HEATS OF MIXING OF AQUEOUS ELECTROLYTES

TEMPERATURE DEPENDENCE

by

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INTRODUCTION

In recent years there have been many studies of the thermodynamic properties of aqueous electrolyte solutions. Much of the economic interest in this work stems from the need to develop a suitable method for converting sea water to potable water. It has been shown that the determination of the heats of mixing of aqueous electrolyte solutions is an excellent way to study specific ion interactions.[1] However, such a study is complicated by a lack of understanding about the role played by water in influencing these interactions. As an introduction to the field of electrolyte solutions, a brief review of some of the available theoretical and experimental information follows.

DOCUMENTATION OF PREVIOUS WORK

The study of electrolyte solutions dates back to van't Hoff,[2] who discovered that solutions which conduct electricity possess freezing points, boiling points, osmotic pressures, and vapor pressures characteristic of a special class of systems, and to Arrhenius,[3] who discovered that these systems contain electrically charged particles, or ions. The next major advance was the realization that the deviations from ideality in dilute solutions differ from those in nonelectrolyte solutions, due to the long-range nature of the electrostatic interionic forces. Among the contributors in this area were Sutherland,[4] Noyes,[5] and Bjerrum.[6] Milner[7] was the first to treat this behavior theoretically, but his expression was so complicated that it could only be approximately evaluated. It was not until 1923 that Debye[8] formulated the first statistical theory of interionic attraction. According to Debye and Huckel the natural logarithm of the activity coefficient in very dilute solutions approaches linearity in the square root of the concentration.

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

where

$\gamma_{\pm}$ = mean activity coefficient

A_{γ} = Debye-Huckel coefficient

$$\frac{2}{1000} \frac{N_0 d_1}{\times 2.303^2} \left[\frac{e^2}{DkT} \right]^3$$

where N_0 = Avogadro's number

d_1 = density of the solvent

e = charge on an electron

D = dielectric constant of the solvent

k = Boltzmann constant

T = temperature

z_{+}, z_{-} = charge on positive, negative ions

I = molal ionic strength

The original equation was

$$\ln \gamma_{\pm} = \frac{-e^2 \kappa \left| z_{+}z_{-} \right|}{2DkT} \qquad \text{Eq. 2}$$

where $\quad \mathsf{K} = \sqrt{\dfrac{4\pi e^2}{DkT} \sum\limits_{j} N_j z_j^2}$

If the definition of ionic strength as originally proposed by Lewis and Randall[9],

$$I = 1/2 \sum_i m_i z_i^2$$

is used, then

$$\mathsf{K} = \sqrt{\dfrac{8\pi e^2 N_0 d_1}{1000 \; DkT} \; I}$$

Substitution of this expression into equation 2 yields equation 1. The assumptions which had to be made to obtain the relatively simple Debye-Huckel equation limit its validity to only very dilute solutions. However, it has proven quite valuable in the practical treatment of electrolyte solutions for extrapolation to zero concentration of activity coefficients, heat capacities, volumes, etc.[10]

At about the same time that Debye's statistical theory was being formulated, there appeared Bronsted's principle of the specific interactions of ions, a phenomenological theory which states, [11] "In a dilute salt solution of constant total concentration, ions will be uniformly influenced by ions of their own sign." The basis for this theory is that specific electrical effects take place between ions and, in dilute solutions, only the ions of unlike sign approach each other closely enough for short-range interactions to manifest themselves. Bronsted noted two effects influencing the activity coefficient of an ion: the interactions between ions of opposite sign and the salting out effects due to the solvent. In a subsequent paper[12] he suggested the combination of the specific ion interactions with the Debye-Huckel limiting law. For a one-to-one electrolyte, MX, this takes the form

$$2.303 \log \gamma_{\pm} = -3\alpha z^2 I^{1/2} + 2\beta_{MX} m \qquad \text{Eq. 3}$$

where
α = universal constant
β = function of the particular salt
m = molality

This equation fit the experimental data up to I = 0.1. In 1935 Guggenheim[13] suggested the use of a standard value of the distance of closest approach of the ions of 3.05 on the basis that this would improve the empirical success of Bronsted's equation. This resulted in the addition of a linear term to account for specific effects of the electrolyte which include ion-pairing and the effects due to size and polarizability. The Guggenheim equation is

$$\log \gamma_{\pm} = -A_\gamma |z_+ z_-| \frac{I^{1/2}}{1 + I^{1/2}} + B_{MX} m \qquad \text{Eq. 4}$$

where B_{MX} is the correction for pairwise interactions.

The above equations apply to single electrolytes, but they may be extended to give the activity coefficient of the electrolyte M'X' in a solution of mixed electrolytes.

$$\log \gamma_{\pm} = -A_\gamma |z_+ z_-| \frac{I^{1/2}}{1 + I^{1/2}} + \frac{\nu_+}{\nu_+ + \nu_-} B_{M'X} m_X +$$
$$\frac{\nu_-}{\nu_+ + \nu_-} B_{MX'} m_X \qquad \text{Eq. 5}$$

where ν is the number of ions per molecule of electrolyte. The Bronsted principle continues to receive discussion. Its defense by Scatchard and its refutation by Friedman and Wood will be presented later. At this point it is necessary to review some of the early experimental work. Three main techniques were used to study solutions of single and mixed electrolytes: electromotive force measurements made by Harned and later by Lietzke, freezing point measurements made by Scatchard and Prentiss,

and isopiestic studies made by Owen and Cook and later Robinson. Harned[14] began his electromotive force studies before the advent of the theories of Bronsted and Debye and Huckel. Using cells of the type

$$H_2 \left| HX \ (m_1), \ MX \ (m_2) \right| AgX\text{-}Ag$$
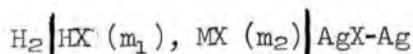
he has shown that the activity coefficient, γ_1, of the acid varies linearly with concentration according to this equation

$$\log \gamma_1 = \log \gamma_1(0) - \alpha_{12} m_2 \qquad \text{Eq. 6}$$

where $\gamma_1(0)$ = the activity coefficient of the pure acid at constant total molality, temperature, and pressure.

         α_{12} = the Harned coefficient, an empirical coefficient which may be a function of total molality

McKay's[15,16] method may be used to find α_{21} in the equation for the activity coefficient, γ_2, of the salt.

$$\log \gamma_2 = \log \gamma_2(0) - \alpha_{21} m_1 \qquad \text{Eq. 7}$$

where $\alpha_{21} m_1 = \left[\log \gamma_2(0) \ / \ \log \gamma_1(0) \right]_{m=m_2}^{m=m} + m_2 \left[\alpha_{12} \right]_{m=m_1}^{m=m} + \int_{m_2}^{m_1} \alpha_{12} \, dm$

Equations 6 and 7 are known as Harned's Rule: The log of the activity coefficient of one electrolyte in a mixture of constant total molality is directly proportional to the molality of the other component. The Harned coefficients may be used to calculate the excess free energy of mixing. This thermodynamic quantity is not usually directly measured, but the excess enthalpy of mixing may be experimentally obtained. It is the temperature derivative of the excess free energy. Lewis and Randall[17] have derived the expression for the excess free energy of mixing

$$\Delta_m G^E = -2.303 \ RT m_2 m_3 \left[\alpha_{23} + \alpha_{32} + 2(m_3 \beta_{23} + m_2 \beta_{32}) + 2/3 \ (\beta_{23} - \beta_{32})(m_2 - m_3) + \ldots \right. \qquad \text{Eq. 8}$$

where α and β are the Harned coefficients. Consequently, the expression for the excess enthalpy of mixing is

$$\Delta_m H^E = 2.303 \ RT^2 m_2 m_3 \frac{\partial}{\partial T} \Big[\alpha_{23} + \alpha_{32} + 2(m_3 \alpha_{23} + m_2 \alpha_{32}) + 2/3(\beta_{23} - \beta_{32})(m_2 - m_3) + \ldots \quad \text{Eq. 9}$$

For the mixture MX - NY (NY = 2, MX = 3), the Harned coefficients are given by the following equations.

$$\alpha_{23} = B_{NY} - 1/2 \ (\ B_{MY} + B_{NX}) \qquad \text{Eq. 10}$$

$$\alpha_{32} = B_{MX} - 1/2 \ (\ B_{MY} + B_{NX}) \qquad \text{Eq. 11}$$

if the coefficients of higher order are zero. Here B represents the specific interaction constants. The sum of α_{23} and α_{32} is

$$\alpha_{23} + \alpha_{32} = B_{NY} + B_{MX} - B_{MY} - B_{NX} \qquad \text{Eq. 12}$$

In the case where the two electrolytes have a common ion, the sum is equal to zero. This agrees with Bronsted's principle of specific ion interaction. Experimental work by Wood and Smith[18] did not yield the zero heats of mixing that would be anticipated form the above analysis.

Using the cell

$$\text{Pt-H}_2 \ (p = 1 \ \text{atm}) \Big| \ \text{HX}(m_2), \text{MX}(m_3) \Big| \text{AgX-Ag}$$
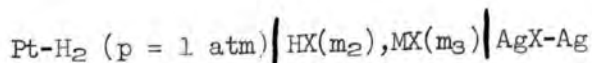
Lietzke [19,20,21] has made electromotice force studies in aqueous solutions at elevated temperatures for a variety of systems over a range of concentration. He reports his work in terms of interaction coefficients B and C. His data may be used to calculate the Harned coefficients according to the following equations.

$$\alpha_{23} = - \ 1/2.303 \Big[2(B_{23} - B_{32}) + 6(C_{223} - C_{222})I \Big] \qquad \text{Eq. 12}$$

This permits the evaluation of α_{23} at any temperature since B and C are defined by the following equations, which give rise to excess enthalpies varying linearly with temperature.

$$B_{iq} = B'_{iq} + B''_{iq}/T + B'''_{iq} \log T \qquad \text{Eq. 13}$$

$$C_{ijq} = C'_{ijq} + C''_{ijq}/T + C'''_{ijq} \log T \qquad \text{Eq. 14}$$

In interpreting the data obtained from freezing point depressions, Scatchard[22,23] has extended the Bronsted specific ion interaction principle to include triplet and pairwise oppositely-charged interactions. He obtained the following expression for the excess free energy:

$$G^E/RT = (G - G^*)/RT + \sum_i n_i(1 - \ln n_i/n_o w_o) + \sum_i n_i A_i \sqrt{I} +$$
$$\sum_{ij} n_i n_j (B_{ij} + C_{ij}\sqrt{I})/n_o w_o + \sum_{ijk} n_i n_j n_k (D_{ijk} + E_{ijk}\sqrt{I}/(n_o w_o)^2$$
$$\text{Eq. 15}$$

where
G = free energy of the system
G^* = the free energy in the standard state of zero concentration of all solutes
w_o = 1/1000 times the molecular weight of the solvent
n_o = the number of moles of solvent
n_i = the number of moles of the i'th solute.
I = ionic strength
A, B, C, D, E = parameters characteristic of the solute, solvent, temperature, and pressure

Scatchard then assumed that the short-range electrostatic forces between two like-charged ions may be neglected unless there is a third ion of opposite sign in their immediate neighborhood. Then the B and C coefficients may be determined from single salt solutions and the D and E coefficients may be determined from the single salt solution and one solution of each mixture with a common ion. This extension of Bronsted's theory gives accurate results up to 1 molal concentrations.

Owen and Cook[24] used the isopiestic method in investigating the

conclusions that the sum of the Harned coefficients is small, that their difference is independent of concentration. They concluded that α_{23} + α_{32} is not zero as assumed by Bronsted nor as small relative to α_{23} - α_{32} as predicted from Scatchard's work. The isopiestic technique has also been employed by Robinson.[25] He overcame the difficulty of making measurements on solutions of exactly the same molality by using the equations of McKay and Perring[26] to calculate the activity coefficients. Robinson[27] also used vapor pressure measurements to demonstrate the validity of the square-cross rule for excess free energies. This rule will be discussed later.

Turning again to theoretical consideration, Mayer[28] derived a more rigorous theory of ionic solutions which exhibits the Debye-Huckel limiting law. It is the only theory for which calculations have been completed enough to provide a basis for a comparison of various models in the experimental concentration range. This theory is actually an adaptation of his cluster theory of imperfect gases. The virial development of the osmotic pressure of a solution is used, provided the force potentials of the solute molecules at infinite dilution are known, to compute the deviations from ideal behavior. Then equations for the evaluation of osmotic and activity coefficients were expressed as power series. For ionic solutions, these power series converge only conditionally: the clusters must be restricted to ring types and the coulomb potential must be multiplied by $e^{-\alpha r}$, where α is finite and positive. Mayer showed that these conditions were consistent with the Debye-Huckel limiting law.[29] The large deviations of ionic solutions from ideality are due in part to the long-range nature of the mutual electrostatic potentials and in part to the large value of these potentials. The difference in energy of two oppositely-charged ions at infinite distance and at closest approach

is large enough to cause considerable ion-pairing even at concentrations of 0.1 to 0.01 molar. Poirier[30] reduced Mayer's equation to forms suitable for practical calculations of the thermodynamic functions of electrolytes. He then carried out numerical calculations and obtained good agreement with experimental values for a variety of valence types below 0.1 molar. The failure of the Mayer-Poirier equations at higher concen - trations and for higher valences is probably due to the neglect of triplet interactions.

In 1959 Friedman[31,32] applied Mayer's cluster theory to electrolyte solutions. The thermodynamic properties of a solution can be obtained from a model for the solution only if the force potentials for sets of ions in the solvent are known as functions of the center-of-mass coordinates of the ions. Friedman used the primitive model consisting of hard spheres in a continuous dielectric, to derive the equation for the excess free energy of mixing.

$$\Delta_m G^E = I^2 RTy \left[(1 - y)\right] \sum_{p=0}^{\infty} g_p Y^p \qquad \text{Eq. 16}$$

where
$\quad I$ = molal ionic strength
$\quad R$ = universal gas constant
$\quad y$ = mole fraction
$\quad g_p$ = coefficient for pairwise like-charged ion interactions
$\quad Y$ = $(1 - 2y)$

He also derived an expression for the heat of mixing.

$$\Delta_m H^E = I^2 RTy \left[(1 - y)\right] \sum_{p=0}^{\infty} h_p Y^p \qquad \text{Eq. 17}$$

where $\quad h_p = -T\left[\partial g_p / \partial T\right]$

Friedman observed that $\Delta_m G^E / I^2$ does not vanish as I approaches zero, as the Bronsted principle would predict. His equation emphasizes the contributions of like-charged ion pairs and triplets. The verification of

the Bronsted principle by some investigators may be the result of the small effects of such interactions at low concentrations. Comparison with experimental results showed roughly consistent agreement in alkali metal chlorides if the distances of approach are composed of additive contributions from a set of radii. The role of solvent structure then is not known even for Friedman's sophisticated model.

But his conclusions are merely indicative of the general state of the understanding of solute-solvent interactions. Kavanau[33] has discussed water structure and solute-water interactions in a comprehensive review. He discusses four of the models that have been proposed for the structure of liquid water. The most widely applicable is the flickering-cluster model of Frank and Wen[34] and Frank[35] which postulates that the formation of hydrogen bonds in liquid water is predominantly a cooperative phenomenon. In other words, the formation of one hydrogen-bonded pair of atoms promotes the formation of many in the neighborhood. By analogy, when one hydrogen bond breaks, several tend to break. Figure 1 represents the short-lived (10^{-10} to 10^{-11} seconds) ice-like, flickering clusters.
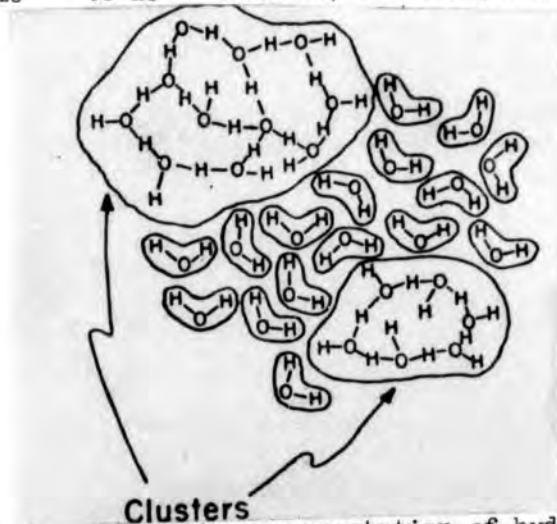

Figure 1: Schematic representation of hydrogen-bonded clusters and unbonded molecules in liquid water according to the flickering cluster theory of Frank and Wen.

Support for this model has been given in the thermodynamic calculations of Nemethy and Scheraga[36] and the near-infrared studies of Buijs and Choppin[37] who resolved the spectra by assigning three species of water: water molecules with zero, one, and two OH groups participating in hydrogen bonding. Miller[38] has shown the existence of an empirical correlation between the temperature dependence of the viscosity of water and the flickering-cluster model. Walrafen[39], on the basis of his Raman studies of water, contends that water possesses an intermolecular structure which involves tetrahedral hydrogen bonding which is disrupted by an increase in temperature. This break-down gives rise to a second species, thought to be a non-hydrogen-bonded monomer. Values for the hydrogen bond enthalpy reported by Scatchard et al.[40] and by Grunberg and Nissan[41] are in reasonable agreement with Walrafen's model. It then becomes readily apparent that there is no widely accepted, completely satisfactory model for the structure of water. The nature of ion interactions with water then becomes even more important in the quest for an understanding of water structure.

Frank and his coworkers [42,43] have described the structure of water surrounding an ion as three concentric regions. See figure 2.
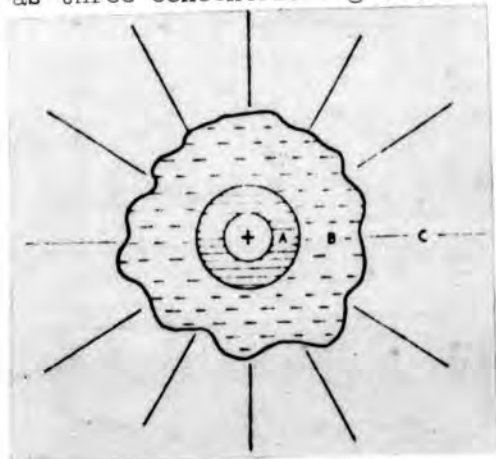

Figure 2: A simple model for the nature of ion-water interactions, Frank and Evans

Region A is the innermost structure-forming region of polarized, immobilized, and electrostricted water molecules. Region B is the intermediate structure-broken region in which the water is more random in organization than ordinary water. Region C is the outer region containing water having the normal liquid structure. On the basis of this Frank-Evans-Wen model, ions may be classified into two groups. Relatively small ions and multivalent ions, such as H^+, Li^+, and Na^+, are said to have net structure-making effects, that is, their high electric fields immobilize and electrostrict nearby water molecules making region A larger than region B. Large monovalent ions, such as K^+ and Cs^+ are considered to be structure-breakers. Dipole-dipole repulsions weaken their electrostatic field to such an extent that region B becomes larger than region A.

The earliest reports of heats of mixing came from Young, and Smith[44]. Young and his coworkers[45,46] have determined heats of mixing for many one-to-one electrolytes at 25 C. and one molal concentration. Their work illustrated that the heats of mixing are independent of a common ion, if one is present. Friedman made a similar observation. Furthermore, from the data obtained in these mixings, $\Delta_m H/I$ does not decrease as required by the Bronsted principle. Young, Wu, and Krawetz[47] have shown that by utilizing the classifications of Frank and Evans, the sign of the heat of mixing can be predicted. When ions of the same classification are mixed, the heat of mixing is endothermic, and when ions of unlike classification are mixed, the heat of mixing is exothermic.

For four single electrolytes which have only two different cations and two different anions, there are six possible mixings. Krawetz[48] has shown empirically that the sum of the experimental heats of mixing represented by the sides of the square in figure 3 equals the sum of the experimental heats of mixing represented by the diagonals. This is
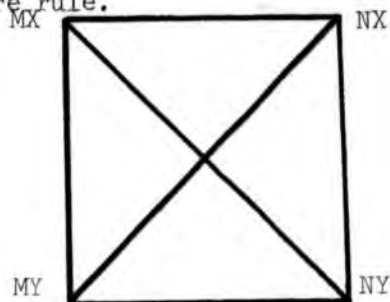
known as the cross-square rule.

Figure 3: The Cross-square Rule fo Heats
of Mixing

Bottcher[49] has shown that this rule holds if the heats of mixing of the
cations in the presence of each anion are nearly equal and the heat of
mixing of the cations in the presence of an equal molal mixture of both
anions has an intermediate value.

Ste n and coworkers[50,51,52] have studied the heat of mixing for sev-
eral systems at varying concentrations and temperatures. The results
were interpreted in terms of Bronsted's principle. Their non-zero heats
were explained as deviations. They observed that agreement with the
principle improved as the concentration decreased.

Wood and Smith[53] studied the concentration dependence of the heats
of mixing of aqueous one-to-one electrolytes in the range of 0.1 to 0.5
molal at 25°C. They found that like-charged ion pai s contribute signi-
ficantly to the heats of mixing; this refuted Bronsted's theory of speci-
fic ion interaction. Their results did agree with Friedman's application
of Mayer's cluster theory. Wood and Anderson[54] measured still mo e
systems and derived a set of general equations which allows the predict-
ion of the total excess free energy and the relative apparent molal heat
content of a multicomponent mixture of electrolytes of the same charge
type from the knowledge of only the thermodynamic properties of the
component pure electrolyte and the common-ion mixed electrolyte solutions.

$$G^E_{MIX} = \sum_{i,j} y_{R_i} y_{X_j} G^E_{R_iX_j} + RTI^2 \sum_{h>i} y_{R_i} y_{R_h} y_{X_j} g^{X_j}_{R_hR_i} +$$

$$\sum_{j>k} y_{X_j} y_{X_k} y_{R_i} g^{R_i}_{X_jX_k} \qquad \text{Eq. 18}$$

$$H^E_{MIX} = \phi^{MIX}_L = \sum_{i,j} y_{R_i} y_{X_j} L^{R_iX_j} + RTI^2/m \sum_{h>i} y_{R_h} y_{R_i} y_{X_j} h^{X_j}_{R_hR_i} +$$

$$\sum_{j>k} y_{X_j} y_{X_k} y_{R_i} h^{R_i}_{X_jX_k} \qquad \text{Eq. 19}$$

where y_{R_i}, etc. = component mole fraction = $m_{R_i}/\sum_k m_{R_k}$

$g^{X_j}_{R_hR_i}$ and $h^{X_j}_{R_hR_i}$ = interaction parameters of ions R_h and R_i in the presence of common ion X_j

$G^E_{R_iX_j}$, $\phi^{R_iX_j}_L$ = pure component properties

Wood and Anderson also studied the heats of mixing of anions in the presence of a common cation to determine whether the classification of ions was based on size or structural properties. Their work led them to the conclusion that it is the latter and that the heat of mixing depends primarily on the structure of water surrounding the like-charged ions. The results of their heats of mixing for tetraalkylammonium chlorides led Wood and Anderson to report that the tetrapropylammonium ion is a structure maker, the tetramethylammonium ion is a structure breaker, and the tetraethylammonium ion is a borderline case, behaving as a structure breaker when mixed with an alkali metal ion and as a structure maker when mixed with tetramethylammonium ion. Wood, Patton, and Ghamkar[55] recently studied the heats of mixing of unsymmetrical electrolytes. Their results also agreed with Friedman's ionic solution theory. Anderson and Petree[56] recently studied the temperature dependence of the heats of mixing of aqueous electrolytes with a common anion. The heat ofmixing of systems involving the sodium ion showed a dependence on temperature. The sodium

ion has been recognized as a borderline ion.   On the basis of their results they have postulated that the interaction which affects the heat of mixing occur in the interface between   regions A and B in the Frank-Evans-Wen model.

This incomplete review has traced major developments in theory and experimental efforts which verified or refuted the theories.

RESEARCH PROPOSAL

It was apparent in the documentation of the work that has been done in the field of aqueous electrolyte solutions that little has been done in the study of the temperature dependence of the heats of mixing. Yet the structure of water has been shown to be strongly dependent on temperature.[57,58] Therefore, the temperature dependence of the heats of mixing should prove useful in understanding the role water plays in influencing the specific ion interactions. Furthermore, the excess free energy of mixing at an elevated temperature can be calculated from the excess free energy at $25°C$ and the heat of mixing as a function of temperature acco ding to this equation[59]:

$$\Delta_m G^E(t_2) = \Delta_m G^E(t_1) + \Delta C_p(m) \bigg]_{t_2}^{t_1} \Delta T - \Delta_m S(t_1) \Delta T - T_2 \Delta C_p(m) \bigg]_{t_1}^{t_2} \ln \frac{T_2}{T_1}$$

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

Thus, kn owledge of the heat of mixing as a function of temperature would make it possible to calculate thermodynamic properties from as few parameters as possible.

Anderson and Petree have already postulated that the interactions which affect the heat of mixing take place at the interface between the primary hydration sphere and the disordered water region. To further this study of the temperature dependence of the heats of mixing, it was proposed to determine the heats of mixing of the systems, at one molal, $CsCl-LiCl-H_2O$, $CsCl-NaCl-H_2O$, $CsCl-KCl-H_2O$ at $60°$ and $80°$ and $HCl-KCl-H_2O$ at $60°$.

EXPERIMENTAL

CALORIMETER

As the heats of mixing of electrolyte solutions involving a common ion are small, a calorimeter with a sensitivity in the microdegree range was desired. The isothermal, double calorimeter designed for the measurements has been described elsewhere.[60]

PROCEDURE

The experimental procedure for carrying out heats of mixing has been reported previously.[61,62,63]

MATERIALS

Stock solutions of Mallinckrodt Analytical Reagent sodium chloride, potassium chloride, and concentrated hydrochloric acid, Research Inorganic Chemical lithium chloride and Penn Rare Metals Division cesium chloride were prepared and analyzed as described previously.[64,65]

TREATMENT OF DATA AND RESULTS

The experimental heats of mixing were fitted by the method of least squares to the two-parameter form of the equation proposed by Friedman.[66]

$$\Delta_mH \text{ (cal/kg solvent)} = RTI^2 y(1-y) \left[h_0 + (1 + 2y)h_1 \right] \qquad \text{Eq. 21}$$

where h_0 is the magnitude of the interaction, h_1 is a measure of asymmetry from the quadratic function with respect to mole fraction, and y is the mole fraction of the component having the largest molecular weight. The parameters for equation 21 are listed in table 1. The details of this

computer fit have already given in the literature.[67] The computer print outs for each set of mixings are included in Appendix A.

ERRORS

An anlysis of the errors in these data has been given.[68] These include inherent errors in the concentration and purity of the solutions and experimental procedure errors in slope extrapolation, electrical heat input, and the heat of opening of the pipet.

TABLE I

Aqueous Heats of Mixing Parameters

Mixture	I	25°C	60°C		80°C	
		RTh_0 [a]	RTh_0	RTh_1	RTh_0	RTh_1
CsCl-LiCl	1.0	-194.6	-176.4 ± 2.7	-5.9 ± 3.8	-170.0 ± 5.0	-10.0 ± 6.0
CsCl-NaCl	1.0	-34.8	-46.7 ± 0.7	---	-51.1 ± 0.9	-1.2 ± 0.2
CsCl-KCl	1.0	6.4	1.38 ± 0.09	---	1.50 ± 0.8	---
HCl-KCl	1.0	-15.0	-13.3 ± 0.8	---		

(a) Y.C. Wu, M.B. Smith, and T.F. Young, J. Phys. Chem., 69, 1870 (1965).

(b) Note: the units for RTh_0 are cal/kg solvent

DISCUSSION

Wood and Smith[69] pointed out in their first paper the importance of the measurement of the heats of mixing of electrolyte solutions in the study of specific ion interactions. If the measurements are made at constant ionic strength, then the effects of the ionic atmosphere are cancelled. If the measurements are made with a common ion, the effects of oppositely charged ion-pairs cancel. Finally, these measurements are independent of the common ion. According to Anderson and Petree the measurements of heats of mixing as functions of temperature should provide information about the nature of the solute-solvent interaction. It has already been shown[70] that the heat of mixing is primarily influenced by the water structure about the like-charged ions. If the mixing involves two ions with the same structural properties, the heat of mixing will be endothermic, while the heat of mixing of ions of unlike structural properties will be exothermic. Figure 4 shows the RTh_0 values plotted against temperature. The heat of mixing of HCl-KCl is negative as would be expected since H^+ is a small structure-maker and K^+ is a medium-sized structure-breaker. It shows no temperature dependence up to $60^{\circ}C$. However, the three mixings involving the cesium ion do exhibit a dependence on temperature. Petree[71] has also observed temperature dependence in mixings involving the sodium ion. These results were interpreted in terms of a gradual change with temperature of the structural properties of the sodium ion, and it was postulated that the interactions which affect the heat of mixing occur in the interface between the primary hydration sphere and the region of disordered water. The apparent insensitivity of the primary hydration sphere up to temperatures of about $130^{\circ}C$. has been reported by both Walrafen[72] on the basis of his Raman studies and by Ackerman[73] on the basis of heat

capacity studies of aqueous alkali halides. Ackerman has also concluded that theregion of disordered water is being destroyed from 30°to 130°C. The outermost region, bulk water, is so temperature sensitive according to studies made by Bonner and Woolsey[74] that none of the heats of mixing could be constant were this the region of solute-solvent interaction.

The present work lends further support to the postulate that the A-B interface is of greatest importance during the mixing process. It is postulated that the cesium ion is also a borderline ion. It has been classified by Frank and Evans [75] as a structure-breaker. However, its behavior in mixings with lithium, potassium, and sodium ions may be interp eted as a increased tendency toward structure making properties as the temperature increases. Referring again to figure 4, when Cs^+ is mixed with Li^+, a small structure-maker, the heat of mixing is exothermic. It may be observed that its heat is becoming less negative as temperature increases. This may indicate that the cesium ion is becoming less of a structure-breaker. An endothermic heat is observed for the Cs^+-K^+ mixing in which both the ions are structure-breakers. Here, the heat is becoming less positive with increasing temperature. Again, this may indicate that the cesium ion is becoming less of a structure-breaker. Finally, then Cs^+ is mixed with Na^+, the heat is endothermic, but it becomes more negative as the temperature increases. This is the only reported instance in which the absolute magnitude of the heat of mixing increases with temperature. If the interpretation for the behavior of the sodium ion in previous work is accepted, then the negative heat which becomes more negative may best be explained by a divergence in the structural properties of the two ions. The sodium is a borderline structure-maker becoming a structure-breaker, and the cesium ion is a borderline structure-breaker becoming a structure-maker. The fact that Cs^+ does show

apparently changing structural properties is additional evidence in support of the idea that the major effects on the heats of mixing occur at the interface between the primary and secondary hydration spheres. However, still more ions should be investigated to verify or refute these conclusions.

Figure 4: Temperature Dependence of Heats of Mixing
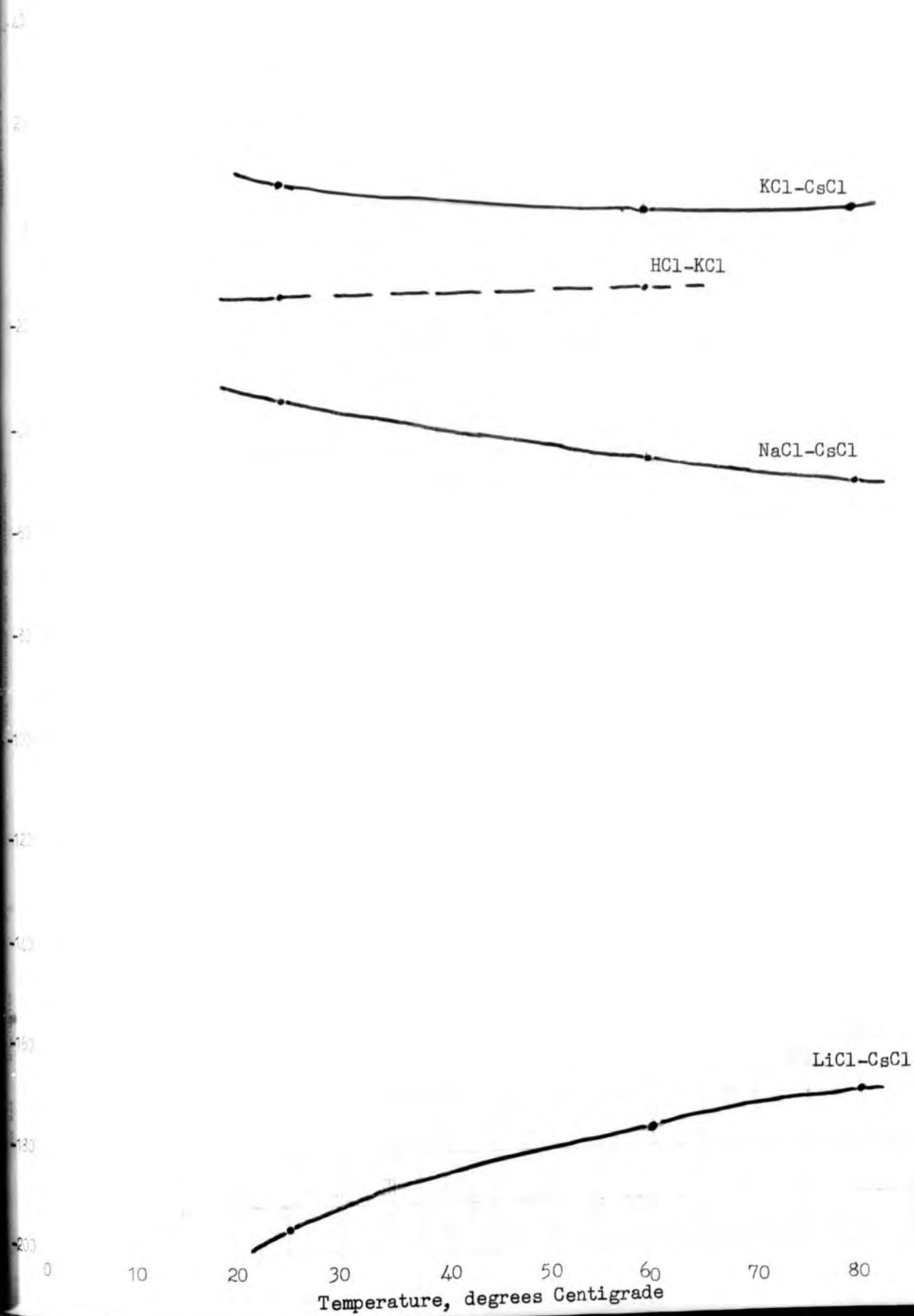
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(64) See footnote (1).

(65) See footnote (54).

(66) See footnote (31).

(67) See footnote (60b).

(68) See fotonote (60b).

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APPENDIX A

HEAT OF MIXING DATA: COMPUTOR FIT

Heat of Mixing: LiCl-CsCl
m = 1.0   T = 60°C.

A = 176.4308 SA =   1.2049 B =   5.8893 SB =   1.7270
SYBC = 0.0447

DELH	HCALC	ERROR	XF	XI	W	F2	F3
2.17160	2.19204	-0.02044	0.052750	0.000000	1.00000	0.0120641	0.0107914
1.99350	1.93222	0.06128	0.102480	0.052750	1.00000	0.0107053	0.0073817
1.75860	1.70511	0.05349	0.149330	0.102480	1.00000	0.0095069	0.0047190
1.87090	1.85905	0.01185	0.885380	0.940390	1.00000	0.0107712	0.0070179
1.73650	1.68452	0.05198	0.833050	0.088538	1.00000	0.0096891	0.0042329
1.56370	1.50366	0.06004	0.784000	0.833050	1.00000	0.0085898	0.0020107
2.20479	2.24782	-0.04303	0.052420	0.000000	1.00000	0.0123708	0.0110739
1.97470	2.00347	-0.02877	0.102370	0.052420	1.00000	0.0110998	0.0076635
1.75455	1.77894	-0.02439	0.149770	0.102380	1.00000	0.0099188	0.0049171
2.10412	2.15611	-0.05199	0.946290	1.000000	1.00000	0.0125960	0.0112430
1.93115	1.93914	-0.00799	0.895900	0.946290	1.00000	0.0002479	0.0076978
1.74262	1.76491	-0.02229	0.840400	0.895900	1.00000	0.0101690	0.0049611

XMI =   10.49424   XM2 =   0.49166
AO =   176.9044   SAO =   1.6783
SUM ERROS SQUARED = 0.433E-01   F =   11.6291
SYB =   0.0627

Heat of Mixing: LiCl-CsCl

m = 1.0   T = 80°C.

A = 169.5778 SA = 1.5401 B = 9.8370 SB = 1.9852

SYBC = 0.0405

DELH	HCALC	ERROR	XF	XI	W	F2	F3
2.14780	2.16445	-0.01665	0.053170	0.000000	1.00000	0.0121347	0.0108443
1.69800	1.69609	0.00191	0.152020	0.104260	1.00000	0.0097268	0.0047414
1.54210	1.49641	0.04569	0.197300	0.152020	1.00000	0.0086727	0.0026135
2.02960	2.01418	0.01542	0.946410	1.000000	1.00000	0.0125264	0.0111838
1.75710	1.81637	-0.05927	0.896260	0.946410	1.00000	0.0111546	0.0076447
1.97840	1.95745	0.02095	0.947910	1.000000	1.00000	0.0121758	0.0109073

XM1 = 6.26070   XM2 = 0.48553

AO = 167.4989   SAO == 3.5313

SUM ERROS SQUARED = 0.468E-01   F = 24.5539

SYB = 0.0968

Heat of Mixing: NaCl-CsCl
m = 1.0   T = 60°C.

A = 46.6892 SA = 0.2783   B = -0.3622 SB = 0.3775
SYBC = 0.0077

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.56428	0.57241	-0.00813	0.053120	0.000000	1.00000	0.0123457	0.0110341
0.51373	0.51166	0.00207	0.103460	0.053120	1.00000	0.0110177	0.0075674
0.46639	0.45514	0.01125	0.150930	0.103460	1.00000	0.0097856	0.0048067
0.59870	0.59700	0.00170	0.945859	1.000000	1.00000	0.0126090	0.0113236
0.52893	0.53479	-0.00586	0.894370	0.945850	1.00000	0.0113941	0.0077530
0.47102	0.46974	0.00128	0.846710	0.894370	1.00000	0.0100236	0.0048331

XM1 = -42.46876 XM2 = 0.50194

AO = 46.6958 SAO == 0.2760
SUM ERROS SQUARED = 0.290E-03   F = 0.9213
SYB = 0.0076

Heat of Mixing: NaCl-CsCl
m == 1.0   T = 80°C.

A =   51.1263 SA =   0.3451 B =   1.2461 SB =   0.4448
SYBC =   0.0092

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.62520	0.63356	-0.00836	0.052200	0.000000	1.00000	0.0121274	0.0108613
0.52530	0.51155	0.01375	0.152250	0.103210	1.00000	0.0098877	0.0048363
0.45196	0.45408	-0.00212	0.198340	0.152250	1.00000	0.0088172	0.0026351
0.65390	0.65865	-0.00475	0.943420	1.000000	1.00000	0.0131675	0.0116774
0.62762	0.63001	-0.00239	0.946110	1.000000	1.00000	0.0112389	0.0125966
0.56796	0.56108	0.00688	0.895680	0.946110	1.00000	0.0111604	0.0076290

XM1 =   14.18201   XM2 =   0.49391
AO =   50.8421 SAO =   0.5079
SUM ERROS SQUARED = 0.100E-02   F =   7.8500
SYB =   0.0142

Heat of Mixing: KCl-CsCl
m = 1.0   T = 60°C.

A = 1.3595 SA = 0.0397 B == -0.0760 SB = 0.0627
SYBC = 0.0010

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.01342	0.01413	-0.00071	0.108070	0.055230	1.00000	0.0108808	0.0072733
0.01379	0.01283	0.00096	0.158530	0.108070	1.00000	0.0096934	0.0045250
0.01715	0.01737	-0.00022	0.948130	1.000000	1.00000	0.0121690	0.0109066
0.01510	0.01390	0.00120	0.852500	0.899230	1.00000	0.0099454	0.0050070
0.02008	0.02024	-0.00016	0.863570	0.929840	1.00000	0.0144157	0.0084594
0.01175	0.01267	-0.00092	0.818940	0.863570	1.00000	0.0091316	0.00333331

XM1 = -5.47878   XM2 = 0.51394

AO = 1.3810 SAO = 0.0371
SUM ERROS SQUARED = 0.516E-05   F = 1.4673
SYB = 0.0010

Heat of Mixing: KCl-CsCl
m = 1.0   T = 80°C..

A =   1.4659 SA =   0.2710 B =   -0.3178 SB =   0.3467
SYBC =   0.0067

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.01735	0.01438	0.00297	0.055990	0.000000	1.00000	0.0121509	0.0107902
0.00888	0.01278	-0.00389	0.159500	0.108900	1.00000	0.0096894	0.0044882
0.01156	0.01280	-0.00123	0.211860	0.159500	1.00000	0.0092273	0.0022943
0.02974	0.02180	0.00794	0.946480	1.000000	1.00000	0.0124598	0.0111261
0.01481	0.02172	-0.00692	0.946290	1.000000	1.00000	0.0124166	0.0110828

    XM1 =   -1.09003   XM2 =   0.55241
AS =   1.5061   SAO =   0.2620
SUM ERROS SQUARED =   0.175E-03   F =   0.8400
SYB =   0.0066

Heat of Mixing: HCl-KCl

m = 1.0   T = 60°C.

A =   13.3503   SA =   0.3457   B =   0.2778   SB =   0.4541

SYBC =   0.0099

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.16878	0.15967	0.00911	0.943839	1.000000	1.00000	0.0121850	0.0108161
0.15717	0.15855	-0.00138	0.944270	1.000000	1.00000	0.0120999	0.0107512
0.13068	0.14543	-0.01475	0.890420	0.944270	1.00000	0.0010475	0.0073950
0.13252	0.13935	0.00317	0.840100	0.891420	1.00000	0.0097828	0.0047103
0.15555	0.016176	-0.00619	0.051910	0.000000	1.00000	0.0118949	-.0106599
0.14414	0.14456	-0.00042	0.101140	0.051910	1.00000	0.0106743	0.0048612
0.14288	0.13095	0.01193	0.148480	0.101140	1.00000	0.0097072	0.0048612

XM1 =   16.52668   XM2 =   0.3202

AO =   13.3070   SAO =   0.3202

SUM ERROS SQUARED =   0.531E-03

SYB =   0.0094

APPENDIX B

PREDICTION OF HEAT OF MIXING AT ELEVATED TEMPERATURES

Several different methods for calculating the excess free energy of mixing have been reviewed in this paper. A practical test of some of these methods is their ability to predict the heat of mixing at some temperature other than 25°C. Lewis and Randall have derived an expression for the excess free energy of mixing:

$$\Delta_m G^E = -2.303 \ RT m_2 m_3 \left[\alpha_{23} + \alpha_{32} + 2(m_2 \beta_{32}) \right]$$

In Table III, J. Phys. Chem., 64, 112, Harned gives the value at 25°C. for the system HCl-KCl

$$\alpha_{12} + \alpha_{21} + 2m_2 \beta_{21} = -0.0104$$

Substitution of this number in the above expression gives a value for the excess free energy at 25°C. of +3.55 cal/kg solvent. Extrapolation of Harned's data gives a value at 60°C. of

$$\alpha_{12} + \alpha_{21} + 2m_2 \beta_{21} = -0.0146$$

which, when substituted, gives a free energy of +5.56 cal/kg solvent.

Lietzke has derived equations for the Harned coefficients:

$$\alpha_{23} = \left[2(B_{23} - B_{22}) + 6(C_{223} - C_{222}) \right] I$$
$$\alpha_{32} = \left[2(B_{23} - B_{33}) + 6(C_{233} - C_{333}) \right] I$$
$$\beta_{32} = \left[3(C_{333} + C_{223} - 2C_{233}) \right] I^2$$

where $B_{iq} = B'_{iq} + B''_{iq}/T + B_{iq}''' \log T$

$$C_{ijq} = C'_{ijq} + C''_{ijq}/T$$

From Table IX, J. Phys. Chem., 72, 4408, the values for the B and C parameters at 25°C. are, for the system HCl-KCl,

$$B_{23} = -0.4093$$
$$B_{22} = -1.5879$$
$$C_{223} = -0.001222$$
$$C_{222} = -0.009703$$
$$B_{33} = -0.0149227$$
$$C_{233} = +0.007259$$
$$C_{333} = 0.00389896$$

Therefore, $\qquad \alpha_{23} = -1.-456$

$$\alpha_{32} = -0.3772$$

$$\beta_{32} = +0.0154$$

and $\qquad \alpha_{23} + \alpha_{32} + \beta_{32}m_2 = -1.4151$

Hence, at 25°C. $\quad \Delta_m G^E = +482.5$ cal/kg solvent.

At 60°C. the B and C parameters are

$$
\begin{aligned}
B_{23} &= -0.4078 \\
B_{22} &= 02.0080 \\
C_{223} &= -0.001781 \\
C_{222} &= -0.004984 \\
B_{33} &= -0.0149227 \\
C_{233} &= 0.001422 \\
C_{333} &= 0.00389896
\end{aligned}
$$

Therefore, $\qquad \alpha_{23} = -1.398$

$$\alpha_{32} = 0.3476$$

$$\beta_{32} = 0.00095$$

Thus at 60°C. Lietzke would predict a free energy of mixing of +400.0 cal/ kg solvent.

The data obtained for the enthalpy of mixing of the HCl-KCl system at 60°C. may be used to test these two predictions, using the equation

$$\Delta_m G^E(60) = \Delta_m G^E(25) + \Delta_m Cp\Big|_{t_1}^{t_2} - \Delta_m S^E(25)\Delta T - T_2 \Delta_m Cp\Big|_{t_1}^{t_2}\ln T_2/T_1$$

where $\quad \Delta_m Cp\Big|_{t_1}^{t_2} = \dfrac{\Delta_M H(t_1) - \Delta_m H(t_2)}{\Delta T}$

Assuming Harned's value at 25°C. for the excess free energy of mixing and using the data for the enthalpy of mixing in Table I, this paper, the free energy of mixing at 60°C. should be +5.83 cal/kg solvent. This is a reasonable prediction and agrees well with Harned's own data. If the value at 25°C. of Lietzke is assumed, the free energy at 60°C. should be +484.8. This is not at all reasonable and does not even agree very well with the predicted value. It is obvious that the vagueness and inconsistency of Lietzke's data makes it far less reliable than Harned's.