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Heats of mixing at 40°, 60°, and 80°C were determined for the following mixtures: $BaCl_2$-$MgCl_2$-H_2O; $BaCl_2$-$CaCl_2$-H_2O; $BaCl_2$-$SrCl_2$-H_2O; and $SrCl_2$-$CaCl_2$-H_2O (only at 60°C). Temperature dependence was observed for all the mixtures, although that dependence was practically insignificant for the $BaCl_2$-$SrCl_2$-H_2O mixture.

The results are interpreted in terms of ion-solvent structural effects. It was found that an interesting correspondence exists between ion-solvent interactions and the total spectroscopic solvation numbers of the cations studied. An attempt was also made to correlate the difference-in-size of the cations in a mixture with the ion-solvent structural effects.

Excess Gibbs free energies of mixing were calculated for the $SrCl_2$-$CaCl_2$-H_2O mixture at 25° and 60°C. The signs of these energies were found to be negative at all concentrations studied.

TEMPERATURE DEPENDENCE OF THE HEATS OF MIXING

AQUEOUS ALKALINE EARTH CHLORIDES

by

Basil G. Vani

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APPROVAL PAGE

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m   molality (moles/kg solvent)

γ activity coefficient

α Harned's coefficient

y   molality fraction

G   Gibb's free energy

H   enthalpy (or simply heat)

S   entropy

I   ionic strength

R   the gas constant

T   temperature (in degrees Kelvin)

UNITS

molality	moles/kg solvent
$\Delta_m H$	calories/kg solvent
$\Delta_m S$	calories/kg solvent/degree absolute
$\Delta_m G$	calories/kg-solvent
RTg_o	calories/kg-solvent
r (radius)	Angstroms

THESIS PROPOSAL

Two isolated systems in thermal equilibrium at constant pressure and coupled together do not normally exchange heat. Another way of saying the same thing is that the net change in heat between the coupled systems (at the same temperature) is zero. However, it is commonly known that when two or more electrolyte solutions are mixed together at the same temperature the net change in heat is in fact not zero, but some real quantity.

This real value of heat has been explained variously as resulting from interactions between ions or interactions between ions and solvent molecules. Wood and Anderson[1] studied heats of mixing alkaline earth halides at 25°C and interpreted their results in terms of such interactions. In using the Young-Wu-Krawetz[2] model they classified the alkaline earth cations as structure makers in the face of solvent molecules, i.e.

$$M^{2+} + \text{solvent} = M^{2+}(\text{solvent.})$$
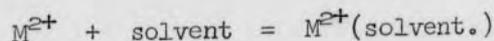
With this information it was felt that temperature dependence studies of the alkaline earth chloride solution mixtures would further elucidate the kinds of interactions that take place in water and also increase the general knowledge about the structure of water in a multicomponent aqueous solution. The size of a particular ion has had the peculiar effect of either enhancing the structuring of water

molecules about itself or disrupting that structuring. Of particular interest then in the case of alkaline earth cations is whether the size and charge effects are complimentary.

It was felt studies at 40°, 60°, and $80^\circ C$ would demonstrate if there were any temperature dependence of the heats of mixing and if such dependence enhanced size and/or charge influence in ion-water interactions. The following mixings were suggested: $BaCl_2$-$MgCl_2$-H_2O; $BaCl_2$-$CaCl_2$-H_2O; $BaCl_2$-$SrCl_2$-H_2O; and $SrCl_2$-$CaCl_2$-H_2O. The method that was to be employed in studying these systems was calorimetry. The salt solutions were to have a concentration of one molal or an ionic strength of 3 upon mixing.

Heats of mixing is a thermodynamic parameter and temperature dependence of such a parameter should be valuable in calculating other thermodynamic parameters. Hence the studies at the suggested temperatures should find ready use in thermodynamic studies and in particular could be of immense value in problems associated with the desalination of sea water.

INTRODUCTION

Heats of mixing aqueous electrolyte solutions as a subject falls in the domain of equilibrium properties of a multicomponent solution. Equilibrium should be emphasized because observations are made when all parts of the system are quasi-static before mixing and after mixing. When two aqueous electrolyte solutions which are in thermal equilibrium are summarily mixed together, a small amount of heat is generated or absorbed. This quantity of heat has been ascribed to the kinds of interactions that take place in solvent water.

Many workers[2,3,4,5] have found that the determination of the heats of mixing is an excellent way of studying the kinds of ion interactions in aqueous electrolyte solutions. The mixings in these works have been done at constant ionic strength, i.e.

$$MX\ (I)\ +\ NX\ (I)\ =\ Mixture(I)$$
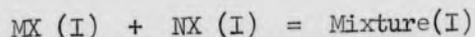
This procedure, which is repeated in this work, has the advantage that terms attributable to Debye-Huckel theory which are ionic strength dependent cancel out. See later discussions. Furthermore in the face of the common anion, X, only heat generated or absorbed from like-charged pair and higher order interactions is of importance.

Some workers, namely Anderson and coworkers[4,5] have used temperature dependence of the heats of mixing aqueous electrolyte solutions as a way of elucidating the ion-solvent interactions in aqueous electrolyte

solutions. This work is intended to compliment their line of thought on electrolyte solutions.

For a good understanding of the mixing processes of electrolyte solutions it is important to review some historical backgrounds of the theories of ion interactions in aqueous electrolyte solutions. Since 1923 when Debye and Huckel[6] applied the Boltzmann Law to the interactions of ions in solution, particularly in dilute solutions, aqueous electrolyte solutions have been subject to many thermodynamic studies. Based purely on the Coulomb law, Bronsted[7] had previously added the concept of specific interactions between ions in aqueous electrolyte solutions. This concept asserted that only interactions of ions of opposite charge were of importance, and interactions between like charge ions were weak because of mutual repulsion. Some of the more important concepts that came up in the course of the early studies were ionic strength, activity, and activity coefficient.

A development which was equally as important as the ion-ion interaction phenomena, but which has only recently gained considerable attention is the ion-solvent (water) interaction. This was introduced in the Debye-Huckel theory in the form of medium of known dielectric constant. This approach was adequate only for concentration dependence of properties of very dilute solutions. In 1919 Bjerrum[8] had first pointed out that solvation must be explicitly taken into account as soon as ions affect an appreciable proportion of solvent molecules. Stokes and Robinson[9] treated concentrated solutions using the concept of solvation.

Ion-solvent interaction is of primary importance in determining the individual molar properties of salts in solution, for example, entropies, specific heats, and molar volumes. The concept of ordering and disordering of solvent molecules by ions has been reviewed extensively by Millero.[10]

Some of the experimental methods that have been used to study ionic solution theories and to calculate thermodynamic functions are EMF measurements, isopiestic method, solubility of slightly soluble salts, and calorimetry. In this work, the latter method has been employed to measure the excess heat of mixing in the manner as first introduced by Young, Wu, and Krawetz.[2]

Apart from the purely thermodynamic interests in the interaction in electrolyte solutions, knowledge of the properties of electrolyte solutions can be useful in the technology of the deionization of sea-water. This of course is a worthy cause since man's potable water supply is quite limited, a fact which becomes quite clear in the summer months! Another area where knowledge of mixed aqueous electrolyte solutions can be of current interest is in the pollution control of lakes, streams, and rivers, and specifically in the deionization of these natural sources of water before they can be used for man's consumption, or as breeding environment for fish and other wildlife.

THEORETICAL SECTION

The two characteristic components of aqueous electrolyte solutions
are the ions of opposite charge and the water molecules, all of which
interact. The unique property of electrolyte solutions is attributable
to the long range nature of the coulomb forces between the ions. The
coulomb energy varies inversely with the interionic distance. As a
result, dilute solutions yield insignificant coulomb potentials.

The simplest model of dilute aqueous electrolyte solutions is a
mixture of charged hard spheres in a continuous dielectric medium,
namely the solvent water. This model in essence is what has often been
referred to as the "primitive model".[11] The molecular nature of water
is completely ignored in this representation. The effect of the ions
on the hydrogen-bonded structure of water, ion-water dipole interactions
and all other features related to the molecular nature of water is
treated in terms of averages, that is, average values of parameters
for ionic interactions.

The Debye-Huckel theory, which has been mentioned in the intro-
duction, is an approximation to the primitive model. It is based on
the following physical assumptions:[12]

1. Violation of the primitive model is only caused by the
the coulomb potential of the hard charged spherical ions.
Short range interactions are not considered important in the
first order.

2. The Poisson equation of electrostatics can on a molecular scale relate the potential (ion) in the solution to the charge density.

3. The charge density, at a distance r from an ion, is determined by Boltzman distribution of positive and negative ions around a given central ion, in agreement with the charges of ions and the electrostatic potential.

4. The resulting Poisson Boltzman equation can be expanded in series retaining only those terms in which the potential is linear in charge thus:

$$\nabla^2 \Psi_j = \frac{-4\pi}{D} \sum n_i^o z_i e^{-Z_j e \Psi_j / kT}$$

where Ψ_g = potential

$z_j e$ = central ion charge

$z_i e$ = ion charge

kT = thermal energy

D = dielectric constant seen by the ions.

The Debye-Huckel theory describes the situation fairly well in dilute, single electrolyte solutions. However, from the first assumption above it becomes quite limited in solutions of moderate concentrations. In this case Bronsted theory of specific ion interaction can be invoked to aid in the theoretical interpretation. This theory asserts that only interactions between ions of opposite charge are important and those between like charges are small or unimportant.

From the knowledge of properties of single electrolyte solutions, considerable effort has been directed toward obtaining properties of mixed electrolyte solutions. Guggenheim[13] has extended Bronsted's theory of specific ion interaction to give

$$\log \gamma_2 = \frac{-A_\gamma m^{\frac{1}{2}}}{1 + m^{\frac{1}{2}}} + m_2 B_{NY} + \tfrac{1}{2}m_3(B_{NX} + B_{MY})$$

$$\log \gamma_3 = \frac{-A_\gamma m^{\frac{1}{2}}}{1 + m^{\frac{1}{2}}} + m_3 B_{MX} + \tfrac{1}{2}m_2(B_{NX} + B_{MY})$$

for a mixture of 1-1 electrolytes of MX-NX (MX = 3, NX = 2) where A_γ is the Debye-Huckel coefficient, γ_2 is the activity coefficient of component 2, γ_3 is the activity coefficient of component 3, m_2 is the molality of component 2, m_3 is the molality of component 3 and m is the sum of m_2 and m_3. The specific ion interaction coefficients (B_{NX}, etc.) are found experimentally from their respective single electrolyte solutions. The above equations have been found to follow experimental data quite nicely up to about 0.1m. The Bronsted-Guggenheim B-coefficients are related to the Harned coefficients (see Literature Review) thus

$$\alpha_{23} = B_{NY} - \tfrac{1}{2}(B_{MY} + B_{NX})$$
$$\alpha_{32} = B_{MX} - \tfrac{1}{2}(B_{MY} + B_{NX})$$

From these equations it is seen the sum of the Harned coefficients equals zero in the common ion case (i.e. X = Y):

$$\alpha_{23} + \alpha_{32} = B_{MX} + B_{NY} - B_{MY} - B_{NY} = 0.$$

From Young's mixture rule (see Literature Review), the Gibb's free energy can be written as

$$\Delta_m G^E = \Delta_m G - \Delta_m G^I$$

where $\Delta_m G$ and $\Delta_m G^I$ are the total and ideal free energy of mixing, respectively, when the total ionic strength, temperature and volume are held constant. By straightforward thermodynamic reasoning and using the generalized Harned's rule, the preceding free energy expression can be written as[14]

$$\Delta_m G^E = -2.303 \ RTm_2 m_3 (\alpha_{23} + \alpha_{32} + 2(m_3 \beta_{23} + m_2 \beta_{32}))$$

$$+ \frac{3}{2} (\beta_{23} - \beta_{32}) (m_2 - m_3) \ . \ . \ .$$

By limiting mixing at constant total ionic strength the terms related to Debye-Huckel limiting law are wiped out and therefore do not enter into the above equations.

Departing from the idea of rules and semi-empirical expressions pertaining to mixtures of electrolyte solutions, efforts have been made in applying statistical theory to the primitive model. Such an approach is provided by the cluster expansion theory. The cluster expansion feature is shared with certain theories of imperfect gases, and this approach was first applied to ionic solutions by Mayer.[15] There are two important features to the Mayer theory in expressing the logarithm of the activity coefficient of an ion: first, the reference state is set at infinite dilution and the working state is set at the desired concentration; second, the way ions interact in solution is treated in combinatorial fashion, i.e., statistically.

A detailed and elegant treatment of the Mayer theory has been given by Friedman. In comparing experimental excess free energy of mixing with that of theory he writes

$$\Delta_m G^E(y,I) = RTI^2 y(1-y)(g_0 + g_1 Y + g_2 Y^2 + \dots)$$

where $Y = 1-2y$, and g_p is independent of mole fraction at constant ionic strength. The experimental quantity, g_p, is closely related to the theoretical g_p. In mixtures nearly obeying Harned's rule (see Literature Review), Friedman found that

$$g_p \gg g_p \;.$$

Consequently the theoretical counterparts have the following

$$\left| g_0 \right| > \left| g_p \right| \;.$$

He concludes that g_0 is the most important term in the cluster expansion, and therefore only contributions to g_0 are significant. For contributions to g_0 he writes

$$g_0 = \sum g_{0,u}, \; u = 2, 3, 4 \dots$$

where $g_{0,2}$ (pairwise interactions) is the most important term. The calculated g_0 is related to g_0 through the expression

$$g_0 \text{ (calc.)} = g_0 k^2/\lambda I$$

where $k^2/\lambda I$ accounts for the different concentration scales. In a case where two similarly charged cations with anions are mixed (i.e. a symmetrical case), $g_{0,2}$ is given as

$$-g_{0,2} = 4\pi z_2^{-2}(z_1 - z_3)^{-2}\int_0^\infty \delta k \exp(q_{11}r^2)dr$$

where species 3 is the common ion, 1 and 2 refer to the hetero ions, r is the distance between two ions, and

$$\delta k = 2k_{12}(r) - k_{22}(r)$$

$$q_{ij} = q_{11} = q_{12} = -z_i z_j \lambda e^{-kr/4\pi r}$$

$$k = \exp(-u_{ij}^*(r_{ij})/kT) - 1$$

$$u_{ij}^* = \text{non-coulombic interaction potential.}$$

At $k = 0$, the integral approaches a finite value. Also at this limit, $dg_{0,2}/dk$, does not vanish, and is given by the following relations:

$$dg_{0,2}/dk = (z_1^2\lambda/4\pi)g_{0,2}, \quad k = 0.$$

In comparing experimental g_0 with calculated, Friedman rewrote the relations for the excess free energy of mixing thus:

$$G(y,I) = RTI^2y(1-y)(w_0 + w_1Y + w_2Y^2 + \ldots)$$

where the w coefficients are determined from the measurement of the activity of the solvent as a function of y at constant ionic strength, I, and w is related to g by the following relation

$$I\, g_0(I) = -\int_0^\infty w(I')\, dI'$$

The Harned α coefficients from isopiestic methods are related to w by

$$w = 2.303(\alpha_{23} + \alpha_{32})$$

The w and g (cal) values plotted <u>versus</u> molality have been shown to have similar linear curves, but differences between experimental and calculated are rather appreciable. Friedman says such differences are not really so severe as to prevent the correlation of the two values since the experimental w can be corrected by minor adjustments of the α parameters of the primitive model.

The excess free energy of mixing arrived at by the Friedman method is related to the enthalpy of mixing by the Gibbs-Helmoltz equation, i.e.

$$\frac{d}{dT} \frac{(\Delta_m G^E)}{T} = - \frac{\Delta H^E}{T}$$

Heat or enthalpy of mixing can be obtained directly by calorimetric method and excess free energy of mixing can be calculated via the above relationship or some variant of it (see Thermodynamic Section). The variation of the heat of mixing with temperature yields heat capacity, i.e.

$$\Delta_m C_p = \frac{\Delta_m H_2 - \Delta_m H_1}{\Delta T}$$

and this relationship is also valuable in calculating the excess free energy.

LITERATURE REVIEW

Most of the work in the area of mixed electrolyte solutions has centered around either the determination of activity coefficients of halogen acids in alkali metal halides from the measurements of the EMF of the cell type:

$$H_2/HX \ (m), \ MX(m) \ /AgX\text{-}Ag$$
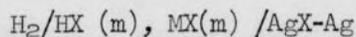
or the determination of the isopiestic coefficients of the mixture type, $MX_n\text{-}NX_n\text{-}H_2O$, where M and N are alkali or alkaline earth cations.

Harned[17],[18], after doing a number of experiments with EMF cell type mentioned above, was able to formulate the rule that the logarithm of the activity coefficient of one electrolyte in a ternary solution at constant ionic strength is a linear function of the composition. This rule can be expressed as

$$\log \gamma_2 = \log \gamma_2(o) - \alpha_{23} m_3$$

and

$$\log \gamma_3 = \log \gamma_3(o) - \alpha_{32} m_2$$

where $\log \gamma_2(o)$ and $\log \gamma_3(o)$ refer to the log of the activity coefficients of solutes 2 and 3 in their respective pure solutions at a concentration

$$m = m_2 + m_3 \quad .$$

The coefficients α's are independent of solute composition but are general functions of molality, temperature, and pressure.

The above empirical rule is often denoted as Harned's rule. It has been shown to be accurate for fairly concentrated solutions. Hawkins[19] has shown that the linearity rule holds even up to as high as 6 molal for mixtures of hydrochloric acid and alkali metal chloride solutions. The isopiestic method has also been used to verify Harned's rule.

While Harned's rule seems to hold for a number of systems, other workers, for example, Argersinger and coworkers[21], have found that the rule has to be extended to account for such phenomena as ion pairing and complex formation. The extended rule has been expressed as

$$\log \gamma_i = \log \gamma_i(o) - \alpha_i I_j - \beta_i I_j^2 - \gamma_i I_j^3$$

where $I = \sum_j I = $ constant, I_j is the ionic strength contribution from the jth electrolyte solution at the same ionic strength as the mixed electrolyte. The coefficients α, β, γ, ... are independent of ionic strength fractions, but are general functions of total ionic strength, temperature, and pressure; they are also subject to the limitations imposed by the Gibbs-Duhem equation and the cross-differentiation relations, respectively represented as follows:

$$\sum_i n_i du = 0$$

and

$$\frac{(du_i)}{(dn_j)_{n_i,n_k}} = \frac{(du_j)}{(dn_i)_{n_j,n_k}}$$

where u is the chemical potential and n is the number of moles of a particular species in question. Harned's rule or the extended form of it has been the subject of too many papers to enumerate here. Currently the best review of the rule and experiments supporting it has been given by Harned and Robinson.[22]

EMF studies dealing with cell type

$$M-Hg \ /MX_2, \ M'X_2, \ H_2O/AgX - Ag$$
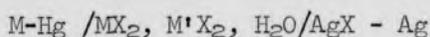
have been very few. Robinson and Farrelly[23] found that in the cell:

$$Zn-Hg \ /ZnCl_2, \ CaCl_2, \ H_2O/AgCl - Ag$$
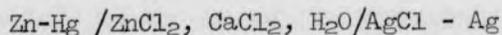
at total molality of 0.45, $ZnCl_2$ followed Harned's rule approximately, but at higher molalities, e.g. at 2.5 and 5.0 molal, large deviations from linearity were found. For $ZnCl_2-MgCl_2-H_2O$, Stokes[24] found by the isopiestic technique that the rule did not hold without some extreme modification. For the system $CaCl_2-ZnCl_2-H_2O$, Meyer[21], applying the EMF technique, found that at low ionic strength (i.e. below 0.9 m) Harned's rule was approximately followed but at higher ionic strengths, terms up to cubic were required. Gregor, Glatz and Schonhorn[25] performed some EMF studies on the systems: $SrCl_2-MgCl_2-H_2O$ and $SrCl_2-CaCl_2-H_2O$. They found that for the former $SrCl_2$ followed Harned's rule at I = 1.0, but not at I = 0.3. For the latter $SrCl_2$ followed Harned's rule at I = 0.3. The results of these experimenters are somewhat doubtful since the measurements were carried out at only a very few points, and the reversibility of the electrodes was

not certain. Wu[26], employing the isopiestic method for the system $SrCl_2$-$CaCl_2$-H_2O found that both salts obeyed Harned's rule within experimental error.

It should be noted that the determination of the activity co-efficient by EMF method or isopiestic method is an indirect way of arriving at important thermodynamic state functions such as, entropy of mixing and enthalpy of mixing. Enthalpy of mixing can be obtained directly by calorimetric method. From a large number of experimental results, Young[2,27] was able to postulate that the mixing of two binary solutions of the same ionic strength to produce a ternary solution may be expressed accurately as the sum of the corresponding excess thermo-dynamic quantities of the binary solutions. He further stated that any deviation from this rule could be expressed as a function both of the ionic strength and of the respective solute fractions of the mixture. The rule and its corollary can be written as follows:

$$\Psi^E = y_A \Psi_A^E + y_B \Psi_B^E$$

and

$$\Delta_m \Psi^E = K I y_A y_B$$

where Ψ^E stands for any excess thermodynamic quantity; the subscripts A and B correspond to the solutes A and B, respectively; K is a pro-portionality constant; and y_A and y_B are ionic strength fractions. Combining the two equations above yields the mixture rule:

$$\Psi^E = y_A \Psi_A^E + y_B \Psi_B^E + \Delta_m \Psi^E$$

where $\Delta_m \Psi^E$ is the deviate.

For the heat of mixing, some workers[28],[29] fitted their data to the following equation:

$$\Delta_m H^E = y_A y_B IK$$

where $K = h_O + h_1(1-2y)$ and is a measure of the magnitude of departure from ideal situation. They found that the mixture rule was fairly well obeyed within experimental error. There are a few times when the expression for K is quite different from the one given above. Such cases have recently been reviewed succinctly by Y. C. Wu.[30]

Wood and his coworkers[1],[3] have also employed calorimetry in determining heats of mixing electrolyte solutions. Anderson[31] found that he had to use Friedman's equation,

$$\Delta_m H^E = RTI^2 y(1-y)(h_O + h_1(1-2y))$$

for a better fit of experimental data rather than the Young's mixture expression. Wood and Anderson[3] in studying alkaline earth halide solution mixtures interpreted their results in terms of water-ion interactions, and suggested that alkaline-earth cations are small structure makers in terms of Frank's model. They also stated that the role the sizes of the cations played in the structuring of water was not yet clear enough to draw any conclusion. Thus, calorimetric studies on the alkaline-earth chloride solutions at various temperatures can prove rather interesting and illuminating.

EXPERIMENTAL SECTION

Preparation of Solutions: The salts used in this work were Mallinckrodt ACS grade reagents. Two to three molal solutions of magnesium chloride, calcium chloride, and strontium chloride were prepared by dissolving the hydrated salts in de-ionized water. On account of the low solubility of barium chloride dihydrate, one to two molal solution was prepared in like manner. The resulting solutions were filtered and stored in polyethylene bottles. A preliminary analysis, utilizing Fajan's method of chloride analysis, was performed on each solution.

The stock solutions were analyzed by standard gravimetric analysis to an accuracy of about a 0.1%. Before use in the mixing process, each stock solution was diluted to 1 molal solution as described by Petree.[32]

The Calorimeter: The Dewar calorimeter used in this research was similar in construction to the calorimeter described by Petree[32], and Wood, et al.[33] The major difference in the present calorimeter was that the vessel and the pipet were approximately two and half times larger. This was particularly advantageous for our purposes since the enthalpies of mixing alkaline earth chloride solutions at $25^{o}C^{I}$ were generally very small quantities. So it was anticipated that mixing larger quantities of alkaline earth chloride solutions at the desired conditions would yield sufficient heat to work with. See Figures 1 and 2 for details of calorimeter and superstructure.

The Vessel: The vessel was made of a 700 ml thermos[34] bottle attached to a brass collar and cemented with silicone rubber cement. The exact measurements were 19.5 cm high and 9 cm in diameter.   The bottom end of the vessel was wrapped around with silicone tape and filled with tar in order to provide a supporting base.   The brass collar was 12.5 cm in diameter (See Figure 3).   The collar had four screw holes that were a match for four holes in the superstructure and it also had circular groove to hold a rubber O-ring.

Pipet: The pipet was made of a blown-up 18 mm thin glass tubing. See Figure 4 for details in measurements.   In order for the pipet to hold the second solution until mixing time, it was fitted with a teflon plunger as described by Petree.[32]   The total volume of the pipet was approximately 45 ml.

Heaters: The calorimeter contained three heaters.   One heater was used for heating the vessel solution up to operating temperature. The second heater was used for heating the pipet solution to operating temperature.   The third (or calibration) heater was used for calibration. The power for the first heater was supplied by a 6 volt dc battery eliminator.   The power for both the second and the calibration heaters was supplied by a regulated power supply.   The vessel solution heater consisted of a 3 cm straight resistance wire soldered at the end of leads from the posts on a panel affixed to the superstructure.   (The solder joints were made of a rosin solder and Nikorode soldering paste[35]). The resistance wire was immersed in an oil bath in a 6 cm X 3 mm glass tubing sealed at one end.   The calibration heater consisted of an

Evanohm chromel wire[36] wound around a glass rod and soldered at the ends of the leads from another set of posts on the panel. This was also immersed in an oil bath in the like manner as the vessel solution heater. These heater probes are illustrated in Figure 2.

In any calorimetry work it is important that heating the solutions be done uniformly. The use of the oil baths was aimed at achieving uniform heating.

Stirrers: In the design of the heating element in any calorimetric vessel it is mandatory that the heat liberated in the heating element be distributed quickly through the specimen and vessel proper. One way of attaining this is to have mechanical stirring to bring new solution to heater surfaces. Another requirement for stirrer design is insuring that the solutions get well mixed quickly, as soon as the pipet is opened into the vessel solution.

The second of these requirements caused considerable trouble and led to a significantly different design in stirrer from that used by Petree[32] (see Figure 5). Several designs were tried. The one that was finally used consisted of 4 sets of propeller shaped blades evenly spaced on a 6 cm X 2 mm glass rod. This new design reduced the time of mixing from about 4 minutes to about one to two minutes when the less dense solution was in the pipet, and to a few seconds when the denser solution was in the pipet.

The stirrer was empowered by a 300 rpm synchronous motor.[37] It was connected to the shaft of this motor vertically with a rubber sleeve and tied with a bare resistance wire in three places.

The Sensing Device: The temperature measuring device was a 10 kilo-ohm ± 0.5% thermistor[38] which was further shielded by wrapping aluminum foil around the thermistor bead. The thermistor was further protected from the vessel solution by inserting it in a glass tubing. The temperature discrimination obtained by the use of such a thermistor was quite good, about 5×10^{-6} degree celsus.

Schematically, the temperature was monitored by a 10 kilo-ohm ± 10% thermistor in a wheatstone bridge circuit (see Figure 6). A microvolt-ammeter[39] was put across the bridge, from which an imbalance in the bridge was recorded on a Sargent chart recorder.[40] When the amplifier was on the 100 microvolt scale and the recorder input was on the 125 millivolt range 1 division on the recorder represented a heat of about 0.002 calorie.

Sunner, et al[41] used a 2 kilo-ohm thermistor with good results and they recommend the current through the thermistor should not exceed 0.1 ma. However, the temperature discrimination obtained was quite inferior compared to a more recent development by Cobble and all[42], who used 10 kilo-ohm thermistor. The temperature discrimination obtained by the latter group was about 10^{-6}, which is about the same as was obtained in this work.

The Timer: During heat capacity measurement the amount of electrical energy supplied to the vessel solution was timed by an electrical timer[43] which had a common switch with the calibration heater.
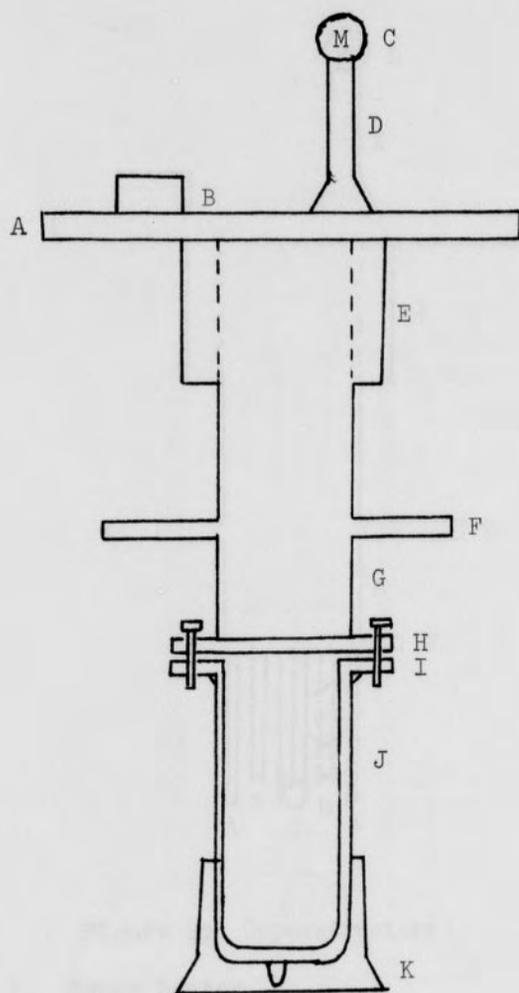
Figure 1: Calorimeter

A. 50 cm X 30 cm X 0.64 cm plywood
B. Electrical panel
C. ½ HP synchronous motor
D. 23 cm steel support
E. Styrofoam
F. 30 cm X 20 cm X 0.64 cm brass plate
G. Hollow brass cylinder
H. Brass lid
I. Brass collar
J. Vessel
K. Tar base
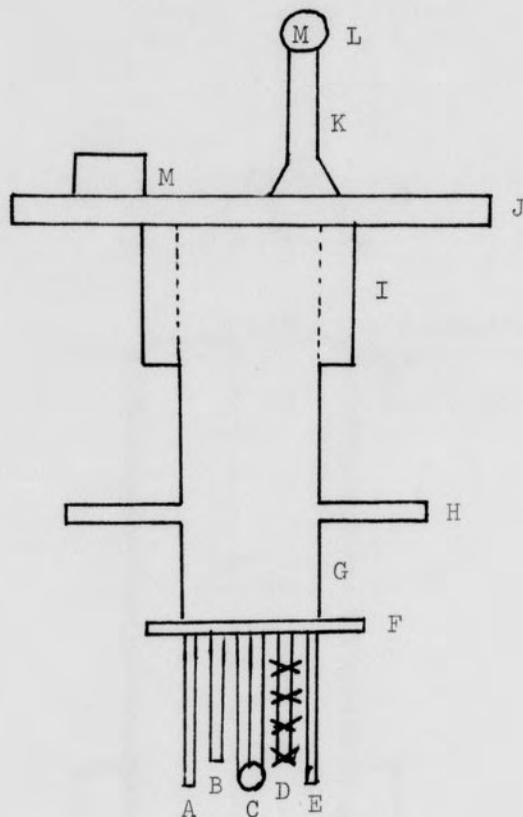
Figure 2: Superstructure

A. Rough heater
B. Calibration heater
C. Teflon pipet basket
D. Stirrer
E. Thermistor
F. Brass collar
G. Hollow brass cylinder
H. 30 cm X 20 cm X 0.64 cm brass plate
I. Styrofoam
J. 50 cm X 30 cm X 0.64 cm brass plate
K. Steel support (for synchronous motor)
L. ½ HP synchronous motor
M. An electrical panel
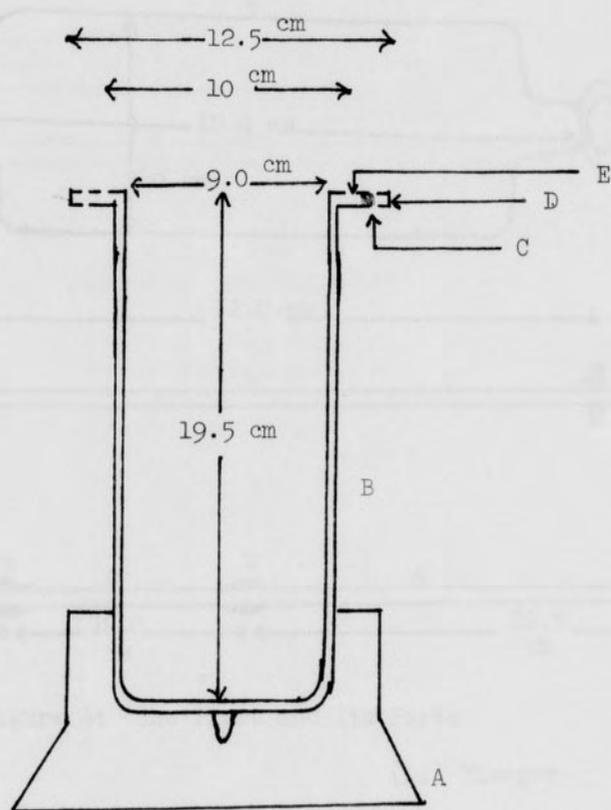
Figure 3: The Vessel

A. Tar base
B. 700 ml thermos bottle
C. A screw hole
D. Brass lid
E. Rubber O-ring groove
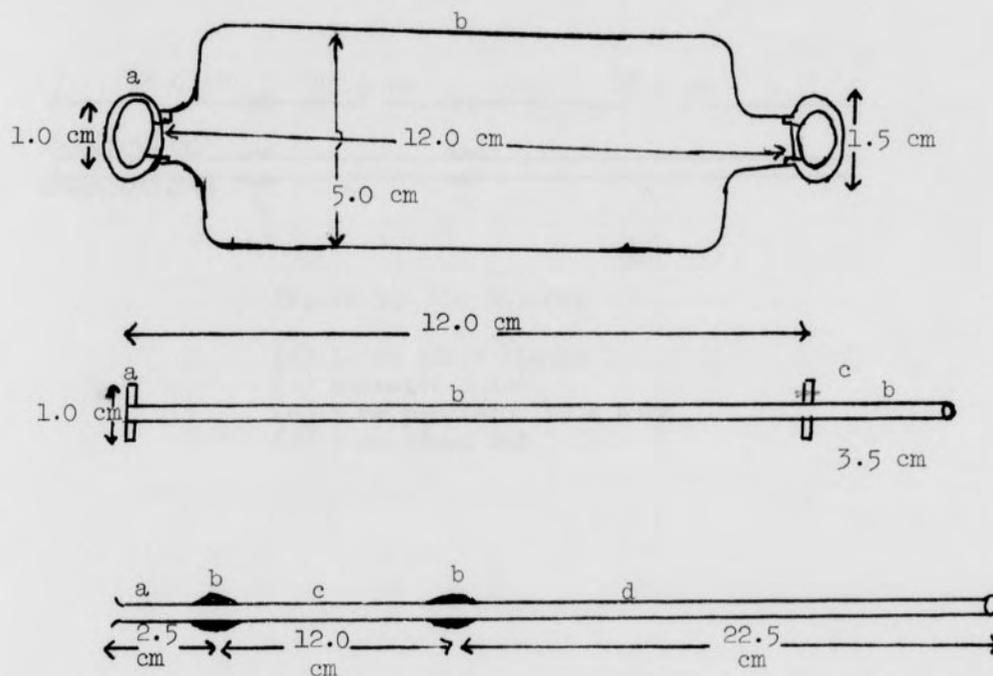
Figure 4: The Pipet and Its Parts

(i) Pipet

    (a) Teflon sleeve
    (b) Blown-up 18 mm glass tubing

(ii) Plunger

    (a) Teflon
    (b) 3 mm glass tubing
    (c) Air vent

(iii) Plunger handle

    (a) 3 mm glass sleeve
    (b) Annealed joint
    (c) 3 mm precision true bore
    (d) 3 mm glass tubing

15.0 cm   15.5 cm   23.0 cm
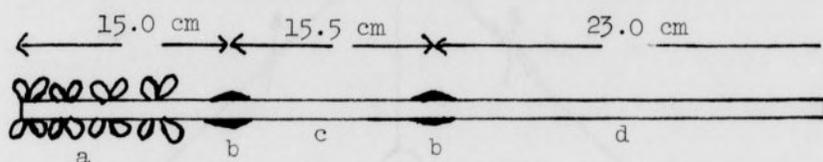
Figure 5:   The Stirrer

(a) 12 mm glass blades
(b) annealed joint
(c) 3 mm precision true bore
(d) 3 mm glass rod

1.34 volts
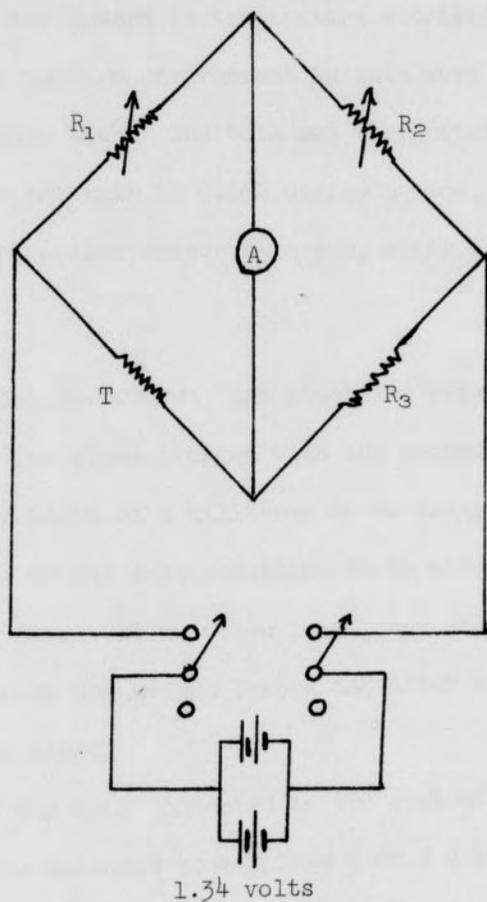
Figure 6: Wheatstone Bridge

R_1 = 1-10 Kilo-ohm adjusting resistor
R_2 = Decade resistor
R_3 = 20 Kilo-ohm standard resistor
T = Thermistor
A = Keithley Model 150A microvolt-ammeter

Thermostated Environment: In any calorimetric work it is important to maintain a uniform temperature environment so that when a reaction or mixing occurs, the change in temperature attributed to the interaction is specific. A uniform environment in this work was provided by a forty gallon water bath. The bath was thermostated by a thermotrol[44] which regulated the bath to 0.002 degree celsus. The bath was mixed by means of a propeller driven by a $\frac{1}{2}$ hp motor (from a Sears quality Sump Pump).

Experimental Procedure: The pipet and vessel were cleaned thoroughly and dried. The pipet plugged with the plunger was then weighed accurately to a tenth of a milligram on an analytical balance. It was filled with one of the salt solutions to be mixed, leaving only 5 to 6 mm vapor space above the solution level, and was weighed again. The difference between the weight before and after was the weight of the solution in the pipet.

The pipet was then connected to the rest of the plunger holder, a hollow true bore annealed to a hollow 6 cm X 2 mm glass tubing by means of Ferrule cement.[45] An eighty ohm heating element was then thrust in through the hollow glass to the pipet so that the heating element had the height equal to the solution depth in the pipet. In this kind of calorimetry it is important to minimize the temperature gradient between the pipet solution and the vessel solution, and so a heater in the pipet was used to heat the pipet solution up tooperating temperature. It is important to minimize the temperature gradient for two reasons: (1) this shortens the time of equilibration considerably, and (2) the fore-slope and after-slope become reasonably parallel, which is a desirable

thing in attaining consistent results.

The vessel was weighed on a platform balance to an accuracy of only a tenth of a gram. It was then filled to within 2.4 cm from the top in allowance of vapor space. Since the experiments were performed at 40°, 60°, and 80^oC, it was absolutely necessary to maintain as little vapor space as possible so as to minimize evaporation. This was particularly critical at 80^oC. The vessel with content (denoted later as solution one) was then reweighed.

The fact that the vessel was weighed on a less accurate balance was not much of a hindrance since the average weight of solution in the vessel was about 650.0 g. A weighing error of about 0.1 g was only 0.015% off.

The vessel was then assembled to the rest of the superstructure by means of four screws. In between the brass collar of the vessel and that of the superstructure laid a rubber 0-ring to prevent both collars from touching, a device which also aided in preventing contamination of the vessel solution. After all four screws were tightened, the calorimeter was then immersed into the thermostated water bath at the desired temperature.

The lead wires from the heaters and thermistor bridge were plugged into their respective posts on a panel bearing leads from the probes in the vessel. The superstructure, and decade resistance box were then grounded to a common ground.

The regulated power supply was switched to 0.5 volt scale and leads from it were connected to the copper wire leads from the pipet heater. Both the vessel solution heater and pipet heater were then turned on.

Heating for the work at 80°C lasted about an hour on the average; at 60°, forty minutes; and at 40°, twenty minutes. The time of equilibration averaged three and a half hours for the work at 80°C; two to two and a half hours at 60°C; and one to one and a half hours at 40°C.

After the system had equilibrated the microvolt-ammeter was turned to the 300 microvolt scale and the recorder was turned to scanning. Scanning at 300 microvolts was a preliminary step to ascertain complete equilibration and when this was true, the scale was moved to 100 microvolts where the scanning was continued for a few minutes so as to establish stable heat curves. The decade resistance reading was recorded and then the pipet was carefully opened by pushing the plunger in. Upon opening the pipet there was a change in the slope of the curve, indicating an absorption of heat (an endothermic reaction). The resistances were adjusted to account for the heat absorbed, and then as the curve resumed a slope similar to that of the pre-opening curve, the resistance reading was recorded. See Figure 7 for a typical experimental curve.

Two to three heat capacity measurements of the calorimeter and solution were then taken. In measuring the heat capacities, the microvolt-ammeter was kept at 100 microvolt scale for a reasonable length of curve wherein the resistance reading was recorded and then heat was pumped into the system by means of the calibration heater at the less sensitive scale of 300 microvolts. The time of heating was generally in the neighborhood of thirty-five seconds. The resistances were then adjusted. After the after-slope resembled the fore-slope, the

resistance (temperature), the voltage, and the time of heating were recorded. Measuring three heat capacities this way provided enough data to determine a reasonable average heat capacity for a particular experiment.

Routine Calculations During the Experiment: Dilution of the stock solutions to the desired concentration was attained by the following relationship:

$$\frac{\text{Wt. stock}}{\text{Kg. solution}} = \frac{m}{m_S} \left(\frac{1000}{(m)(mw) + 1000}\right)(m_S\,(mw) + 1000)$$

where m is the desired concentration, m_S is the molality of the stock solution, and mw is the molecular weight of the salt. This relationship was programmed for the Wang computer so that when the desired concentration, molality of the stock solution, and molecular weight of the salt were fed into the computer, the weight of the stock to be diluted per kg. solution was obtained. See Petree's thesis.[32]

As it has already been pointed out, one molal salt solutions were weighed out for the experiments. The number of moles in each weighed one molal salt solution (either pipet or vessel solution) was calculated through the following relationship:

$$n = \frac{w}{1000 + K}$$

where n is the number of moles, w is the weight of the one molal salt solution, and K is the molecular weight of the particular salt in question. For the first mixing the mole fraction was obtained in the
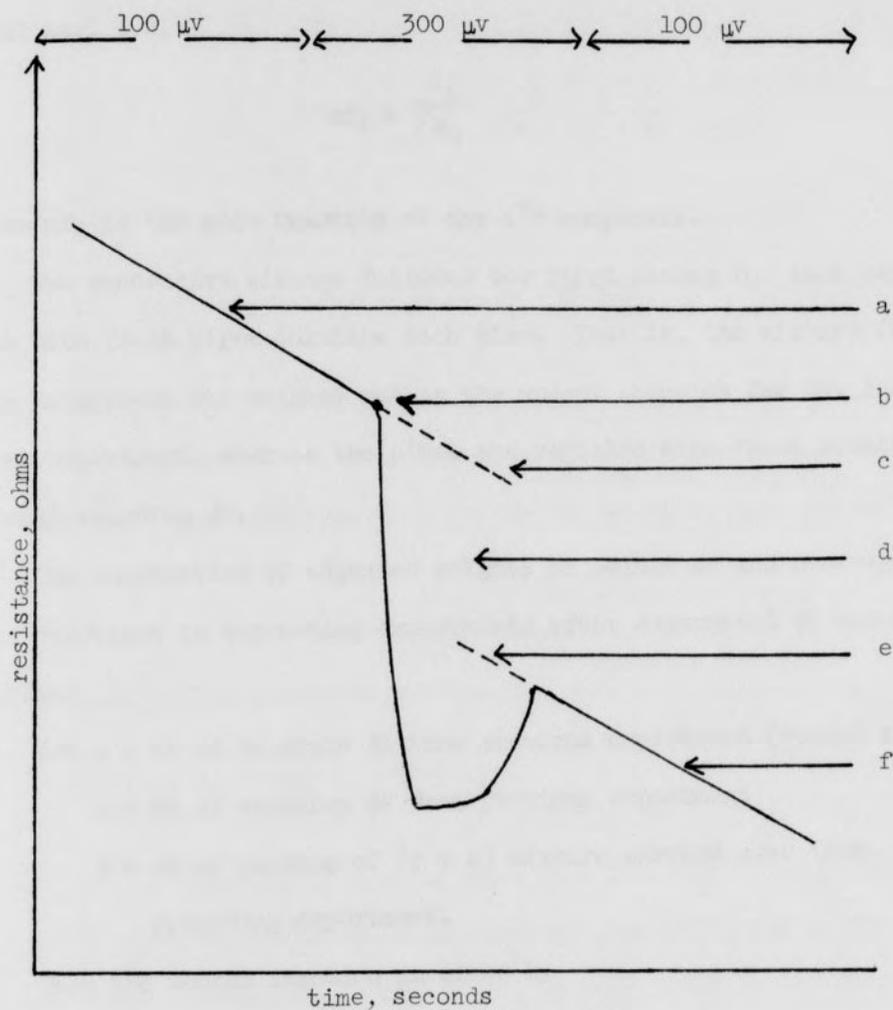
Figure 7: A Typical Experimental Curve

(a) Foreslope
(b) Open pipet
(c) Projection of foreslope
(d) Change in resistance (at 50% heating time)
(e) Afterslope projection
(f) Afterslope

usual way, i.e.

$$mf_i = \frac{n_i}{\sum n_i}$$

where mf_i is the mole fraction of the ith component.

Two successive mixings followed the first mixing for each experiment with fresh pipet solution each time. That is, the mixture from each experiment was weighed out as the vessel solution for the subsequent experiment, whereas the pipet was refilled with fresh solution of salt solution #2.

The computation of adjusted weights of solutions and corresponding mole fractions in succeeding experiments after experiment #1 are as follows:

Let r = wt of solution #1 from previous experiment (vessel solution)

s = wt of solution #2 from previous experiment

t = wt of portion of (r + s) mixture carried over from preceding experiment.

Then the weight fraction is given by

$$F = \frac{t}{r + s}$$

Now if r contains n moles of salt #1 and s contains m moles of salt #2, then the number of moles of salts' number 1 and 2 carried over are given respectively by F X n and F X m. If a is the weight of fresh salt solution #2 in the pipet, then the number of moles of salt #2 in a is given by

$$b = \frac{a}{1000 + K}$$; where K is the molecular weight of salt #2.

Therefore the mole fraction of salt #2 is given by

$$mf(salt\ \#2) = \frac{Fm + b}{Fm + Fn + b}$$

The corresponding mole fraction of salt #1 is given by

$$mf(salt\ \#1) = \frac{Fn}{Fm + Fn + b}$$

At the conclusion of three such mixings the order of the salt solutions in the pipet and vessel was reversed, beginning with fresh solutions; the salt solution that was in the previous experiments in the pipet was now in the vessel, and the vessel solution in the pipet.

The electrical heat in the heat capacity measurement was obtained by the means of the following equation:

$$Q = \frac{E^2 t}{R \times 4.184}$$

where Q is the quantity of heat in calories, E is the voltage, t is the time in seconds, and R is the resistance in ohms and 4.184 is the conversion factor to calories. From the above relationship the heat capacity was derived as

$$Cp = \frac{Q}{\Delta T} = \frac{Q}{\Delta R + x/s}$$

where ΔR is the difference in resistance readings before heating and after heating, x/s is the correction term and x means the number of divisions measured between pre- and after-heating curves about 15 seconds from the initial time of heating, and s means sensitivity, i.e., the number of divisions per ohm. Making use of the heat capacity data,

the quantity of heat absorbed in a particular experiment was calculated as

$$DELH = C_p(\Delta_m R + x/s)$$

where C_p is the average heat capacity, $\Delta_m R$ is the ohmage change upon opening the pipet and x/s is the correction term. DELH was then recorded and analyzed as is done in the treatment of the data.

Results and Treatment of Data: Following in the manner of Anderson[31], the experimental heats of mixing were fitted to the equation:

$$\Delta_m H \text{ (cal/kg solvent)} = RTI^2 y(1 - y)(h_0 + (1 - 2y)h_1) \qquad (1)$$

where R is the gas constant, T is the temperature in degree absolute, I is the total ionic strength, y is the mole fraction of the salt having the largest formula weight, h_0 is the magnitude of the interaction and h_1 is a measure of the first order deviation from the quadratic dependence of the heat of mixing on ionic strength. The experimental heats were corrected to account for the heat of opening the pipet which varied from 0.005 to 0.009 calorie over the temperature range studied.

A statistical "F" test (at 95% confidence level) was performed on each mixture to test for the significance of RTh_0. In those cases where RTh_1 was unimportant, it was set equal to zero and the data was refitted using only RTh_0. It should be pointed out here also that in cases where second and third points were dubious, only first points were taken for the F-test. For example only first point experiments were recorded for the system $SrCl_2$-$CaCl_2$-H_2O. In the case of $BaCl_2$-$CaCl_2$-H_2O, only

second and third points were taken due to the precipitation of minute amount of $BaSO_4$ (SO_4 from impurities in the calcium chloride solution) in the first point experiment.

The results of these statistical tests, which are in effect the parameters of eq. #1 are listed in Table 1.

For each system, MCl_2-$M'Cl_2$-H_2O, eight to twelve experimental determinations were made at 1.0 molal. It has been shown[1,32] that this is sufficient to determine the mixing parameters.

To facilitate computation of the parameters and to fit each experimental heat (DELH) of the Friedman equation without a prior knowledge of the previous heat on the mole fraction curve, the equation was modified thus:

$$HCALC = (\Delta H)(WTSF) - (\Delta H)(WTSI)$$
$$= A(F2) \qquad - B(F3)$$

where F2 = XF(1-XF)(WTSF) - XI(1-XI)(WTSI)

F3 = XF(1-XF)(1-2xF)(WTSF) - XI(1-XI)(1-2XI)(WTSI)

The letters I and F refer to initial and final conditions for a given pipet opening. The least squares program was written for the modified equation in FORTRAN. The FORTRAN program for this work has been quite well treated by Petree[32] and therefore will not be repeated here. The results of the program are given in the appendix.

Discussion of Errors: Anderson[31] found that the sources of error in this kind of calorimetric work are in general: ion impurities,

Table 1: Parameters for Heat of Mixing Equations

Temperature	Mixture	I^a	N^b	$RTh_0{}^c$	$RTh_1{}^c$	$\Delta_m H^d (y = 0.5)$
	$BaCl_2$-$MgCl_2$	3	11	6.4±0.2	0.9±0.2	14.4
40°C	$BaCl_2$-$CaCl_2$	3	10	2.9±0.1	0.7±0.2	6.5
	$BaCl_2$-$SrCl_2$	3	10	1.56±0.07	0.21±0.09	3.50
	$BaCl_2$-$MgCl_2$	3	7	5.3±0.1	0.4±0.1	11.8
	$BaCl_2$-$CaCl_2$	3	8	2.7±0.2	0.4±0.3	6.0
60°C	$BaCl_2$-$SrCl_2$	3	10	1.53±0.07	0.12±0.09	3.45
	$SrCl_2$-$CaCl_2$	3	6	0.39±0.03	0.16±0.03	0.88
	$BaCl_2$-$MgCl_2$	3	8	5.0±0.2	0.6±0.2	11.3
80°C	$BaCl_2$-$CaCl_2$	3	7	1.9±0.2	0.5±0.2	4.3
	$BaCl_2$-$SrCl_2$	3	8	1.2±0.1	0.3±0.1	2.6

a, ionic strength; b, number of experiments; c, units are cal/kg solvent/ional; d, units are cal/kg solvent.

concentration uncertainties, and the experimental precision for the one molal mixtures. He estimated the total experimental accuracy as follows:

$$\text{Total accuracy} = \left(\sum (\text{errors})^2 \right)^{\frac{1}{2}}.$$

The following errors for the mixtures in this work are listed in (his) Table XXII as: $BaCl_2$-$MgCl$-H_2O, 1.0%; $BaCl_2$-$CaCl_2$-H_2O, 2.9%; $BaCl_2$-$SrCl_2$-H_2O, 3.6%; and $SrCl_2$-$CaCl_2$-H_2O, 5.1%. For all practical purposes these errors were negligible because the heats of mixing as calculated from the least squares program were only accurate to a tenth of a calorie on the whole.

Two other major sources of errors were the instrument and uncontrollable shifts in the ambient temperature. These were accounted for in the least squares fit of the experimental data. Thus the error as reported in the Appendix is a result of instrumental problems, sudden shifts in the ambient temperature and possibly bias on the part of the experimenter in reading numbers from the instrument.

DISCUSSION

Symmetry: The variation of the heats of mixing with respect to mole fraction as represented by the Friedman equation[11] is parabolic about $y = 0.5$. The intercepts on the mole fraction axis are $y = 0$ and $y = 1$, where the heats of mixing are zero. This prediction seems to hold within narrow limits for all the 1-1 and 2-1 electrolyte solution mixtures so far studied. Anderson[31] found that the maximum in the heats of mixing alkaline earth chloride solutions lies between 0.47 and 0.53 mole fraction units. The upper limit here lies about 12% below that of Anderson's; likewise the lower limit lies about 12% below his. This implies that there is some asymmetry in the present work.

The calculation of $d(\Delta_m H)/dy = 0$, was included in the least squares program. The mole fraction at this zero slope was denoted at XM2. See Appendix.[46]

The skew term in the Friedman equation is represented by RTh_I. All the values of RTh_I in this work (see Table 1) seem appreciable enough to point to the fact that there is indeed some asymmetry at higher temperatures. The $CaCl_2$-$SrCl_2$-H_2O mixture at 60°C has the most skew. The RTh_I value for this mixture is about 41% of the RTh_0 value, which means there is a considerable amount of asymmetry. The $BaCl_2$-$MgCl_2$-H_2O and $BaCl_2$-$SrCl_2$-H_2O mixtures at 60°C have the smallest RTh_I values, which are 7.5% and 8.5% of their RTh_0 values, respectively.

On the average the $BaCl_2$-$CaCl_2$-H_2O mixture at 40°, 60°, and $80^\circ C$ has more skew (save the $CaCl_2$-$SrCl_2$-H_2O mixture at $60^\circ C$) than the other mixtures; but again the work at $60^\circ C$ even for this mixture has smaller skew term.

As can be seen, there is some relationship between skew and temperature variation for this work. However, such a relationship is not simply a linear one. As the matter of fact the least skew term at $60^\circ C$ for the mixtures: $BaCl_2$-$MgCl_2$-H_2O, $BaCl_2$-$CaCl_2$-H_2O and $BaCl_2$-$SrCl_2$-H_2O is probably due to the fact that the time-heating curves at this temperature were much better behaved than at other temperatures. Of peculiar interest is the fact that all the experiments (save $BaCl_2$-$SrCl_2$-H_2O mixing) at $40^\circ C$ did not yield the least skew terms. No simple explanations concerning the random variation with temperature can be given at this time, although the randomness could most probably be accrued to experimental errors.

In terms of the conclusions drawn by Wood and Anderson[1] concerning skew, the variation in skew with temperature probably involves triplet interactions of like charges and the phenomenon of ion-pairing. The presence of triplet interactions in this work is in contrast to the findings of Wood and Anderson[1] and Anderson and Petree[4], who found that triplet interactions were unimportant in their work. For the interaction between the highly charged alkaline earth cations and the chloride anions it is highly probable that ion-pairing becomes appreciable as the temperature increases. This postulate may in fact be true because the dielectric constant of water is very sensitive to temperature. The

constant drops from about 80 at $25^{\circ}C$ to 60 at $80^{\circ}C$. Thus the ability of the charged ions to pair increases.

Solvent-Solute Structure: The ion-water interaction in aqueous electrolyte solution has been reviewed by J. L. Kavanau.[47] Liquid water has long been known to possess distinctive structural features similar to ice. The ice-like orderliness may be altered by changes in temperature and pressure. It was observed early that ions in water also altered its structure. For example, a 0.1 M solution of CsCl has been found to more fluid than pure liquid water at the same temperature. This observation was interpreted by Bernal and Fowler[48], and Cox and Wolfenden[49] as meaning that ions were somehow breaking water structure.

In studying entropy of hydration of metal ions in aqueous solutions, Frank and Evans[50] reached a conclusion similar to that of Bernal and Fowler. The numerical values for entropy of hydration are obtained by subtraction between the partial molal entropies of the salt and the statistically calculated molal entropies of ions as perfect gases. Frank and Evans compared such numerical results with the estimated entropy losses arising from: (1) restriction of the ions in "free volume" cells in the condensed phase; (2) immobilization of first layer water; and (3) dielectric polarization of more distant water. This model is represented by Figure 8. Frank and Evans further imagined that region A always existed, composed of nearest-neighbor waters, and that an ion which is small, or multiple charged, or both (e.g. Li^+, F^-, Mg^{2+}) might induce additional structure (entropy loss) of some sort beyond the first
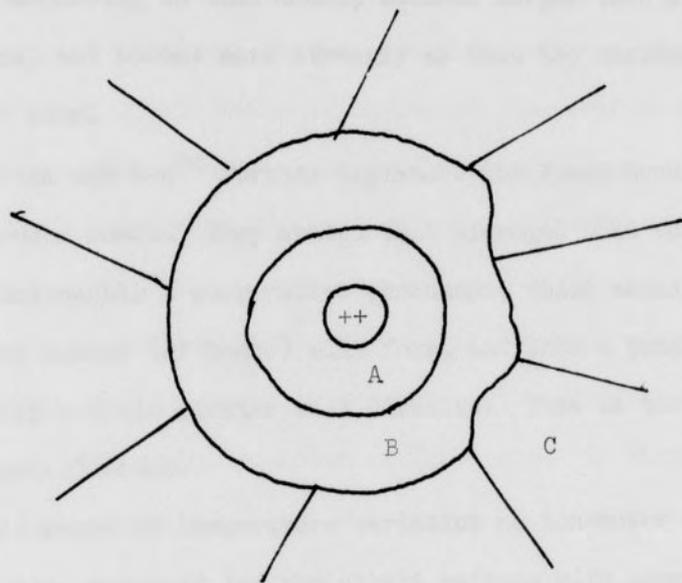
Figure 8: A simple model for structure alteration produced by a small
ion. A, region of immobilization of water molecules;
B, region of structure breaking; C, structurally "normal"
water.

water layer. Whereas larger ions may induce encroachment of regions B on C. According to this model, cations larger than K^+ are net structure breakers, and become more strongly so than the smaller and more highly charged ions.

Frank and Wen[51] further explained the Frank-Evans model in terms of hydrogen bonds. They stated that hydrogen bond formation in water is predominantly a cooperative phenomena, which means when a bond forms, a larger number (of bonds) will form, and when a bond breaks, then typically a whole cluster will dissolve. This is the so-called "flickering cluster" model.

Influence of temperature variation on ion-water structure have mostly been reported for the alkali cations with common anion mixtures. Anderson and Petree[4] found that the heats of mixing for the mixtures: $LiCl-KCl-H_2O$; $LiCl-(CH_3)_4NCl-H_2O$; $KCl-(CH_3)_4NCl-H_2O$ are all independent of temperature variation at 40°, 60°, and $80^\circ C$. Making use of an earlier study[52] they concluded that these systems must involve interactions in the primary hydration sphere of the Frank-Evans-Wen model. The primary hydration sphere has been found to be temperature insensitive within the temperature range $25-80^\circ C$. On the other hand, Bonner and Woosley[53] estimated that 'normal' water becomes disordered by about fifty percent within the temperature range $25-80^\circ C$.

Anderson and Petree say they arrived at their conclusion on the basis of mixtures involving the borderline ion, Na^+, which behaves either as structure maker or a structure breaker. They found that the heats of mixing for the mixtures: $HCl-NaCl-H_2O$, $LiCl-NaCl-H_2O$, and $NaCl-KCl-H_2O$ are all highly temperature dependent.

Anderson, Wilson and Smith[5] have similarly reported that the heats

of mixing for the mixtures: $KF-KC_2H_3O_2-H_2O$ and $KBr-KCl-H_2O$ are

temperature insensitive whereas for the mixtures: $KCl-KF-H_2O$ and

$KCl-KC_2H_3O_2-H_2O$, the heats of mixing are temperature dependent. They

came to the same conclusion as Anderson and Petree[4] that the water in

the region of the structure-making, structure-breaking interface is

either invariant with temperature or very nearly invariant for the

anions and cations studied. This is in contrast with the present work

in which all the mixtures have shown some temperature dependence. That

they are temperature dependent is illustrated in Figure 9.

In terms of the cluster theory, h_0 is represented by the expression

$$h_{R_hR_i}^{xj} = \frac{-T \, dg^{xj}}{dT} = T \, d(B^{ih} - B^{ii} - B^{hh})$$

where the B's are cluster integrals involving the cations h and i.

Utilizing the Anderson-Petree idea about the insensitivity of the

interface region, one would expect the heat of mixing as reflected by

the integrals, e.g. $Ba^{2+}-Ba^{2+}$, $Ba^{2+}-Mg^{2+}$, etc., to be temperature

independent, if the mixing effect took place at the interface. However,

on account of the large charge on the alkaline earth cations, the ions

probably do not approach as close to one another as the alkali cations

in aqueous chloride solutions; thus the water further away from the

(A-B) interface region should determine the heats of mixing. This water

(sometimes denoted as bulk water) has been shown[53] to be quite sensitive

to temperature. It is not surprising then that the heats of mixing in

this work are all temperature dependent.
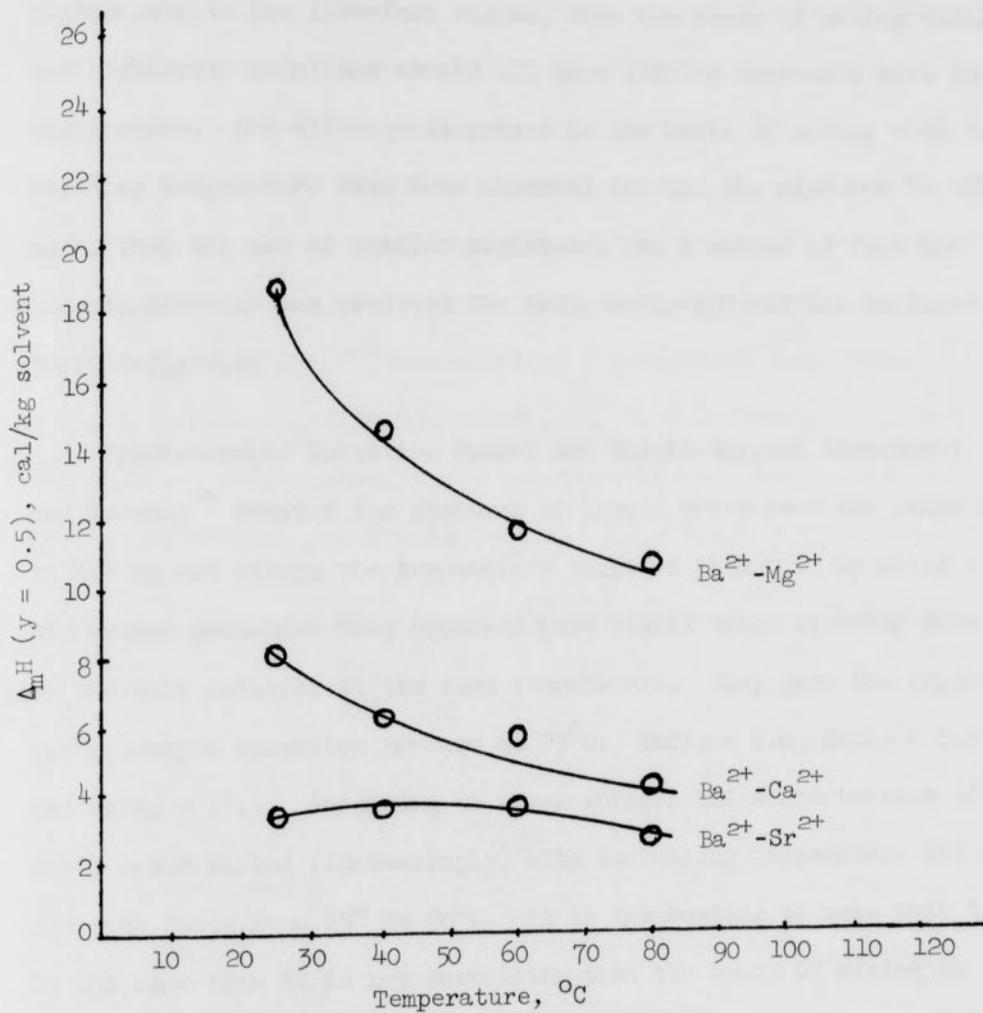
Figure 9: $\Delta_m H$ (y = 0.5) _versus_ Temperature

[Plotted from Table 1]

If the charges of the alkaline earth cations indirectly command the region outside the interface region, then the heats of mixing alkaline earth chloride solutions should all show similar decreases with increasing temperature. But although decreases in the heats of mixing with increasing temperature have been observed for all the mixtures in this work, they are not of similar magnitude. As a matter of fact the largest decrease was observed for $BaCl_2-MgCl_2-H_2O$ and the smallest for $BaCl_2-SrCl_2-H_2O$.

Spectroscopic Solvation Number and Solute-Solvent Structure: Bonner and Woosley[53] studied the spectrum of liquid water over the range 600 to 800 mu and within the temperature range of $25-80^{o}C$. By using a difference technique they compared pure liquid water spectrum with that of the salt solution at the same temperature. They gave the following spectroscopic solvation numbers at $25^{o}C$: $BaCl_2 = 5.0$, $CaCl_2 = 8.2$, and $MgCl_2 = 11.5$. According to these workers the concentration of monomeric water varied (increasingly) with increasing temperature and doubled over the range from 25° to $80^{o}C$. It is interesting to note that if this is the case then it is not surprising that the heats of mixing in this work are temperature dependent.

The picture could be looked at in this fashion: In the mixture $BaCl_2-MgCl_2-H_2O$, there are a total of 16.5 water-ion bonds to be broken and replaced by the only significant $Ba^{2+}-Mg^{2+}$ bonds. This requires thermal energy -- i.e., heat of mixing. As the temperature is raised there are fewer bonds to be broken, hence there is a decrease in the heat of mixing. Similarly there are a total of 13.2 bonds to be broken

in the $BaCl_2$-$CaCl_2$-H_2O mixture, but this number decreases with increasing temperature. It is not surprising then the heat of mixing $BaCl_2$-$CaCl_2$-H_2O should also fall in magnitude with increasing temperature. The spectroscopic solvation number was not determined for $SrCl_2$, but it would be expected to follow the general trend. It is noteworthy that the magnitude of the heats of mixing of alkaline earth chloride solutions seem to vary directly with the total number of spectroscopic solvation numbers, at a specified temperature. For example, $BaCl_2$-$MgCl_2$-H_2O mixture has the largest heat of mixing, 18.59 calories/kg solvent and the largest total spectroscopic solvation number, 16.5, at $25^{o}C$. For comparison see the following Table 2 constructed from data at $25^{o}C$.

Table 2: Heat of Mixing (in cal/kg solvent) and Spectroscopic Solvation Numbers

Mixture	$\Delta_m H$ (y = 0.5)	S. S. N.
$BaCl_2$-$MgCl_2$	18.59	16.5
$BaCl_2$-$CaCl_2$	8.07	13.2
$BaCl_2$-$SrCl_2$	3.32	5.0 + ?

Size of Cations and Solute-Solvent Structure: Anderson and Wood[1] have followed Frank and Evans in classifying the alkaline earth ions as structure makers on the basis that the ions are small and highly charged. In following Young, Wu and Krawetz[2], Anderson and Wood[1] have predicted the sign of the heats of mixing alkaline earth chloride solutions to be positive. According to the Young-Wu-Krawetz model the sign of the heats of mixing two structure breakers or makers in the

face of a common anion is positive, whereas the sign of the heats of mixing a structure maker and a structure breaker is negative. The sign prediction has been proven to hold even for the mixings in the present work. But it seems to be inconclusive to correlate the positive sign of the heats of mixing alkaline earth chloride solutions with the structure making ability of the cations because some of the alkaline earth cations have been classified as structure breakers by Greyson and Snell.[54]

Through heats of solution measurements at $25^{\circ}C$, Greyson and Snell[54] found that the order of structure-breaking influence for alkaline earth cations is $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ with Mg^{2+} behaving as a structure maker. Thus structural influences on water of the alkaline earth cations seem to be size dependent. Noyes[55] goes on further to state that for cations having the electronic structure of an inert gas, the free energies of hydration indicate effective dielectric constants are size-of-ion dependent and virtually charge independent. The effective dielectric constants for the alkaline earth cations are given in the order $Mg^{2+} < Ca^{2+} \approx Sr^{2+} < Ba^{2+}$. The spectroscopic solvation numbers: $BaCl_2 = 5.0$, $CaCl_2 = 8.2$, and $MgCl_2 = 11.5$, also seem to indicate the structural influences of the alkaline earth cations upon the solvent water can be more aptly discussed in terms of the size of the cations.

It is interesting that when the ratio, r_c/r_i, (for $r_i \leq r_c$, where r_c is the Pauling crystal radius of the barium cation and r_i is the radius of the other cation in the mixture) is plotted against the heats of mixing alkaline earth chlorides, an essentially linear curve is

obtained. The lower limiting point where r_c/r_i is 1, is taken intuitively to have zero heat of mixing, as in the absence of any other influences, mixing the same solution will yield a zero heat of mixing. The points in each plot fall on the line through that zero limit with a large deviation occurring for the Ba^{2+}-Sr^{2+} mixing at 25°, 40°, 60° and $80^\circ C$. See Figures 10 to 13. The linearity is particularly striking for the 25° and $40^\circ C$ mixings where two of the points fall right down in line with the zero point. The other two curves show quite a bit of scatter, but this is most probably due to experimental difficulties at those temperatures.

The fact that the ratio, r_c/r_i varies linearly with heats of mixing is a further revelation that the heats of mixing alkaline earth chloride solutions are size-of-cations dependent (and virtually charge independent). Why there is sudden increase in the heat of mixing at $r_c/r_i = 1.11$, as observed in all the figures, is probably attributable to charge or higher order effect. In other words as the sizes of different cations approach one another in magnitude, charge or higher order effect seems to become important and causes an additive effect to the heat of mixing.

Figure 14 shows that the size-dependent curves are all temperature dependent. As the plots indicate the Ba^{2+}-Sr^{2+} mixtures yield about the same heat of mixing at 25° and $60^\circ C$, which probably means that as the sizes of the cations in the alkaline earth chloride mixtures approach one another the heat of mixing of such mixtures become insensitive to temperature variation. Plots similar to those in Figure 14 have been constructed for the alkali chloride solution mixtures. See Figure 15. In these mixtures there is a tendency for the curves to go through zero
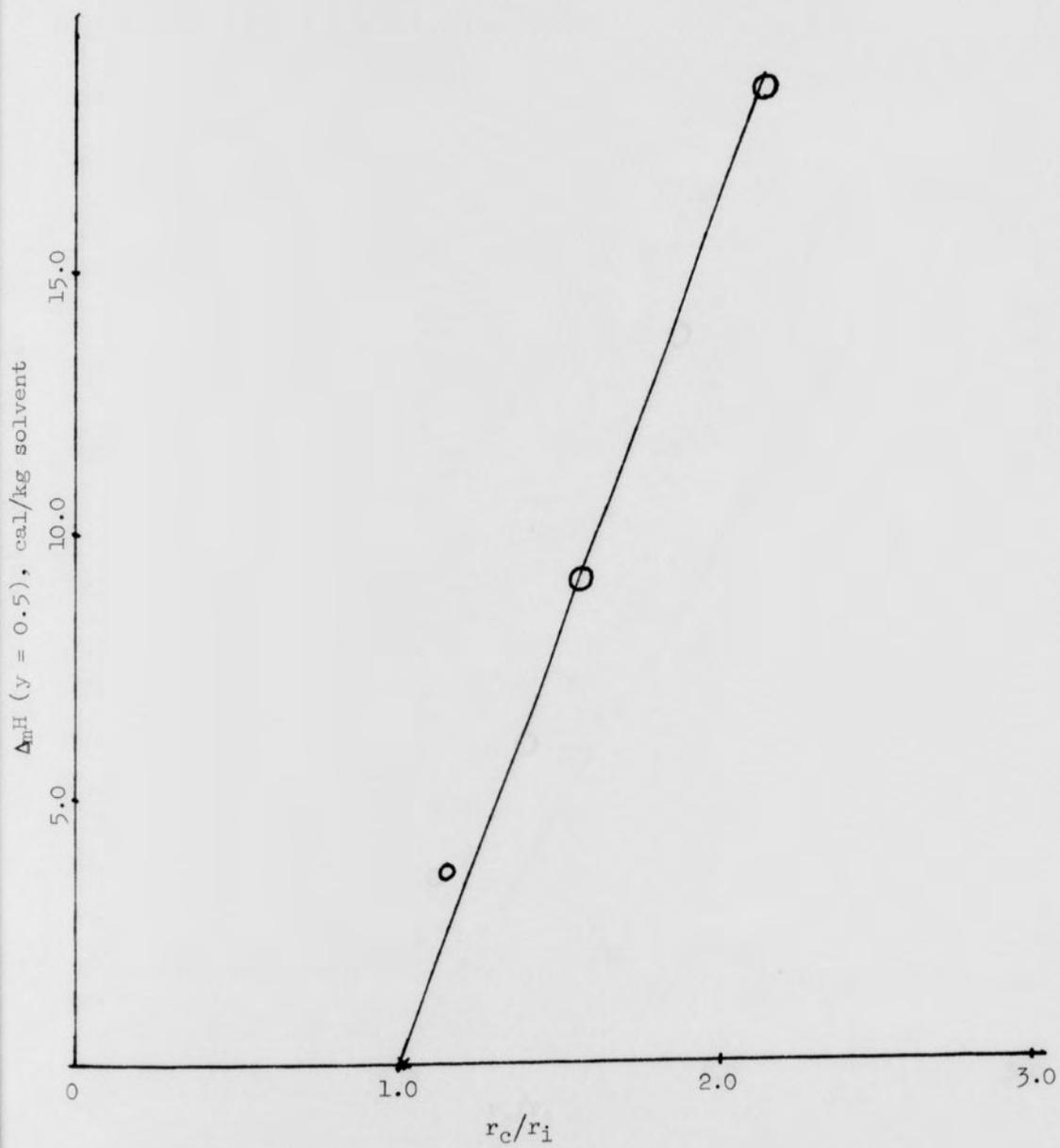
Figure 10: $\Delta_m H$ $(y = 0.5)$ _versus_ r_c/r_i at $25^\circ C$
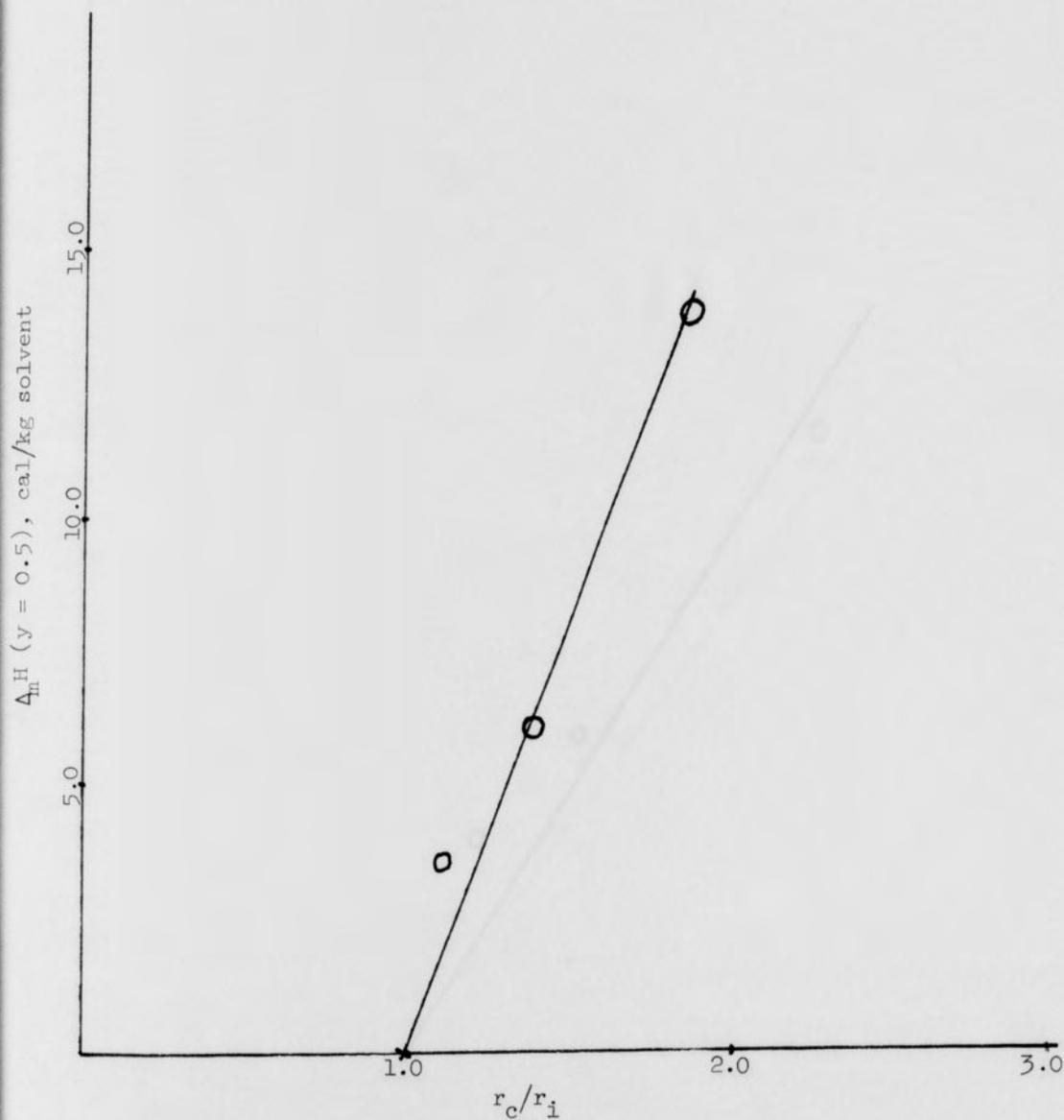
Figure 11: $\Delta_m H$ (y = 0.5) _versus_ r_c/r_i at $40^{\circ}C$
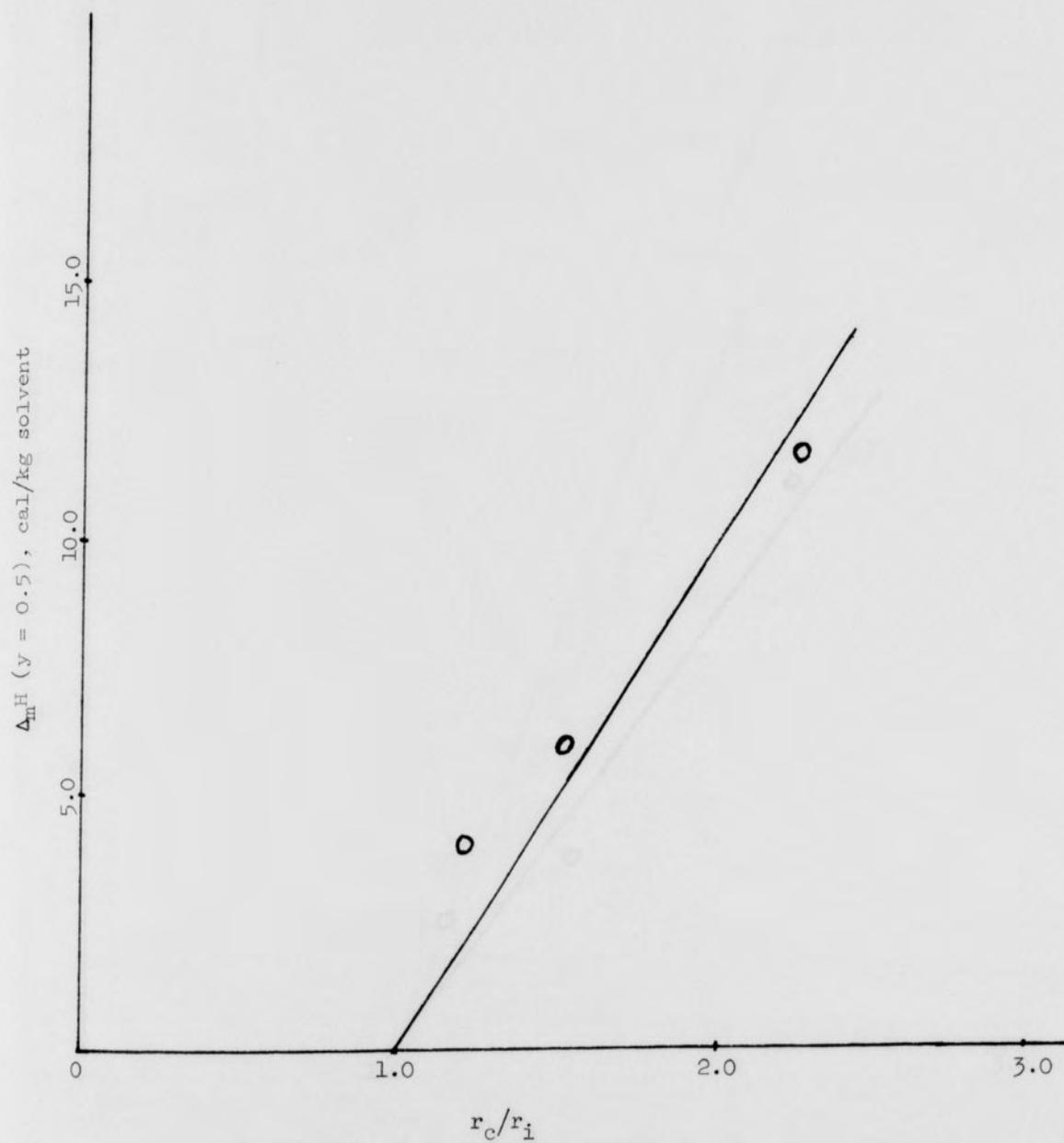
Figure 12: $\Delta_m H$ (y = 0.5) versus r_c/r_i at 60°C
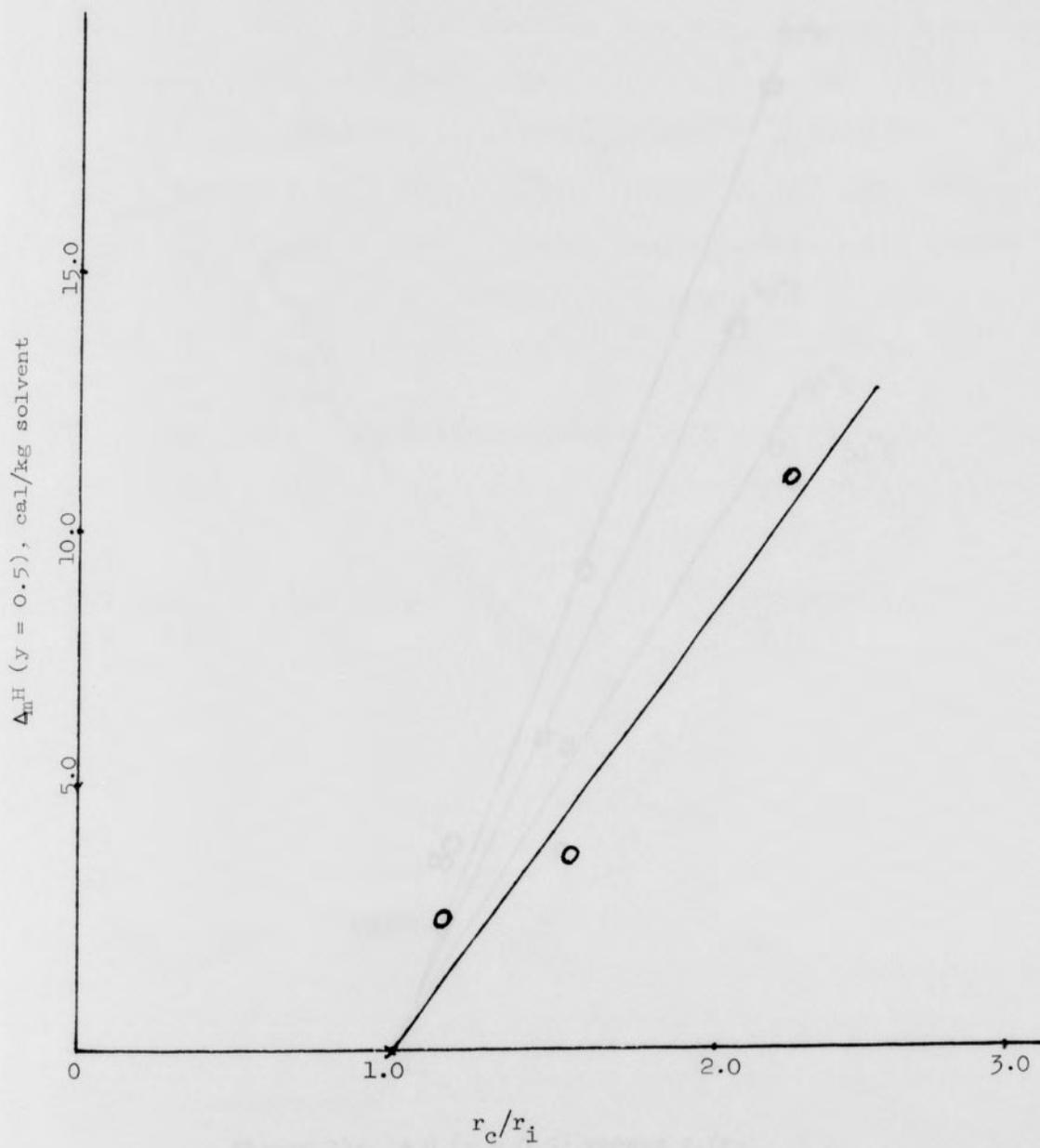
Figure 13: $\Delta_m H$ (y = 0.5) <u>versus</u> r_c/r_i at 80°C

Figure 14: $\Delta_m H$ (y = 0.5) <u>versus</u> r_c/r_i
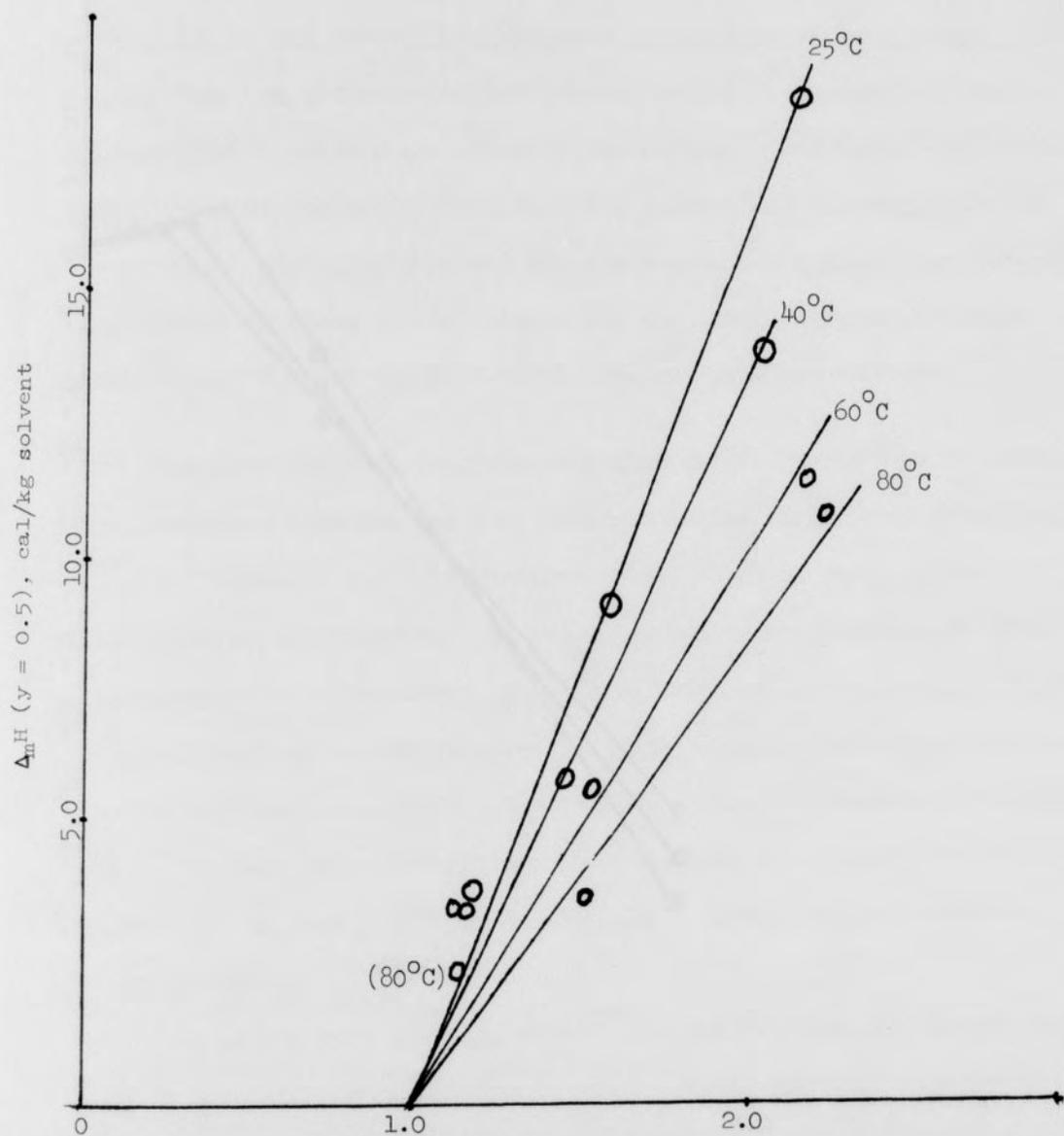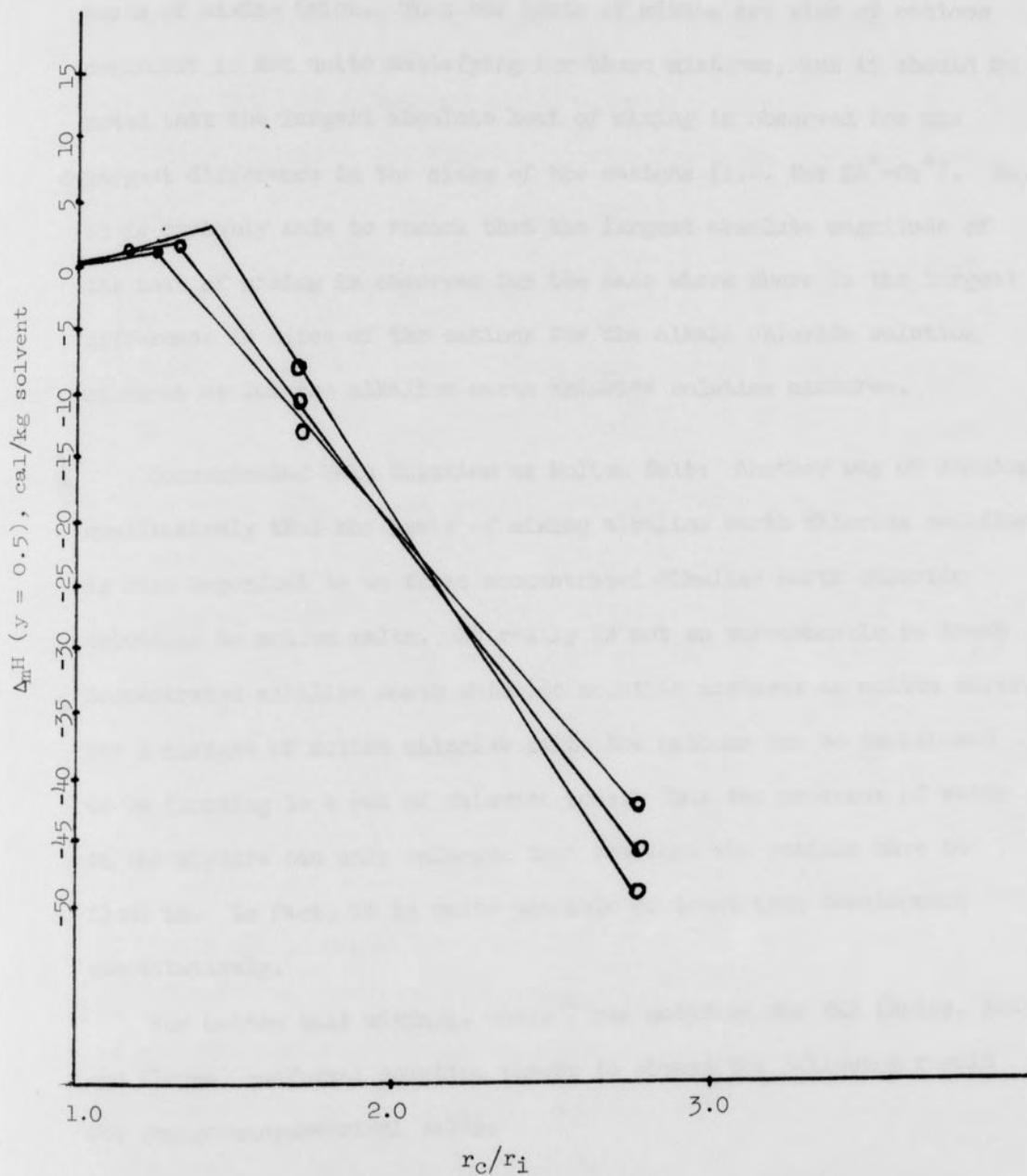
Figure 15: $\Delta_m H \ (y = 0.5)$ <u>versus</u> r_c/r_i

heats of mixing twice. That the heats of mixing are size of cations dependent is not quite satisfying for these mixtures, but it should be noted that the largest absolute heat of mixing is observed for the largest difference in the sizes of the cations (i.e. for Li^+-Cs^+). So, it is probably safe to remark that the largest absolute magnitude of the heat of mixing is observed for the case where there is the largest difference in sizes of the cations for the alkali chloride solution mixtures or for the alkaline earth chloride solution mixtures.

Concentrated Salt Solution as Molten Salt: Another way of showing qualitatively that the heats of mixing alkaline earth chloride solutions is size dependent is to treat concentrated alkaline earth chloride solutions as molten salts. It really is not so unreasonable to treat concentrated alkaline earth chloride solution mixtures as molten salts, for a mixture of molten chloride salts the cations can be envisioned to be floating in a sea of chloride ions. Thus the presence of water in the mixture can only enlargen that sea that the cations have to float in. In fact, it is quite possible to treat this development quantitatively.

For molten salt mixings, Davis[56] has modified the RKK (Reiss, Katz, and Kleppa) conformal solution theory to obtain the following result for charge-unsymmetrical salts:

$$\lim_{x_2 \to 0} \frac{\Delta A_m}{x_2} = \lim_{x_2 \to 0} \frac{(-kT\theta_{12})}{x_2} + \left[(z-1)\alpha_1 + \frac{(\partial \alpha_{12})}{\partial x_2}\right] \delta_{12} \Big|_{x_2 = 0}$$

where α_1, α_{12}, are universal functions of the reduced temperature and volume, k and T stand for their usual meaning, θ_{12} is the interaction

Table 3:   Data From Which Figures 10-15 Were Constructed

A. Ionic radii of alkali and alkaline earth cations

Alkali cations	radius (A)	Alkaline earth cations	radius
Li^+	0.60	Mg^{2+}	0.65
Na^+	0.95	Ca^{2+}	0.99
K^+	1.33	Sr^{2+}	1.13
Rb^+	1.48	Ba^{2+}	1.35
Cs^+	1.69	Ra^{2+}	1.40

B. The ratio r_c/r_i (where r_i is less than r equal to r_c)

v.s. $\Delta_m H(y = 0.5)$

Alkaline earth cation mixture	r_c/r_i	$\Delta_m H, 25^{o}$ [1]	$\Delta_m H, 40^o$	$\Delta_m H, 60^o$	$\Delta_m H, 80^o$
$Ba^{2+}-Mg^{2+}$	2.08	18.59	14.4	11.8	11.3
$Ba^{2+}-Ca^{2+}$	1.47	8.03	6.5	6.0	4.3
$Ba^{2+}-Sr^{2+}$	1.11	3.31	3.5	3.5	2.6
$Ba^{2+}-Ba^{2+}$	1.00				

C. Alkali cation mixtures [5]

	r_c/r_i				
Li^+-Cs^+	2.82	-49		-47	-43
Na^+-Cs^+	1.78	-9		-12	-13
K^+-Cs^+	1.27	1.6		0.4	
Rb^+-Cs^+	1.14	0.4			
Cs^+-Cs^+	1.00				

parameter, and δ_{12} is the distance between the centers of the two cations in a mixture. The heats of mixing have the same form as the free energies so that the above equation predicts that for fixed values of z, T and Θ the limiting heats of mixing vary linearly as δ_{12} with the same slope for all mixtures.

In using the Davis-Rice modification of the RKK conformal solution theory, i.e.

$$\Delta_m H = X_1 X_2 (U_0' + U_1' d' + U_2' (d')^2)$$

where $d' = \dfrac{d_1 - d_2}{d_1 d_2}$, and d_1 and d_2 are the interionic separations characteristic of the pure salts, McCarty and coworkers[57] found the enthalpies of mixing for the alkaline earth-alkali nitrate solutions varied linearly or nearly linearly with d'.

Robbins and all[58] found that the excess partial molar free enthalpies of mixing molten potassium chloride in molten alkaline earth chlorides showed a negative deviation from the Temkin ideal mixing model (a random mixing scheme) in the order $Ca^{2+} > Sr^{2+} > Ba^{2+}$, which is obviously size dependent. All these observations seem to add up to the general trend that the heats of mixing alkaline earth chloride solutions are size of cation dependent. This work also adds that the heats of mixing alkaline earth chloride solutions are also temperature dependent.

Thermodynamics: Heats of mixing at various temperatures furnish adequate data for heat capacity calculations. This work provides such a data.

The results of the heat capacity calculations can be used to calculate the temperature variation of the excess free energy of mixing.

For free energy of mixing, using heat capacity data, Criss and Cobble[59] give

$$\Delta_m G^E_{T_2} = \Delta_m G_{T_1} + \Delta_m C_p \Big]^{T_2}_{T_1} \Delta T - \Delta_m S^E_{T_1} \Delta T \Big]^{T_2}_{T_1} - T_2 \Delta_m C_p \Big]^{T_2}_{T_1} \ln \frac{T_2}{T_1} \qquad (2)$$

where $\Delta_m C_p = \dfrac{\Delta_m H_{T_2} - \Delta_m H_{T_1}}{\Delta T}$. This equation is satisfied if $\Delta_m G_{T_1}$ is known at some reference temperature, T_1. The remaining unknown is simply calculated from the free energy expression at constant temperature and pressure:

$$\Delta_m G_T = \Delta_m H_T - T \Delta_m S_T$$

or

$$\Delta_m S_T = \frac{\Delta_m H_T - \Delta_m G_T}{T} \qquad (3)$$

Thus in order to calculate the free energy of mixing at T_2 for this work it is only necessary to know the free energy of mixing at some reference temperature, T_1.

The reference free energy is usually the one at $25^o C$. A number of experiments dealing with activities of multicomponent electrolyte solutions have been carried out at $25^o C$. Most of these studies come from either EMF measurements of $HX-MX-H_2O$ mixtures where X is a halide ion and M is an alkali or alkaline earth cation, or from isopiestic measurements of $MX-NX-H_2O$ mixtures. The relationship between free energy and the data from either method is usually of the form[14]

$$\Delta_m G = -2.303 \ RTm_2 m_3 \left[\alpha_{23} + \alpha_{32} + 2(m_3 \beta_{23} + m_2 \beta_{32}) + \right.$$
$$\left. {}^2/_3 (\beta_{23} - \beta_{32})(m_2 - m_3) + \ldots \right]$$

or [60]

$$\Delta_m G = -2.303 \ RTI^2 y(1 - y) \left[\alpha_{23} + \alpha_{32} + 2(m_3 \beta_{23} + m_2 \beta_{32}) + \right.$$
$$\left. {}^2/_3 (\beta_{23} - \beta_{32})(m_2 - m_3) + \ldots \right] \qquad (4)$$

where the sum $(\alpha_{23} + \alpha_{32})$ is the leading term in the expansion. Most often the other terms are neglected.

Excess free energy of mixing data for alkaline earth halide solution mixtures are scarce. Of the mixtures studied in this work the only available data are from Wu's isopiestic studies[26] on $SrCl_2$-$CaCl_2$-H_2O at $25^{\circ}C$. Assuming Wu's data are reasonably reliable, free energies of and entropies of mixing have been calculated via equations 2, 3, and 4, and the results are recorded in the following Table 4:

Table 4: (the units for $\Delta_m G$ and $\Delta_m H$ are cal/kg solvent, for $\Delta_m S$ is cal/kg solvent $^{\circ}K$)

T	$\Delta_m H$	$\Delta_m G^E$	$\Delta_m S^E$
$298^{\circ}K$	0.64	-3.98	0.0157
$333^{\circ}K$	0.88	-4.54	0.0163

In the absence of numerical values from other workers to compare with, one should not put too much emphasis on the magnitude of the values nor the way they vary in the table. However, it is interesting to note that the sign of the excess free energy is negative. For the entire concentration

range of Wu's data the signs for the calculated free energies of mixing are all negative. See the following Table 5.

Platford[61] has estimated the excess Gibbs energies for $MgCl_2$-$CaCl_2$-H_2O at $25^{\circ}C$ and at various ionic strengths. The signs of these energies are all positive and the magnitudes of the free energies increase with increasing ionic strength. At an ionic strength of 3 Platford gives the free energy as 1 cal/kg solvent. This is in contrast to the value of 2 cal/kg solvent evaluated by Robinson and Bower.[62] The difference in these values is probably due to the type of equation employed in calculating the excess free energy. Platford applied an equation which is ionic strength dependent whereas Robinson and coworker did not.

Robinson and Bower found that the sum $(\alpha_{23} + \alpha_{32})$ varied linearly with molal concentration going from relatively large negative numbers at lower concentrations through zero at a concentration of 4 molal. This means a plot of excess free energies versus molal concentration is linear. If the alkaline earth cations have similar structural effects on water and the ion-water interaction contributes more to the over-all interactions in a multicomponent alkaline earth chloride solution, the one would expect that the sign of the free energy of mixing for $SrCl_2$-$CaCl_2$-H_2O would also be positive. But this work indicates that although the free energies of $SrCl_2$-$CaCl_2$-H_2O are of small magnitude, the signs are negative at all concentrations studied by Wu. Also plotting the RTg_0 (in calories/kg solvent) versus molal concentration from Table 5 yields not a linear curve but a saw-tooth curve. See the following Figure 16. An interesting point about the curve is that there is no tendency for RTg_0 to go through zero as the concentration is increased, which is a striking contrast to the curve deduced from the Robinson-Bower data.

Table 5: (Calculated RTg_0's from Wu's data)

m	α_{12}	α_{21}	$\alpha_{12} + \alpha_{21}$	RTg_0	$5.18RTg_0$
0.1	0.0164	-0.0151	0.0013	-0.77	-3.98
0.2	0.0156	-0.0145	0.0011	-0.65	-3.38
0.4	0.0151	-0.0143	0.0008	-0.48	-2.45
0.5	0.0148	-0.0145	0.0003	-0.18	-0.98
0.6	0.0156	-0.0147	0.0009	-0.53	-2.76
0.8	0.0158	-0.0153	0.0005	-0.30	-1.53
1.0	0.0166	-0.0158	0.0008	-0.48	-2.43
1.2	0.0166	-0.0162	0.0004	-0.24	-1.24
1.4	0.0174	-0.0162	0.0012	-0.71	-3.66
1.6	0.0173	-0.0164	0.0009	-0.53	-2.76
1.8	0.0182	-0.0169	0.0013	-0.77	-3.98
2.0	0.0182	-0.0171	0.0011	-0.65	-3.38
2.2	0.0186	-0.0175	0.0011	-0.65	-3.38
2.4	0.0192	-0.0179	0.0013	-0.77	-3.98
2.5	0.0194	-0.0179	0.0015	-0.89	-4.58
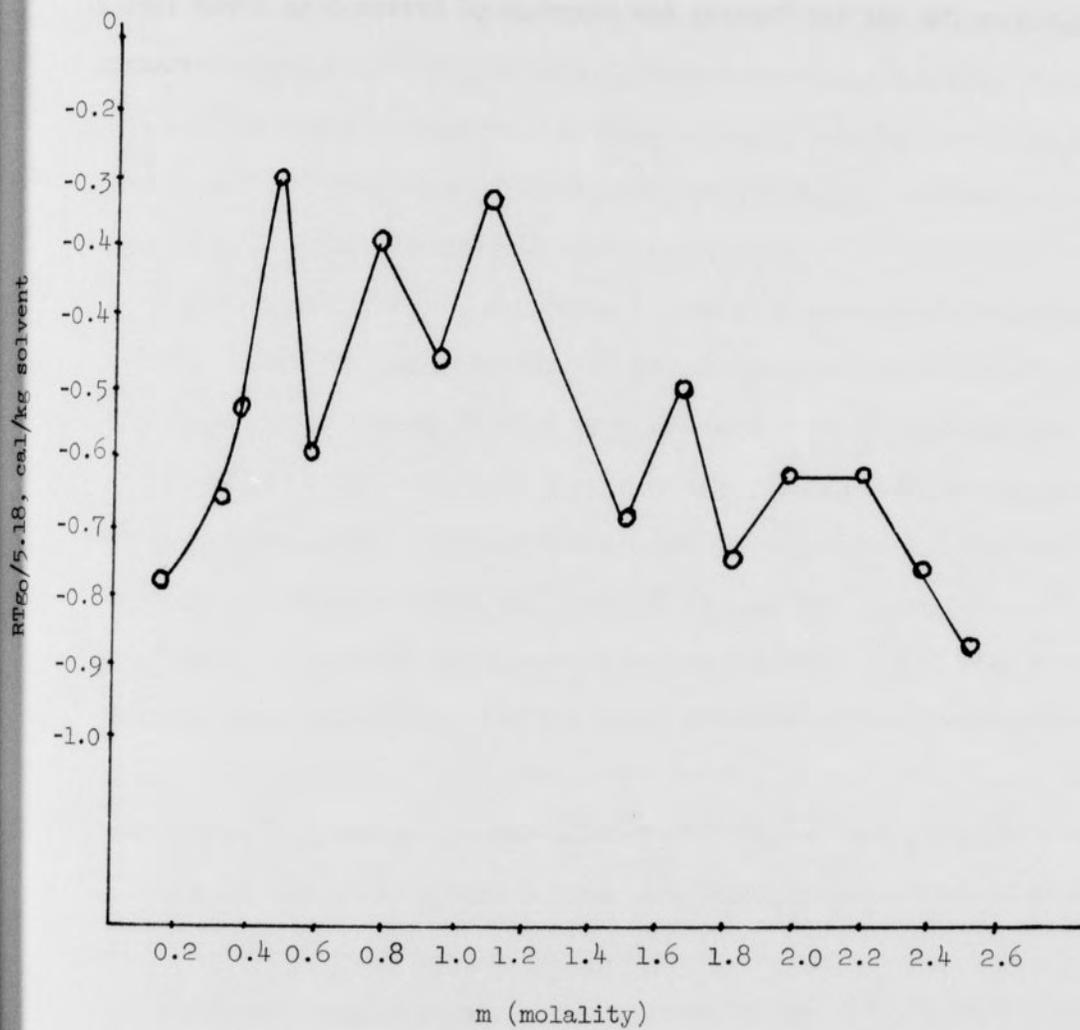
Figure 16: RTg_o *versus* Concentration (in molal units)

There is very little conclusion that can be drawn from the way
the free energies of mixing vary with temperature in this work since
there are only two points. About the only remark that can be made is
that there is a large decrease in the free energy at 60°C, which may be
a real trend as observed by Anderson and Petree[4] for the HCl-NaCl-H_2O
mixture.

SUMMARY

Heats of mixing at 40°, 60°, and $80^\circ C$ have been determined for the following mixtures: $BaCl_2-MgCl_2-H_2O$; $BaCl_2-CaCl_2-H_2O$; $BaCl_2-SrCl_2-H_2O$; and $SrCl_2-CaCl_2-H_2O$ (only at $60^\circ C$). Temperature dependence of the heats of mixing was observed for $BaCl_2-MgCl_2-H_2O$ and $BaCl_2-CaCl_2-H_2O$. Except at $80^\circ C$, the heat of mixing for $BaCl_2-SrCl_2-H_2O$ seemed to have stayed pretty much around that observed at $25^\circ C$.

These results were interpreted in terms of ion-solvent structural effects. From the point of view of the cluster theory and the fact that all the heats of mixing in this work were endothermic, the alkaline earth cations were denoted as structure makers. However, in the light of studies of single alkaline earth chloride solutions and the fact that in terms of the magnitude, the heats of mixing were largest for a mixture with the largest difference in cations' sizes, it has been concluded that the heats of mixing alkaline earth chlorides are difference-in-size-of-cations dependent. In other words, it is probably safe to say that the statistical theory (in the name of the cluster theory) becomes applicable where the sizes of the cations are almost equal and any skew term can be interpreted as arising from like charge triplet and/or higher order interaction. However, when the sizes of the cations in a mixture are quite different then it becomes apparent that the structural influences of ion-solvent interactions are difference-in-size-of-cations dependent.

This is probably a reasonable conclusion for the order of the structure breaking ability of the cations in this work is $BaCl_2$-$SrCl_2$ > $BaCl_2$-$CaCl_2$ > $BaCl_2$-$MgCl_2$ with the latter structuring more water molecules.

Excess Gibbs free energies of mixing were determined for $SrCl_2$-$CaCl_2$-H_2O mixture at 25° and 60^oC. As opposed to other works on alkaline earth halide mixtures, the sign of these excess free energies have been found to be negative at all concentrations studied. A conclusive statement has been avoided here because the data from which the reference free energy was calculated were derived results rather than experimental.

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TABLE I. A

$BaCl_2$-$MgCl_2$-H_2O Mixings at 40°C

A = 57.3942; SA = 0.6332; B = 8.2086; SB = 0.8036; SYBC = 0.0557

DELH	HCALC	ERROR	XF	XI	W	F2	F3
2.22456	2.28887	-0.06431	0.0611100	0.0000000	1.0000	0.0354317	0.0311012
2.03348	1.96045	0.07303	0.1189600	0.0611100	1.0000	0.0312938	0.0200237
1.74216	1.68742	0.05474	0.1687200	0.1143700	1.0000	0.0276831	0.0120090
2.27266	2.29624	-0.02358	0.0613100	0.0000000	1.0000	0.0355476	0.0311887
1.73703	1.78128	-0.04425	0.9383100	1.0000000	1.0000	0.0354848	-0.0311067
1.79903	1.77598	0.02306	0.9384900	1.0000000	1.0000	0.0353812	-0.0310286
1.63581	1.63355	0.00226	0.8808000	0.9384900	1.0000	0.0313227	-0.0200020

XM1 = 2.86589; XM2 = 0.46478

AO = 57.7557; SAO = 2.6988

SUM ERRORS SQUARED = 0.339E 00; F = 104.3291

SYB = 0.2377

APPENDIX

HEAT OF MIXING DATA: COMPUTER FIT

Symbols used in this Appendix

DELH = experimental heat of mixing

HCALC = least squares heat in calories

A = I^2RTh_0

B = I^2RTh_1

XF = final mole fraction of $BaCl_2$

XI = initial mole fraction of $BaCl_2$

W = weighting factor

TABLE I. B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
2.22456	2.04638	0.17818	0.0611100	0.0000000	1.0000	0.6175400	0.5798000
2.03348	1.80739	0.22609	0.1189600	0.0611100	1.0000	0.6139900	0.5761600
1.74216	1.59885	0.14331	0.1687200	0.1143700	1.0000	0.6127600	0.5751700
2.27266	2.05307	0.21959	0.0613100	0.0000000	1.0000	0.6176700	0.5798000
1.73703	2.04945	-0.31242	0.9383100	1.0000000	1.0000	0.6130300	0.5752100
1.79903	2.04346	-0.24443	0.9384900	1.0000000	1.0000	0.6129100	0.5752100
1.63581	1.80906	-0.17325	0.8808000	0.9384900	1.0000	0.6164300	0.5785400

TABLE I. B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
2.22456	2.04638	0.17818	0.0611100	0.0000000	1.0000	0.6175400	0.5798000
2.03348	1.80739	0.22609	0.1189600	0.0611100	1.0000	0.6139900	0.5761600
1.74216	1.59885	0.14331	0.1687200	0.1143700	1.0000	0.6127600	0.5751700
2.27266	2.05307	0.21959	0.0613100	0.0000000	1.0000	0.6176700	0.5798000
1.73703	2.04945	-0.31242	0.9383100	1.0000000	1.0000	0.6130300	0.5752100
1.79903	2.04346	-0.24443	0.9384900	1.0000000	1.0000	0.6129100	0.5752100
1.63581	1.80906	-0.17325	0.8808000	0.9384900	1.0000	0.6164300	0.5785400

TABLE II. A

$MgCl_2$-$BaCl_2$-H_2O Mixings at $60^{\circ}C$

A = 47.4017; SA = 0.3864; B = 3.3682; SB = 0.4886; SYBC = 0.0318; t = 2.571

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.52672	1.53314	-0.00642	0.9400200	1.0000000	1.0000	0.0345010	-0.0303622
1.36051	1.38168	-0.02117	0.8838300	0.9400200	1.0000	0.0305545	-0.0197902
1.42840	1.43346	-0.00506	0.9403600	1.0000000	1.0000	0.0322595	-0.0284116
1.35923	1.34078	0.01845	0.8858100	0.9403360	1.0000	0.0296602	-0.0193474
1.27490	1.25169	0.02321	0.8308400	0.8838300	1.0000	0.0272370	-0.0116943
1.77943	1.73873	0.04070	0.0590700	0.0000000	1.0000	0.0345179	0.0304399
1.70126	1.74605	-0.04479	0.0593200	0.0000000	1.0000	0.0346642	0.0305517

XM1 = 5.20884; XM2 = 0.48230

AO = 46.7677; SAO = 1.1106

SUM ERRORS SQUARED = 0.531E-01; F = 47.5281

SYB = 0.0941

TABLE II. B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
1.52672	1.61353	-0.08681	0.9400200	1.0000000	1.0000	0.6119100	0.5752100
1.36051	1.42897	-0.06846	0.8838300	0.9400200	1.0000	0.6152400	0.5784600
1.42840	1.50871	-0.08031	0.9403600	1.0000000	1.0000	0.5752100	0.0000000
1.35923	1.38714	-0.02791	0.8858100	0.9403360	1.0000	0.6140600	0.5784300
1.27490	1.27381	0.00109	0.8308400	0.8838300	1.0000	0.6186300	0.5815300
1.77943	1.61432	0.16511	0.0590700	0.0000000	1.0000	0.6210400	0.5843600
1.70126	1.62117	0.08009	0.0593200	0.0000000	1.0000	0.6212100	0.5843600

TABLE III. A

BaCl$_2$-MgCl$_2$-H$_2$O Mixings at 80°C

A = 45.1846; SA = 0.7049; B = 5.3470; SB = 0.8494; SYBC = 0.0714

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.80500	1.81788	-0.01288	0.0618000	0.0000000	1.0000	0.0364519	0.0319465
1.51000	1.49295	0.01705	0.9361400	1.0000000	1.0000	0.0368442	-0.0321384
1.85900	1.83990	0.01910	0.0624700	0.0000000	1.0000	0.0368987	0.0322886
1.53300	1.50526	0.02774	0.9359200	1.0000000	1.0000	0.0371460	-0.0323853
1.43400	1.51422	-0.08022	0.9352000	1.0000000	1.0000	0.0373599	-0.0325180
1.90500	1.83337	0.07163	0.0625300	0.0000000	1.0000	0.0367682	0.0321700
1.41600	1.34958	0.06642	0.8768300	0.9359200	1.0000	0.0322556	-0.0201758
1.45400	1.56778	-0.11378	0.1206800	0.0618000	1.0000	0.0322720	0.0204940

XM1 = 3.34612; XM2 = 0.47072

AO = 45.1573; SAO = 1.7994

SUM ERRORS SQUARED = 0.232E 00; F = 39.6106

SYB = 0.1822

TABLE III. B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
1.80500	1.64607	0.15893	0.0618000	0.0000000	1.0000	0.6286900	0.5898400
1.51000	1.66378	-0.15378	0.9361400	1.0000000	1.0000	0.6163100	0.5769500
1.85900	1.66624	0.19276	0.0624700	0.0000000	1.0000	0.6300200	0.5906600
1.53300	1.67741	-0.14441	0.9359200	1.0000000	1.0000	0.6193700	0.5796800
1.43400	1.68707	-0.25307	0.9352000	1.0000000	1.0000	0.6164900	0.5765400
1.90500	1.66035	0.24465	0.0625300	0.0000000	1.0000	0.6272300	0.5880100
1.41600	1.45658	-0.04058	0.8768300	0.9359200	1.0000	0.6225600	0.5832600
1.45400	1.45732	-0.00332	0.1206800	0.0618000	1.0000	0.6233200	0.5842000

TABLE IV. A

BaCl$_2$-CaCl$_2$-H$_2$O Mixings at 40°C

A = 26.5269; SA = 0.5043; B = 6.4859; SB = 0.6818; SYBC = 0.0513

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.10022	1.13878	-0.03856	0.0613600	0.0000000	1.0000	0.0353472	0.0310094
0.96885	0.95633	0.01252	0.1193400	0.0613600	1.0000	0.0311825	0.0199131
0.86433	0.79957	0.06476	0.1738600	0.1193400	1.0000	0.0273735	0.0113219
1.11381	1.13913	-0.02532	0.0613800	0.0000000	1.0000	0.0353585	0.0310179
0.95565	0.95200	0.00365	0.1190900	0.0613800	1.0000	0.0310384	0.0198356
0.85342	0.80096	0.05246	0.1736800	0.1190900	1.0000	0.0274162	0.0113627
0.79065	0.74378	0.04687	0.9379700	1.0000000	1.0000	0.0356803	-0.0312538
0.66073	0.69833	-0.03760	0.8799400	0.9379700	1.0000	0.0311659	-0.0197981
0.76382	0.74152	0.02230	0.9377200	1.0000000	1.0000	0.0355663	-0.0311362
0.61309	0.70101	-0.08792	0.8796000	0.9377200	1.0000	0.0312800	-0.0198514

XM1 = 1.92191; XM2 = 0.44139

AO = 26.8942; SAO = 1.6635

SUM ERRORS SQUARED = 0.260E 00; F = 90.5089

SYB = 0.1698

TABLE IV. B (Contd.)

DELH	HCALC	ERROR	XF	XI	W	WTSF	WTSI
1.10022	0.95064	0.14958	0.0613600	0.0000000	1.0000	0.6137200	0.5760600
0.96885	0.83863	0.13022	0.1193400	0.0613600	1.0000	0.6107000	0.5279800
0.86433	0.73619	0.12814	0.1738600	0.1193400	1.0000	0.6077300	0.5701000
1.11381	0.95094	0.16287	0.0613800	0.0000000	1.0000	0.6137300	0.5760600
0.95565	0.93475	0.12090	0.1190900	0.0613800	1.0000	0.6105300	0.5729800
0.85342	0.73734	0.11608	0.1736800	0.1190900	1.0000	0.6077900	0.5701300
0.79065	0.95959	-0.16894	0.9379700	1.0000000	1.0000	0.6132500	0.5752100
0.66073	0.83818	-0.17745	0.8799400	0.9379700	1.0000	0.6117900	0.5752100
0.76382	0.95653	-0.19271	0.9377200	1.0000000	1.0000	0.6090000	0.5710700
0.61309	0.84125	-0.22816	0.8796000	0.9377200	1.0000	0.6118700	0.5739500

TABLE V. A

$BaCl_2-CaCl_2-H_2O$ Mixings at $60^{\circ}C$

$A = 23.8987$; $SA = 0.8443$; $H = 3.9328$; $SB = 1.0935$; $SYBC = 0.0772$

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.58780	0.65537	-0.06757	0.8822300	0.9395300	1.0000	0.0306707	-0.0197373
0.75750	0.69943	0.05807	0.9392100	1.0000000	1.0000	0.0342117	-0.0300522
0.72950	0.70357	0.02593	0.9388600	1.0000000	1.0000	0.0344096	-0.0302020
0.58520	0.66148	-0.07628	0.8806100	0.9388600	1.0000	0.0309305	-0.0197627
0.87335	0.95447	-0.08112	0.0605700	0.0000000	1.0000	0.0348919	0.0306651
0.78170	0.69709	0.08461	0.1714400	0.1172600	1.0000	0.0272718	0.0115252
0.92703	0.94364	-0.01661	0.0603500	0.0000000	1.0000	0.0344937	0.0303303
0.90482	0.81942	0.08540	0.1179300	0.0603500	1.0000	0.0310041	0.0199494

$XM1 = 2.56590$; $XM2 = 0.45966$

$AO = 23.7882$; $SAO = 1.3878$

SUM ERRORS SQUARED = $0.113E\ 00$; $F = 12.9383$

$SYB = 0.1269$

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TABLE V. B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.58780	0.72960	-0.14180	0.8822300	0.9395300	1.0000	0.6067100	0.5697000
0.75750	0.81383	-0.05633	0.9392100	1.0000000	1.0000	0.5992100	0.5628000
0.72950	0.81854	-0.08904	0.9388600	1.0000000	1.0000	0.5994500	0.5628000
0.58520	0.73578	-0.15058	0.8806100	0.9388600	1.0000	0.6029900	0.5655800
0.87335	0.83001	0.04334	0.0605700	0.0000000	1.0000	0.6132000	0.5760600
0.78170	0.64875	0.13295	0.1714400	0.1172600	1.0000	0.6075000	0.5702100
0.92703	0.82054	0.10649	0.0603500	0.0000000	1.0000	0.6082700	0.5715600
0.90482	0.73753	0.16729	0.1179300	0.0603500	1.0000	0.6104400	0.5730300

TABLE VI. A

$BaCl_2$-$CaCl_2$-H_2O Mixings at $80^{\circ}C$

A = 17.2946; SA = 0.6346; B = 4.8413; SB = 0.8801; SYBC = 0.0564

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.54485	0.49259	0.05226	0.9341100	1.0000000	1.0000	0.0376277	-0.0326691
0.39832	0.46518	-0.06686	0.8727500	0.9341100	1.0000	0.0324773	-0.0199320
0.48584	0.48899	-0.00315	0.9345700	1.0000000	1.0000	0.0373651	-0.0324754
0.60641	0.66809	-0.06168	0.1268100	0.0646500	1.0000	0.0329398	0.0203265
0.64164	0.66005	-0.01841	0.1260400	0.0654500	1.0000	0.0325441	0.0200803
0.67895	0.63672	0.04223	0.1181300	0.0606100	1.0000	0.0312036	0.0200489
0.68836	0.63588	0.05248	0.1184800	0.0609900	1.0000	0.0311733	0.0199838

XM1 = 1.75706; XM2 = 0.43371

AO = 16.9792; SAO = 1.5321

SUM ERRORS SQUARED = 0.112E 00; F = 30.2607

SYB = 0.1367

TABLE VI. B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.54485	0.63889	-0.09404	0.9341100	1.0000000	1.0000	0.6113500	0.5710700
0.39832	0.55144	-0.15312	0.8727500	0.9341100	1.0000	0.6064600	0.5666200
0.48584	0.63443	-0.14859	0.9345700	1.0000000	1.0000	0.6110500	0.5710700
0.60641	0.55929	0.04712	0.1268100	0.0646500	1.0000	0.6068800	0.5665500
0.64164	0.55257	0.08907	0.1260400	0.0654500	1.0000	0.6145900	0.5747500
0.67895	0.52981	0.14914	0.1181300	0.0606100	1.0000	0.6151600	0.5775000
0.68836	0.52930	0.15906	0.1184800	0.0609900	1.0000	0.6151300	0.5774800

TABLE VII. A

BaCl$_2$-SrCl$_2$-H$_2$O Mixings at 40°C

A = 14.0308; SA = 0.2714; B = 1.8710; SB = 0.3671; SYBC = 0.0277

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.55605	0.55464	0.00141	0.0616600	0.0000000	1.0000	0.0353929	0.0310283
0.47400	0.47132	0.00268	0.1192900	0.0616600	1.0000	0.0309576	0.0197541
0.43772	0.40589	0.03183	0.1738000	0.1192900	1.0000	0.0274160	0.0113454
0.53555	0.55551	-0.01996	0.0612900	0.0000000	1.0000	0.0354453	0.0311004
0.48933	0.47418	0.01515	0.1188000	0.0612900	1.0000	0.0311392	0.0199236
0.45363	0.43976	0.01387	0.9378600	1.0000000	1.0000	0.0354864	-0.0310762
0.36554	0.40064	-0.03510	0.8797600	0.9378600	1.0000	0.0311969	-0.0198175
0.47864	0.43954	0.03910	0.9378900	1.0000000	1.0000	0.0354693	-0.0310632
0.37355	0.39883	-0.02528	0.8800500	0.9378900	1.0000	0.0310589	-0.0197497
0.33746	0.36504	-0.02758	0.8255500	0.8800500	1.0000	0.0275266	-0.0113190

XM1 = 3.03259; XM2 = 0.46709

AO = 14.0309; SAO = 0.5261

SUM ERRORS SQUARED = 0.259E-01; E = 25.8121

SYB = 0.0537

TABLE VII. B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.55605	0.49659	0.05946	0.0616600	0.0000000	1.0000	0.6117200	0.5740000
0.47400	0.43436	0.03964	0.1192900	0.0616600	1.0000	0.6099400	0.5724800
0.43772	0.38467	0.05305	0.1738000	0.1192900	1.0000	0.6087500	0.5710700
0.53555	0.49733	0.03822	0.0612900	0.0000000	1.0000	0.6160800	0.5783200
0.48933	0.43691	0.05242	0.1188000	0.0612900	1.0000	0.6144500	0.5768000
0.45363	0.49791	-0.04428	0.9378600	1.0000000	1.0000	0.6089100	0.5710700
0.36554	0.43772	-0.07218	0.8797600	0.9378600	1.0000	0.6103400	0.5725300
0.47864	0.49767	-0.01903	0.9378900	1.0000000	1.0000	0.6088900	0.5710700
0.37355	0.43578	-0.06223	0.8800500	0.9378900	1.0000	0.6101700	0.5725400
0.33746	0.38622	-0.04876	0.8255500	0.8800500	1.0000	0.6118000	0.5739100

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TABLE VIII.   A

BaCl$_2$-SrCl$_2$-H$_2$O Mixings at 60°C

A = 13.8594; SA = 0.2584; B = 1.1310; SB = 0.3496; SYBC = 0.0260

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.47393	0.44602	0.02791	0.9379600	1.0000000	1.0000	0.0346592	-0.0303586
0.40600	0.40854	-0.00254	0.8787900	0.9379600	1.0000	0.0310843	-0.0196919
0.42582	0.41530	-0.02548	0.9381400	1.0000000	1.0000	0.0350707	-0.0307318
0.41151	0.40142	0.01009	0.8800000	0.9381400	1.0000	0.0305499	-0.0194383
0.35729	0.36428	-0.00699	0.8249600	0.8800000	1.0000	0.0271937	-0.0111473
0.55318	0.51280	0.04038	0.0596900	0.0000000	1.0000	0.0345198	0.0303989
0.46871	0.45298	0.01573	0.1178000	0.0596900	1.0000	0.0310500	0.0200280
0.49377	0.51202	-0.01825	0.0600500	0.0000000	1.0000	0.0344687	0.0303290
0.41400	0.45438	-0.04038	0.1179300	0.0600500	1.0000	0.0311477	0.0200604
0.38840	0.39245	-0.00405	0.1722800	0.1179300	1.0000	0.0273788	0.0114876

XM1 = 4.60505; XM2 = 0.47970

AO = 13.8610; SAO = 0.3706

SUM ERRORS SQUARED = 0.125E-01; F = 10.5098

SYB = 0.0373

TABLE VIII.   B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.47393	0.48041	-0.00648	0.9379600	1.0000000	1.0000	0.5956100	0.5586600
0.40600	0.43086	-0.02486	0.8787900	0.9379600	1.0000	0.5978000	0.5600900
0.42582	0.48612	-0.06030	0.9381400	1.0000000	1.0000	0.6043200	0.5669400
0.41151	0.42345	-0.01194	0.8800000	0.9381400	1.0000	0.5971000	0.5600900
0.35729	0.37693	-0.01964	0.8249600	0.8800000	1.0000	0.5989000	0.5614400
0.55318	0.47848	0.07470	0.0596900	0.0000000	1.0000	0.6150300	0.5783200
0.46871	0.43039	0.03832	0.1178000	0.0596900	1.0000	0.6056700	0.5682300
0.49377	0.47777	0.01600	0.0600500	0.0000000	1.0000	0.5106700	0.5740000
0.41400	0.43174	-0.01774	0.1179300	0.0600500	1.0000	0.6100900	0.5725200
0.38840	0.37950	0.00890	0.1722800	0.1179300	1.0000	0.6086000	0.5711000

TABLE IX.   A

BaCl$_2$-SrCl$_2$-H$_2$O Mixings at 80°C

A = 10.4949; SA = 0.3843; B = 2.8643; SB = 0.4882; SYBC = 0.0346

0.26971	0.27143	-0.00172	0.9406100	1.0000000	1.0000	0.0340529	-0.0300081
0.31106	0.26234	0.04872	0.8840200	0.9406100	1.0000	0.0303691	-0.0196820
0.24725	0.27459	-0.02733	0.9397161	0.0000000	1.0000	0.0344267	-0.0302759
0.24835	0.25706	-0.00871	0.9944700	0.9397100	1.0000	0.0297601	-0.0192952
0.41774	0.44214	-0.02440	0.0591600	0.0000000	1.0000	0.0339577	0.0299398
0.39973	0.37338	0.02635	0.1152400	0.0591600	1.0000	0.0302085	0.0196717
0.43830	0.40555	0.03275	0.0538000	0.0000000	1.0000	0.0310743	0.0277307
0.33214	0.37219	-0.04005	0.1153000	0.0593800	1.0000	0.0301159	0.0195946

XM1 = 1.78615; XM2 = 0.43521

AO = 10.4335; SAO = 0.9231

SUM ERRORS SQUARED = 0.483E-01; F = 34.4164

SYB = 0.0830

TABLE IX.   B (Contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.26971	0.35529	-0.08558	0.9406100	1.0000000	1.0000	0.6095800	0.5706600
0.31106	0.31685	-0.00579	0.8840200	0.9406100	1.0000	0.6101000	0.5761200
0.24725	0.35919	-0.11194	0.9397161	0.0000000	1.0000	0.6077100	0.5710700
0.24835	0.31050	-0.06215	0.8844700	0.9397100	1.0000	0.6091200	0.5733200
0.41774	0.35430	0.06344	0.0591600	0.0000000	1.0000	0.6100900	0.5740000
0.39973	0.31518	0.08455	0.1152400	0.0591600	1.0000	0.6088300	0.5725400
0.43830	0.32421	0.11409	0.0538000	0.0000000	1.0000	0.6104300	0.5741800
0.33214	0.31421	0.01793	0.1153000	0.0593800	1.0000	0.6087400	0.5725500

TABLE X. A

$SrCl_2$-$CaCl_2$-H_2O Mixings at 60°C

A = 3.5186; SA = 0.1051; B = 1.4778; SB = 0.1198; SYBC = 0.0091

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.07604	0.07847	-0.00243	0.9384900	1.0000000	1.0000	0.0353067	-0.0309633
0.08251	0.07869	0.00382	0.9383300	1.0000000	1.0000	0.0353989	-0.0310327
0.15890	0.16918	-0.01028	0.0609800	0.0000000	1.0000	0.0351282	0.0308439
0.07714	0.07850	-0.00136	0.9384700	1.0000000	1.0000	0.0353180	-0.0309718
0.16674	0.16998	-0.00324	0.0612800	0.0000000	1.0000	0.0353012	0.0309747
0.18347	0.16995	0.01352	0.0612700	0.0000000	1.0000	0.0352953	0.0309702

XM1 = 1.38755; XM2 = 0.40611

AO = 3.5158; SAO = 0.5871

SUM ERRORS SQUARED = 0.129E-01; F = 151.9284

SYB = 0.0508

TABLE X.   B (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.07604	0.12413	-0.04809	0.9384900	1.0000000	1.0000	0.6116200	0.5740000
0.08251	0.12446	-0.04195	0.9383300	1.0000000	1.0000	0.6117300	0.5740000
0.15890	0.12350	0.03540	0.0609800	0.0000000	1.0000	0.6134700	0.5760600
0.07714	0.12417	-0.04703	0.9384700	1.0000000	1.0000	0.6116300	0.5740000
0.16674	0.12411	0.04263	0.0612800	0.0000000	1.0000	0.6136700	0.5760600
0.18347	0.12409	0.05938	0.0612700	0.0000000	1.0000	0.6136600	0.5760600