt. (3) = 67.226  
 $\phi_v(3) = 7.322$   
 $I(3) = 1.0056$

$m(3)^a$	$m(2)^a$	$y_3$	$10^3\Delta d^b$	$\phi_v(2,3)^c$	$\Delta V_m^c$
0.3343	1.0003	0.20271	21.629	17.350	0.053
		0.20271	21.631	17.348	0.052
		0.20271	21.624	17.355	0.059
0.3352	1.0012	0.29420	23.670	16.520	0.066
		0.29420	23.703	16.517	0.063
		0.29420	23.702	16.518	0.063
		0.40602	26.218	15.413	0.069
		0.40602	26.218	15.413	0.069
		0.40602	26.217	15.414	0.070
0.3352	1.0012	0.50435	28.440	14.359	0.074
		0.50435	28.441	14.357	0.072
		0.50435	28.449	14.348	0.065
0.3343	1.0003	0.60350	30.644	13.188	0.062
		0.60350	30.646	13.185	0.060
		0.60350	30.653	13.177	0.053
		0.80260	35.180	10.538	0.054
		0.80260	35.180	10.538	0.054
		0.80260	35.197	10.516	0.037

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: gm·cm<sup>-3</sup>. <sup>c</sup>Units: cm<sup>3</sup>·kg<sup>-1</sup>.

## APPENDIX B-Continued

Mixture: HCl(2)-CuCl<sub>2</sub>(3), I=3.0

$10_3\Delta d(2) = 48.138$   
 $m_2 = 3.0123$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 19.550$   
 $I(2) = 3.0123$   
 mean I = 3.007725

$10_3\Delta d(3) = 114.213$   
 $m_3 = 1.00105$   
 Eq. Wt. (3) = 67.226  
 $\phi_v(3) = 9.008$   
 $I(3) = 3.00315$

$10_3\Delta d(2) = 48.138$   
 $m_2 = 3.0123$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 19.550$   
 $I(2) = 3.0123$   
 mean I = 3.0087

$10_3\Delta d(3) = 114.284$   
 $m_3 = 1.0017$   
 Eq. Wt. (3) = 67.226  
 $\phi_v(3) = 9.009$   
 $I(3) = 3.0051$

$m(3)^a$	$m(2)^a$	$y_3$	$10^3\Delta d^b$	$\phi_v(2,3)^b$	$\Delta V_m^b$
1.0011	3.0123	0.20672	61.004	18.133	0.403
		0.20672	61.014	18.130	0.393
		0.20672	61.024	18.126	0.383
1.0017		0.30140	67.027	17.392	0.532
		0.30140	67.027	17.390	0.527
		0.30140	67.032	17.391	0.531
1.0011		0.40816	73.962	16.444	0.556
		0.40816	73.950	16.448	0.568
		0.40816	73.949	16.449	0.569
		0.50616	80.347	15.517	0.617
		0.50616	80.360	15.512	0.605
		0.50616	80.379	15.505	0.587
		0.60770	87.104	14.440	0.590
		0.60770	87.123	14.432	0.572
		0.60770	87.156	14.419	0.540
		0.80672	100.662	11.967	0.378
		0.80672	100.650	11.972	0.389
		0.80672	100.672	11.963	0.368

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: gm·cm<sup>-3</sup>. <sup>c</sup>Units: cm<sup>3</sup>·kg<sup>-1</sup>.

## APPENDIX B-Continued

Mixture: HCl(2)-MnCl<sub>2</sub>(3), I=1.0

$10_3\Delta d(2) = 17.163$   
 $m_2 = 1.0003$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 18.982$   
 $I(2) = 1.0003$   
 mean I = 1.00025

$10_3\Delta d(3) = 34.402$   
 $m_3 = 0.3334$   
 Eq. Wt. (3) = 62.922  
 $\phi_v(3) = 10.835899$   
 $I(3) = 1.0002$

$10_3\Delta d(2) = 17.178$   
 $m_2 = 1.00124$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 18.984$   
 $I(2) = 1.0012$   
 mean I = 1.00325

$10_3\Delta d(3) = 34.572$   
 $m_3 = 0.3351$   
 Eq. Wt. (3) = 62.922  
 $\phi_v(3) = 10.841$   
 $I(3) = 1.0053$

$m(3)^a$	$m(2)^a$	$y_3$	$10^3\Delta d^b$	$\phi_v(2,3)^c$	$\Delta V_m^c$
0.3334	1.0003	0.20111	20.569	17.843	0.030
		0.20111	20.569	17.843	0.030
		0.20111	20.564	17.849	0.034
0.3351	1.0012	0.27756	21.913	17.366	0.039
		0.27756	21.918	17.360	0.033
		0.27756	21.913	17.366	0.039
0.3334	1.0003	0.40035	23.974	16.523	0.043
		0.40035	23.974	16.523	0.043
		0.40035	23.977	16.520	0.041
		0.50118	25.706	15.771	0.047
		0.50118	25.709	15.768	0.044
		0.50118	25.710	15.766	0.043
		0.60194	27.455	14.940	0.038
		0.60194	27.458	14.936	0.035
		0.60194	27.447	14.949	0.045
		0.80129	30.923	13.074	0.022
		0.80129	30.918	13.081	0.027
		0.80129	30.927	13.069	0.018

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: gm·cm<sup>-3</sup>. <sup>c</sup>Units: cm<sup>3</sup>·kg<sup>-1</sup>.

## APPENDIX B-Continued

Mixture: HCl(2)-MnCl<sub>2</sub>(3), I=3.0

$10_3\Delta d(2) = 48.138$   
 $m_2 = 3.0123$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 19.550$   
 $I(2) = 3.0123$   
 mean I = 3.01005

$10_3\Delta d(3) = 99.708$   
 $m_3 = 1.0026$   
 Eq. Wt. (3) = 62.922  
 $\phi_v(3) = 11.899$   
 $I(3) = 3.0078$

$10_3\Delta d(2) = 48.272$   
 $m_2 = 3.0216$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 19.552$   
 $I(2) = 3.0216$   
 mean I = 3.0147

$10_3\Delta d(3) = 99.708$   
 $m_3 = 1.0026$   
 Eq. Wt. (3) = 62.922  
 $\phi_v(3) = 11.899$   
 $I(3) = 3.0078$

$m(3)^a$	$m(2)^a$	$y_3$	$10^3\Delta d^b$	$\phi_v(2,3)^c$	$\Delta V_m^c$
1.0026	3.0123	0.20428	58.296	18.471	0.111
		0.20428	58.299	18.470	0.108
		0.20428	58.296	18.471	0.110
	3.0216	0.30409	63.458	17.877	0.139
		0.30409	63.460	17.876	0.137
		0.30409	63.467	17.873	0.130
	3.0123	0.40687	68.573	17.206	0.148
		0.40687	68.574	17.205	0.147
		0.40687	68.584	17.201	0.137
		0.50774	73.751	16.494	0.155
		0.50774	73.755	16.492	0.151
		0.50774	73.755	16.492	0.151
		0.60665	78.879	15.731	0.144
		0.60665	78.891	15.726	0.133
		0.60665	78.898	15.723	0.126
		0.80522	89.304	13.978	0.093
		0.80522	89.298	13.980	0.099
		0.80522	89.296	13.981	0.101

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: gm·cm<sup>-3</sup>. <sup>c</sup>Units: cm<sup>3</sup>·kg<sup>-1</sup>.

## APPENDIX B-Continued

Mixture: HCl(2)-ZnCl<sub>2</sub>(3), I=1.0

$10_3\Delta d(2) = 17.163$   
 $m_2 = 1.0003$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 18.982$   
 $I(2) = 1.0003$   
 mean I = 0.999725

$10_3\Delta d(3) = 39.833$   
 $m_3 = 0.33305$   
 Eq. Wt. (3) = 68.143  
 $\phi_v(3) = 7.874$   
 $I(3) = 0.99915$

$10_3\Delta d(2) = 17.178$   
 $m_2 = 1.00124$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 18.984$   
 $I(2) = 1.0012$   
 mean I = 1.0016

$10_3\Delta d(3) = 39.940$   
 $m_3 = 0.3340$   
 Eq. Wt. (3) = 68.143  
 $\phi_v(3) = 7.881$   
 $I(3) = 1.0020$

$m(3)^a$	$m(2)^a$	$y_3$	$10^3\Delta d^b$	$\phi_v(2,3)^c$	$\Delta V_m^c$
0.3331	1.0003	0.20118	21.410	17.674	0.269
		0.20118	21.416	17.668	0.263
		0.20118	21.417	17.666	0.262
0.3340	1.0012	0.30140	23.637	16.872	0.332
		0.30140	23.635	16.875	0.335
		0.30140	23.639	16.871	0.331
0.3331	1.0003	0.40272	25.872	15.943	0.351
		0.40272	25.872	15.943	0.351
		0.40272	25.866	15.950	0.357
0.3340	1.0012	0.50351	28.205	14.924	0.349
		0.50351	28.195	14.936	0.359
		0.50351	28.120	14.930	0.355
0.3331	1.0003	0.60265	30.454	13.773	0.300
		0.60265	30.450	13.778	0.304
		0.60265	30.451	13.778	0.303
		0.80252	35.149	11.086	0.159
		0.80252	35.149	11.086	0.159
		0.80252	35.155	11.078	0.153

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: gm·cm<sup>-3</sup>. <sup>c</sup>Units: cm<sup>3</sup>·kg<sup>-1</sup>.

## APPENDIX B-Continued

Mixture: HCl(2)-ZnCl<sub>2</sub>(3), I=3.0

$10_3\Delta d(2) = 48.138$   
 $m_2 = 3.0123$   
 Eq. Wt. (2) = 36.4609  
 $\phi_v(2) = 19.550$   
 $I(2) = 3.0123$   
 mean I = 3.00614

$10_3\Delta d(3) = 110.094$   
 $m_3 = 0.99999$   
 Eq. Wt. (3) = 68.143  
 $\phi_v(3) = 11.681$   
 $I(3) = 2.99997$

$m(3)^a$	$m(2)^a$	$y_3$	$10^3\Delta d^b$	$\phi_v(2,3)^c$	$\Delta V_m^c$
1.0000	3.0123	0.20486	56.792	19.731	3.742
		0.20486	56.796	19.729	3.738
		0.20486	56.801	19.728	3.733
		0.29997	61.720	19.494	4.583
		0.29997	61.726	19.492	4.577
		0.29997	61.713	19.497	4.590
		0.40656	67.598	19.082	5.197
		0.40656	67.617	19.075	5.178
		0.40656	67.631	19.069	5.165
		0.50485	73.765	18.388	5.058
		0.50485	73.767	18.387	5.055
		0.50485	73.767	18.388	5.056
		0.61027	80.945	17.370	4.401
		0.61027	80.942	17.370	4.403
		0.61027	80.970	17.359	4.377
		0.80271	95.010	14.904	2.426
		0.80271	95.020	14.900	2.417
		0.80271	95.012	14.903	2.425

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: gm·cm<sup>-3</sup>. <sup>c</sup>Units: cm<sup>3</sup>·kg<sup>-1</sup>.

## **Appendix C**

**Experimental Heat and Enthalpy of Mixing Data for Each  
of the Mixtures at  $I=1.0$  and  $I=3.0$  at  $25^{\circ}\text{C}$**

## APPENDIX C

Experimental Heat and Enthalpy of Mixing Data for each  
of the Mixtures at  $I=1.0$  and  $I=3.0$  at  $25^{\circ}\text{C}$

Mixture:  $\text{HCl}(2)\text{-CdCl}_2(3)$ ,  $I=1.0$

$10_3\Delta d(2) = 17.180$   
 $m_2 = 1.0014$   
 Eq. Wt. (2) = 36.4609  
 $I(2) = 1.0014$   
 mean  $I = 0.99915$

$10_3\Delta d(3) = 51.506$   
 $m_3 = 0.3323$   
 Eq. Wt. (3) = 91.658  
 $I(3) = 0.9969$

$m(2)^a$	$m(3)^a$	$y_3$	$Q_{\text{mix}}^b$	$\Delta H_m^c$
1.0014	0.3323	0.20000	0.563	118.0
		0.19968	0.572	119.6
		0.20025	0.577	120.7
		0.40169	0.744	157.1
		0.39962	0.744	156.1
		0.39950	0.750	157.6
		0.50147	0.592	152.5
		0.49851	0.574	151.7
		0.50309	0.567	149.2
		0.60446	0.639	134.2
		0.60545	0.637	133.9
		0.60310	0.650	135.7
		0.80196	0.380	78.41
		0.80671	0.366	76.51
		0.80175	0.362	75.34

<sup>a</sup>Units: Initial molality,  $\text{mol}\cdot\text{kg}^{-1}$ . <sup>b</sup>Units: J. <sup>c</sup>Units:  $\text{J}\cdot\text{kg}^{-1}$ .

## APPENDIX C-Continued

Mixture: HCl(2)-CdCl<sub>2</sub>(3), I=3.0

$10_3\Delta d(2) = 48.038$   
 $m_2 = 3.0054$   
 Eq. Wt. (2) = 36.4609  
 $I(2) = 3.0054$   
 mean I = 3.00825

$10_3\Delta d(3) = 150.056$   
 $m_3 = 1.0037$   
 Eq. Wt. (3) = 91.658  
 $I(3) = 3.0111$

$m(2)^a$	$m(3)^a$	$y_3$	$Q_{\text{mix}}^b$	$\Delta H_m^c$
3.0054	1.0037	0.20877	3.537	781.2
		0.21219	3.741	821.7
		0.20961	3.654	807.6
		0.41610	4.366	944.8
		0.41336	4.389	955.0
		0.41640	4.385	950.9
		0.51275	2.843	754.4
		0.51055	2.934	782.3
		0.51397	2.887	769.2
		0.60734	2.758	594.1
		0.60970	2.603	585.9
		0.60885	2.699	575.6
		0.80834	0.911	193.8
		0.80271	0.849	185.9
		0.80033	0.856	190.6

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: J. <sup>c</sup>Units: J·kg<sup>-1</sup>.

## APPENDIX C-Continued

Mixture: HCl(2)-CuCl<sub>2</sub>(3), I=1.0

$10_3\Delta d(2) = 17.160$   
 $m_2 = 1.0002$   
 Eq. Wt. (2) = 36.4609  
 $I(2) = 1.0002$   
 mean I = 0.9999

$10_3\Delta d(3) = 39.62771206$   
 $m_3 = 0.3332$   
 Eq. Wt. (3) = 67.226  
 $I(3) = 0.9996$

$m(2)^a$	$m(3)^a$	$y_3$	$Q_{\text{mix}}^b$	$\Delta H_m^c$
1.0002	0.3332	0.20514	0.322	67.24
		0.20427	0.308	64.19
		0.20535	0.313	65.38
		0.41041	0.471	97.73
		0.40563	0.457	95.32
		0.40997	0.462	95.98
		0.50682	0.377	96.85
		0.50526	0.374	99.52
		0.50576	0.372	98.73
		0.60370	0.340	82.26
		0.60356	0.413	85.10
		0.61038	0.421	86.07
		0.80591	0.278	56.89
		0.80431	0.281	57.93
		0.80333	0.285	58.47

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: J. <sup>c</sup>Units: J·kg<sup>-1</sup>.

## APPENDIX C-Continued

Mixture: HCl(2)-CuCl<sub>2</sub>(3), I=3.0

$10_3\Delta d(2) = 48.008$   
 $m_2 = 3.0034$   
 Eq. Wt. (2) = 36.4609  
 $I(2) = 3.0034$   
 mean I = 2.9954

$10_3\Delta d(3) = 113.648$   
 $m_3 = 0.9958$   
 Eq. Wt. (3) = 67.226  
 $I(3) = 2.9874$

$m(2)^a$	$m(3)^a$	$y_3$	$Q_{\text{mix}}^b$	$\Delta H_m^c$
3.0034	0.9958	0.20728	2.339	507.1
		0.20581	2.344	507.0
		0.20820	2.308	501.7
		0.40029	3.442	756.7
		0.40505	3.415	756.7
		0.40748	3.490	759.9
		0.51011	2.847	758.8
		0.51114	2.876	759.2
		0.51269	2.878	758.6
		0.60420	3.379	724.7
		0.60347	3.381	727.9
		0.61085	3.357	729.4
		0.80248	2.152	459.3
		0.80564	2.118	453.5
		0.80441	2.102	452.9

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: J. <sup>c</sup>Units: J·kg<sup>-1</sup>.

## APPENDIX C-Continued

Mixture:  $\text{HCl}(2)\text{-MnCl}_2(3)$ ,  $I=1.0$ 

$10_3\Delta d(2) = 17.160$   
 $m_2 = 1.0002$   
 $\text{Eq. Wt. (2)} = 36.4609$   
 $I(2) = 1.0002$   
 $\text{mean } I = 1.00065$

$10_3\Delta d(3) = 34.428$   
 $m_3 = 0.3337$   
 $\text{Eq. Wt. (3)} = 62.922$   
 $I(3) = 1.0011$

$m(2)^a$	$m(3)^a$	$y_3$	$Q_{\text{mix}}^b$	$\Delta H_m^c$
1.0002	0.3337	0.20605	0.064	13.28
		0.20225	0.063	13.30
		0.20515	0.067	14.11
		0.41121	0.122	25.38
		0.41037	0.087	18.16
		0.40754	0.121	25.29
		0.50314	0.096	24.70
		0.50666	0.101	26.38
		0.50700	0.098	25.07
		0.59889	0.132	27.43
		0.59898	0.108	22.36
		0.60004	0.113	23.31
		0.80750	0.083	17.17
		0.80221	0.089	18.31
		0.80112	0.088	18.09

<sup>a</sup>Units: Initial molality,  $\text{mol}\cdot\text{kg}^{-1}$ . <sup>b</sup>Units: J. <sup>c</sup>Units:  $\text{J}\cdot\text{kg}^{-1}$ .

## APPENDIX C-Continued

Mixture:  $\text{HCl}(2)\text{-MnCl}_2(3)$ ,  $I=3.0$ 

$10_3\Delta d(2) = 48.008$   
 $m_2 = 3.0034$   
 $\text{Eq. Wt. (2)} = 36.4609$   
 $I(2) = 3.0034$   
 $\text{mean } I = 2.9999$

$10_3\Delta d(3) = 99.342$   
 $m_3 = 0.9988$   
 $\text{Eq. Wt. (3)} = 62.922$   
 $I(3) = 2.9964$

$m(2)^a$	$m(3)^a$	$y_3$	$Q_{\text{mix}}^b$	$\Delta H_m^c$
3.0034	0.9988	0.20748	0.414	90.40
		0.20704	0.405	88.66
		0.20660	0.415	90.92
		0.39790	0.655	145.4
		0.40152	0.659	146.3
		0.39948	0.664	146.8
		0.50045	0.564	157.8
		0.50596	0.558	156.4
		0.50153	0.549	153.7
		0.61380	0.724	159.5
		0.60700	0.729	159.3
		0.61357	0.722	159.1
		0.80421	0.544	117.4
		0.80231	0.526	114.0
		0.80443	0.539	111.6

<sup>a</sup>Units: Initial molality,  $\text{mol}\cdot\text{kg}^{-1}$ . <sup>b</sup>Units: J. <sup>c</sup>Units:  $\text{J}\cdot\text{kg}^{-1}$ .

## APPENDIX C. Continued

Mixture: HCl(2)-ZnCl<sub>2</sub>(3), I=1.0

$10_3\Delta d(2) = 17.160$   
 $m_2 = 1.0002$   
 Eq. Wt. (2) = 36.4609  
 $I(2) = 1.0002$   
 mean I = 0.999

$10_3\Delta d(3) = 39.782$   
 $m_3 = 0.3326$   
 Eq. Wt. (3) = 68.143  
 $I(3) = 0.9978$

$m(2)^a$	$m(3)^a$	$y_3$	$Q_{\text{mix}}^b$	$\Delta H_m^c$
1.0002	0.3326	0.20302	1.272	266.0
		0.20480	1.257	261.9
		0.20409	1.298	270.4
		0.39932	1.614	344.1
		0.39512	1.581	337.6
		0.40034	1.604	341.9
		0.50596	1.217	324.9
		0.49602	1.207	323.7
		0.49777	1.215	327.0
		0.60446	1.373	292.0
		0.60153	1.346	288.7
		0.60384	1.367	292.1
		0.80212	0.692	144.3
		0.80248	0.708	147.8
		0.80266	0.688	144.4

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: J. <sup>c</sup>Units: J·kg<sup>-1</sup>.

## APPENDIX C-Continued

Mixture: HCl(2)-ZnCl<sub>2</sub>(3), I=3.0

$10_3\Delta d(2) = 48.008$   
 $m_2 = 3.0034$   
 Eq. Wt. (2) = 36.4609  
 $I(2) = 3.0034$   
 mean I = 3.00995

$10_3\Delta d(3) = 110.625916$   
 $m_3 = 1.0055$   
 Eq. Wt. (3) = 68.143  
 $I(3) = 3.0165$

$m(2)^a$	$m(3)^a$	$y_3$	$Q_{\text{mix}}^b$	$\Delta H_m^c$
3.0034	1.0055	0.20709	14.753	3194.
		0.20512	14.504	3144.
		0.20628	13.703	2973.
		0.41276	20.831	4454.
		0.41393	20.872	4515.
		0.41420	20.507	4419.
		0.51422	16.290	4340.
		0.51026	16.096	4245.
		0.51051	16.070	4259.
		0.60769	17.775	3766.
		0.60425	18.251	3905.
		0.60745	17.882	3824.
		0.80555	8.807	1861.
		0.80736	8.646	1829.
		0.80735	8.513	1811.

<sup>a</sup>Units: Initial molality, mol·kg<sup>-1</sup>. <sup>b</sup>Units: J. <sup>c</sup>Units: J·kg<sup>-1</sup>.

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