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The heats of mixing of aqueous electrolytes provide an excellent method of studying specific ion interactions. Numerous systems have been studied at 25°, but as yet few measurements have been made at elevated temperatures. In order to extend the thermodynamic calculations and further the knowledge of solute-solvent interactions, a study of systems at temperatures other than 25° is necessary.

The heats of mixing for the systems $NaCl$-HCl-H_2O, $NaCl$-$LiCl$-H_2O, $NaCl$-KCl-H_2O, and $LiCl$-KCl-H_2O at 1.0 molal and $LiCl$-$(CH_3)_4NCl$-H_2O and KCl-$(CH_3)_4NCl$-H_2O at 0.5 molal and constant ionic strength were measured at 40, 60, and 80°. An isothermal, double microcalorimeter was used for the experimental work.

The heat of mixing for systems involving the Na^+ ion showed temperature dependence, but the other systems had heats of mixing independent of temperature. It is postulated that the heat of mixing is mainly influenced by interactions occurring in the water which is at the interface of the primary and secondary hydration spheres of the ions.

It is shown how the complete excess thermodynamic functions of mixing for electrolyte solutions can be calculated from the heat of mixing as a function of temperature and the excess free energy of mixing at a reference temperature. In addition, the heat of mixing as a function of temperature allows for the extension of general equations for calculating the free energy and heat content of multicomponent electrolyte solutions.

HEATS OF MIXING OF AQUEOUS ELECTROLYTES.
TEMPERATURE DEPENDENCE

by

Linda Anne Petree

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INTRODUCTION

Aqueous electrolyte solutions have long been of interest from both theoretical and experimental considerations. As early as the last decade of the eighteenth century many of their fundamental properties were known. Beginning in the last decade of the nineteenth century, a systematic theoretical and experimental investigation of electrolyte solutions began to emerge as a result of work by van't Hoff[1] and Arrhenius.[2] Continuing until the present time, countless men have studied electrolyte solutions and have contributed to our present knowledge of them.

Today electrolyte solutions are of fundamental importance in areas ranging from desalination to biochemistry and from ionic equilibria to water pollution. A better understanding of electrolyte solutions is desired not only by physical chemists but also by biochemists, organic, inorganic, and analytical chemists whose work relates to electrolyte solutions.

The complete understanding of aqueous electrolyte solutions is, however, complicated by many factors. The most complicating factor is the solvent. An understanding of water structure and its influence on electrolyte solutions is inextricably related to an understanding of electrolyte solution theory. Samoilov[3] has written, " . . . any theory of liquid solutions must be considered in relation to the structure of the solvent concerned. This is especially true for aqueous electrolyte solutions, and extension of the theory of them must involve structural investigation." Kavanau,[4] in his review, discusses the theories of water and water structure. Many theories have been proposed to explain water structure, but as yet none is completely adequate. There is much disagreement among the theories and a wide range of interpretations of intermolecular interactions in water.

Another complicating factor in the study of electrolyte solutions is the difficulty of obtaining good data for dilute solutions. Many of the theories of electrolyte solutions are limiting laws and apply only to very dilute solutions. In order to test these theories, it is necessary to obtain data in very dilute solutions.

In spite of the problems encountered, both inherent and experimental, a vast amount of data is available on electrolyte solutions. This data has been important both in the development of electrolyte solution theories and in the explanation of the behavior of electrolyte solutions. Often it is difficult to explain the behavior of electrolyte solutions. Caution must be exercised in relating different properties of electrolyte solutions because unrelated factors may be influencing the properties. The property may be influenced by an external factor (magnetic field, electric field, pressure) or an internal factor (concentration gradient, dipole interactions, concentration). The time scale may be different for the various properties. There may be no time scale, which is the case for thermodynamic properties, or there may be a very short time scale, which occurs in spectroscopic and kinetic properties.

It is hoped that the "ultimate theory" of electrolyte solutions will incorporate all aspects of electrolyte solutions and demonstrate their relationships. Until the "ultimate theory" is developed, the process of trying to understand the various aspects of electrolyte solutions must continue. By putting together the separate parcels of knowledge, the entire picture may someday emerge.

DOCUMENTATION OF PREVIOUS WORK

To understand the reasons for undertaking this research project and to better appreciate the current state of knowledge of electrolyte solutions, a documentation of previous work on electrolyte solutions is relevant. Even though more emphasis will be placed on work which has been done in areas relating to this research, it is hoped that by discussing other areas of electrolyte solution studies the entire picture will be clearer.

In the development of electrolyte solution knowledge certain ideas, theories, and experimental results have tended to change the previous course of development and to dramatically influence later development. The Debye-Hückel theory has been a powerful influence and a definite turning point in the development of electrolyte solution theory. Prior to 1923, when Debye and Hückel published the first paper on their theory,[5] Milner[6] had successfully described mathematically the problem--interionic attraction--, but his treatment was too involved to be widely applicable. Before Milner's work, men such as Sutherland,[7] Noyes,[8] and Bjerrum[9] had felt that the behavior of strong electrolytes in dilute solution could be explained by considering the ions to be completely dissociated and yet under the effects of interionic attraction. The idea of complete dissociation goes back even further to Arrhenius[10] who, along with van't Hoff,[11] Ostwald,[12] and Kohlrausch,[13] made significant early contributions to the study of electrolyte solutions. Their papers on conductance, freezing point depression, osmotic pressure, boiling point elevation, and vapor pressure are classics in the early development of electrolyte theory.

The Debye-Hückel treatment was, however, the first real turning point in the development of electrolyte solution theory. The basic Debye-Hückel equation is,

$$\ln \gamma_{\pm} = -A_{\gamma} \left| z_{+} z_{-} \right| I^{1/2} \qquad \text{Eq. 1}$$

where: $\gamma_{\pm}$ = mean activity coefficient
A_{γ} = Debye-Hückel coefficient

$$= \sqrt{\frac{2\pi N_0 d_1}{1000 \times 2.303^2} \left(\frac{e^2}{DkT}\right)^3}$$

N_0 = Avogadro's number
d_1 = density of solvent
e = charge on electron
D = dielectric constant of solvent
k = Boltzmann constant
T = temperature
z_{+}, z_{-} = charge on positive, negative ion
I = ionic strength

Although this equation is applicable only in dilute solutions, experimental results have confirmed the <u>a priori</u> results calculated from the Debye-Hückel equation, and today their theory is well established. The limiting law derived by them has been invaluable for extrapolation to zero concentration of activity coefficients, heat capacities, heat contents, volumes, etc. It is noteworthy that in their expression a term for the ionic atmosphere, I, is present. This term is the ionic strength and was first proposed by

Lewis and Randall.[14]

There are limitations in the Debye-Hückel treatment which have restricted its applicability. The fact that approximations were used in its derivation make it a limiting law. In addition, the solvent is incorporated in the treatment only to the extent of its dielectric effect on charged particle interactions. No account is taken of solvent structure in bulk, nor are the properties of the solvent closely surrounding the ions considered.

The Debye-Hückel equation may be applied to solutions of mixed electrolytes as well as single electrolyte solutions. The principle of ionic strength[15] is used to extend the Debye-Hückel equation to mixed electrolyte solutions. This principle states that the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.

Another principle which governed the treatment of mixed electrolyte solutions at this time was Brønsted's principle of specific ion interaction.[16] This principle states, "In a dilute salt solution of constant total concentration, ions will be uniformly influenced by ions of their own sign." Furthermore, Brønsted stated that the activity coefficient of an ion is a function of the nature of the ion itself, the solvent containing it, and the action upon it of ions of opposite charge.

Brønsted's papers on solubility and the theory of specific ion interaction and Debye and Hückel's papers on the theory of interionic attraction greatly affected subsequent research on electrolyte solutions. Many papers were published commenting on and extending the Debye-Hückel treatment. Other limiting laws for conductance[17] and viscosity[18] and general laws of diffusion[19] were developed. Concurrent with the theoretical advances was the collection of extensive data on the properties of electrolyte solutions. These data included activity coefficients from electromotive force measurements, solubility, freezing point, isopiestic, and diffusion determinations. Conductance experiments were numerous as were viscosity and partial molal quantity experiments. Much of this work, which is discussed in Harned and Owen[20] or Lewis and Randall,[21] was concerned with solutions of a single electrolyte.

The determination and tabulation of activity coefficients is especially important for electrolyte solutions. Utilizing the Debye-Hückel theory and Brønsted's principle of specific ion interaction, Guggenheim[22] developed an equation for the treatment of 1-1 electrolytes at concentrations from 0 to 0.1 M. Employing an ideal electrolyte obeying the Debye-Hückel equation, and letting the mean distance of approach of the ions be 3.05 Å at 25°, Guggenheim added a linear term to the Debye-Hückel equation to account for specific effects of the electrolyte, which include ion-pairing and effects due to size and polarizability. His equation for a single, simple electrolyte MX is,

$$\log \gamma_{\pm} = -A_{\gamma}\left|z_{+}z_{-}\right|\frac{I^{1/2}}{1 + I^{1/2}} + B_{MX}\, m \qquad \text{Eq. 2}$$

where B_{MX} is the correction for + - interactions, and the other symbols are the same as for Equation 1. This equation may be expanded to provide for the activity coefficient of the electrolyte M'X' in a solution of mixed electrolytes. The equation then takes the form,

$$\log \gamma_{\pm} = -A_{\gamma}\left|z_{+}z_{-}\right|\frac{I^{1/2}}{1 + I^{1/2}} + \frac{\nu_{+}}{\nu_{+}+\nu_{-}}\sum_{X} B_{M'X}m_{X} + \frac{\nu_{-}}{\nu_{+}+\nu_{-}}\sum_{M} B_{MX'}m$$

Eq. 3

where ν is the number of ions per molecule of electrolyte and the various B terms are adjustable constants for ionic interactions. Guggenheim's B values, which are essentially deviations from the Debye-Hückel limiting term, have been used to tabulate activity coefficients. Other deviation functions have also been used (see Lewis and Randall[23]) and are helpful because they vary more slowly with concentration than the activity coefficient. This allows tabulation of activity coefficients to be made at wider concentration intervals without sacrificing accuracy.

Experimental study of electrolyte solutions has not been devoted exclusively to single electrolyte solutions. A significant amount of the work has been concerned with mixed electrolyte solutions. From the beginning, work with mixed electrolytes has been particularly valuable in developing the theory of electrolyte solutions and is, of course, of great practical value.

Two early techniques for the study of mixed electrolytes were solubility and electromotive force measurements from which the activity of one electrolyte in the presence of another can be determined. Early work with the effect of salts on the solubility of other salts was done by Noyes and

Bray,[24] Noyes, Boggs, Farrell, and Stewart,[25] Bray and Winninghoff,[26] and Bray.[27] In their work they made use of the concept of activity which had been proposed by Lewis[28] a few years earlier. The work of Noyes and collaborators was later used by Lewis and Randall[29] in developing their ionic strength principle. Solubility studies were also published by Brønsted.[30]

About the same time as these early solubility studies, Harned[31] began his work on electromotive force measurements. The electromotive force technique was found to be particularly advantageous because the concentration of both electrolytes can be varied, whereas in solubility measurements the concentration of one salt is fixed. A discussion of most of Harned's work may be found in Harned and Owen.[32]

Harned used cells of the type,

$$H_2 \left| HX_{(m_2)}\ MX_{(m_3)} \right| AgX\text{-}Ag$$

for much of his work. From his results with several systems, he developed a very important empirical relationship for the activity coefficient of one electrolyte in the presence of another. Considering a ternary solution of HX, MX, and water with a constant total molality of m, and a variable molality of MX, m_3, the log of the activity coefficient of HX as a function of m_3 may be expressed as,

$$\log \gamma_2 = \log \gamma_2(0) - \alpha_{23} m_3. \qquad \text{Eq. 4}$$

In this equation $\gamma_2(0)$ is the activity coefficient of HX in a pure solution of HX at molality m. α_{23}, called the Harned coefficient, is an empirical coefficient which may be a function of the total molality m. The corresponding equation for MX is,

$$\log \gamma_3 = \log \gamma_3(0) - \alpha_{32} m_2. \qquad \text{Eq. 5}$$

Equations 4 and 5, known as Harned's Rule, have been found to hold for many ternary systems, and the Harned coefficients have been particularly convenient for reporting data.

Harned's work with the cell,

$$H_2 \big| HCl(m_2)\ NaCl(m_3) \big| AgCl\text{-}Ag$$

is of special interest to this research. He measured the activity coefficient of HCl in the mixture HCl-NaCl-H_2O at total molalities of one, two, and three and at temperatures from 0° to 50°.[33] From his experimental data, α_{23} could be obtained, and using the method of McKay,[34] α_{32} was obtained. It was necessary to employ an additional term in the expression for log γ_3 giving the equation,

$$\log \gamma_3 = \log \gamma_3(0) - \alpha_{32} m_2 - \beta_{32} m_2^2. \qquad \text{Eq. 6}$$

The Harned coefficients may be used to calculate the excess free energy and enthalpy of mixing. As shown by Lewis and Randall,[35] the Harned coefficients for a mixture of 1-1 electrolytes MX and NY (NY = 2, MX = 3) at molality m may be expressed as,

$$\alpha_{23} = B_{NY} - 1/2(B_{MY} + B_{NX}) \qquad \text{Eq. 7}$$

$$\alpha_{32} = B_{MX} - 1/2(B_{MY} + B_{NX}) \qquad \text{Eq. 8}$$

with β_{23}, etc. equal to zero and where B_{NY}, etc. are the specific interaction constants in the Brønsted-Guggenheim extension of the Debye-Hückel equation (see Equations 2 and

3). The equation for the excess free energy of mixing (derived in Lewis and Randall[36]) is,

$$\Delta_m G^E = -2.303RTm_2m_3[\alpha_{23} + \alpha_{32} + 2(m_3\beta_{23} + m_2\beta_{32}) + 2/3(\beta_{23} - \beta_{32})(m_2 - m_3) + \cdot \cdot \cdot]. \qquad \text{Eq. 9}$$

Taking the temperature derivative of Equation 9 gives the excess enthalpy of mixing.

$$\Delta_m H = 2.303RT^2m_2m_3\frac{\partial}{\partial T}\left[\alpha_{23} + \alpha_{32} + 2(m_3\beta_{23} + m_2\beta_{32}) + 2/3(\beta_{23} - \beta_{32})(m_2 - m_3) + \cdot \cdot \cdot\right]. \qquad \text{Eq. 10}$$

Referring to Equations 7, 8, 9, and 10, notice that for mixings involving a common ion the leading term, $\alpha_{23} + \alpha_{32}$, in the equations for excess free energy and enthalpy of mixing would be zero. This is in agreement with Brønsted's principle. Experimental values (to be discussed later) of heats of mixing are not zero, even in 0.1 m solutions.

Another important series of electromotive force determinations of activity coefficients has been conducted by Lietzke.[37] His studies cover a wide range of systems at varying concentrations and at different temperatures. His results for the HCl-NaCl-H_2O system at total ionic strengths ranging from 0.4 to 1.0 and temperatures of 25-175° are of particular interest, since from them values of the Harned coefficients may be calculated. Unfortunately it was found that the Harned coefficients calculated from Lietzke's work do not agree well with those obtained from Harned's study. This disagreement points out the difficulty associated with the determination of activity coefficients.

Solubility and electromotive force techniques are not the only methods available for studying mixed electrolytes. Scatchard and co-workers[38] published a series of papers dealing with the activity of single and mixed electrolytes in both aqueous and non-aqueous solvents. Their data were obtained from freezing point depression determinations. By extending Brønsted's theory to include both triplet (+-+ or -+-) and pairwise oppositely-charged (+-) interactions, they derived equations for mixed electrolytes and were able to show that their results supported Brønsted's theory of specific ion interaction.

Owen and Cook[39] and later Robinson[40] applied the isopiestic technique to obtain activities of electrolytes in mixed solutions. Much of this work has been reported in terms of the Harned coefficients and is also discussed in terms of Harned's Rule. The $LiCl-KCl-H_2O$ system, which was studied by Owen and Cooke, was found to obey Harned's Rule, but the sum $(\alpha_{23} + \alpha_{32})$ of the Harned coefficients was not zero as predicted by Brønsted, nor was it small relative to the difference $(\alpha_{23} - \alpha_{32})$, as it should be according to Scatchard. Use is made in another section of this thesis of Owen and Cooke's data to calculate the excess free energy of mixing for this system at one molal.

Robinson has made numerous contributions in the area of activity coefficients from the isopiestic method, and of particular interest are his results with the $NaCl-KCl-H_2O$ mixture[41] and the $LiCl-NaCl-H_2O$ mixture.[42] In his work with the $NaCl-KCl-H_2O$ mixture, the equation of McKay and Perring[43] was used to evaluate the activity coefficients of both components. The log of the activity coefficient of KCl was found to vary linearly with the NaCl concentration in solutions of constant total molality, but the log of the activity coefficient of NaCl showed some departure from linearity. His data for the activity coefficients may be used to calculate the Harned coefficients and the excess free energy of mixing.

The previously discussed work is certainly not all which was done on single or mixed electrolyte solutions following the Debye-Hückel treatment and reviews of other work are available.[44,45] Before discussing more recent experimental results, it is necessary to present other theoretical developments which began appearing in the 1950's and which have profoundly affected the present state of understanding of electrolyte solutions.

In a series of papers, Mayer[46] developed a theory of ionic solutions based on the statistical mechanical treatment of imperfect gases and utilizing cluster integrals to describe interionic attractions. The interionic attractions are considered in terms of potentials of average force of sets of ions and are calculated from a molecular model for the solution. The molecular model, termed the primitive model, considers the ions as hard spheres of the same dielectric as the solvent. The solvent is considered as an ideal structureless dielectric. Essential to his calculations is the assumption that the total potential of average force for all the solute may be represented as a sum of pair energies. The potential of interaction for two ions is proportional only to the distance separating them and is not affected by other ions. This amounts to saying that only pairwise interactions are important (triplet and higher order interactions are not considered), and this is one reason the theory does not give good results for concentrated solutions. Mayer's theory is applicable in solutions more concentrated than those covered by the Debye-Hückel treatment, which is essentially a limiting law, and reduces to the Debye-Hückel equation in the limit of zero concentration. Mayer's equations cannot be compared with experimental values without first correcting to standard pressure, because his equations are given for total pressure (standard pressure plus osmotic pressure).

Two papers published by Poirier[47] in 1953 significantly extended Mayer's theory by reducing the equations to forms suitable for calculation of thermodynamic properties of single electrolyte solutions. For solutions of 1-1 electrolytes, Poirier obtained good agreement between experimental and calculated results of activity coefficients up to 0.4 M. For higher valence types, the limit of agreement was approximately 0.01 M. The formation of triplets may account for the lack of agreement in more concentrated solutions of higher valence.

Significantly, Mayer's theory and Poirier's extension of it are the first equations from which precise activity coefficients, osmotic coefficients, partial and apparent molal volumes, partial and apparent molal heat contents, etc. can be calculated without using the Debye-Hückel theory as a starting point.

Another important extension of Mayer's theory has been made by Friedman.[48] Besides performing calculations for single electrolyte solutions, Friedman has extended Mayer's theory to apply to solutions of symmetrical and unsymmetrical mixed electrolytes with a common ion. In his work the concept of excess thermodynamic functions, first introduced by Lewis and Randall[49] and later Scatchard,[50] is used and is defined as the difference in properties of a real solution and a hypothetical ideal reference solution at the same temperature, pressure, and composition. Excess thermodynamic functions for mixtures may also be thought of as the sum of contributions of the component single electrolyte solutions at the same temperature, pressure, and composition.

Two important equations were developed by Friedman. The first, for the excess free energy of mixing, is

$$\Delta_m G^E = I^2 RTy(1 - y)\sum g_p Y^p \qquad p = 0, 1, 2, \cdots \text{Eq. 11}$$

where:

$Y = 1 - 2y$
y = mole fraction
I = molal ionic strength
R = gas constant
T = temperature
g_p = measure of pairwise like-charged ion interactions

and the second, for the excess enthalpy of mixing, is

$$\Delta_m H^E = I^2 RTy(1 - y)\sum h_p Y^p \qquad p = o, 1, 2, \cdots \text{Eq. 12}$$

where:

$h_p = -T[\partial g_p/\partial T]$.

Calculations of g_0 for several mixtures of aqueous alkali metal chloride solutions by Friedman, using the primitive model, gave results consistent with available experimental data. One result of his calculations is that the Brønsted principle of specific ion interaction is shown to be quite inaccurate.[51] Brønsted's principle would imply that g_0, the leading term in the excess free energy equation, would go to zero as the concentration goes to zero, but according to Friedman, g_0 does not approach zero as $I \rightarrow 0$.

A major problem in Friedman's treatment is the assigning of the distance of separation for the ++, --, and +- interactions. In his equations, no account is taken of the effect of the solvent on the ions with respect to hydration or charge shielding, nor is the effect of the ions on the solvent considered. Presently it is not known to what extent solvent structure must be incorporated into a theoretical model in order to obtain agreement with experimental results.

The effect of solvent structure on ionic interactions and the nature of solute-solvent interactions is a problem which occupies a central role in studies of electrolyte solutions. The effect of ions on the structure of water has long been recognized. Bernal and Fowler[52] noted in 1933 the influence of ions on water viscosity. In a recent review, Kavanau[53] discusses the different ideas concerning water structure and solute-solvent interactions.

Prerequisite to understanding solute-solvent interactions is an understanding of the solvent. Numerous models have been proposed to account for the properties of water, most of which are reviewed in Kavanau. The model which has yielded perhaps the best results in terms of explaining the properties of water, both physical and thermodynamic, and being applicable to experimental techniques (infrared and Raman spectroscopy) is the flickering cluster model of Frank and Wen[54] and Frank.[55] This model postulates that the formation of hydrogen bonds in water is a cooperative phenomenon. The formation of one hydrogen bond (due to a local energy fluctuation) leads to the formation of many in its area and causes a cluster of hydrogen bonds to form. Likewise, the disruption of one hydrogen bond in such a cluster leads to the disruption of the entire cluster. Hence the overall picture is one of flickering clusters of ice-like regions in water. These clusters have an average half-life of 10^{-10} to 10^{-11} sec.

Statistical thermodynamic calculations using the flickering cluster model have been made by Némethy and Scheraga.[56] Fairly good agreement was obtained between their calculated values of free energy, internal energy, entropy, and heat capacity and experimental values. They calculated that the percentage of hydrogen bonds in liquid water decreased from 52.8% at 0° to 32.5% at 100°.

Near-infrared studies of water by Buijs and Choppin[57] have produced results which agree generally with Némethy and Scheraga's results and, hence, support the flickering cluster model. By resolving the absorption band of water between 1.1 and 1.3 μ into three bands, assigning each band to a species of water (i.e., water molecules with zero, one, and two OH groups participating in hydrogen bonds), and studying the molar absorptivity of these three bands as a function of temperature, they were able to obtain information on the cluster size, concentration, and the percentage of hydrogen bonds as a function of temperature. They found 54% hydrogen bonds present at 0° and 39% at 72°.

Others who have studied water structure disagree with Buijs and Choppin and their model. Among those disagreeing is Walrafen,[58] who, from his Raman studies of water, contends that the three species model of Buijs and Choppin is not possible. Instead, he proposes a two species model consisting of bound and unbound water.

The situation at present is that there is simply no completely satisfactory explanation of the structure and properties of water. The fact that the problem of water structure still remains largely unsolved, makes the interpretation of solute-water interactions even more difficult. It is known that ions exhibit an effect on water structure which goes beyond the simple dielectric polarization and compression of adjacent water in the hydration shell. These effects of ions on water may be observed, for example, in changes in the intensity and frequency of Raman[59] and infrared[60] spectra, in changes in the viscosity,[61] heat capacity,[62] temperature of maximum density,[63] and dielectric constant.[64]

The structure of water surrounding an ion has been described by Frank and co-workers[65] as consisting of three regions (see Figure 1). In the region nearest the ion, region A, the water is highly oriented. It is polarized, immobilized, and electrostricted by the electric field of

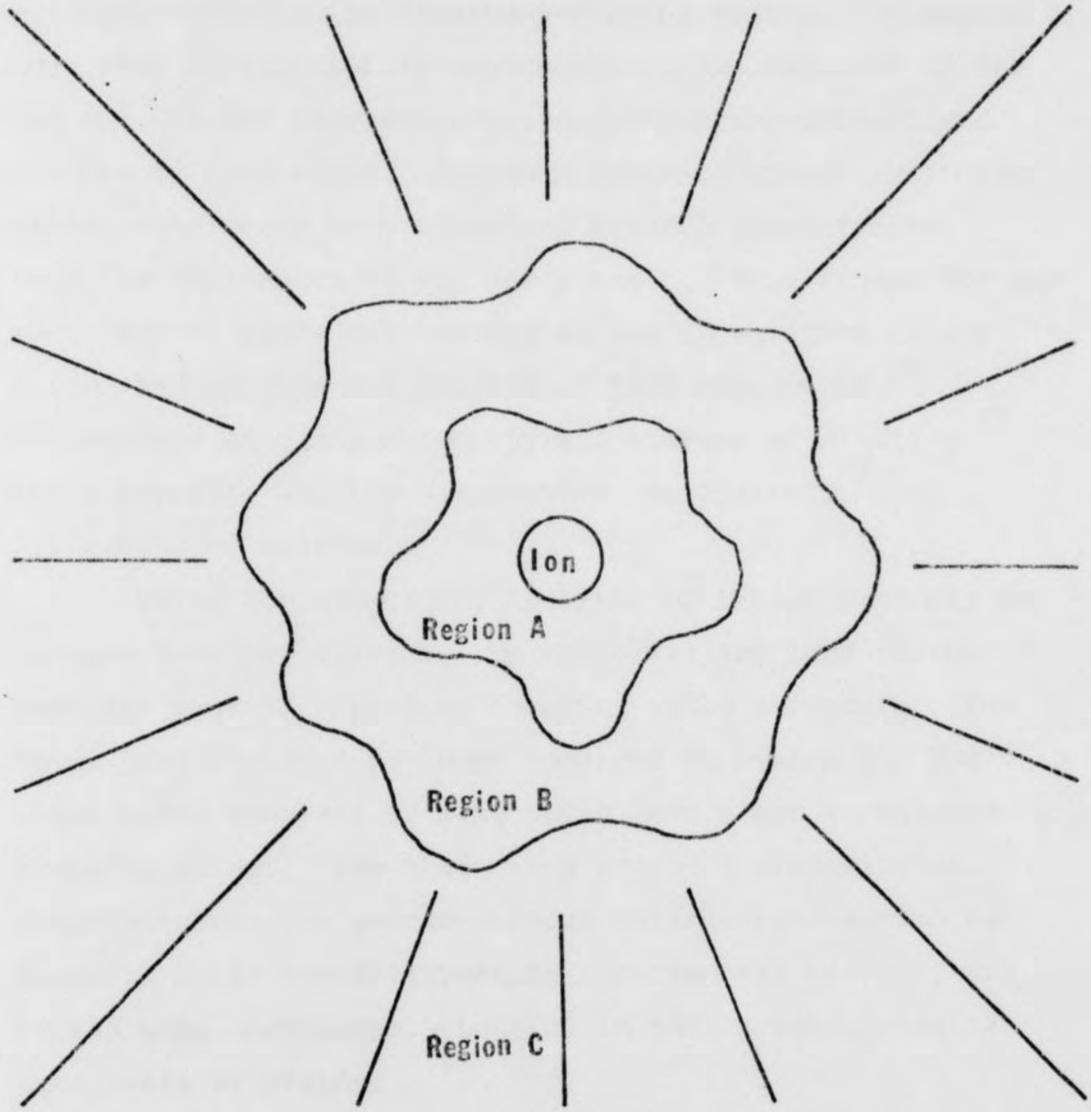

Figure 1. Structure of an Ion in Water.

Region A:	Highly oriented, electrostricted water.
Region B:	Structure-broken water.
Region C:	Bulk water.

the ion. This is the structure-forming region. In region C, the water is essentially unaffected by the presence of the ion and has the same structure and structure-orienting effects as pure water. Region B contains structure broken water. The water here is caught between the different ordering influences of regions A and C. This scheme for the structure of water surrounding an ion in solution is supported by experimental studies of heat capacities,[66] temperature of maximum density and entropy of dilution,[67] ionic mobility and its temperature coefficient,[68] and dielectric relaxation.[69]

Using the structural analysis of Frank, ions may be grouped into two classes. In one class are ions which have the overall effect of creating water structure. For these ions region A is large compared to region B. The other class consists of ions which have a net structure-breaking effect. For these ions region B predominates. Frank's scheme for solute-solvent interactions serves as a useful guide for interpreting experimental results, and it has been particularly helpful in interpreting results from heats of mixing.

Heats of mixing are an excellent way of looking at solute-solvent interactions and specific ion effects. Furthermore, they give the temperature coefficient for the activity coefficient. The first heats of mixing were reported by Young and Smith[70] who studied the mixtures $NaCl-KCl-H_2O$ and $NaCl-LiCl-H_2O$ at one molal and 25°. In subsequent publications, Young and co-workers[71] determined the heats of mixing for a large variety of 1-1 electrolytes at 25° and one molal, including mixtures with and without a common ion. The heats of mixing were found to be independent of the common ion. In addition, the heat of mixing was quadratic in mole fraction. Young and co-workers fitted their data to the equation,

$$\Delta_m H/x_2 x_3 = \alpha + \beta(x_2 - x_3) + \cdot \cdot \cdot \qquad \text{Eq. 13}$$

where x is the mole fraction and α and β are empirical constants.

Young observed that for common anion mixings, the cations could be placed into two groups. The heat of mixing for cations of the same group was endothermic, and the heat of mixing for cations of different groups was exothermic.

An empirical rule which resulted from early heat of mixing data is the cross-square rule.[72] For the six mixings possible with four single electrolytes which have only two different cations and two different anions (see Figure 2), it was found that the sum of the heats of mixing represented by the sides of the square was approximately equal to the sum of the cross heats of mixing. It has been shown by Bottcher[73] that this rule will be valid if the heats of mixing of the cations in the presence of each anion are nearly equal ($\Delta H_{\text{cation in X}} = \Delta H_{\text{cation in Y}}$), and if the heat of mixing of the cations in the presence of an equal molal mixture of both anions ($\Delta H_{\text{cation in (X + Y)}}$) has a value intermediate between $\Delta H_{\text{cation in X}}$ and $\Delta H_{\text{cation in Y}}$.

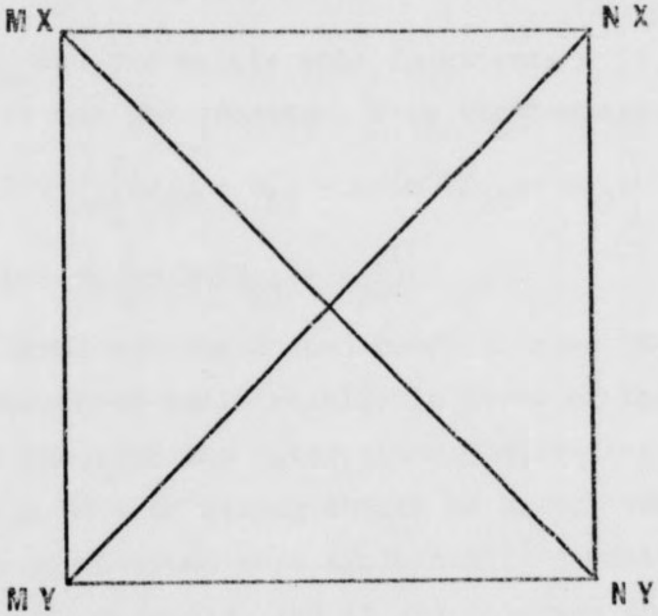

Figure 2. Cross-Square Rule

Example[a]

Salt Pair	$\Delta_m H$ (cal/mole)
LiCl-KCl	-16.06
LiCl-LiBr	0.80
LiBr-KBr	-17.06
KBr-KCl	0.81
$\sum\square$ =	-31.51
LiCl-KBr	0.17
LiBr-KCl	-31.75
$\sum\times$ =	-31.58

(a) See footnote (72).

Stern and Anderson[74] studied the heat of mixing for the systems KCl-NaCl-H_2O and LiCl-NaCl-H_2O at 25° and concentrations from 0.5 m to saturation. The data were fitted to the equation,

$$\Delta_m H = 2.302RT^2 m x_2(1 - x_2)(A - Bx_2) \qquad \text{Eq. 14}$$

x_2 and $1 - x_2$ are the solute mole fractions, m is the total molality, R is the gas constant, T is the temperature, and

$$A = \frac{\partial}{\partial T}\left[(\alpha_{23} + \alpha_{32} + 2/3m(2\beta_{23} + \beta_{32})\right] \qquad \text{Eq. 15}$$

$$B = \frac{\partial}{\partial T}\left[-2/3m(\beta_{23} - \beta_{32})\right]. \qquad \text{Eq. 16}$$

The α and β terms are the Harned coefficients. Stern and Anderson interpreted their results in terms of the Brønsted principle of specific ion interaction. According to this principle, the heat of mixing should be zero. The non-zero heats of mixing obtained were explained as deviations from Brønsted's principle, and it was observed that as the concentration decreased better agreement with Brønsted's principle was reached.

The heats of mixing for the systems HCl-KCl-H_2O at two and three molal and HCl-NaCl-H_2O at one, two, and three molal were studied at temperatures of 0, 10, 25, and 40° by Stern, Anderson, and Passchier[75] and Stern and Passchier.[76] Again the data were fitted to Equation 14 and the results interpreted in terms of Brønsted's principle. A particularly interesting conclusion obtained from extrapolation of the data was the prediction that the heat of mixing for the HCl-NaCl-H_2O system should be zero around 80°.

The heats of mixing of aqueous electrolytes have been extensively studied by Wood and Smith,[77] Wood and Anderson,[78] and Wood, Patton, and Ghamkhar.[79] It was found that, contrary to Brønsted's principle, like-charged ions do have specific interactions and that like-charged pair interactions are usually more important than triplet interactions for the alkali metal halide mixings. For alkaline earth halides more contribution to the heat of mixing by triplet interactions was indicated. The success of general equations for the excess free energy and relative apparent molal heat content of a multicomponent mixture of electrolytes of the same charge type further supported their conclusion that like-charged pair interactions are mainly responsible for the heat of mixing. The general equations are based on only pair-wise (++, --) and triplet (+-+, -+-) interactions and take the forms,

$$G^{E}_{mix} = \sum_{i,j} y_{R_i} y_{X_j} G^{E}_{R_i X_j} + RTI^{2}\left[\sum_{h>i} y_{R_h} y_{R_i} y_{X_j} g^{X_j}_{R_h,R_i} + \sum_{j>k} y_{X_j} y_{X_k} y_{R_i} g^{R_i}_{X_j,X_k}\right] \qquad \text{Eq. 17}$$

$$H^{E}_{mix}/m = \phi_{L}^{mix} = \sum_{i,j} y_{R_i} y_{X_j} \phi_{L}^{R_i X_j} + \frac{RTI^{2}}{m}\left[\sum_{h>i} y_{R_h} y_{R_i} y_{X_j} h^{X_j}_{R_h,R_i} + \sum_{j>k} y_{X_j} y_{X_k} y_{R_i} h^{R_i}_{X_j,X_k}\right] \qquad \text{Eq. 18}$$

where y_{R_i}, etc. = mole fraction of cations = $m_{R_i}/\sum_h m_{R_h}$; y_{X_j}, etc. = mole fraction of anions = $m_{X_j}/\sum_k m_{X_k}$; $g^{X_j}_{R_h,R_i}$, $h^{X_j}_{R_h,R_i}$ = interaction parameters of ions R_h and R_i in the presence of common X_j ion. This parameter is a measure of the heat of mixing R_hX_j with R_iX_j; $G^{E}_{R_iX_j}$, $\phi_L^{R_iX_j}$, etc. = pure component thermodynamic properties; G^E_{mix}, H^E_{mix} = excess free energy and enthalpy of mixture (cal/kg of solvent); $\emptyset_L^{mix}$ = excess heat of mixture (cal/mole). These equations were derived using Friedman's[80] results and allow for the calculation of the thermodynamic properties of mixed electrolyte solutions from knowledge only of the pure electrolyte properties and the common ion mixed electrolyte properties.

Wood and Anderson[81] studied the heats of mixing of the potassium salts of the fluoride, chloride, bromide, and acetate ions in an effort to determine why the heat of mixing of ions of the same group is endothermic and of different groups is exothermic. It was felt that the classification of the ions into different groups was based on size and/or ionic structural properties--structure-making, structure-breaking. The results of this work led them to conclude that the classification is based on ionic structural properties, and that the heat of mixing is primarily influenced by the water structure around the like-charged ions.

From studies on the heats of mixing of tetraalkylammonium chlorides, Wood and Anderson[82] observed that the tetramethylammonium and tetraethylammonium ions behave as structure breakers toward alkali cations, but they behave as opposites when mixed with each other. This seems to indicate that the tetraethylammonium cation is borderline between structure-making and structure-breaking. The structural influences of the tetraalkylammonium ions are different from those of the alkali, alkaline and halide ions. As discussed by Frank and Evans[83] the tetraalkylammonium ions should become hydrophobic structure makers as the size of the alkyl group increases. These ions seem to induce hydrogen bonding or structure in the water surrounding them because of the repulsion between the water and their non-polar surface.

The heats of mixing of unsymmetrical electrolytes (1-1 with 1-2) have recently been studied at 25° and 0.5, 1.0, 2.0, and 3.0 m.[84] The results agree generally with Friedman's prediction that the value of RTh_0 should $\rightarrow + \infty$ as the concentration $\rightarrow 0$. The heats were about the same as those observed for charge symmetrical mixtures. It was found that the calculated cation-cation interactions obeyed the structure rule for the sign of the heat of mixing except for the KCl-$MgCl_2$-H_2O mixing.

The heats of mixing for 15 systems were studied by Zdanovskii and Deryabina.[85] These mixings were determined for solutions containing a constant concentration of one salt with solutions of variable concentration of the other salt. The results were discussed in terms of the type of curve obtained from the heat of mixing versus concentration graph.

In another heat of mixing study,[86] the variation of the heat of mixing with concentration for the systems $LiCl$-MCl-H_2O ($M = Rb^+, Cs^+$), $NaCl$-$CsCl$-H_2O, and $LiCl$-$LiNO_3$-H_2O was interpreted in terms of changes in the hydration shell around the ions. Values of the excess entropy of mixing were calculated from published values of the excess free energy of mixing. It was noted that the thermodynamic excess functions do not conform to the Brønsted-Guggenheim principle. For the heat of mixing of the systems LiCl-KCl-H_2O, LiCl-NaCl-H_2O, and NaCl-KCl-H_2O at 25° and one to six molal, it was found that the LiCl-KCl-H_2O system, whose ions differ most in size, gave the largest enthalpy effect.[87]

The temperature dependence of the heat of mixing for the systems LiCl-CsCl-H_2O, LiCl-RbCl-H_2O, and LiCl-KCl-H_2O at 1/4 m from 0-40° has been studied by Stakhanova and co-workers.[88] They found that the heat of mixing was more exothermic at 0° than at 25° and the suggestion was made that there exists a temperature at which the heat of mixing is zero. The method of comparative calculation[89] was used to compare the heats of mixing at the temperatures studied, and a satisfactory linear relationship was obtained. Stakhanova's heats of mixing were obtained at constant molality.

This documentation of the development of electrolyte solution theory and of the experimental work with electrolyte solutions is, of necessity, incomplete. An attempt was made, however, to include enough material to give a general idea of the basic trends and developments and to include work particularly relevant to this research.

RESEARCH PROPOSAL

Heats of mixing have been studied rather extensively at 25°, yet there is a paucity of data at other temperatures. A study of the temperature dependence of the heat of mixing was undertaken to gain additional thermodynamic and structural information on electrolyte solutions.

From the equation,[90]

$$\Delta_m G^E(t_2) = \Delta_m G^E(t_1) + \Delta C_p(m)\Big]_{t_2}^{t_1} \Delta T - \Delta_m S(t_1)\Delta T - T_2 \Delta C_p(m)\Big]_{t_1}^{t_2} \ln T_2/T_1 \qquad \text{Eq. 19}$$

where $\Delta C_p(m) = \dfrac{\Delta_m H(t_2) - \Delta_m H(t_1)}{\Delta T}$, Eq. 20

the complete excess thermodynamic properties of electrolyte solutions can be calculated provided $\Delta_m G^E(t_1)$ and the heat of mixing as a function of temperature are known. Some values of $\Delta_m G^E$ at 25° are available from electromotive force and isopiestic work, but without $\Delta_m H$ as a function of temperature the equation cannot be used. By extending the heat of mixing data to higher temperatures and including additional systems, the complete thermodynamic properties of these systems can be calculated.

One of the goals of the study of electrolyte solutions is to develop general equations applicable to all systems. If the heats of mixing were found to be a regular function of temperature, then it would perhaps be possible to calculate the heat of mixing and other thermodynamic properties for many systems as a function of temperature from only a few representative system studies.

Another reason for undertaking the study of heats of mixing as a function of temperature was the desire to learn more about the role of water structure in heats of mixing and the nature of ion-solvent interactions. Studies of water structure indicate that it is changing its structure significantly in the temperature range 25° to 80°. If water structure is significantly involved in the heats of mixing, then one would expect this change to affect the heats of mixing. In addition, since Friedman's theory does not involve solvent structure, if heats of mixing are made at temperatures where solvent structure is no longer important, then better agreement between Friedman's theory and experiment might be obtained.

It was proposed to measure the heat of mixing at 40, 60, and 80° for the systems $HCl-NaCl-H_2O$, $NaCl-LiCl-H_2O$, $NaCl-KCl-H_2O$, $LiCl-KCl-H_2O$ at one molal, and $LiCl-(CH_3)_4NCl-H_2O$ and $LiCl-(CH_3)_4NCl-H_2O$ at 0.5 molal.

EXPERIMENTAL

Calorimeter

Introduction. In order to measure accurately the very small experimental heats (less than 1.0 cal), a very sensitive instrument was necessary. In addition, the instrument needed to be one in which the mixing experiments could be expeditiously conducted. Both of these requirements can be met by a microcalorimeter.

In designing the calorimeter several points had to be considered. The size of the calorimeter had to be such that the volumes of solutions mixed would be large enough to give heats of mixing which could be determined accurately. On the other hand, if the calorimeter were too large problems in manipulation and time of heating and mixing would overshadow any accuracy gained by the larger size. Another point which had to be considered was the thermal leak. Thermal leak considerations were particularly important since the measurements were absolute. Finally, design of each component of the calorimeter (pipets, stirrers, heaters, etc.) had to be tailored to meet requirements of accuracy, time to accomplish purpose, size, and integration with other components.

In the discussion of the design of the calorimeter some of the problems encountered in obtaining optimum experimental conditions will also be included.

The isothermal, double microcalorimeter built for conducting the heat of mixing experiments was originally designed to serve as a twin calorimeter. The advantage of a twin calorimeter is that the thermal leak error, while not eliminated, may be evaluated very accurately by suitable rating periods.[91] The thermal leak involves heat exchange between the calorimeter and its surrounding jacket. For some processes, slow ones especially, appreciable error in the data can result unless it is known how much of the apparent heat of the process results from thermal leak.

The twin concept was not employed for this calorimeter, however, because error from the large "noise level" produced when both thermistors were in the circuit overshadowed any thermal leak correction. As it turned out, the mixing process was rapid enough and the thermal leak small enough so that no correction for heat exchange was necessary. Having two calorimeter vessels was advantageous none-the-less because of the long heating times. By heating two experiments simultaneously the heating time per experiment was reduced by one half.

Vessels. The major features of the calorimeter are shown in Figure 3. The Dewar vessels,[92] I, hold 240 ml. The use of Dewar vessels minimized radiation and conduction contributions to the thermal leak. Each vessel is attached by silicone rubber to a 13.3 cm in diameter brass collar, D, which has a 4.7 cm in diameter opening into the vessel. The collar is bolted to the brass lid, C, and sealed with a 2 7/8 X 3 1/4 rubber "O-ring", K. Prior to the mixings involving HCl, the brass collar and brass lid were coated

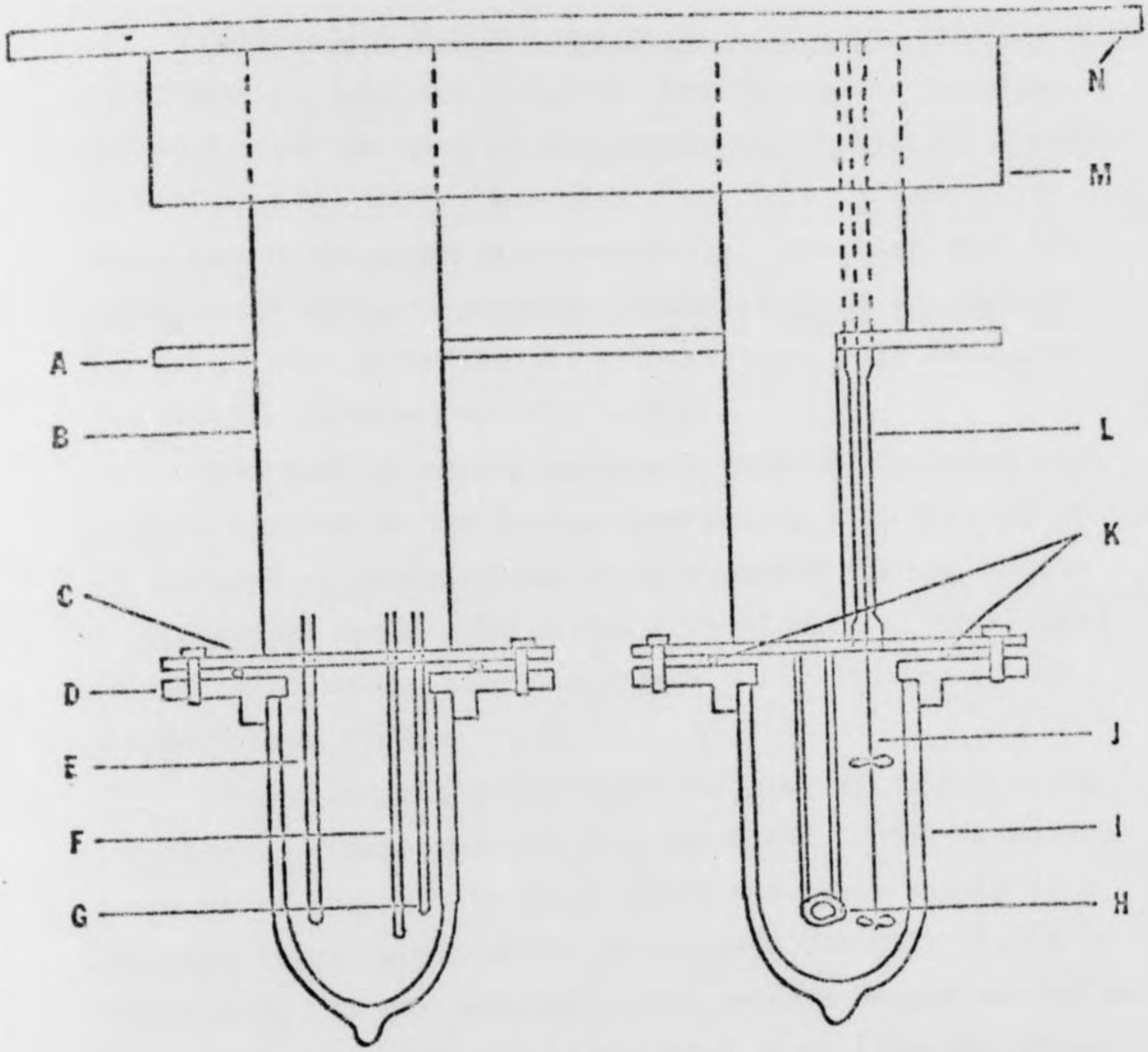

Figure 3. Calorimeter

A	12" × 8" × 1/4" brass plate
B	half-cylinder brass superstructure
C	brass lid
D	brass collar
E	Thermistor
F	rough heater
G	calibration heater
H	Teflon® pipet holder
I	10 oz. Dewar flask
J	glass stirrer
K	"O-rings"
L	5 mm precision bore bearing
M	styrofoam
N	20" × 12" × 1/2" plywood

Note: right calorimeter rotated 90°

with an epoxy enamel paint to prevent corrosion.

Calibration Heaters and Heating Circuit. Most modern calorimeters, this one included, are in essence instruments for comparing the heat of some chemical or physical process with electrical heat. One reason for this is that electrical heats can be measured very accurately. Provided that the calorimeter has been properly constructed and adequately tested so that no systematic error occurs, very accurate data can be obtained by this method.

The heat of mixing data were obtained by comparing thermal changes in the system upon mixing with thermal changes in the same system produced by an accurately known amount of electrical heat. The circuit for electrical heat imput to the calorimeter, shown in Figure 4, is similar to the one described by Wood et al.[93]

A double-pole-double-throw toggle switch activates the timer[94] simultaneously with the heater. The timer was found to be accurate to ±0.02 sec. The power supply is a Heathkit Power Supply Model IP-20, 0-50 V supply (0.01% stability). It was checked on all voltage ranges at 150 mA and found to be steady. On the 20 V range (the operating voltage for heat capacities) it was steady to ±0.3 mV. The voltmeter is a Keithley Model 660A guarded DC differential voltmeter employing a null scale mode of operation.

The calibration heaters, G of Figure 3 and R_2 of Figure 4, were constructed from about four feet of Evanohm (126 ohm/ft) wire. Number 24 Teflon® sheathed wire was used for the lead wire. The solder joints were made with rosin

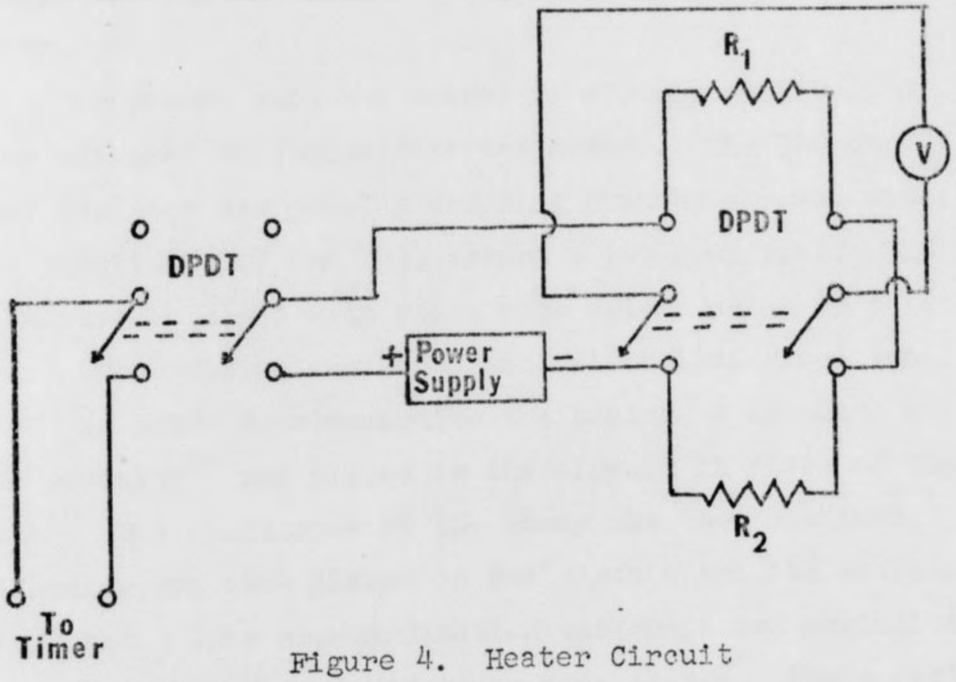

Figure 4. Heater Circuit

R_1 dummy resistor

R_2 heater

core solder and Nokorode Soldering Paste.[95] The heater wire was coiled around the Teflon® sheath of the lead wire. A glass well, G of Figure 3, made from 5 mm Pyrex tubing, encases the heater. Silicone oil inside the well facilitates thermal contact and heating of the calorimeter solution. The oil level is below the calorimeter lid to prevent excessive heat leak. The heater well enters the calorimeter through the superstructure to which it is sealed with silicone rubber.

In series with the heater is a dummy resistor, R_1, which was used to standardize the heater. The 500 ohm dummy resistor was made by wrapping Evanohm chromel wire, size 0.0071 (16.07 ohm/ft), around a two gram vial. The leads were soldered with rosin core solder using an acid flux. The resistor was wound with electrical glass tape.

In order to standardize the heater, a standard one kohm resistor[96] was placed in the circuit in place of the heater. The resistance of the dummy was then obtained. The heater was then placed in the circuit and its resistance determined. This standardization was conducted periodically and the heaters were found to be very stable. Their resistance could be determined to 0.02%.

For best results it was desired that the electrical heats be approximately the same as the experimental heats (less than 1.0 cal). At the same time, the heating times had to be long enough to obtain the desired precision as well as to permit the actual physical manipulations. The electrical heats were usually around 1.5 cal and were reproducible to 0.04%.

Auxiliary Heaters. In addition to the calibration heaters, each calorimeter vessel contains an auxiliary heater, F of Figure 3, for heating of the system from room temperature to near the mixing temperature. These heaters (approximately 2 ohm) were constructed of chromel B and S 30 wire in a manner similar to the calibration heaters and were used with a power supply of 6 V at 3 A or in series with 15 V at 3 A.

Thermistor Circuit. Temperature changes effected in the calorimeter were detected by a thermistor which composes one leg of a Wheatstone bridge. The thermistor circuit, which is similar to the one described by Jekel, Criss, and Cobble,[97] is shown in Figure 5. Two 1.34 V batteries in parallel power the Wheatstone bridge. A General Radio Precision 20 kohm resistor, an adjustable resistor (1-10 kohm),[98] and a dialed Decade resistor[99] compose three legs of the Wheatstone bridge. The Decade resistor is dialed to 0.1 ohm and was set on approximately 20 kohm for this work. The accuracy of the Decade was ±0.01%, traceable to the National Bureau of Standards.

The fourth leg of the Wheatstone bridge is the thermistor. Originally matched 10 kohm thermistors[100] were used. Later, unmatched 10 kohm ±5% thermistors[101] were employed. The thermistors are imbedded in 0.100 in. glass probes and are soldered to the lead wires. The solder joints are taped with electrical tape. All soldering in the thermistor circuit is low thermal emf solder. The thermistors are covered with aluminum foil, and the thermistor leads

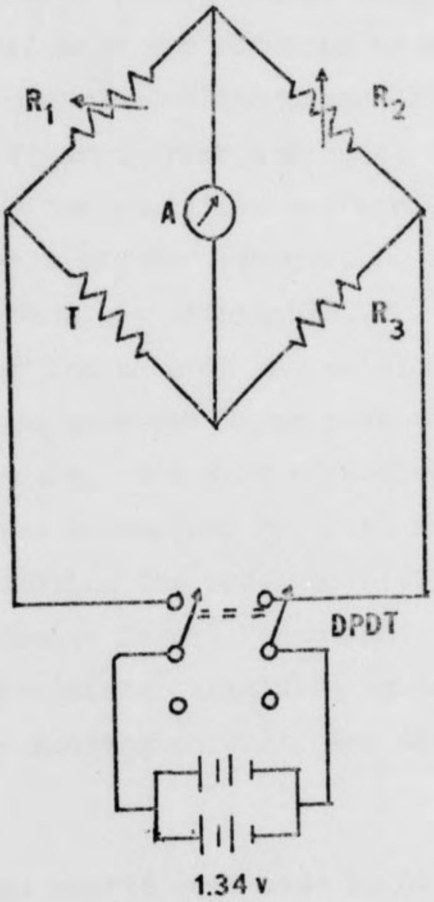

Figure 5. Thermistor Circuit

R_1	1-10 kilo ohm adjustable resistor
R_2	Decade resistor
R_3	20 kilo ohm standard resistor
T	thermistor 1 or thermistor 2
A	Keithley Model 150A microvolt-ammeter

are encased by a shielding cable. The thermistor and a portion of the shielded lead wire are contained in a 5 mm Pyrex well (E of Figure 3) which is sealed to the superstructure with silicone rubber.

A coarse balance of the bridge before and after each mixing or electrical heat was obtained by means of the Decade. A Keithley Model 150A microvolt-ammeter detected any off-balance of the bridge and drove a Sargent Model SR Recorder. The 10 µV scale for the amplifier was used in conjunction with the 125 mV scale of the recorder. A sensitivity of about 5×10^{-6} degrees was attainable.

Grounding of the circuit and shielding from atmospheric interference were the major problems associated with the thermistor circuit. The most effective grounding and shielding system was determined by trial and error. It was found that grounding the water-bath stirrer resulted in a significant "noise level" reduction. Other ground wires led to the thermistor shielding cable, the water bath cooling coils, the heating circuit, and the calorimeter stirring system.

<u>Pipets</u>. The pipets were made by blowing out the sides of 15 x 65 mm Pyrex tubing (see Figure 6). A circular Teflon® sheath, F, was epoxied to each end of the pipet. The pipets were opened and closed at each end by means of Teflon® plugs, C, fitted with 1/4 x 3/8 rubber "O-rings", E. The plugs fit inside the Teflon® rings at each end of the pipet. By opening the pipets at both ends better and faster mixing was possible.

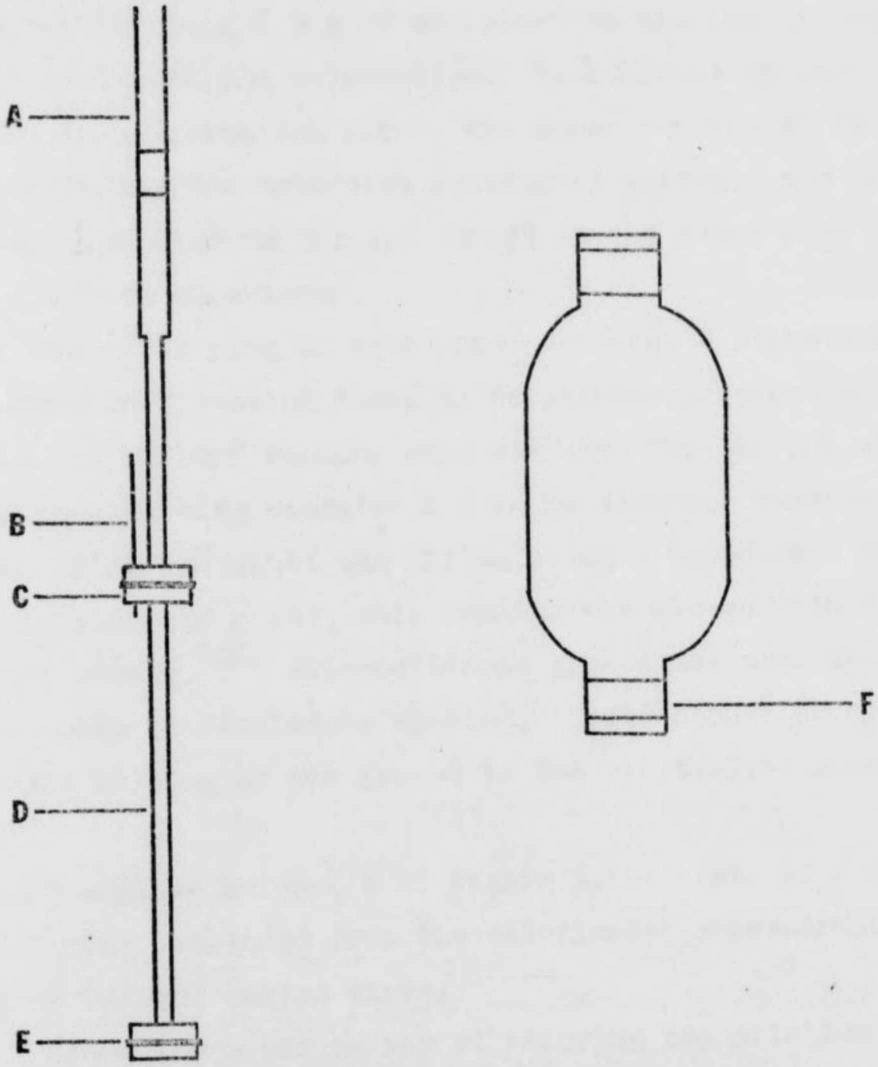

Figure 6. Pipet and Pipet Plunger

A 5 mm true bore bearing
B venting tube
C Teflon® plug
D 3 mm glass tubing
E "O-ring"
F Teflon® sheath

Note: actual size

The plugs were epoxied to a shaft, D, of 3 mm glass tubing. The shaft was operated from outside the calorimeter by pushing it down to open the pipet. The shaft exited the calorimeter <u>via</u> a 5 X 90 mm true-bore bearing, A, which reduced heat leak and evaporation. As a matter of convenience in weighing the pipet, the upper portion of the shaft including the true-bore bearing is separate and was cemented with Clark's Ferrule cement to the pipet plug shaft for each experiment.

The upper plug of each pipet contains a stainless steel capillary venting tube, B, to release pressure upon heating. A Teflon® venting tube was used for the HCl mixings. The upper plug also contains a 1 mm in diameter opening through which the pipet was filled using a hypodermic syringe. After loading the pipet, this opening was closed with fluorosilicone grease.[102] Fluorosilicone grease was also used on the plugs to facilitate opening. Tests showed no appreciable melting of the grease in the electrolyte solutions at 80°.

The pipet holder, H of Figure 3, consists of a 2.2 cm Teflon® ring suspended from the calorimeter superstructure by three Teflon® coated wires.

Since there was no way of stirring the solution inside the pipet, it had a considerable heat lag. After large heat imputs, about one hour was required for the pipet solution to reach thermal equilibrium with the solution in the calorimeter. Shorter heat imputs required less time.

The heat of opening of the pipets was determined periodically at each temperature and the corrections applied to the heat of mixing. The heats of opening ranged from 0.000 to 0.008 ±0.004 cal. (For some of the 80° work the heat of opening was as high as 0.034 ±0.008 cal.)

Stirrers. Initially, brass stirrers which were coated with polyethylene using the procedure of Anderson[103] were used. Problems arising from chipping of the polyethylene and corrosion of the brass led to the employment of glass stirrers. The glass stirrers, J of Figure 3, consist of four paddles attached to the end of a 3 mm solid shaft and 5 cm above these four additional paddles are attached. The stirrer and pipet were situated in the best position relative to one another to give the fastest mixing time. The stirrer shaft had a true-bore bearing as it exited the calorimeter (see Figure 3, L). The half cylindrical design of the superstructure (see Figure 3) allowed the stirrer shaft and its enclosure to be in contact with the water bath. Much of the heat of stirring was thus dissipated into the water bath. The stirrers were driven at 427.5 rpm by a synchronous motor.[104]

Water Bath. The calorimeter was submerged in a 47 gal water bath. The temperature of the water bath was maintained about 0.02 degrees warmer than the calorimeter to lessen evaporation and condensation of the calorimeter solution.

The water bath consists of a two foot in diameter, cylindrical, stainless steel vat inside a 29 × 29 × 28 in. wooden box. Insulation is provided by 2 in. fiber glass padding. Originally, a cubic, stainless steel 60 gal vat was used. It was found, however, that more efficient stirring and hence better temperature control was possible with the cylindrical vat. Several types of motors for stirring of the water bath were used during the course of the experimental data collection. A 0.5 hp motor which rotated at 1880 rpm a 1.7 cm shaft equipped with two sets of flanged blades gave the most satisfactory performance. Temperature control of the water bath, as monitored by a quartz thermometer,[105] ranged from ±0.001° at 25° to ±0.004° at 80°.

The temperature control system of the water bath consists of a Thermotrol[106] sensing device in conjunction with a 500 W knife heater. Cooling water flows through 25 feet of coiled copper tubing in the bath.

Standardization. The internal comparative method used to obtain the heat of mixing data necessitated the standardization of the calorimeter. If some systematic, inherent error had been present which affected both the electrical and mixing heat measurements, it would have been possible to obtain very precise but inaccurate data. Until recently there had been no generally accepted standard for solution calorimetry. In a paper by Gunn,[107] the criteria for processes used in checking and comparing calorimeters are given. Of the four processes he describes, the reaction of tris-(hydroxymethyl) aminomethane (TRIS) with HCl appears the most promising with respect to purity, cost, and ease of preparation, handling, and weighing.

The reaction of TRIS with 0.1 M HCl at 25° was chosen as the method for standardization of this calorimeter. The

Fisher Certified Reagent TRIS was dried at 80° <u>in vacuo</u> for 36 hours before use. The 0.100 M HCl was prepared from Mallinckrodt Analytical Reagent HCl and was standardized with TRIS using bromocresol green, methyl red mixed indicator.[108]

The dried TRIS was weighed into a glass ampoule, which was made from 4 mm glass tubing, and the ampoule was sealed in the atmosphere. The ampoules were cemented with Clark's Ferrule cement to a 4 mm glass shaft, which was similar to the pipet shaft. The ampoules were broken inside the calorimeter by crushing them in a bottomless, spiked glass basket. There was no heat of breaking the ampoule. From four determinations, the average heat of neutralization obtained at 25° was 7147.3 ±12.1 cal/mole which is within 0.5% of Gunn's value of 7107.3 ±0.9 cal/mole[109] and Irving and Wadsö's value of 7105 ±4 cal/mole.[110] It was thus assumed that the calorimeter was capable of giving accurate results.

Solutions

<u>Preparation, Standardization, and Analysis</u>. Stock solutions of HCl, NaCl, KCl, LiCl, and $(CH_3)_4NCl$ (approximately 4 m) were prepared using water which had been passed through two deionizing columns. The stock solutions, as well as the 1.0 and 0.5 m solutions were stored in polyethylene bottles. NaCl and KCl stock solutions were prepared directly from the Mallinckrodt Analytical Reagent salts. Research Inorganic Chemical (99.9%) LiCl was used to prepare directly from the salt this stock solution.

The stock solutions were filtered to remove any inert particles. The HCl stock solution was prepared by dilution of concentrated Mallinckrodt Analytical Reagent HCl. These stock solutions were then standardized to better than 0.1% by the standard gravimetric AgCl procedure. Before standardization of the HCl stock solution, it was neutralized with NaOH following the procedure of Pierce, Haenisch, and Sawyer.[111]

Purification of the Eastman Organic $(CH_3)_4NCl$ was necessary prior to preparation of the stock solution. The salt was dissolved to saturation in hot methanol, filtered, and precipitated with anhydrous diethyl ether similar to the procedure described by Conway[112] and by Unni.[113] The recrystallized salt was dried at 80° in vacuo for three days. To test the dried salt for the presence of any amine impurity a sample was dissolved in water and the pH adjusted to approximately 11 with 0.1 M NaOH. The pH was then recorded as the solution was titrated with 0.1 M HCl. Comparison of the titration curve obtained for the salt with the blank showed the presence of less than 0.1% amine impurity. In addition, the purity of the salt was found to be 99.9% by gravimetric AgCl determination of the halide content. The $(CH_3)_4NCl$ stock solution was then prepared and standardized by the gravimetric AgCl procedure.

The stability of a solution of $(CH_3)_4NCl$ at 80° was determined by heating a sample of the stock solution at this temperature for 24 hours. The amine content of the heated sample was then determined by HCl titration following the procedure previously described. There was no detectable decomposition to the amine.

The magnitude of the heat of mixing of cations has been found to be considerably larger than the magnitude of the heat of mixing of anions.[114] Consequently it was necessary to know whether any cation impurities were present in the solutions and if there were to make necessary corrections to the heat of mixing. The NaCl, KCl, and LiCl stock solutions were analyzed for Na^+, K^+, and Li^+ impurities using a Beckman Model 1301 Atomic Absorption System. The absorption system utilizes an acetylene-air flame. A Beckman DB Spectrophotometer and Beckman Recorder were used with the atomic absorption system. The Li^+ source was a hollow cathode lamp, the Na^+ and K^+ sources were Osram-type lamps. The percentage transmission for each cation at its characteristic wavelength (Na^+ at 5890 Å, K^+ at 7665 Å, and Li^+ at 6708 Å)[115] was obtained for each of the appropriate stock solutions. This percentage transmission was compared with that obtained from solutions containing a known amount of the cation. Less than 0.1 mole per cent cation impurity was present in the stock solutions. Consequently, no correction of the mixing heats was necessary.

After each mixing experiment at 80° a concentration check of the solution was made by either Fajan's or Mohr's[116] volumetric AgCl method. This was done to detect any increase in concentration due to evaporation. Evaporation of the solution from the calorimeter was no problem; evaporation during transfer of the hot solution from the calorimeter to storage bottles presented some problem. A technique for this transfer was developed employing a Tygon® transfer tube.

This technique greatly reduced evaporation, and concentration changes which did occur were not significant. Concentration changes due to evaporation at 40 and 60° were not encountered.

Dilution of Stock Solutions. The stock solutions were diluted by weight to 0.1% accuracy.

Experimental Procedure

Mixing Procedure. The pipet and vessel were filled at room temperature with the solutions to be mixed. The contents of the pipet and vessel were weighed to 0.1%. The procedure for filling the pipets, each of which held approximately 20 ml, has been previously described. By using a portion of the previously mixed solution in the vessel, the heats of mixing could be determined in the mole fraction range of 0.0 to 0.2 and 0.8 to 1.0.

In order to minimize the air space within the calorimeter, the solution levels in both the vessel and the pipet were carefully controlled with allowance being made for changes in the volume of the solution on heating. By keeping the air space at a minimum, concentration changes due to evaporation were reduced. In addition, a small air space reduced heat leak by convection.

The calorimeter, once loaded, was secured in the water bath and its contents were heated to the mixing temperature. After heating, about one hour was allowed for the pipet solution to reach thermal equilibrium with the vessel contents. After this time, the foreslope (recorder trace of change in thermistor resistance versus time) was begun. After recording a satisfactory, horizontal, linear foreslope, A of Figure 7, with the amplifier on the 10 μV scale and the recorder on the 125 mV scale, the amplifier was switched to the 100 μV scale and the pipet opened at point B. The foreslope, A, with the resistance of the decade R_D^i, was obtained as nearly horizontal as possible in order that the afterslope, D, with decade resistance R_D^f, would also be nearly horizontal. The reason for desiring a horizontal afterslope was to reduce extrapolation error. The time between the pipet opening and detection of the heat of mixing was negligible. Detection of 50% of the heat of mixing, point G, occurred within 12 sec, but for 99% of the heat of mixing, the detection time was 2.5 min. After changing the decade resistance, E, to rebalance the Wheatstone bridge and compensate for the heat of mixing, the amplifier was returned to the 10 μV scale and the afterslope, D, was recorded. All of the resistance change of the thermistor could not usually be compensated for by changing the decade resistance. The correction, C, was computed at point G after 50% of the heat of mixing had been detected. The total resistance change was obtained as the difference in the final and initial decade resistance plus the correction term.

$$R_D = R_D^f - R_D^i + C. \qquad \text{Eq. 21}$$

Heat capacities of the calorimeter and contents were obtained after the mixing experiments. The heat of mixing was then obtained, taking into account any pipet opening heat.

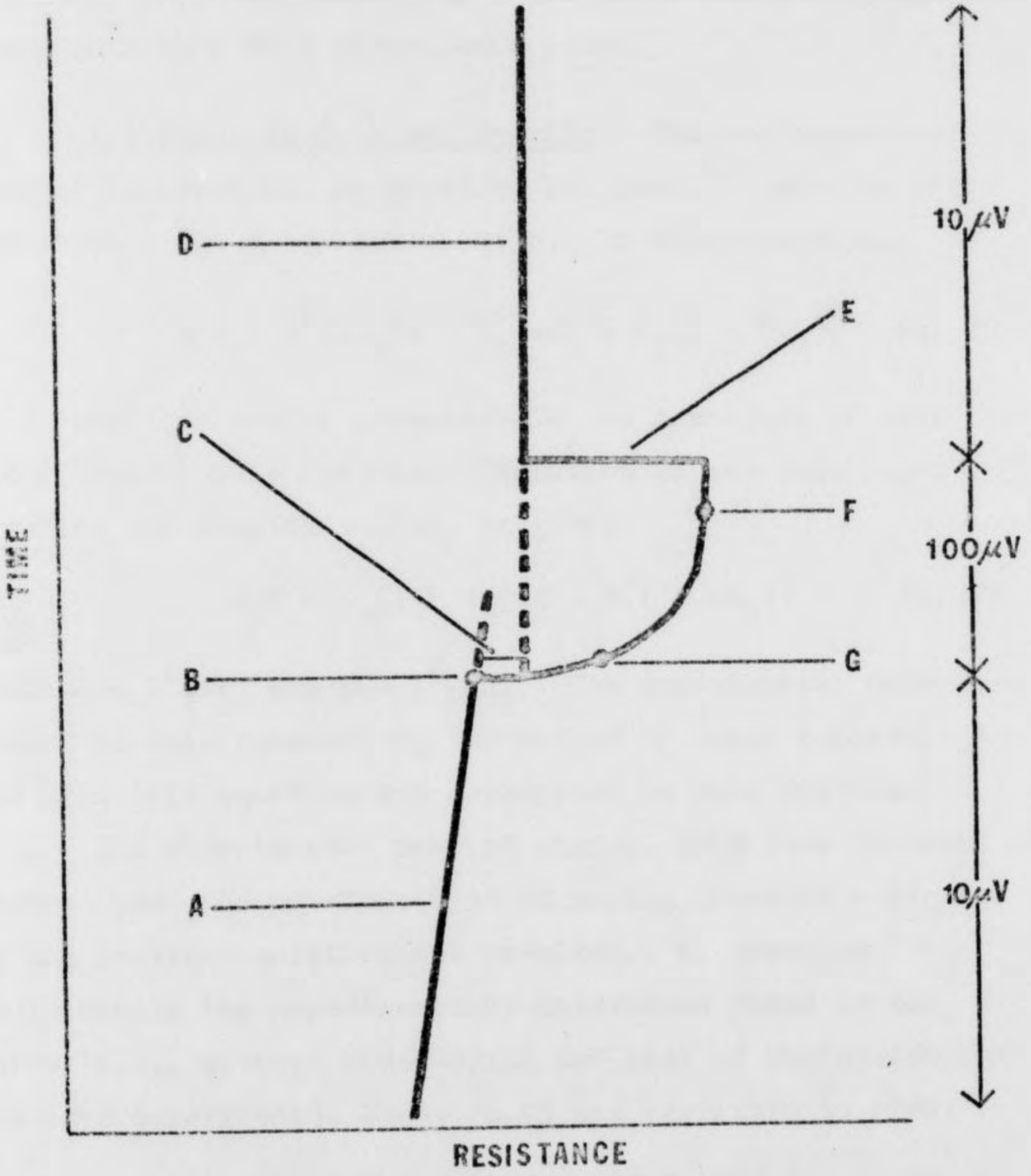

Figure 7. Schematic of Mixing Experiment

A foreslope
B open pipet
C correction
D afterslope

E decade resistance change
F detection of 99% heat of mixing
G detection of 50% heat of mixing

The heat of mixing was determined in duplicate for each mole fraction, resulting in at least twelve experiments for each mixing at a given temperature.

Treatment of Data and Results. The two parameter form of Equation 12, proposed by Friedman,[117] was the basis for fitting the experimental data. In this equation,

$$\Delta_m H = I^2 RTx_2(1 - x_2)[h_0 + h_1(1 - 2x_2)] \qquad \text{Eq. 22}$$

h_0 is the interaction parameter, h_1 is a measure of skew, and x_2 is the mole fraction. Equation 22 was rearranged, grouping the constant terms, to give,

$$\Delta_m H = x_2(1 - x_2)[A + B(1 - 2x_2)] \qquad \text{Eq. 23}$$

where $A = I^2 RTh_0$ and $B = I^2 RTh_1$. The experimental data were fitted to this equation by the method of least squares. A and B in this equation are orthogonal in mole fraction.

The experimental heat of mixing, DELH (see Appendix A), depends upon the previous heat of mixing, because a portion of the previous solution was re-mixed. In order to fit individually the experimentally determined heats to the curve (i.e., without considering the heat of mixing for the previous experiment), Equation 23 was rewritten to give,

$$\text{HCALC} = \Delta_m H_f(\text{WTS}_f) - \Delta_m H_i(\text{WTS}_i) \qquad \text{Eq. 24}$$

$$= A(\text{F2}) + B(\text{F3})$$

where HCALC is the least squares heat in calories, A and B are as defined previously, and

$$F2 = x_{2_f}(1 - x_{2_f})(WTS_f) - x_{2_i}(1 - x_{2_i})(WTS_i)$$

$$F3 = x_{2_f}(1 - x_{2_f})(1 - 2x_{2_f})(WTS_f) - x_{2_i}(1 - x_{2_i})(1 - 2x_{2_i})(WTS_i).$$

The subscripts f and i refer to final and initial conditions for a mixing. The data were fitted twice by computer to Equation 24. One fit utilized both parameters A and B. The second fit utilized only A. The program for the fitting was written in Fortran.

The equations for evaluating the constants A and B are discussed in Bennett and Franklin.[118] The equations for K experimental points are:

$$A = \frac{\begin{vmatrix} S12 & S23 \\ S13 & S33 \end{vmatrix}}{\begin{vmatrix} S22 & S23 \\ S23 & S33 \end{vmatrix}} = \frac{S13}{S23} - B\left(\frac{S33}{S23}\right) \qquad \text{Eq. 25}$$

$$B = \frac{\begin{vmatrix} S22 & S23 \\ S12 & S13 \end{vmatrix}}{\begin{vmatrix} S22 & S23 \\ S23 & S33 \end{vmatrix}} = \frac{\frac{S12}{S22} - \frac{S13}{S23}}{\frac{S23}{S22} - \frac{S33}{S23}} \qquad \text{Eq. 26}$$

where,

$$S12 = \sum_K [DELH_{(K)}][F2_{(K)}][W_{(K)}]$$

$$S13 = \sum_K [DELH_{(K)}][F3_{(K)}][W_{(K)}]$$

$$S22 = \sum_K [F2_{(K)}][F2_{(K)}][W_{(K)}]$$

$$S23 = \sum_K [F2_{(K)}][F3_{(K)}][W_{(K)}]$$

$$S33 = \sum_K [F3_{(K)}][F3_{(K)}][W_{(K)}]$$

$\mathrm{DELH}_{(K)}$ = Experimental heat
$W_{(K)}$ = weighting factor = 1.0.

A refers to the constant for the two parameter fit and AO, to the one parameter fit. AO can be expressed as,

$$AO = \frac{S12}{S22}$$

The computer print out which contains the experimental data and results is given in Appendix A. The results of the leasts squares fit are summarized in Table I.

Bennett and Franklin[119] show that the confidence interval for β_i at a probability level of α can be written as,

$$b_i - t_{DF}{}^{\alpha}S\sqrt{C_{ii}} < \beta_i < b_i + t_{DF}{}^{\alpha}S\sqrt{C_{ii}} \qquad \text{Eq. 27}$$

where,

b_i = constants found by least squares fit of Equation 24
t = students distribution[120]
DF = degrees of freedom = n - number of constants in Equation 24
n = K
α = probability level chosen at 0.05 level (95% confidence) for all least squares fits in this work.
S = standard deviation of a given experimental DELH with S = SYBC or SYB where,

$$SYBC = \left[\frac{S11 - A(S12) - B(S13)}{DF}\right]^{1/2}$$

$$SYB = \left[\frac{S11 - AO(S12)}{DF - 1}\right]^{1/2}$$

TABLE I

Aqueous Heats of Mixing Parameters

		25°C	40°C		60°C		80°C	
Mixture	I	RTh_o	RTh_o	RTh_1	RTh_o	RTh_1	RTh_o	RTh_1
LiCl-KCl	1.0	-64.2[a]	-63.9 ± 0.7	-3.3 ± 1.0	-63.0 ± 0.3	-2.8 ± 0.5	-61.1 ± 1.6	4.7 ± 2.3
LiCl-$(CH_3)_4$NCl	0.5	-160.8[b]	-157.1 ± 1.9	-5.5 ± 2.8	-161.3 ± 1.5	-6.6 ± 2.1	-162.8 ± 4.5	---
KCl-$(CH_3)_4$NCl	0.5	118.9[b]	118.4 ± 1.0	---	114.7 ± 1.4	---	112.9 ± 6.5	---
NaCl-KCl	1.0	-38.1[c]	-36.6 ± 0.4	---	-35.1 ± 0.3	---	-31.2 ± 0.6	---
LiCl-NaCl	1.0	84[a]	64.2 ± 0.3	3.8 ± 0.4	44.5 ± 0.4	2.4 ± 0.6	33.0 ± 1.1	---
HCl-NaCl	1.0	124[c]	112.3 ± 0.8	8.0 ± 1.0	95.5 ± 1.1	5.6 ± 1.4	82.2 ± 1.1	3.6 ± 1.5

(a) R. H. Wood and R. W. Smith, J. Phys. Chem., 69, 2974 (1965).

(b) R. H. Wood and H. L. Anderson, ibid., 71, 1871 (1967).

(c) Y. C. Wu, M. B. Smith, and T. F. Young, ibid., 69, 1868 (1965).

$$C22 = \frac{S33}{(S22)(S33) - (S23)^2}$$

$$C33 = \frac{S22}{(S22)(S33) - (S23)^2}$$

$$C11 = \frac{1}{S22}$$

Thus the confidence interval for the constants can be expressed as

$$\text{confidence of A} = (SYBC)\sqrt{C_{22}}\, t_{n-2}^{\alpha} \qquad \text{Eq. 28}$$

$$= SYBC\left[\frac{S33}{(S22)(S33) - (S23)^2}\right]^{1/2} t_{n-2}^{0.05}$$

$$\text{confidence of B} = SYBC\sqrt{C_{33}}\, t_{n-2}^{\alpha} \qquad \text{Eq. 29}$$

$$= SYBC\left[\frac{S22}{(S22)(S33) - (S23)^2}\right]^{1/2} t_{n-2}^{0.05}$$

$$\text{confidence of A0} = SYB\sqrt{C_{11}}\, t_{n-1}^{\alpha} \qquad \text{Eq. 30}$$

$$= SYB\left[\frac{1}{S22}\right]^{1/2} t_{n-1}^{0.05}.$$

Due to the fact that students' t varies with the number of experimental points, the confidence interval was not computed directly. Rather, the following terms were computed:

$$SA = SYBC\left[\frac{S33}{(S22)(S33) - (S23)^2}\right]^{1/2} \qquad \text{Eq. 31}$$

$$SB = SYBC\left[\frac{S22}{(S22)(S33) - (S23)^2}\right]^{1/2} \qquad \text{Eq. 32}$$

$$SA0 = SYB\left[\frac{1}{S22}\right]^{1/2} \qquad \text{Eq. 33}$$

To obtain the confidence of A, B, or AO Equations 31, 32, or 33 were then multiplied by the appropriate students' t.

The F test (ratio of variances) as described in Bennett and Franklin[121] was used to test for the significance of B. F was determined by means of the equation,

$$F_{1,\ n-2} = \frac{SEB - SEBC}{SEBC}(n - 2) \qquad \text{Eq. 34}$$

where,

$$SEBC = S11 - (A)(S12) - (B)(S13)$$

$$SEB = S11 - (AO)(S12).$$

F values[122] were read for one degree of freedom (vertical column) and n - 2 degrees of freedom (horizontal column) at the 95% confidence level.

Errors. The accuracy attainable in the heat of mixing data is, of course, limited by the least accurate step in obtaining the data. It is convenient in discussing the errors limiting the final accuracy to consider two categories. In the first category are inherent errors of the solutions (concentration, ion impurities), and in the second category are experimental procedure errors (uncertainty of pipet opening heat, extrapolation of slope).

The inherent errors in the stock solution include uncertainty of concentration and ion impurities. In a discussion by Anderson,[123] it was shown that if the concentration of the solutions is known to within 0.1% and the ion impurity is less than 0.1 mole per cent, then the experimental results will be as accurate as the experimental procedure precision.

The experimental procedure precision involves uncertainties in the slope extrapolation, electrical heat input, and heat of opening of the pipet. On the 10 μV amplifier scale and the 125 mV recorder scale, the combined uncertainty in the extrapolation of the fore- and afterslopes of the temperature versus time curve to the time of detection of 50% of mixing heat input was ±3 divisions or ±0.005 calories. The electrical heat input uncertainty was 0.2% which caused an uncertainty in the experimental heat of mixing of ±0.001 calories. The heat of opening of the pipet uncertainty was within ±0.004 calories in most experiments.

The most uncertain step in the experimental procedure was the slope extrapolation. This uncertainty of ±0.005 calories amounted to about 1% of the experimental heats.

DISCUSSION

A common anion mixing may be shown as follows:

$$MX_{(I)} + NX_{(I)} \rightarrow \text{Mixture}_{(I)}.$$

Solutions of MX and NX, both of the same ionic strength, are combined to give a mixture, also of the same ionic strength I. Several features of this type of mixing, first pointed out by Wood and Smith,[124] result in it being an excellent way of looking at specific ion interactions. The term specific ion interactions is used in the Brønsted[125] sense and includes pairwise like-charged (M^+N^+) and higher order interactions ($N^+X^-M^+$, $X^-M^+X^-$, $X^-N^+X^-$, . . .). The first important feature is that pairwise, oppositely-charged interactions (M^+X^-, N^+X^-) occur to the same extent before mixing as after mixing, so that effects arising from such interactions cancel. (See Appendix B for a mathematical proof.) The only new interactions present in the mixture must include like-charged ions. A second feature of importance is the cancellation of effects due to the ionic atmosphere. This is a result of maintaining constant ionic strength. The third feature regarding this type of mixing is that the heat of mixing is independent of the common ion. Wu, Smith, and Young[126] were the first to show this.

The excess heat of mixing, which is given by the equation,

$$\Delta_m H^E = \Delta_m H - \Delta_m H^i, \qquad \text{Eq. 35}$$

is the difference between the observed heat of mixing and the calculated heat of mixing for a hypothetical, ideal solution at the same temperature, pressure, and concentration. Since the ideal heat of mixing is zero, the excess heat of mixing is the heat of mixing.

On examining the results, given in Table I, it is seen that the sign of the heat of mixing for all temperatures is in accord with Young's[127] observation that for cation, common-anion mixings the heat of mixing is endothermic for cations of the same group and exothermic for cations of different groups. Wood and Anderson[128] have shown that ions should be grouped according to the ion-water structural relationships. Following the Frank, Wen, and Evans[129] classification, the two groups are structure-makers and structure-breakers.

It is also observed in Table I that the values of RTh_1 are small. This indicates little skew in the heat of mixing. In fact, for all heats of mixing reported in the literature, the maximum in the heat of mixing ($d\Delta_m H/dx_2 = 0$) occurs in the mole fraction range of 0.47 to 0.53. The present results indicate that interactions contributing to skew in the heat of mixing are relatively unimportant in the temperature range studied, and that such interactions are not significantly changing with an increase in temperature. It is not, however, appropriate to try to make correlations concerning the skew term because of its inaccuracy. The inaccuracy is a result of the fact that heats of mixing are not measured in the critical mole fraction range of 0.47 to 0.53 and that the magnitude of the asymmetric interactions is too small to determine accurately.

It should be pointed out that the heat of mixing is quadratic in mole fraction. This is illustrated in Figure 8 for the LiCl-KCl-H_2O system. It has been shown[130] that the measurement of the heats of mixing in the mole fraction ranges of 0.0 to 0.2 and 0.8 to 1.0 is sufficient to accurately determine the curve.

The major objective of this research was to determine the heat of mixing as a function of temperature. In Figure 9 RTh_0 is plotted versus temperature for the mixtures studied. In this figure, it is seen that the three mixings involving the Na^+ ion show temperature dependences larger than experimental error. The other three mixings have heats that are constant within experimental error over the temperature range studied.

Solute-Solvent Structure

The behavior of the heats of mixing is best explained in terms of the influence of solute-solvent interactions. It has been shown[131] that the heat of mixing is mainly influenced by the structure of water around the like-charged ions. Referring to Figure 9, it is seen that the heat of mixing is constant with temperature for three of the mixings. These three involve mixing the Li^+ ion, a small structure-maker, with the $(CH_3)_4N^+$ ion, a large

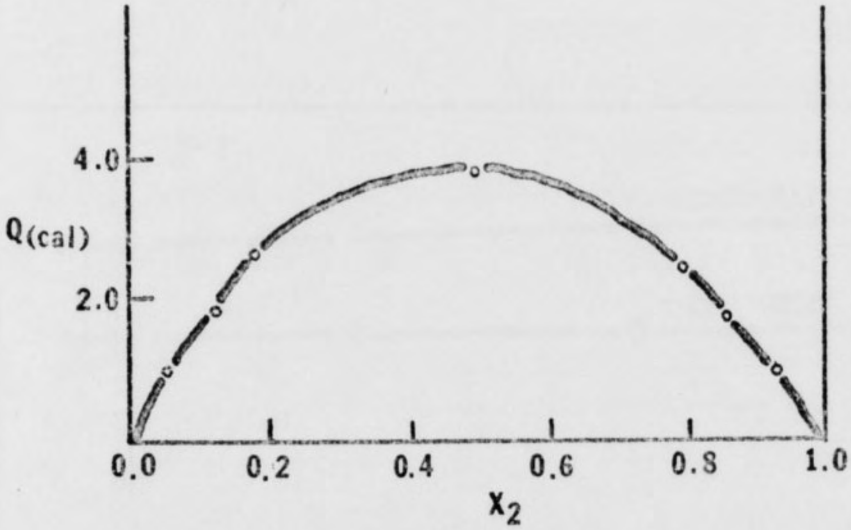

Figure 8. Heat of Mixing Versus Mole Fraction

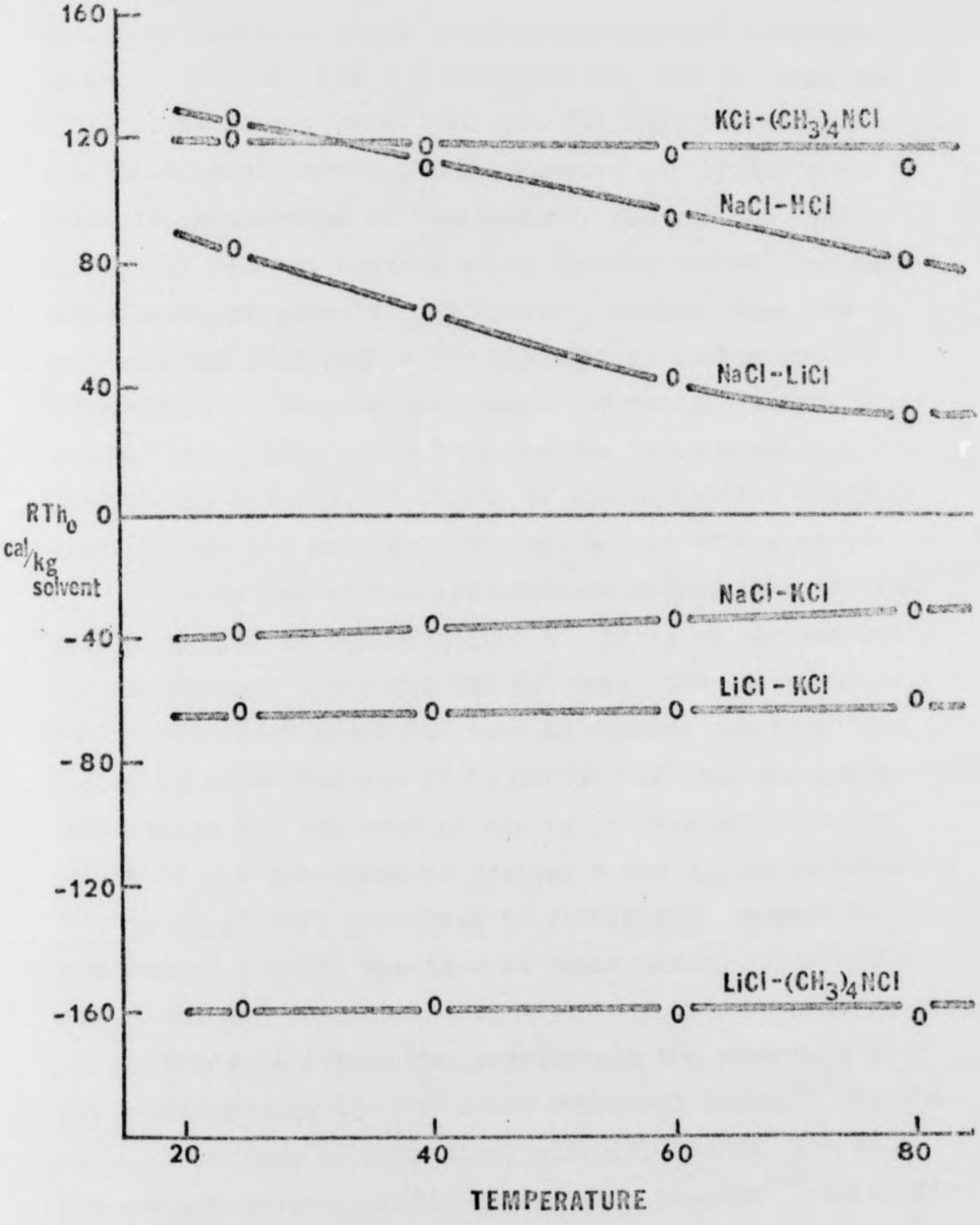

Figure 9. RTh$_o$ Versus Temperature

structure-breaker; the K^+ ion, a medium-sized structure-breaker, with the $(CH_3)_4N^+$ ion; and the Li^+ ion with the K^+ ion. It hardly seems coincidental that the heat of mixing for these three systems, which involve widely different ions, is independent of temperature, and yet the heat of mixing for all the systems which contain the Na^+ ion shows temperature dependence. It appears, rather, that the interactions responsible for the heat of mixing are independent of temperature except for mixings which include the Na^+ ion. This means that for the three temperature independent systems, the heats of mixing involve energies greater than the available thermal energy of the system.

The nature of the interactions responsible for the heat of mixing is postulated on the basis of the results for the mixings involving the Na^+ ion. The Frank, Evans, Wen[132] structure model for ions in aqueous solution (see Figure 1) is evoked and it is postulated that the interactions responsible for the heat of mixing involve water in the region of the interface of regions A and B. It is believed that water at this interface is stable with respect to temperature for all the ions in these mixing experiments except the Na^+ ion.

Evidence exists for questioning the structure of water surrounding the Na^+ ion. Frank and Evans,[133] on the basis of entropy of hydration, classify the Na^+ ion as a structure-breaker. On the other hand, Bingham[134] classifies it as a structure-maker on the basis of fluidity measurements. From the sign of the heats of mixing it is a structure-maker. Another aspect of the unusual character of the Na^+ ion is that the log of its activity coefficient in the $NaCl-HCl-H_2O$[135] and $NaCl-KCl-H_2O$[136] mixtures does not obey Harned's rule unless an additional term is added.

The fact that the Na^+ ion appears to be on the borderline between a structure-maker and a structure-breaker could mean that the interface between regions A and B is not as well defined for it as for other ions and may be unstable with respect to such external conditions as temperature. The instability of the interface could in turn cause the heats of mixing involving the Na^+ ion to be temperature dependent, provided that interactions in this area are responsible for the heat of mixing.

The apparent constancy of the primary hydration sphere of ions over a temperature range of 25-140° has been reported by Walrafen on the basis of Raman studies.[137] Ackermann <u>et al</u>.[138] studied the heat capacities of aqueous solutions of alkali halides, and on the basis of their results concluded that the primary hydration sphere of an ion is essentially unaltered at 130°, the highest temperature they studied. These conclusions of Walrafen and Ackermann support the postulate that the heat of mixing is influenced by interactions at the surface of the primary hydration sphere.

Ackermann, and in addition Criss and Cobble,[139] found that the partial molal heat capacities exhibit a maximum in the region of 60-80°. The interpretation given to this behavior by Ackermann is that between room temperature and, in most cases, 130° the second hydration shell is being degraded. The maximum in the partial molal heat capacity is a result of this degradation of the second hydration shell, which, they say, is bound with little energy to the ions.

In Figure 9 it is seen that the heats of mixing which vary with temperature appear to be approaching a constant value at some higher temperature. This is especially apparent for the $LiCl-NaCl-H_2O$ mixing. This approach to a constant value for the heat of mixing of the systems involving the Na^+ ion suggests that whatever the instability is at the interface of regions A and B for the Na^+ ion it is destroyed by thermal energy at higher temperatures, so that only the temperature stable region A (primary hydration sphere) influences the heat of mixing. This suggestion is in agreement with Ackermann's conclusions regarding the primary and secondary hydration spheres as a function of temperature. Of course, the heat of mixing would have to be determined at higher temperatures to test this suggestion.

That the heat of mixing is not influenced to any great extent by bulk water structure can be concluded on the basis of the changes known to occur in bulk water structure in the range of 25 to 80°. For example, Bonner and Woolsey[140] estimated that in this temperature range the amount of monomer water increases by about 50%. Némethy and Scheraga [141] and Buijs and Choppin[142] reported about a 20% decrease in hydrogen bonds in this temperature range. It is hardly conceivable that the heat of mixing could be constant with temperature (as it is for three mixtures) and yet involve bulk-water interactions to any great extent.

There are several reasons for discounting interactions involving the structure-broken region B as influencing the heat of mixing. The conclusion of Ackermann <u>et al</u>.[143] that this region is being destroyed over the temperature range 30 to 130° is one. Another reason is the minimum for some electrolyte solutions in the viscosity versus temperature curve. As pointed out by Gurney,[144] the co-spheres of ions (spherical portion of solvent surrounding an ion and modified by presence of the ion) should be expected to contribute toward a change in viscosity. The viscosity B-coefficient in the Jones-Dole equation for viscosity[145] has been attributed to solute-solvent interactions. Suryanarayana and Venkatesan[146] found for NaCl at 1 m that the relative viscosity has a minimum at 35°. For KCl, on the other hand, there is no minimum.[147] Kaminsky[148] reported that the single ion viscosity B-coefficients for Na^+, K^+, Cl^-, and I^- have a minimum value at 35°. The variations of the viscosity B-coefficients seem to indicate changes occurring in the co-spheres or outer hydration shells of the ions. If such changes do actually occur, then one would not expect the heat of mixing to involve interactions in this region and yet remain constant with temperature.

The postulated explanation for the interactions responsible for the heat of mixing can, at this time, only be tentative. Additional systems must be studied before a definite conclusion can be reached.

Thermodynamics

One of the goals of the study of electrolyte solutions is the a priori calculation of their thermodynamic properties under a variety of conditions, including temperature and composition. At present this is not possible, but there are available equations which rely on only a few experimental parameters for the calculation of the free energy and heat content of mixed electrolyte solutions.[149] The present work allows for the extension of these equations to temperatures other than 25°.

Referring to Equation 17, it is seen that in order to calculate the free energy of a mixture at any given temperature, the excess free energy of the component single electrolyte solutions at that temperature and the excess free energy of mixing for common-ion mixings at the given temperature are needed. The excess free energy of the component single electrolyte solutions may be obtained from data of osmotic and activity coefficients. Osmotic and activity coefficients for single electrolyte solutions at 25° are readily available. The excess free energy of mixing for common-ion mixings at 25°, as explained on page 9, is obtained from electromotive force, isopiestic, and freezing point lowering data using Equation 9. There is not, however, a large amount of data available for use in this equation, and the accuracy of some of the available data is questionable.

In Appendix C the calculations for the free energy of the $NaCl-HCl-H_2O$ mixture at 25 and 60° are given to illustrate the use of Equations 17 and 19. In order to perform the calculation at 60° (or any other temperature), values for the activity and osmotic coefficients at that temperature must be known. Some data is available in the literature, but more is needed. In addition, for the calculation of the excess free energy of mixing at a given temperature, the excess free energy and heat of mixing at a reference temperature and the heat of mixing as a function of temperature are needed. Equation 19 can then be utilized to obtain the excess free energy of mixing at the desired temperature.

Equation 19 is an important relationship because it allows for the calculation of the complete excess thermodynamic quantities of mixing at any temperature. It is important to note, however, that accurate values of the excess free energy of mixing at the reference temperature are extremely difficult to obtain. The reasons for this are threefold. First, the excess free energy of mixing is not determined directly, but rather is computed indirectly from partial molal quantities. Second, the excess free energy of mixing is actually the difference between very small numbers (Harned coefficients in Equation 9). Third, the magnitude of the excess free energy of mixing is very small. The inaccuracy of excess free energies of mixing at the reference temperature means that, even if the heat of mixing as a function of temperature is known quite accurately, the calculated excess free energy of mixing as a function of temperature is not necessarily accurate. The source of the inaccuracy in calculating the excess free energy of mixing as a function of temperature may be seen in Equation 19. In this equation, the second and fourth terms are nearly self-compensating. In addition, as pointed out by Anderson and Petree,[150] for the mixings which show no temperature dependence of the heat of mixing this equation reduces to

$$\Delta_m G^E_{(t_2)} = \Delta_m G^E_{(t_1)} - \Delta_m S^E_{(t_1)} \Delta T. \qquad \text{Eq. 36}$$

Thus, it is imperative to have an accurate value of $\Delta_m G^E_{(t_1)}$ in order to calculate $\Delta_m G^E_{(t_2)}$.

Using Equations 19 or 36 and available literature values for the excess free energy of mixing at 25°, the excess free energy and entropy of mixing have been calculated for the systems HCl-$NaCl$-H_2O, $NaCl$-KCl-H_2O, $NaCl$-$LiCl$-H_2O, and $LiCl$-KCl-H_2O and are reported in Table II along with the excess heat of mixing.

Stern and Passchier,[151] who studied the heat of mixing for the HCl-$NaCl$-H_2O system from 0-40°, reported a value of 22 cal/kg solvent for the heat of mixing at 40°. This value represents about a 20% difference from the value of 28.1 cal/kg solvent which was obtained in this work. Repetition of the heat of mixing at 40° was performed in the same laboratory by another person[152] about one year later and agreement with the value of 28.1 cal/kg solvent was obtained. Despite this discrepancy, Anderson and Petree[153] have shown that the excess free energy of mixing is not greatly affected.

In Table III the values for the excess free energy

TABLE II

Excess Thermodynamic Properties at $x_2 = 0.5$, $I = 1.0$

Mixture	t	$\Delta_m H$	$\Delta_m G^E$	$\Delta_m S^E$
HCl-$NaCl$-H_2O	25	32.5[e]	8.7[a]	0.80
	40	28.1	7.6	0.65
	60	23.9	6.4	0.63
	80	20.6	5.4	0.43
$NaCl$-KCl-H_2O	25	-9.53[f]	-4.0[b]	-0.01_8
	40	-9.15	-3.7	-0.01_7
	60	-8.78	-3.4	-0.01_8
	80	-7.80	-3.1	-0.01_3
$LiCl$-KCl-H_2O	25	-15.8[e]	-9.4[c]	-0.02_1
	40	-15.8	-9.1	-0.02_1
	60	-15.8	-8.7	-0.02_1
	80	-15.8	-8.2	-0.02_2
$LiCl$-$NaCl$-H_2O	25	21.0[e]	3.6[d]	0.05_8
	40	16.0	2.9	0.04_2
	60	11.0	2.1	0.02_7
	80	8.3	1.5	0.01_9

(a) H. S. Harned, *J. Phys. Chem.*, **63**, 1299 (1959).

(b) A. K. Covington, T. H. Lilly, and R. A. Robinson, *ibid.*, **72**, 2759 (1968).

(c) B. B. Owen and T. F. Cooke, *J. Amer. Chem. Soc.*, **59**, 2273 (1937).

(d) R. A. Robinson and C. K. Lim, *Trans. Faraday Soc.*, **49**, 1144 (1953).

(e) T. F. Young, Y. C. Wu, and A. A. Krawetz, *Discussions Faraday Soc.*, **24**, 37 (1957).

(f) R. H. Wood and R. W. Smith, *J. Phys. Chem.*, **69**, 2974 (1965).

TABLE III

$HCl-NaCl-H_2O$ (I = 1.0)

t	$\Delta_m G^E$(expt.)	$\Delta_m G^E$(calc.)
0	10.94	
10	9.78	
20	9.19	
25	8.70	8.70
30	8.67	
40	8.78	7.61
50	8.87	
60		6.39
80		5.36

of mixing for the $HCl-NaCl-H_2O$ system as a function of temperature are given as calculated from Harned's[154] emf data (column one) and as calculated using Harned's 25° excess free energy of mixing, the heat of mixing as a function of temperature, and Equation 19 (column two). The values calculated in these two ways do not agree very well. Harned's values, column one, have a minimum between 30 and 40°, but no minimum occurs in the values calculated from the heat of mixing data.

There is a method for obtaining a better value of the excess free energy of mixing at 25° from Harned's measurements. This method consists of assuming the heat of mixing values to be correct and using Equation 19 to correct Harned's excess free energies of mixing to 25° and then averaging these corrected values. The heat of mixing at 20, 30, and 50° was obtained by extrapolation. In Table IV the corrected excess free energies are given. The fact that the corrected excess free energy of mixing shows a steady increase, no minimum, and gives an average 9% larger than the calculated value seems to indicate an inconsistency in either Harned's electromotive force data or the heat of mixing data. Column two of Table IV gives the values the heat of mixing would have to be in order to correct Harned's excess free energies of mixing to the same value, 8.70, at 25°. In column three the experimental heats of mixing are given for comparison. It hardly seems possible that the heat of mixing could be in error by as much as 180%. On the other hand, the values the excess free energy of mixing should be in order to correct to 8.70 at

TABLE IV

$HCl-NaCl-H_2O$ (I = 1.0)

t	$\Delta_m G^E$(25°) (corrected from t)	$\Delta_m H$(calc.)	$\Delta_m H$(expt.)	$\Delta_m G^E$(calc.)	$\Delta_m G^E$(expt.)
20	8.78	+0.7	34.4	8.29	9.19
25	(8.70)	(+32.5)	(32.5)	(8.70)	(8.70)
30	9.05	-11.8	30.8	8.65	8.67
40	9.81	-19.2	28.1	7.67	8.78
50	10.45	-20.6	25.9	7.12	8.87
	Av = 9.52				

25° (given in column four) represent at most an error of 20% from the experimental values given in column five.

An error of as much as 20% in the excess free energy of mixing is possible. At 25° α_{23} is 0.0315 and α_{32} is -0.0560. The sum, which is the leading term in the expression for the excess free energy of mixing, is then -0.0245. It is believed that this sum is accurate to only two significant figures which could give a 20% error in the excess free energy of mixing. Harned and Robinson[155] note that the α and β coefficients are very sensitive to even small error in the experimental data.

SUMMARY

The heat of mixing for the systems $LiCl-KCl-H_2O$, $LiCl-(CH_3)_4NCl-H_2O$, $LiCl-NaCl-H_2O$, $NaCl-KCl-H_2O$, $NaCl-HCl-H_2O$, and $KCl-(CH_3)_4NCl-H_2O$ was measured at 40, 60, and 80°. The heat of mixing for the three systems involving the Na^+ ion showed temperature dependence, whereas the heat of mixing for the other three systems was independent of temperature. It is postulated that the interactions which affect the heat of mixing occur in the region of the interface between the primary hydration sphere and the region of disordered water surrounding the ions. Evidence from other experiments with electrolyte solutions supports this conclusion.

The excess free energy as a function of temperature is calculated for all the systems except those involving the $(CH_3)_4N^+$ ion. It is shown how the complete thermodynamic properties of mixed electrolyte solutions can be calculated from only a few parameters.

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APPENDIX A

HEAT OF MIXING DATA: COMPUTER FIT

The symbols in this appendix are the same as those defined in the discussion of the treatment of the data and results with the following exceptions:

XF = X_{2_f}
XI = X_{2_i}
W = weighting factor

TABLE A. I

SODIUM CHLORIDE - POTASSIUM CHLORIDE

MOLALITY = 1.0 X = POTASSIUM CHLORIDE TEMPERATURE = 40°

A = -36.6490; SA = 0.1654; B = 0.1604; SB = 0.2324; SYBC = 0.0076

DELH	HCALC	ERROR	XF	XI	W	F2	F3
-0.55400	-0.55145	-0.00255	0.0647500	0.0000000	1.0000	0.0151042	0.0131482
-0.55500	-0.54833	-0.00667	0.0642800	0.0000000	1.0000	0.0150190	0.0130881
-0.48500	-0.49737	0.01237	0.1271099	0.0647500	1.0000	0.0136079	0.0083863
-0.48200	-0.48203	0.00003	0.1246400	0.0642800	1.0000	0.0131885	0.0082053
-0.42500	-0.43133	0.00633	0.1851100	0.1271099	1.0000	0.0117885	0.0044276
-0.44100	-0.43163	-0.00937	0.1822700	0.1246400	1.0000	0.0117973	0.0045558
-0.57000	-0.57237	0.00237	0.9333400	1.0000000	1.0000	0.0155585	-0.0134842
-0.57500	-0.56774	-0.00726	0.9333200	1.0000000	1.0000	0.0154327	-0.0133746
-0.51000	-0.50385	-0.00615	0.8766100	0.9333400	1.0000	0.0137099	-0.0087030
-0.49500	-0.50148	0.00648	0.8779800	0.9333200	1.0000	0.0136451	-0.0087302
-0.43200	-0.43845	0.00645	0.8217000	0.8766100	1.0000	0.0119426	-0.0047371

XM1 = 0.50108; XM2 = -75.64165; AO = -36.6481; SAO = 0.1609

SUM ERRORS SQUARED = 0.541E-03; F = 0.4706; SYB = 0.0074

TABLE A. I (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
-0.55400	-0.55354	-0.00046	0.0647500	0.0000000	1.0000	0.2494200	0.2332700
-0.55500	-0.55042	-0.00458	0.0642800	0.0000000	1.0000	0.2497000	0.2336500
-0.48500	-0.49871	0.01371	0.1271099	0.0647500	1.0000	0.2499959	0.2333300
-0.48200	-0.48333	0.00133	0.1246400	0.0642800	1.0000	0.2496099	0.2335100
-0.42500	-0.43203	0.00703	0.1851100	0.1271099	1.0000	0.2494000	0.2328200
-0.44100	-0.43235	-0.00865	0.1822700	0.1246400	1.0000	0.2503400	0.2338600
-0.57000	-0.57019	0.00019	0.9333400	1.0000000	1.0000	0.2500700	0.2334000
-0.57500	-0.56558	-0.00942	0.9333200	1.0000000	1.0000	0.2479800	0.2314399
-0.51000	-0.50244	-0.00756	0.8766100	0.9333400	1.0000	0.2590400	0.2299899
-0.49500	-0.50007	0.00507	0.8779800	0.9333200	1.0000	0.2610300	0.2300900
-0.43200	-0.43767	0.00567	0.8217000	0.8766100	1.0000	0.2646599	0.2480699

TABLE A. II

LITHIUM CHLORIDE - SODIUM CHLORIDE

MOLALITY = 1.0

X = SODIUM CHLORIDE

TEMPERATURE = 40°

A = 64.2380; SA = 0.1302; B = 3.8304; SB = 0.1808; SYBC = 0.0073

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.90500	0.91773	-0.01273	0.9340500	1.0000000	1.0000	0.0150663	-0.0130790
0.96900	0.95400	0.01500	0.9309300	1.0000000	1.0000	0.0156556	-0.0134929
0.83300	0.83106	0.00194	0.8677900	0.9309300	1.000	0.0134151	-0.0080148
0.65600	0.65471	0.00129	0.7558800	0.8104600	1.0000	0.0102732	-0.0013631
1.07900	1.07210	0.00690	0.0667590	0.0000000	1.0000	0.0158696	0.0137507
0.91100	0.91869	-0.00769	0.9355400	1.0000000	1.0000	0.0150849	-0.0131401
0.96300	0.95643	0.00657	0.9317400	1.0000000	1.0000	0.0156970	-0.0135540
0.82900	0.83106	-0.00206	0.8741400	0.9355400	1.000	0.0134333	-0.0083199
0.85300	0.84702	0.00598	0.8680699	0.9317400	1.0000	0.0136746	-0.0081997
0.70500	0.70976	-0.00476	0.8187799	0.8741400	1.0000	0.0113090	-0.0043634
0.74300	0.74796	-0.00496	0.8086200	0.8680699	1.0000	0.0118942	-0.0042027
0.97000	0.97229	-0.00229	0.0609700	0.0000000	1.0000	0.0143828	0.0126289
1.04400	1.03870	0.00530	0.0661400	0.0000000	1.0000	0.0153740	0.0133404
0.88600	0.89166	-0.00566	0.1216500	0.0609700	1.0000	0.0133744	0.0083895

TABLE A. II(contd.)

0.89000	0.89666	-0.00666	0.1280400	0.0661400	1.0000	0.0134672	0.0082371
0.75800	0.76076	-0.00276	0.1779200	0.1216500	1.0000	0.0115664	0.0046365
0.77800	0.77556	0.00244	0.1861899	0.1280400	1.0000	0.0118115	0.0043885

XMI = 6.10510; XM2 = 0.48514; AO = 63.8436; SAO = 0.6934

SUM ERRORS SQUARED = 0.246E-01; F = 448.5466; SYB = 0.0392

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.90500	0.96189	-0.05689	0.9340500	1.0000000	1.0000	0.2445800	0.2284499
0.96900	0.99951	-0.03051	0.9309300	1.0000000	1.0000	0.2434800	0.2266600
0.83300	0.85647	-0.02347	0.8677900	0.9309300	1.0000	0.2448300	0.2282200
0.65600	0.65588	0.00012	0.7558800	0.8104600	1.0000	0.2490100	0.2322400
1.07900	1.01317	0.06583	0.0667590	0.0000000	1.0000	0.2547200	0.2377200
0.91100	0.96307	-0.05207	0.9355400	1.0000000	1.0000	0.2501430	0.2340200
0.96300	1.00215	-0.03915	0.9317400	1.0000000	1.0000	0.2468060	0.2299600
0.82900	0.85763	-0.02863	0.8741400	0.9355400	1.0000	0.2502900	0.2338690
0.85300	0.87303	-0.02003	0.8680699	0.9317400	1.0000	0.2474000	0.2304820
0.70500	0.72201	-0.01701	0.8187799	0.8741400	1.0000	0.2495000	0.2337010
0.74300	0.75937	-0.01637	0.8086200	0.8680699	1.0000	0.2474480	0.2305120

TABLE A. II(contd.)

0.97000	0.91825	0.05175	0.0609700	0.0000000	1.0000	0.2512160	0.2358990
1.04400	0.98154	0.06246	0.0661400	0.0000000	1.0000	0.2489100	0.2324460
0.88600	0.85387	0.03213	0.1216500	0.0609700	1.0000	0.2509350	0.2347190
0.89000	0.85980	0.03020	0.1280400	0.0661400	1.0000	0.2495140	0.2329770
0.75800	0.73844	0.01956	0.1779200	0.1216500	1.0000	0.2500400	0.2340220
0.77800	0.75409	0.02391	0.1861899	0.1280400	1.0000	0.2495900	0.2329440

TABLE A. III

LITHIUM CHLORIDE - POTASSIUM CHLORIDE

MOLALITY = 1.0 X = POTASSIUM CHLORIDE TEMPERATURE = 40°

A = -63.8608; SA = 0.3137; B = -3.3255; SB = 0.4403; SYBC = 0.0136

DELH	HCALC	ERROR	XF	XI	W	F2	F3
-0.96200	-0.94374	-0.01826	0.9335300	1.0000000	1.0000	0.0154769	-0.0134194
-0.95100	-0.96744	0.01644	0.9309400	1.0000000	1.0000	0.0158610	-0.0136703
-0.82500	-0.83105	0.00605	0.8715200	0.9335300	1.0000	0.0134405	-0.0082000
-0.87600	-0.86423	-0.01177	0.8657600	0.9309400	1.0000	0.0139645	-0.0082865
-0.73000	-0.72966	-0.00034	0.8142700	0.8715200	1.0000	0.0116513	-0.0043290
-0.72200	-0.73716	0.01516	0.8068800	0.8657600	1.0000	0.0117546	-0.0040586
-0.98900	-0.99857	0.00957	0.0636120	0.0000000	1.0000	0.0149569	0.0130540
-1.02900	-1.02986	0.00086	0.0666860	0.0000000	1.0000	0.0154303	0.0133723
-0.91800	-0.89911	-0.01889	0.1300650	0.0666860	1.0000	0.0136482	0.0082777
-0.73300	-0.73582	0.00282	0.1863199	0.1300650	1.0000	0.0113061	0.0041518

XM1 = 0.48701; XM2 = 6.91408; AO = -63.5362; SAO = 0.8355

SUM ERRORS SQUARED = 0.120E-01; F = 57.0459; SYB = 0.0366

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
-0.96200	-0.98334	0.02134	0.9335300	1.0000000	1.0000	0.2494190	0.2328399
-0.95100	-1.00775	0.05675	0.9309400	1.0000000	1.0000	0.2467080	0.2296700

TABLE A. III (contd.)

-0.82500	-0.85396	0.02896	0.8715200	0.9335300	1.0000	0.2487040	0.2321870
-0.87600	-0.88725	0.01125	0.8657600	0.9309400	1.0000	0.2474689	0.2301460
-0.73000	-0.74028	0.01028	0.8142700	0.8715200	1.0000	0.2499599	0.2335500
-0.72200	-0.74684	0.02484	0.8068800	0.8657600	1.0000	0.2474200	0.2305940
-0.98900	-0.95030	-0.03870	0.0636120	0.0000000	1.0000	0.2510999	0.2351300
-1.02900	-0.98038	-0.04862	0.0666860	0.0000000	1.0000	0.2479200	0.2313900
-0.91800	-0.86716	-0.05084	0.1300650	0.0666860	1.0000	0.2475340	0.2307200
-0.73300	-0.71834	-0.01466	0.1863199	0.1300650	1.0000	0.2470100	0.2310410

TABLE A. IV

LITHIUM CHLORIDE - TETRAMETHYLAMMONIUM CHLORIDE

MOLALITY = 0.5 X = TETRAMETHYLAMMONIUM CHLORIDE TEMPERATURE = 40°

A = -39.2829; SA = 0.2152; B = -1.3851; SB = 0.3145; SYBC = 0.0103

DELH	HCALC	ERROR	XF	XI	W	F2	F3
-0.60700	-0.61570	0.00870	0.9278600	1.0000000	1.0000	0.0161610	-0.0138293
-0.52600	-0.52159	-0.00441	0.8628200	0.9278600	1.0000	0.0135557	-0.0078808
-0.47800	-0.45842	-0.01958	0.8021800	0.8628200	1.0000	0.0118070	-0.0038963
-0.62200	-0.62197	-0.00003	0.0656140	0.0000000	1.0000	0.0153626	0.0133466
-0.54200	-0.54787	0.00587	0.1286800	0.0656140	1.0000	0.0136525	0.0083473
-0.47700	-0.47235	-0.00465	0.1875800	0.1286800	1.0000	0.0118706	0.0043623
-0.61900	-0.61772	-0.00128	0.9289700	1.0000000	1.0000	0.0162154	-0.0139118
-0.54300	-0.53990	-0.00310	0.8618400	0.9289700	1.0000	0.0140317	-0.0081611
-0.43600	-0.45591	0.01991	0.8014989	0.8618400	1.0000	0.0117411	-0.0038355
-0.62300	-0.62960	0.00660	0.0670130	0.0000000	1.0000	0.0155524	0.0134680
-0.53400	-0.52757	-0.00643	0.1278099	0.0670130	1.0000	0.0131472	0.0080244
-0.46700	-0.46165	-0.00535	0.1851330	0.1278099	1.0000	0.0115990	0.0043393

XM1 = 0.49119; XM2 = 9.96265; AO = -39.2676; SAO = 0.3517

SUM ERRORS SQUARED = 0.312E-02; F = 19.3828; SYB = 0.0168

TABLE A. IV (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
-0.60700	-0.63460	0.02760	0.9278600	1.0000000	1.0000	0.2414400	0.2240199
-0.52600	-0.53230	0.00630	0.8628200	0.9278600	1.0000	0.2415580	0.2246250
-0.47800	-0.46363	-0.01437	0.8021800	0.8628200	1.0000	0.2427239	0.2256660
-0.62200	-0.60325	-0.01875	0.0656140	0.0000000	1.0000	0.2505770	0.2341360
-0.54200	-0.53610	-0.00590	0.1286800	0.0656140	1.0000	0.2484500	0.2316800
-0.47700	-0.46613	-0.01087	0.1875800	0.1286800	1.0000	0.2480699	0.2313000
-0.61900	-0.63674	0.01774	0.9289700	1.0000000	1.0000	0.2457440	0.2282880
-0.54300	-0.55099	0.00799	0.8618400	0.9289700	1.0000	0.2425300	0.2250040
-0.43600	-0.46105	0.02505	0.8014989	0.8618400	1.0000	0.2427710	0.2257740
-0.62300	-0.61071	-0.01229	0.0670130	0.0000000	1.0000	0.2487500	0.2320800
-0.53400	-0.51626	-0.01774	0.1278099	0.0670130	1.0000	0.2479380	0.2317830
-0.46700	-0.45546	-0.01154	0.1851330	0.1278099	1.0000	0.2483150	0.2319950

TABLE A. V

POTASSIUM CHLORIDE - TETRAMETHYLAMMONIUM CHLORIDE

MOLALITY = 0.5 X = TETRAMETHYLAMMONIUM CHLORIDE TEMPERATURE = 40°

A = 29.6072; SA = 0.1123; B = -0.4481; SB = 0.1493; SYBC = 0.0059

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.44800	0.44842	-0.00042	0.0666350	0.0000000	1.0000	0.0153469	0.0133016
0.43900	0.44188	-0.00288	0.0647455	0.0000000	1.0000	0.0151241	0.0131656
0.46900	0.46136	0.00764	0.0684105	0.0000000	1.0000	0.0157888	0.0136286
0.38800	0.38319	0.00481	0.1246400	0.0647455	1.0000	0.0130653	0.0081165
0.39800	0.39827	-0.00027	0.1316500	0.0684105	1.0000	0.0135751	0.0081433
0.29000	0.30149	-0.01149	0.2363700	0.1827100	1.0000	0.0102081	0.0016520
0.28600	0.29161	-0.00561	0.2425800	0.1896400	1.0000	0.0098697	0.0013379
0.47700	0.47135	0.00565	0.9310200	1.0000000	1.0000	0.0157151	-0.0135470
0.48100	0.48483	-0.00383	0.9280500	1.0000000	1.0000	0.0161658	-0.0138395
0.42100	0.41862	0.00238	0.8609599	0.9280500	1.0000	0.0140163	-0.0081015
0.47900	0.47382	0.00518	0.9303640	1.0000000	1.0000	0.0157976	-0.0135974
0.48100	0.47722	0.00378	0.9294200	1.0000000	1.0000	0.0159116	-0.0136655
0.39400	0.40020	-0.00620	0.8671300	0.9303640	1.0000	0.0133963	-0.0079708
0.41000	0.41548	-0.00548	0.8629100	0.9294200	1.0000	0.0139100	-0.0081325

TABLE A. V (contd.)

XM1 = -21.52667; XM2 = 0.50378; AO = 29.6602; SAO = 0.1410

SUM ERRORS SQUARED = 0.736E-02; F = 8.9871; SYB = 0.0075

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.44800	0.45519	-0.00719	0.0666350	0.0000000	1.0000	0.2467560	0.2303140
0.43900	0.44858	-0.00958	0.0647455	0.0000000	1.0000	0.2497640	0.2335920
0.46900	0.46830	0.00070	0.0684105	0.0000000	1.0000	0.2477440	0.2307960
0.38800	0.38752	0.00048	0.1246400	0.0647455	1.0000	0.2491980	0.2332390
0.39800	0.40264	-0.00464	0.1316500	0.0684105	1.0000	0.2472100	0.2304320
0.29000	0.30278	-0.01278	0.2363700	0.1827100	1.0000	0.2491240	0.2327680
0.28600	0.29274	-0.00674	0.2425800	0.1896400	1.0000	0.2461399	0.2300600
0.47700	0.46611	0.01089	0.9310200	1.0000000	1.0000	0.2447000	0.2278200
0.48100	0.47948	0.00152	0.9280500	1.0000000	1.0000	0.2420999	0.2246799
0.42100	0.41573	0.00527	0.8609599	0.9280500	1.0000	0.2426700	0.2251379
0.47900	0.46856	0.01044	0.9303640	1.0000000	1.0000	0.2438400	0.2268600
0.48100	0.47194	0.00906	0.9294200	1.0000000	1.0000	0.2425600	0.2254400
0.39400	0.39734	-0.00334	0.8671300	0.9303640	1.0000	0.2443060	0.2276930
0.41000	0.41257	-0.00257	0.8629100	0.9294200	1.0000	0.2423780	0.2250420

TABLE A. VI

SODIUM CHLORIDE - HYDROCHLORIC ACID

MOLALITY = 1.0

X = SODIUM CHLORIDE

TEMPERATURE = 40°

A = 112.3371; SA = 0.3190; B = 8.0280; SB = 0.4420; SYBC = 0.0139

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.35800	1.36607	-0.00807	0.8176600	0.8795500	1.0000	0.0125132	-0.0049355
1.57300	1.56869	0.00431	0.8795500	0.9468600	1.0000	0.0146475	-0.0095621
1.30500	1.30940	-0.00440	0.9468600	1.0000000	1.0000	0.0124512	-0.0111279
1.06300	1.08911	-0.02611	0.1652000	0.1194800	1.0000	0.0094056	0.0040502
1.23900	1.23087	0.00813	0.1194800	0.0706100	1.0000	0.0104922	0.0065032
1.93100	1.94133	-0.01033	0.0706100	0.0000000	1.0000	0.0162820	0.0139827
1.46200	1.43550	0.02650	0.0509460	0.0000000	1.0000	0.0120078	0.0107843
1.51600	1.52036	-0.00436	0.8633900	0.9293100	1.0000	0.0141248	-0.0082686
1.71000	1.71123	-0.00123	0.9293100	1.0000000	1.0000	0.0162288	-0.0139344
1.34100	1.34717	-0.00617	0.8014100	0.8630900	1.0000	0.0122809	-0.0040401
1.51800	1.51564	0.00236	0.8630900	0.9289800	1.0000	0.0140796	-0.0082245
1.73400	1.72009	0.01391	0.9289800	1.0000000	1.0000	0.0163119	-0.0139950

XM1 = 5.18220; XM2 = 0.48220; AD = 110.1106; SAO = 1.6373

SUM ERRORS SQUARED = 0.652E-01; F = 329.9359; SYB = 0.0770

TABLE A. VII

LITHIUM CHLORIDE - SODIUM CHLORIDE

MOLALITY = 1.0 X = SODIUM CHLORIDE TEMPERATURE = 60°

A = 44.5207; SA = 0.1840; B = 2.4017; SB = 0.2619; SYBC = 0.0084

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.65400	0.65314	0.00086	0.9327199	1.0000000	1.0000	0.0153890	-0.0133183
0.57700	0.57836	-0.00136	0.8698850	0.9327199	1.0000	0.0134293	-0.0081275
0.73200	0.72488	0.00712	0.0676221	0.0000000	1.0000	0.0155562	0.0134523
0.61000	0.62288	-0.01289	0.1306990	0.0676221	1.0000	0.0135499	0.0081755
0.51500	0.52736	-0.01236	0.1888450	0.1306990	1.0000	0.0116191	0.0041933
0.73200	0.72343	0.00857	0.0673980	0.0000000	1.0000	0.0155247	0.0134320
0.63300	0.62766	0.00534	0.1309710	0.0673980	1.0000	0.0136538	0.0082369
0.51800	0.52741	-0.00941	0.1891200	0.1309710	1.0000	0.0116209	0.0041813
0.66100	0.65842	0.00258	0.9322100	1.0000000	1.0000	0.0155124	-0.0134092
0.58600	0.58708	-0.00108	0.8684140	0.9322100	1.0000	0.0136287	-0.0081942
0.52000	0.51226	0.00774	0.8094960	0.8684140	1.0000	0.0117313	-0.0041741

XM1 = 6.69259; XM2 = 0.48654; AO = 44.5842; SAO = 0.5610

SUM ERRORS SQUARED = 0.662E-02; F = 84.0904; SYB = 0.0257

TABLE A. VII (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.65400	0.68611	-0.03211	0.9327199	1.0000000	1.0000	0.2452300	0.2287300
0.57700	0.59874	-0.02174	0.8698850	0.9327199	1.0000	0.2456990	0.2291530
0.73200	0.69356	0.03844	0.0676221	0.0000000	1.0000	0.2467300	0.2300500
0.61000	0.60411	0.00589	0.1306990	0.0676221	1.0000	0.2471099	0.2303900
0.51500	0.51803	-0.00303	0.1888450	0.1306990	1.0000	0.2463599	0.2298860
0.73200	0.69215	0.03985	0.0673980	0.0000000	1.0000	0.2469900	0.2303399
0.63300	0.60874	0.02426	0.1309710	0.0673980	1.0000	0.2471400	0.2302909
0.51800	0.51811	-0.00011	0.1891200	0.1309710	1.0000	0.2464600	0.2299700
0.66100	0.69161	-0.03061	0.9322100	1.0000000	1.0000	0.2454700	0.2288300
0.58600	0.60763	-0.02163	0.8684140	0.9322100	1.0000	0.2460000	0.2291650
0.52000	0.52303	-0.00303	0.8094960	0.8684140	1.0000	0.2459800	0.2292950

TABLE A. VIII

POTASSIUM CHLORIDE - SODIUM CHLORIDE

MOLALITY = 1.0 X = POTASSIUM CHLORIDE TEMPERATURE = 60°

A = -35.0509; SA = 0.1531; B = 0.0171; SB = 0.2229; SYBC = 0.0072

DELH	HCALC	ERROR	XF	XI	W	F2	F3
-0.41500	-0.41115	-0.00385	0.8092170	0.8685900	1.0000	0.0117280	-0.0041707
-0.45600	-0.46833	0.01233	0.8685900	0.9316700	1.0000	0.0133576	-0.0080214
-0.54200	-0.54428	0.00228	0.9316700	1.0000000	1.0000	0.0155218	-0.0134006
-0.39700	-0.40168	0.00468	0.1868970	0.1292100	1.0000	0.0114620	0.0042154
-0.46400	-0.46454	0.00054	0.1292100	0.0670220	1.0000	0.0132573	0.0080543
-0.54500	-0.53754	-0.00746	0.0670220	0.0000000	1.0000	0.0153424	0.0132858
-0.43000	-0.42020	-0.00980	0.8094299	0.8698699	1.0000	0.0119861	-0.0042983
-0.46100	-0.46246	0.00146	0.8698699	0.9321540	1.0000	0.0131901	-0.0079673
-0.54900	-0.54064	-0.00836	0.9321540	1.0000000	1.0000	0.0154180	-0.0133259
-0.40600	-0.41365	0.00765	0.1859300	0.1267689	1.0000	0.0118037	0.0044218
-0.45800	-0.46337	0.00537	0.1267689	0.0649275	1.0000	0.0132238	0.0081538
-0.52400	-0.52161	-0.00239	0.0649275	0.0000000	1.0000	0.0148878	0.0129545

XM1 = 0.50000; XM2 = -683.26025; A0 = -35.0510; SA0 = 0.1459

SUM ERRORS SQUARED = 0.513E-03; F = -0.0129; SYB = 0.0068

TABLE A. VIII (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
-0.41500	-0.41108	-0.00392	0.8092170	0.8685900	1.0000	0.2441000	0.2274140
-0.45600	-0.46820	0.01220	0.8685900	0.9316700	1.0000	0.2437969	0.2272940
-0.54200	-0.54406	0.00206	0.9316700	1.0000000	1.0000	0.2438200	0.2271600
-0.39700	-0.40175	0.00475	0.1868970	0.1292100	1.0000	0.2443700	0.2281840
-0.46400	-0.46468	0.00068	0.1292100	0.0670220	1.0000	0.2448130	0.2284940
-0.54500	-0.53776	-0.00724	0.0670220	0.0000000	1.0000	0.2453600	0.2289200
-0.43000	-0.42012	-0.00988	0.8094299	0.8698699	1.0000	0.2449999	0.2279750
-0.46100	-0.46233	0.00133	0.8698699	0.9321540	1.0000	0.2434600	0.2271979
-0.54900	-0.54042	-0.00858	0.9321540	1.0000000	1.0000	0.2437900	0.2272500
-0.40600	-0.41373	0.00773	0.1859300	0.1267689	1.0000	0.2450800	0.2284729
-0.45800	-0.46351	0.00551	0.1267689	0.0649275	1.0000	0.2448800	0.2286879
-0.52400	-0.52183	-0.00217	0.0649275	0.0000000	1.0000	0.2452199	0.2293000

TABLE A. IX

LITHIUM CHLORIDE - POTASSIUM CHLORIDE

MOLALITY = 1.0 X = POTASSIUM CHLORIDE TEMPERATURE = 60°

A = -62.9762; SA = 0.1537; B = -2.7823; SB = 0.2096; SYBC = 0.0079

DELH	HCALC	ERROR	XF	XI	W	F2	F3
-0.93600	-0.94175	0.00575	0.9315600	1.0000000	1.0000	0.0155469	-0.0134188
-0.84000	-0.84063	0.00063	0.8668820	0.9315600	1.0000	0.0137100	-0.0081833
-0.74300	-0.73764	-0.00536	0.8067160	0.8668820	1.0000	0.0118954	-0.0041301
-1.02300	-1.01963	-0.00337	0.0676650	0.0000000	1.0000	0.0155950	0.0134845
-0.86400	-0.86612	0.00212	0.1301450	0.0676650	1.0000	0.0133955	0.0080960
-0.72900	-0.73510	0.00610	0.1877609	0.1301450	1.0000	0.0114878	0.0041836
-1.01100	-1.01614	0.00514	0.0674998	0.0000000	1.0000	0.0155414	0.0134433
-0.99700	-1.00872	0.01172	0.0670330	0.0000000	1.0000	0.0154272	0.0133590
-0.89400	-0.88253	-0.01147	0.1307070	0.0670330	1.0000	0.0136491	0.0082512
-0.76800	-0.75327	-0.01473	0.1897970	0.1307070	1.0000	0.0117745	0.0042270
-0.95100	-0.94928	-0.00172	0.9311000	1.0000000	1.0000	0.0156706	-0.0135112
-0.85700	-0.85300	-0.00400	0.8654990	0.9311000	1.0000	0.0139094	-0.0082510
-0.93500	-0.93962	0.00462	0.9316600	1.0000000	1.0000	0.0155118	-0.0133917

XM1 = 0.48897; XM2 = 8.05601; AO = -63.0188; SAO = 0.6072

TABLE A. IX (contd.)

SUM ERRORS SQUARED = 0.115E-01; F = 176.3537; SYB = 0.0310

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
-0.93600	-0.97975	0.04375	0.9315600	1.0000000	1.0000	0.2438500	0.2271600
-0.84000	-0.86399	0.02399	0.8668820	0.9315600	1.0000	0.2445199	0.2275400
-0.74300	-0.74964	0.00664	0.8067160	0.8668820	1.0000	0.2450800	0.2280700
-1.02300	-0.98278	-0.04022	0.0676650	0.0000000	1.0000	0.2472000	0.2305300
-0.86400	-0.84417	-0.01983	0.1301450	0.0676650	1.0000	0.2464700	0.2299500
-0.72900	-0.72395	-0.00505	0.1877609	0.1301450	1.0000	0.2454799	0.2292220
-1.01100	-0.97940	-0.03160	0.0674998	0.0000000	1.0000	0.2469100	0.2302400
-0.99700	-0.97221	-0.02479	0.0670330	0.0000000	1.0000	0.2466800	0.2301400
-0.89400	-0.86015	-0.03385	0.1307070	0.0670330	1.0000	0.2465900	0.2297600
-0.76800	-0.74202	-0.02598	0.1897970	0.1307070	1.0000	0.2459400	0.2292210
-0.95100	-0.98754	0.03654	0.9311000	1.0000000	1.0000	0.2442700	0.2274400
-0.85700	-0.87655	0.01955	0.8654990	0.9311000	1.0000	0.2449800	0.2277200
-0.93500	-0.97754	0.04254	0.9316600	1.0000000	1.0000	0.2436300	0.2269800

TABLE A. X

LITHIUM CHLORIDE - TETRAMETHYLAMMONIUM CHLORIDE

MOLALITY = 0.5 X = TETRAMETHYLAMMONIUM CHLORIDE TEMPERATURE = 60°

A = -40.3218; SA = 0.1672; B = -1.6579; SB = 0.2373; SYBC = 0.0076

DELH	HCALC	ERROR	XF	XI	W	F2	F3
-0.62600	-0.63083	0.00483	0.0648910	0.0000000	1.0000	0.0151045	0.0131442
-0.55700	-0.55199	-0.00500	0.1262110	0.0648910	1.0000	0.0133506	0.0082478
-0.47100	-0.47371	0.00271	0.1831700	0.1262110	1.0000	0.0115670	0.0044100
-0.61800	-0.61391	-0.00408	0.9307400	1.0000000	1.0000	0.0157844	-0.0135979
-0.53800	-0.53286	-0.00513	0.8669900	0.9307400	1.0000	0.0135469	-0.0080667
-0.46600	-0.46920	0.00320	0.8074400	0.8669900	1.0000	0.0118057	-0.0041183
-0.60200	-0.60777	0.00577	0.9312600	1.0000000	1.0000	0.0156272	-0.0134788
-0.53700	-0.54101	0.00401	0.8664900	0.9312600	1.0000	0.0137541	-0.0081905
-0.64200	-0.64176	-0.00023	0.0660220	0.0000000	1.0000	0.0153676	0.0133384
-0.54300	-0.55156	0.00856	0.1275000	0.0660220	1.0000	0.0133427	0.0081786
-0.48800	-0.47083	-0.01716	0.1843500	0.1275000	1.0000	0.0114988	0.0043274

XM1 = 0.48973; XM2 = 8.61713; AO = -40.3437; SAO = 0.4021

SUM ERRORS SQUARED = 0.338E-02; F = 48.8052; SYB = 0.0183

TABLE A. X (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
-0.62600	-0.60937	-0.01662	0.0648910	0.0000000	1.0000	0.2489200	0.2327600
-0.55700	-0.53861	-0.01838	0.1262110	0.0648910	1.0000	0.2491800	0.2328500
-0.47100	-0.46665	-0.00434	0.1831700	0.1262110	1.0000	0.2486000	0.2323880
-0.61800	-0.63680	0.01880	0.9307400	1.0000000	1.0000	0.2448600	0.2279000
-0.53800	-0.54653	0.00853	0.8669900	0.9307400	1.0000	0.2451000	0.2283100
-0.46600	-0.47628	0.01028	0.8074400	0.8669900	1.0000	0.2455400	0.2286800
-0.60200	-0.63046	0.02846	0.9312600	1.0000000	1.0000	0.2441200	0.2273400
-0.53700	-0.55489	0.01789	0.8664900	0.9312600	1.0000	0.2450800	0.2280400
-0.64200	-0.61999	-0.02200	0.0660220	0.0000000	1.0000	0.2492200	0.2327600
-0.54300	-0.53829	-0.00470	0.1275000	0.0660220	1.0000	0.2487400	0.2323600
-0.48800	-0.46390	-0.02409	0.1843500	0.1275000	1.0000	0.2479600	0.2317940

TABLE A. XI

POTASSIUM CHLORIDE - TETRAMETHYLAMMONIUM CHLORIDE

MOLALITY = 0.5   X = TETRAMETHYLAMMONIUM CHLORIDE   TEMPERATURE = 60°

A = 28.6633; SA = 0.1662; B = 0.0036; SB = 0.2425; SYBC = 0.0078

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.43700	0.43739	-0.00039	0.0661370	0.0000000	1.0000	0.0152579	0.0132396
0.39200	0.38628	0.00571	0.1285400	0.0661370	1.0000	0.0134754	0.0082289
0.32600	0.32726	-0.00126	0.1853600	0.1285400	1.0000	0.0114170	0.0042493
0.46600	0.45582	0.01017	0.9300400	1.0000000	1.0000	0.0159046	-0.0136792
0.39900	0.39353	0.00546	0.8652300	0.9300400	1.0000	0.0137307	-0.0081085
0.33300	0.34220	-0.00920	0.8046700	0.8652300	1.0000	0.0119392	-0.0040570
0.44300	0.43584	0.00715	0.0653840	0.0000000	1.0000	0.0152039	0.0132157
0.37900	0.38521	-0.00621	0.1273100	0.0653840	1.0000	0.0134383	0.0082594
0.33300	0.33663	-0.00363	0.1850600	0.1273100	1.0000	0.0117440	0.0044073
0.45000	0.45587	-0.00587	0.9301800	1.0000000	1.0000	0.0159063	-0.0136852
0.38800	0.38099	0.00700	0.8674500	0.9301800	1.0000	0.0132929	-0.0079128
0.33600	0.34958	-0.01358	0.8057300	0.8674500	1.0000	0.0121967	-0.0042238

XM1 = 2626.01230; XM2 = 0.49996; AO = 28.6632; SAO = 0.1585

SUM ERRORS SQUARED = 0.623E-03; F = 0.0001; SYB = 0.0075

TABLE A. XI (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.43700	0.43734	-0.00034	0.0661370	0.0000000	1.0000	0.2470400	0.2307000
0.39200	0.38625	0.00574	0.1285400	0.0661370	1.0000	0.2477800	0.2312100
0.32600	0.32725	-0.00125	0.1853600	0.1285400	1.0000	0.2466600	0.2305800
0.46600	0.45587	0.01012	0.9300400	1.0000000	1.0000	0.2444400	0.2273400
0.39900	0.39356	0.00543	0.8652300	0.9300400	1.0000	0.2448600	0.2277960
0.33300	0.34221	-0.00921	0.8046700	0.8652300	1.0000	0.2450000	0.2278500
0.44300	0.43579	0.00720	0.0653840	0.0000000	1.0000	0.2488000	0.2325400
0.37900	0.38518	-0.00618	0.1273100	0.0653840	1.0000	0.2486600	0.2321800
0.33300	0.33662	-0.00362	0.1850600	0.1273100	1.0000	0.2495200	0.2330000
0.45000	0.45592	-0.00592	0.9301800	1.0000000	1.0000	0.2449200	0.2278200
0.38800	0.38101	0.00698	0.8674500	0.9301800	1.0000	0.2442800	0.2278000
0.33600	0.34959	-0.01359	0.8057300	0.8674500	1.0000	0.2452900	0.2278500

TABLE A. XII

SODIUM CHLORIDE - HYDROCHLORIC ACID

MOLALITY = 1.0
X = SODIUM CHLORIDE
TEMPERATURE = 60°

A = 95.5070; SA = 0.4942; B = 5.5949; SB = 0.6264; SYBC = 0.0236

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.46700	1.46058	0.00642	0.9297700	1.0000000	1.0000	0.0161037	-0.0138418
0.99100	0.99437	-0.00337	0.8980400	0.9474600	1.0000	0.0108507	-0.0074979
1.29700	1.30610	-0.00910	0.8636800	0.9297700	1.0000	0.0141624	-0.0083118
1.07700	1.08359	-0.00659	0.9483100	1.0000000	1.0000	0.0119746	-0.0107367
1.43900	1.46005	-0.02105	0.9301100	1.0000000	1.0000	0.0160986	-0.0138483
1.02100	0.98915	0.03185	0.8991690	0.9483100	1.0000	0.0107964	-0.0075054
1.31400	1.29984	0.01416	0.8642200	0.9301100	1.0000	0.0140959	-0.0082976
1.61100	1.61490	-0.00390	0.0710870	0.0000000	1.0000	0.0160997	0.0138107
1.19200	1.22025	-0.02825	0.0513310	0.0000000	1.0000	0.0121385	0.0108923
1.38800	1.40215	-0.01415	0.1386200	0.0710870	1.0000	0.0141982	0.0082432
1.19000	1.20954	-0.01954	0.0511510	0.0000000	1.0000	0.0120317	0.0108009
1.65590	1.60734	0.04856	0.0683580	0.0000000	1.0000	0.0160194	0.0138293

XM1 = 6.20478; XM2 = 0.48539; A0 = 95.1469; SA0 = 1.4070

SUM ERRORS SQUARED = 0.502E-01; F = 79.7700; SYB = 0.0675

TABLE A. XIII

POTASSIUM CHLORIDE - TETRAMETHYLAMMONIUM CHLORIDE

MOLALITY = 0.5 X = TETRAMETHYLAMMONIUM CHLORIDE TEMPERATURE = 80°

A = 28.2936; SA = 0.6321; B = -0.6950; SB = 0.9446; SYBC = 0.0275

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.38800	0.43030	-0.04230	0.0675840	0.0000000	1.0000	0.0155386	0.0134383
0.35800	0.38265	-0.02465	0.1317700	0.0675840	1.0000	0.0137272	0.0082541
0.34800	0.32997	0.01803	0.1907600	0.1317700	1.0000	0.0117650	0.0041761
0.44900	0.43113	0.01787	0.0676240	0.0000000	1.0000	0.0155686	0.0134629
0.43000	0.38385	0.04615	0.1318500	0.0676240	1.0000	0.0137698	0.0082764
0.37000	0.39676	-0.02676	0.8621300	0.9280500	1.0000	0.0138260	-0.0080240
0.33900	0.33684	0.00216	0.8004200	0.8621300	1.0000	0.0118107	-0.0038399
0.47900	0.47036	0.00864	0.9262200	1.0000000	1.0000	0.0162832	-0.0138805
0.39500	0.39791	-0.00291	0.8585100	0.9262200	1.0000	0.0138696	-0.0078981
0.34700	0.33736	0.00964	0.7962800	0.8585100	1.0000	0.0118336	-0.0036634

XM1 = -13.07567; XM2 = 0.50614; AO = 28.2360; SAO = 0.6110

SUM ERRORS SQUARED = 0.648E-02; F = 0.5414; SYB = 0.0268

TABLE A. XIV

LITHIUM CHLORIDE - TETRAMETHYLAMMONIUM CHLORIDE

MOLALITY = 0.5 X = TETRAMETHYLAMMONIUM CHLORIDE TEMPERATURE = 80°

A = 40.7079; SA = 0.5112; B = 0.7915; SB = 0.7519; SYBC = 0.0248

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.64000	0.64302	-0.00302	0.9296900	1.0000000	1.0000	0.0160645	-0.0138055
0.57400	0.56599	0.00801	0.8630980	0.9296900	1.0000	0.0140638	-0.0082353
0.48400	0.49075	-0.00675	0.8014800	0.8630980	1.0000	0.0121331	-0.0039937
0.63600	0.64903	-0.01303	0.9286800	1.0000000	1.0000	0.0162140	-0.0139012
0.58000	0.55711	0.02289	0.8631000	0.9286800	1.0000	0.0138426	-0.0080780
0.46700	0.49239	-0.02539	0.8013300	0.8631000	1.0000	0.0121734	-0.0040033
0.62900	0.64571	-0.01671	0.0672760	0.0000000	1.0000	0.0155996	0.0135007
0.60100	0.57165	0.02935	0.1315700	0.0672760	1.0000	0.0138801	0.0083600
0.45900	0.47896	-0.01996	0.1907700	0.1315700	1.0000	0.0116859	0.0041117
0.62500	0.65785	-0.03285	0.0684540	0.0000000	1.0000	0.0158935	0.0137176
0.59900	0.56361	0.03539	0.1319300	0.0684540	1.0000	0.0136858	0.0082009
0.51800	0.48902	0.02898	0.1913800	0.1319300	1.0000	0.0119310	0.0042163

XM1 = 17.64825; XM2 = 0.49514; AO = 40.7023; SAO = 0.5137

SUM ERRORS SQUARED = 0.685E-02; F = 1.1083; SYB = 0.0250

TABLE A. XV

LITHIUM CHLORIDE - POTASSIUM CHLORIDE

MOLALITY = 1.0 X = POTASSIUM CHLORIDE TEMPERATURE = 80°

A = 61.0735; SA = 0.6934; B = 4.6718; SB = 1.0002; SYBC = 0.0326

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.88500	0.91054	-0.02554	0.9293500	1.0000000	1.0000	0.0159570	-0.0137023
0.90300	0.90852	-0.00552	0.9293900	1.0000000	1.0000	0.0159218	-0.0136733
0.82200	0.80214	0.01986	0.8638600	0.9293900	1.0000	0.0137510	-0.0080650
0.82000	0.80749	0.01251	0.8630000	0.9288300	1.0000	0.0138396	-0.0080777
0.72750	0.72116	0.00634	0.8011900	0.8630000	1.0000	0.0121123	-0.0039776
0.97300	1.02627	-0.05327	0.0689300	0.0000000	1.0000	0.0157642	0.0135910
0.87700	0.89088	-0.01388	0.1344600	0.0689300	1.0000	0.0139538	0.0082777
0.78600	0.75411	0.03189	0.1955800	0.1344600	1.0000	0.0120346	0.0040911
1.06000	1.03811	0.02189	0.0692050	0.0000000	1.0000	0.0159467	0.0137396
0.94180	0.89176	0.05004	0.1344700	0.0692050	1.0000	0.0139681	0.0082782
0.71300	0.74866	-0.03566	0.1946900	0.1344700	1.0000	0.0119461	0.0040818

XM1 = 4.87662; XM2 = 0.48096; AO = 61.1901; SAO = 1.2164

SUM ERRORS SQUARED = 0.328E-01; F = 21.8153; SYB = 0.0573

TABLE A. XVI

LITHIUM CHLORIDE - SODIUM CHLORIDE

MOLALITY = 1.0   X = SODIUM CHLORIDE   TEMPERATURE = 80°

A = 33.3779; SA = 0.4541; B = 1.4071; SB = 0.6759; SYBC = 0.0187

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.51400	0.50697	0.00703	0.9309500	1.0000000	1.0000	0.0157613	-0.0135847
0.44000	0.44833	-0.00833	0.8662100	0.9309500	1.0000	0.0137770	-0.0081879
0.51700	0.51572	0.00128	0.9299600	1.0000000	1.0000	0.0160322	-0.0137864
0.42500	0.44628	-0.02128	0.8658500	0.9299600	1.0000	0.0137126	-0.0081126
0.35900	0.39196	-0.03296	0.8061200	0.8658500	1.0000	0.0119158	-0.0040982
0.48100	0.45338	0.02762	0.8656100	0.9307400	1.0000	0.0139314	-0.0082572
0.41200	0.39440	0.01760	0.8052800	0.8656100	1.0000	0.0119888	-0.0040976
0.56200	0.55895	0.00305	0.0704840	0.0000000	1.0000	0.0161608	0.0138827
0.47100	0.47461	-0.00361	0.1355800	0.0704840	1.0000	0.0138755	0.0081569
0.41100	0.40490	0.00610	0.1961400	0.1355800	1.0000	0.0119612	0.0040253

XM1 = 8.41772; XM2 = 0.48948; AO = 33.0286; SAO = 0.4940

SUM ERRORS SQUARED = 0.430E-02; F = 4.3342; SYB = 0.0219

TABLE A. XVII

SODIUM CHLORIDE - POTASSIUM CHLORIDE

MOLALITY = 1.0 X = POTASSIUM CHLORIDE TEMPERATURE = 80°

A = 31.1701; SA = 0.3285; B = 0.7047; SB = 0.4572; SYBC = 0.0152

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.46700	0.47945	-0.01245	0.0659550	0.0000000	1.0000	0.0150858	0.0130958
0.41800	0.41903	-0.00103	0.1280770	0.0659550	1.0000	0.0132598	0.0081143
0.40000	0.36986	0.03014	0.1872700	0.1280770	1.0000	0.0117677	0.0043461
0.49600	0.49513	0.00087	0.0678660	0.0000000	1.0000	0.0155804	0.0134656
0.41500	0.43061	-0.01561	0.1321800	0.0678660	1.0000	0.0136301	0.0081768
0.51600	0.49628	0.01972	0.0682460	0.0000000	1.0000	0.0156167	0.0134851
0.42250	0.42658	-0.00408	0.1316400	0.0682460	1.0000	0.0135025	0.0081046
0.34900	0.36939	-0.02039	0.1909170	0.1316400	1.0000	0.0117564	0.0041725
0.45300	0.46312	-0.01012	0.9328200	1.0000000	1.0000	0.0151544	-0.0131183
0.42600	0.42517	0.00083	0.8671200	0.9328200	1.0000	0.0138280	-0.0082952
0.48100	0.47387	0.00713	0.9311800	1.0000000	1.0000	0.0155051	-0.0133710
0.36900	0.36353	0.00547	0.8055400	0.8654800	1.0000	0.0117535	-0.0040197

XM1 = 15.24993; XM2 = 0.49435; AO = 31.3145; SAO = 0.3340

SUM ERRORS SQUARED = 0.286E-02; F = 2.3754; SYB = 0.0161

TABLE A. XVIII

SODIUM CHLORIDE - HYDROCHLORIC ACID

MOLALITY = 1.0 X = SODIUM CHLORIDE TEMPERATURE = 80°

A = 82.1928; SA = 0.5227; B = 3.6279; SB = 0.6857; SYBC = 0.0252

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.00900	1.04257	-0.03357	0.0520880	0.0000000	1.0000	0.0122020	0.0109308
1.01500	1.02373	-0.00873	0.0509110	0.0000000	1.0000	0.0119802	0.0107604
0.93100	0.92461	0.00639	0.1014800	0.0520880	1.0000	0.0109154	0.0075629
1.40600	1.38289	0.02311	0.0695570	0.0000000	1.0000	0.0162090	0.0139538
0.79360	0.81839	-0.02479	0.1480500	0.1014800	1.0000	0.0097415	0.0048800
1.20200	1.17341	0.02859	0.1341000	0.0695670	1.0000	0.0139124	0.0082454
1.04100	1.01269	0.02831	0.1944800	0.1341000	1.0000	0.0121373	0.0041611
0.98800	1.01413	-0.02613	0.0510400	0.0000000	1.0000	0.0118680	0.0106565
1.29500	1.28457	0.01043	0.9287500	1.0000000	1.0000	0.0162436	-0.0139289
1.15300	1.12450	0.02850	0.8625000	0.9287500	1.0000	0.0140423	-0.0081796
0.94200	0.97123	-0.02923	0.9459300	1.0000000	1.0000	0.0123008	-0.0109705
1.28700	1.28741	-0.00041	0.9287400	1.0000000	1.0000	0.0162795	-0.0139593
1.11600	1.13873	-0.02273	0.8617400	0.9287400	1.0000	0.0142190	-0.0082608

XM1 = 8.06293; XM2 = 0.48898; AO = 82.3321; SAO = 0.9410

SUM ERRORS SQUARED = 0.248E-01; F = 27.9941; SYB = 0.0454

APPENDIX B

CANCELLATION OF PAIRWISE OPPOSITELY-CHARGED INTERACTIONS

For the mixing

$$MX_{(I)} + NX_{(I)} \rightarrow \text{Mixture}_{(I)},$$

a given weight, g, of MX (concentration m moles/kg solvent) and, for simplicity, the same weight, g, of NX (concentration m moles/kg solvent) are mixed. In the mixture of weight 2g, the concentration of M^+ and of N^+ is 1/2 m, but the concentration of X^- is m. Before mixing the number of M^+X^- interactions can be expressed as,

$$n_{M^+X^-} = \frac{m_{M^+}m_{X^-}}{K} \times wt \qquad \text{Eq. A. 1}$$

$$= \frac{m^2}{K} \times g$$

$$= \frac{m^2 g}{K}$$

where: K is the dissociation constant and can be expressed as $a_{M^+}a_{X^-}/a_{MX}$, where a is the activity.

After mixing the same number of M^+X^- interactions are present and this can be expressed as,

$$n_{M^+X^-} = \frac{m_{M^+}m_{X^-}}{K} \times wt \qquad \text{Eq. A. 2}$$

$$= \frac{1/2m \times m \times 2g}{K}$$

$$= \frac{m^2 g}{K}$$

The same expressions can be written for the N^+X^- interactions. Since K is the same in Equations A. 1 and A. 2, the number of pairwise oppositely-charged interactions is the same before mixing as after mixing. Hence, effects due to these types of interactions cancel.

APPENDIX C

FREE ENERGY OF NaCl-HCl-H_2O SYSTEM: CALCULATIONS

In the following calculations 1.0 molal equimolal solutions will be considered for simplicity. The first term in Equation 17 may be calculated from activity and osmotic coefficients at 25° as follows:

$$\sum_{i,j} y_{R_i} y_{X_j} G^E_{R_iX_j} = 1/2 \left[G^E_{HCl} + G^E_{NaCl}\right]$$

where;

$$G^E_{R_iX_j} = \nu RTm \left[1 - \varnothing_{R_iX_j} + \ln \gamma_{\pm} (R_iX_j)\right]$$

thus,

$$1/2 \left[G^E_{HCl} + G^E_{NaCl}\right] = RT\left[2 - \varnothing(HCl) - \varnothing(NaCl) + \ln \gamma_{NaCl} + \ln \gamma_{HCl}\right]$$

$$= RT\left[2 - 1.039 - 0.936 - 0.422 - 0.212\right]$$

$$= -359 \text{ cal/kg.}$$

The remaining terms in Equation 17 involve the excess free energy of mixing for the common-ion mixings. For the NaCl-HCl-H_2O system only the excess free energy of mixing parameter, $G^{Cl}_{H,Na}$, is needed. Thus the remaining terms in Equation 17 reduce to

$$\Delta_m G^E = \frac{RTI^2}{4} g^{Cl}_{H,Na}.$$

At 25° the excess free energy of mixing for this system is 8.7 cal/kg solvent (see Table II). Therefore,

$$G^E_{mix}\ (25°) = -359 + 8.7 = -350 \text{ cal/kg solvent.}$$

At 60°, the first term of Equation 17 is calculated from literature values of the activity and osmotic coefficients and found to be -456.7 cal/kg solvent. Equation 19 may be used to calculate the excess free energy of mixing at 60°, and the value was found to be 6.4 cal/kg solvent. Therefore

$$G^E_{mix}\ (60°) = -450.7 - 6.4 - -444 \text{ cal/kg solvent.}$$

APPENDIX D

ABBREVIATIONS AND UNITS

The abbreviations and style used in this thesis are recommended in "Handbook for Authors of Papers in the Journals of the American Chemical Society," American Chemical Society Publications, Washington, D. C. 1967.

The units for some of the thermodynamic properties discussed in this thesis are as follows, unless denoted otherwise:

$\Delta_m H$	cal/kg solvent
$\Delta_m G^E$	cal/kg solvent
$\Delta_m S^E$	cal/kg solvent degree
$\phi_L \mathrm{mix}$	cal/mole salt