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The recent increase of interest in high temperature thermodynamic data has revealed that very little precise data exists. Also, the data that does exist contains some large uncertainties. An efficient and accurate method is needed by which high temperature thermodynamic data can be obtained. This is essential not only for extending the present knowledge of aqueous electrolyte solutions, but also to remove the uncertainties now existing in published data.

The heats of dilution of sodium chloride have been measured over a concentration range of 0.1 m to 6.0 m at 40°, 50°, 60°, 70°, and 80°. These measurements were made using a micro-degree calorimeter. The experimental data was extrapolated to infinite dilution using the extended Debye-Hückel equation.

The partial molal heat contents of solute and solvent were calculated from the experimental heats of dilution. These values in turn were used to correct existing activity coefficients and osmotic coefficients at 25° to higher temperatures. The calculated values were found to be in excellent agreement with existing data. The apparent molal heat capacity of solute was also calculated from partial molal heat content of solute; however, no real conclusions as to the accuracy of these values could be reached. It is concluded that use of heat of dilution data to correct existing values of thermodynamic quantities to higher temperatures is an efficient and precise technique.

HEATS OF DILUTION OF SODIUM CHLORIDE
TEMPERATURE DEPENDENCE

by

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INTRODUCTION

The thermodynamic properties of aqueous electrolyte solutions have been under investigation for many years. Early work by Arrhenius[1] led to many attempts to correlate experimental results with theoretical considerations. The Debye-Hückel limiting law[2] was the most successful of these attempts in predicting the behavior of electrolytes. This simple theory considers only interionic attraction effects in a continuous dielectric solvent, and provides a method for extrapolation of electrolyte data in the real concentration range to infinite dilution. The Debye-Hückel limiting law was the subject of many investigations to prove its validity; therefore, it is not surprising that extensive data exists for 1-1 electrolytes at 25°.

The importance of electrolyte solutions cannot be overlooked. The extent of electrolyte's role in one's life ranges from the starting of a car in the morning to the performing of vital life processes in the blood stream. In recent years, man has become aware that his demand for fresh water is increasing while the supply is steadily dwindling. This trend makes the development of a quick and efficient method for the conversion of sea water to fresh water a necessity. Most methods now under investigation for desalination of sea water involve high temperature processes. In order for these procedures to be economical and efficient, the behavior of electrolyte solutions must be well characterized at elevated temperatures. However, very little thermodynamic properties of electrolyte solutions at high temperatures exists.

There are two procedures for obtaining high temperature thermodynamic properties. The first method entails the direct measurement of the properties at the desired temperature. However, difficulties are encountered in experimental procedures which make direct measurements susceptable to limitations. For example, activity coefficients are measured at high temperatures using three different techniques: electromotive force measurements which can be made up to 40°, data from vapor pressure lowering which is valid above 70° and boiling point elevation data which can be used in the temperature range of 60° to 100°. The data from these sources still leave areas of large uncertainties due to experimental limitations present in the methods.

The second method for obtaining high temperature thermodynamic properties is to extend by calculation existing 25° data to the desired temperature using heat capacity data. Direct measurement of the heat capacity of a system at elevated temperatures is limited by experimental difficulties. The experimental error present in measurements below 0.4 m makes it impossible to directly obtain data. An upper limit of 2.0 m is also placed upon heat capacity measurements for a similar reason. The heat of solution of a substance has also been used to obtain partial molal heat capacity data, but this method can only be used to secure values at infinite dilution.

The task of obtaining high temperature thermodynamic data is a difficult one no matter which method is used, since both methods are limited by experimental technique. The second method is preferred since the experimental drawbacks are not so large as the ones associated with direct measurements. However, it can easily be seen that there is a definite need for a relatively quick and accurate method for obtaining high temperature thermodynamic data.

THERMODYNAMIC RELATIONSHIPS

The heat content of solutions has always been of interest to physical chemists. The heat content cannot be determined but is of theoretical importance for describing all other thermal properties of solutions. It is convenient to break the heat content up into its partial molal components, defined by the relation,

$$H = n_1\overline{H}_1 + n_2\overline{H}_2 \qquad \text{Eq. 1}$$

$\underline{H}$ = total heat content
$\overline{H}_1$ = partial molal heat content of solvent
$\overline{H}_2$ = partial molal heat content of solute
n_1 = number of moles of solvent
n_2 = number of moles of solute

The absolute values of the partial molal heat contents are also not measurable. An arbitrarily defined reference state is chosen and a relative partial molal heat content is introduced, defined as,

$$L = H - H^{\circ} \qquad \text{Eq. 2}$$

the difference between the heat content of the system and some reference state, H°. The relative heat content of the solution in partial molal quantities is defined as,

$$L = n_1(\overline{H}_1 - \overline{H}_1^{\circ}) + n_2(\overline{H}_2 - \overline{H}_2^{\circ}) \qquad \text{Eq. 3}$$

The reference state chosen for the solvent is the pure liquid. The reference state chosen for the solute is the state in which the solute particles are separated by an infinite amount of solvent. The term, infinite dilution, is used to describe the reference state of the solute.

The relative partial molal heat content of the solute and solvent can now be described as

$$\overline{L}_1 = \overline{H}_1 - \overline{H}_1^{o} \qquad \text{Eq. 4}$$

$$\overline{L}_2 = \overline{H}_2 - \overline{H}_2^{o} \qquad \text{Eq. 5}$$

Upon substitution into Equation 3, one has

$$L = n_1(\overline{L}_1) + n_2(\overline{L}_2). \qquad \text{Eq. 6}$$

The relative partial heat contents are not measurable but can be derived using another thermodynamic quantity, the apparent molal heat content, defined as

$$\Phi H = \frac{H - n_1\overline{H}_1^{o}}{n_2} \qquad \text{Eq. 7}$$

ΦH = apparent molal heat content

This quantity, ΦH, is not directly measurable. Equation 7 can be rearranged to

$$H = n_1\overline{H}_1^{o} + n_2\ \Phi H. \qquad \text{Eq. 8}$$

It can easily be seen that when Equation 8 is set equal to Equation 1, at infinite dilution,

$$\Phi H^{o} = \overline{H}_2^{\ o} \qquad \text{Eq. 9}$$

Using this relationship, Equation 3 becomes

$$L = n_1\overline{H}_1 - n_1\overline{H}_1^{o} + n_2\overline{H}_2 - n_2\ \Phi H^{o} \qquad \text{Eq. 10}$$

The first three terms of this equation can then be rearranged to give

$$L = \frac{n_2(H - n_1\overline{H}_1^{\ o})}{n_2} - n_2\Phi H^{o} \qquad \text{Eq. 11}$$

Using the Equation 7 which defines apparent molal heat contents, the above equation can be expressed as

$$L = n_2\Phi H - n_2\Phi H^{o} = n_2(\Phi H - \Phi H^{o}) \qquad \text{Eq. 12}$$

$$L = n_2\ (\Phi L) \qquad \text{Eq. 13}$$

$$\Phi L = (\Phi H - \Phi H^{o}) = \text{relative apparent molal heat content} \qquad \text{Eq. 14}$$

The relative apparent molal heat content is equal to, but of opposite sign to the heat of dilution, ΔH_D, defined as the heat evolved from the isothermal isobaric addition of an infinite quantity of a pure solvent to a solution containing one mole of solute in n_1/n_2 moles of solvent.

$$\Delta H_D = \frac{H^o - n_1\overline{H}_1^o}{n_2} - \frac{H - n_1\overline{H}_1^o}{n_2} = \frac{H^o - H}{n_2} = -\Phi L \qquad \text{Eq. 15}$$

The heat of dilution can then be described as simply the difference of the heat content at infinite dilution and the heat content of a real solution. This is still not a measurable quantity since the state of infinite dilution is unobtainable in the laboratory.

The heat of dilution measured in the laboratory is $\Delta\Phi L$ or the heat evolved in going from initial concentration to final concentration. The Debye-Hückel limiting law in its extended form is then used to extrapolate the $\Delta\Phi L$ to infinite dilution. The exact method by which the experimentally obtained $\Delta\Phi L$ is extrapolated to infinite dilution is explained in the experimental section.

The Debye-Hückel theory was first used to treat activity coefficients. The limiting law for activity coefficients is expressed as

$$\ln \gamma_{\pm} = -A_y/z + z-/I^{\frac{1}{2}} \qquad \text{Eq. 16}$$

$\gamma_{\pm}$ = activity coefficient
A_y = Debye-Hückel limiting slope = $\sqrt{\frac{2\pi N_o d_1}{1000 \times 2.303^2}} \left(\frac{e^2}{DkT}\right)^3$
N_o = Avogadro number
d_1 = density of solvent
e = charge on electron
D = dielectric constant of solvent
k = Boltzmann constant
$z + z-$ = charge on positive and negative ions
I = ionic strength

This treatment, due to the approximations, is valid only in dilute solutions. Nevertheless, it is an invaluable aid in extrapolating to infinite dilution quantities such as heat content, heat capacities, and activities.

The theory assumes that the solvent is a continuous dielectric in which electrical contribution to chemical potential can be calculated for ion interaction by Coulomb's law. Since the solvent contribution is considered only as the dielectric effect on charged particles and there is no accounting for bulk solvent structure, this assumption restricts the theory to dilute concentrations. A second assumption made in the Debye-Huckel theory is that the contribution of all ions is the same because every ion effects every other ion in the same way.

The extended Debye-Hückel equation is used to derive the equation for ΦL. This equation for the activity coefficient takes the form

$$\ln \gamma_{\pm} = -Ay/z+z-/\frac{Am^{\frac{1}{2}}}{1 + Am^{\frac{1}{2}}} + \frac{2\nu+\nu-}{\nu}\ Bm + \frac{2\nu+\nu-}{\nu}\ Cm^{3/2} \qquad \text{Eq. 17}$$

A = distance of closest approach parameter
B,C = coefficients specific for solute and temperature

The B and C terms account for all interactions which occur, except for the very close specific interactions of ions as hard spheres. This is accounted for by the distance of closest approach parameter, A. Using the relationships for ΦL,

$$L = m\Phi L = H - H^{o} \qquad \text{Eq. 18}$$

$$H - H^{o} = -\nu RT^{2}\left(\frac{\partial \ln \gamma \pm}{\partial T}\right. \qquad \text{Eq. 19}$$

Substituting Equation 19 into Equation 16 and carrying out the required differentiation, the extended Debye-Hückel equation for ΦL takes the form

$$\Phi L = \frac{\nu}{2} AH/z+z-/Am^{\frac{1}{2}}\left[1\ \frac{1}{+Am^{\frac{1}{2}}} - \frac{\sigma(m^{\frac{1}{2}})}{3}\right] \qquad \text{Eq. 20}$$

$$+\ 2.303RT^{2}\ \frac{dB}{dT}\ m\nu+\nu+ \ +\ 2.303RT^{2}\ \frac{dC}{dT}\ m^{3/2}$$

where

$$\sigma(m^{\frac{1}{2}}) = 3(m^{\frac{1}{2}})^{-3}\left[1 + m^{\frac{1}{2}} - 2\ln(1+m^{\frac{1}{2}} - \frac{1}{1+m^{\frac{1}{2}}}\right]$$

The differential portions of ${}^{dB}/dT$ and ${}^{dC}/dT$ are usually written as coefficients B and C. The extended Debye-Hückel equation for ΦL takes the form

$$\Phi L = AHm^{\frac{1}{2}}\left[\frac{1}{1+Am^{\frac{1}{2}}} - \sigma\frac{(Am^{\frac{1}{2}})}{3}\right] + Bm + Cm^{3/2} \qquad \text{Eq. 21}$$

Once ΦL is determined it is possible to derive an expression for partial molal heat contents as a function of ΦL. Differentiation of relationship

$$L = n_2\ \Phi L \qquad \text{Eq. 13}$$

with respect to n_2 at constant temperature, pressure, and n_1 yields

$$\overline{L}_2 = \frac{\partial L}{\partial n_2} = \Phi L + n_2\frac{\partial \Phi L}{\partial n_2} \qquad \text{Eq. 22}$$

A more convenient way of expressing $\overline{L}_2$ is in terms of molality,

$$\overline{L}_2 = \Phi L + \frac{\sqrt{m}}{2}\ \frac{\partial \Phi L}{\partial \sqrt{m}} \qquad \text{Eq. 23}$$

The reason for writing $\overline{L}_2$ in this way is that the slope of ΦL vs. $\sqrt{m}$ curve, $\partial\Phi L/\partial\sqrt{m}$, is nearer linearity than the previous expression 22.

This expression for $\overline{L}_2$ is then substituted back into Equation 6 and the relationship describing $\overline{L}_1$ in terms of ΦL can be derived,

$$\overline{L}_1 = \frac{-M_1 m^{3/2}}{2000}\ \frac{\partial \Phi L}{\partial m} \qquad \text{Eq. 24}$$

Heat capacities, the heat content change with respect to temperature, can be derived.

$$Cp = \partial H/\partial T \qquad \text{Eq. 25}$$

The relative partial molal heat capacity of solute, $\overline{J}_2$, can be determined from $\overline{L}_2$ as a function of temperature.

$$\overline{J}_2 = \partial\overline{L}_2/\partial T \qquad \text{Eq. 26}$$

The relative partial molal heat capacity is related to the partial molal heat capacity, $\overline{Cp}_2$, by the relation

$$\overline{J}_2 = \overline{Cp}_2 - \overline{Cp}_2^{\,o} \qquad \text{Eq. 27}$$

where $\bar{C}p_2^{\circ}$ is the partial molal heat capacity of the solute at infinite dilution. The partial molal heat capacity relationships are analogous to the previously described partial molal heat content relationships.

HISTORICAL BACKGROUND

The study of electrolyte solutions can be traced to the early work of Arrhenius[3] and the discovery that certain solutes dissociate into charged species. Other authors[4,5] investigated this behavior using experimental techniques such as conductance, freezing point depression, osmotic pressure, and vapor pressure lowering. The deviations from ideality in dilute electrolyte solution were rocognized, due to the work of Sutherland[6], Noyes[7], and Bjerrum[8], as the result of long range interactions of the ions. Milner[9], in 1912, treated the problem of electrostatic interactions of the ions mathematically and derived a complicated expression which was successful, but not easily adapted to practical situations.

The development of the Debye-Hückel theory had a tremendous effect upon the investigation of electrolyte solutions. This uncomplicated theory dealt with the interionic attractions in dilute solution. The limiting law derived by Debye-Hückel provided an _a priori_ method of extrapolating thermodynamic properties such as activity coefficients, heat contents, volumes, and heat capacities to infinite dilution. This theory spurred much experimental work to check its validity. In every case the Debye-Hückel limiting law has proved accurate, and it is now accepted by most investigators.

The investigations of the heat of dilution of electrolytes before the publishing of the Debye-Hückel theory was severely handicapped by two experimental limitations. First, the instrumentation needed to measure the small heats evolved from dilutions in less concentrated ranges was not yet developed. This limited the researchers to high concentration work. Secondly, no method was available by which the experimental data could be accurately extrapolated to infinite dilution. Several early workers[10,11,12] studied the heats of dilution of sodium chloride at room temperature or below. Richard and Rowe[13,14] extrapolated heat of dilution data using a method based upon Kirchhoff's laws and the measurement of $\Delta\Phi L$ at two temperatures. In 1921, they published ΦL data for a number of electrolytes including NaCl.

In order to prove the validity of the Debye-Hückel limiting law, accurate measurements at extreme dilution were necessary. This necessitated the development of calorimeters capable of detecting very small temperature changes. The first accurate measurements of heats of dilution at low concentrations was accomplished by Nernst and Orthmann[15] and Lange and Messner[16]. Their experiments were at dilutions great enough to yield positive heats not observed previously. These measurements were made using a multijunction thermoelement in conjunction with a highly sensitive galvanometer which had a sensitivity of about 2×10^{-7} degree. The early work in this area has been reviewed by Lange and Robinson[17].

Robinson[18] and Gulbransen and Robinson[19] studied the ΦL of NaCl at temperatures of 10°, 15°, 20°, and 25°. Their measurements in the dilute range (0.1 m. to 0.000318 m.) were used to construct a curve whose slope was then compared with the Debye-Hückel limiting slope. A rather large deviation was observed with the theoretical values being from 14% to 49% larger.

The chord-area method developed by Young and co-workers[20,21,22,23] was a precise method for treatment of ΦL curves. Each dilution experiment was used to calculate a chord, which was plotted on a graph and a derivative curve was constructed by drawing a smoothed curve through the mid-points of each chord. The data of Gulbransen and Robinson was subjected to this treatment. The recalculated slopes were within a range of 0 to 5% of the theoretical values.

The heat capacities of NaCl solutions have also been investigated very extensively at 25° or below. Some of the more prominent papers were by Drucker,[24] and Randall and Rossini.[28] Rossini[29] has published the heat capacities for a number of 1-1 electrolytes at 25°. At temperatures above 25°, only a few precise studies have been made. Hess and Gramkee[30] measured heat capacities of NaCl from 1.03 m to 0.01 m at 15°, 25°, 35°, and 45°. White[31] used the above data and his own measurements from 0.2 m to 0.01 m at the same temperatures to calculate ΦCp. The data was plotted versus $m^{\frac{1}{2}}$ and parabolic curves were obtained at the higher temperatures. This behavior is contrary to the observations of Harned and Owen[32] and Gucker[33] who have observed that ΦCp varies linearly with $m^{\frac{1}{2}}$ over a wide concentration range (0.05 to 3.0 m) for a large number of 1-1 electrolytes.

Eigen and Wicke[34] measured the heat capacities of a sodium chloride solution over a large temperature range at concentrations of 1.12 m to 0.41 m. Ackermann,[35] using the data from the above paper, reported heat capacity values of aqueous sodium chloride solutions at 0.5 m, 1.0 m, and 2.0 m for a wide temperature range.

The usual experimental method employed to determine the heat capacity of a solution is the twin calorimeter technique. One calorimeter contains water and the other contains the solution under investigation. The experiment is designed so that passage of electrical current through the two calorimeters will cause the same temperature rise. The accurate determination of the ratio of the resistances of the heating elements is essential. The heat capacity of the solution is then calculated.

This technique is capable of measuring specific heats to precision of 0.01%. Values of Cp_2 and ΦCp cannot be derived to a satisfactory accuracy at low concentrations from the specific heats. This unfortunate circumstance is due to an unavoidable magnification of experimental error. The apparent molal heat capacity of the solute, ΦCp, can be calculated from the specific heat of the solution using

$$\Phi Cp = \frac{(1000 + mM_2)\ Cp - 1000Cp^{o}}{m} \qquad \text{Eq. 28}$$

where

m = molality of solution
M_2 = Molecular weight of solute
Cp = specific heat of solution
Cp^{o} = specific heat of pure solvent

When Equation 28 is differentiated and rearranged into the forms

$$\partial\Phi Cp = \left[\frac{1000}{m}\ (Cp^{o} - Cp)\right] \partial m/m \qquad \text{Eq. 29}$$

and

$$\partial\Phi Cp = \left[\frac{1000}{m}\ Cp^{o} + \Phi Cp\right] \partial Cp/Cp \qquad \text{Eq. 30}$$

it can be seen that ΦCp is more sensitive to errors in the value of Cp than in the value of m. Harned and Owen[36] have shown that an error of 0.1% in concentration would yield an error of 0.05 calorie per degree in ΦCp. However, using Equation 30, an uncertainty of just 0.01% in Cp will cause an error of 10 calories per degree in ΦCp at 0.01 m. As a result of this situation, measurements below 0.4 m are practically useless.

The partial molal heat capacities quantities can then be calculated from ΦCp using

$$C\bar{p_2} = \Phi Cp + m\ \partial Cp/\partial m \qquad \text{Eq. 31}$$

The partial molal heat capacity of the solute at infinite dilution can be obtained from Equation 31 by the fact that at infinite dilution

$$\bar{Cp}_2^{\,o} = \Phi Cp^o \qquad \text{Eq. 32}$$

Howevever, the $\bar{Cp}_2^{\,o}$ values obtained by this extrapolation are approximate values since the experimental slopes in the real concentration range vary considerably from the theoretical slopes predicted by Debye-Hückel theory.

Another method for obtaining $\bar{Cp}_2^{\,o}$ of NaCl was used by Gulbransen and Robinson[37]. They used the heat of dilution at two temperatures, 20° and 25°, combined with the heat of solution at the same two temperatures to calculate $\bar{Cp}_2^{\,o}$ at 22.5°.

The $\bar{Cp}_2^{\,o}$ can also be determined using the "integral heat method" of Criss and Coble[38]. This involves only the measurement of heats of solution as a function of temperature and concentration. The heat of solution can be described as the amount of heat given off when a solute is dissolved in a solvent. In terms of partial molal heat contents, the heat of solution can be expressed as

$$\Delta H_s = n_1\bar{H}_1 + n_2\bar{H}_2 - n_1\bar{H}_1^{\,o} - n_2H_2 \qquad \text{Eq. 33}$$

where

$\bar{H}_1$, $\bar{H}_2$ = partial molal heat content of solvent, solute
$\bar{H}_1^{\,o}$ = heat content of pure solvent
H_2 = heat content of pure solute

At infinite dilution the heat of solution is defined by

$$\Delta H_s^{\,o} = n_2\bar{H}_2^{\,o} - n_2H_2 \qquad \text{Eq. 34}$$

ΔCp^o = change in heat capacity of reaction in Equation
$\bar{Cp}_2^{\,o}$ = partial molal heat capacity of solute at infinite dilution
Cp_2 = heat capacity of pure solute

Therefore, $\bar{Cp}_2^{\,o}$ can be calculated if the $\Delta H_s^{\,o}$ is accurately known at two temperatures. The limitation of this method is that it cannot be used to determine $\bar{Cp}_2$ at real concentrations.

The values of $\overline{Cp}_2$ for a large number of electrolytes, including NaCl, have been reported by Cobble and co-workers.[38,39,40,41] A comparison of values derived by this method and those derived from the extrapolation of ΦCp does not show good agreement. An example of this is the comparison of $\overline{Cp}_2$ for NaCl, using Criss and Cobble's data and Ackermann's values[43] can be found in Table I.

It is evident that additional high temperature thermodynamic information is needed to help establish the realiability of existing data for all electrolyte solutions. The high temperature partial molal quantities of sodium chloride solutions are especially needed since it is used as a standard one to one electrolyte.

TABLE I

COMPARISON OF $C\bar{p}_2^{\circ}$ VALUES

Temperature	Ackermann[43]	Criss and Cobble[42]
10	-16.4	-29.0
20	-14.0	-20.9
40	-11.0	-15.3
60	-10.1	-15.2
80	-11.3	-16.5
100	-13.5	-18.0

RESEARCH PROPOSAL

The goal of this investigation was to develop a method for obtaining heat capacity data in an expedient and precise manner. These heat capacities would then be used to calculate high temperature data by extending existing 25° thermodynamic data. Previous methods used to obtain heat capacity data are limited to specific concentration ranges due to experimental difficulties. The method employed by this research was to measure the heat of dilution ΦL, as a function of temperature and concentration.

The heat of dilution can be related to heat capacity functions using the following relationships:

$$\overline{L}_2 = -\Phi L - N_2 \, {}^{\partial \Phi L}/\partial N_2 \qquad \text{Eq. 22}$$

$$\overline{J}_2 = \partial \overline{L}_2 / \partial T \qquad \text{Eq. 26}$$

$$\overline{Cp}_2 - \overline{Cp}_2^{o} \equiv \overline{J}_2 \qquad \text{Eq. 27}$$

It was then possible by using the derived values to extend existing 25° data by calculation. An example of such a calculation would be the extention of activity coefficients using Equation 36.

$$d \ln \gamma_{\pm} = -\overline{L}_2 / {}_{\nu} R T^2 \, dT \qquad \text{Eq. 36}$$

$\gamma_{\pm}$ = activity coefficient
ν = number of ions
R = gas constant

The accuracy and quickness by which the high temperature data could be obtained was dependant upon how precisely the slope of a ΦL vs. $\sqrt{m}$ curve was determined. Previous methods utilized some type of large scale polts which are difficult and time-consuming. To facilitate the slope determination procedure, the ΦL data was fitted to a polynomial equation as a function of concentration. This equation could then be easily differentiated. Subsequent calculations involving $\bar{L}_2$, such as Equation 36 used an equation describing $\bar{L}_2$ as a function of temperature.

This investigation proposed to measure the ΦL of NaCl at 40°, 50°, 60°, 70°, and 80° over a concentration range of 0.1 m to 6.0 m. The choice of NaCl as the electrolyte to be investigated was based upon several factors. First, the need to develop a method for conversion of sea water to fresh water makes the knowledge of high temperature thermodynamic properties of NaCl, the principle component of sea water, extremely important. Second, much data for NaCl at high temperatures has already been published and the validity of the method can be checked using it. Criss and Cobble[44] have published $\bar{Cp}_2^{\circ}$ values for NaCl at a variety of temperatures. Eigen and Wicke[45] have performed heat capacity measurements of NaCl solutions up to a temperature of 120°. From this work, Ackermann[46] has calculated partial molal heat capacities for NaCl ($\bar{Cp}_2$). The consistency of the $\bar{J}_2$ values derived from this research can be checked by using $\bar{Cp}_2$ and $\bar{Cp}_2^{\circ}$ values in Equation 27.

The final reason for using NaCl for this research was that it is used as a standard for 1-1 electrolyted in many thermodynamic studies. For example, the activity coefficients of electrolytes are determined using the isopiestic method in which NaCl is used as the reference electrolyte. The validity of such studies depends upon the accuracy of the activity coefficients or the osmotic coefficients of the reference electrolyte. These properties have been determined for NaCl at elevated temperatures; however, some large uncertainties exist in the temperature range of 40°

to 70°. It was hoped that this investigation would remove these uncertainties and help to establish high temperature properties of NaCl to a greater certainty.

EXPERIMENTAL

Preparation of Solution

In this research, doubly recrystalized "Baker Analyzed Reagent" sodium chloride was used. After recrystalization, the salt was baked at 400°C for two hours and was determined, by silver chloride gravimetric analysis, to be 99.9% pure.

A near saturated stock solution (approximately 6 m) was prepared using the purified sodium chloride and doubly deionized water. The molality of the solution was determined by gravimetric analysis. From this stock solution, all other solutions were made by diluting a known weight of stock solution with a known weight of deionized water. All weights were measured to the nearest 0.1 mg with an analytical balance. The solutions were stored in polyethylene bottles. The molality of the stock solution was checked every two months and was found to vary no more than 0.02% over a six-month period.

Calorimeter

The heats of dilution of sodium chloride in the 0.1 m range are small for a low dilution ratio calorimeter (1 to 40). In order to accurately detect the small heats in this dilution range, which were essential to the extrapolation procedure used, a very sensitive calorimeter was necessary. The calorimeter used in this investigation was the left side of the microdegree double calorimeter, previously described by Petree.[47] It had a sensitivity of 5×10^{-6} °C, which was satisfactory for measurements in the dilute range.

The Vessel

The vessel was a 250 ml Thermos bottle refill,[48] attached to a brass collar with silicone rubber. The collar was fastened to a brass superstructure by four brass screws with wing nuts. The contents of the vessel were sealed using a rubber O-ring which fitted in a machined groove in the brass collar.

The level of solution in the vessel was adjusted at the various temperatures to allow for expansion. The air space above the solution was kept at a minimum to keep the loss of solution due to evaporation negilible.

The solution in the vessel was stirred by a glass stirrer equiped with two sets of blades. A portion of the stirrer's glass shaft was precision bore glass, which fitted into a precision glass bearing located immediately above the vessel in the superstructure of the calorimeter. This arrangement allowed the vessel to remain sealed. The stirring mechanism was driven at a rate of 427.5 by a synchronous motor.[49]

Heaters

Two heaters were present in the calorimeter. A rough heater was used to raise the vessel solution to the approximate temperature of the bath and a calibration heater which was used to accurately determine the heat capacity of the system. Each heater was situated in 5 mm pyrex tubing, which was sealed to the superstructure with silicone rubber. The heaters were covered with silicon oil to insure uniform heating.

The rough heater was made from four cm of resistance wire and had a resistance of 4.5 ohms. The heater was powered by a 12 volt power supply. The heating times necessary to raise the temperature of the vessel to the operating temperature, increased from ten minutes at 40°C to forty five minutes at 80°C. This rapid addition of heat caused a heat lag between the water in the vessel and the solution in the sealed pipet. After the vessel had been heated to slightly below the temperature of the bath, a period of time was allowed so that the pipet and the solution could thermally equilibrate. This equilibration time increased with the amount of heat added and ranged from forty five minutes at 40°C to two hours at 80°C.

The calibration heater was powered by a regulated power supply.[50] A double pole double throw toggle switch was used to activate the heater and the timer[51] simultaneously. The voltage drop across the heater was measured with a differential voltmeter[52] to a thousandth of a volt. The resistance of the heater was determined with the aid of a dummy resistor incorporated in the heating circuit. The resistance of the dummy was determined using a standard one kilohm resistor.[53] Once the resistence of dummy was obtained it was then used to determined the resistance of the calibrated heater. This resistance was checked at each operating temperature. For a complete list of the resistance, see Appendix A.

Temperature Detection

The temperature of the vessel was measured with a ten kilohm thermistor[54] which was submerged in the solution. The thermistor was incorporated as one leg of a wheatstone bridge and the temperature change in the vessel was registered as a resistance change on a decade resistor located on the opposite side of the wheatstone bridge from the thermistor. A Keithly Model 150A Microvolt-Ammeter was used as a null instrument in balancing the bridge. The bridge's unbalance was amplified by the microvolt-ammeter and recorded by a Sargent Model SR recorder. The sensitivity of the thermistor circuit was 5×10^{-6} °C when using the 10 v scale of the amplifier in connection with the 125 v scale of the recorder. This circuit was described in greater detail by Petree[55].

Water Bath

The water bath consisted of a fifty-five gallon stainless steel tank, insulated with two inches of fiberglass. The stirrer consisted of a 3/4 inch diameter brass shaft with two sets of four inch diameter blades. It was turned by a one-half horse power motor operating at 1880 rpm. The temperature of the bath was regulated by a Thermotrol[56] using a 500 watt blade heater. At the lower temperatures (40°, 50°) it was necessary to run cold water through the cooling coil submerged in the bath to achieve the desired regulation of the bath temperature. The temperature was found to be constant to 0.001°C at 40°C; this value increased to 0.003°C at 80°C. The bath regulation was checked every day using a Hewlett Packard quartz thermometer.[57]

Pipets

The pipets were made from 15 mm Pyrex tubing which had two sides blown out to increase the capacity (see Figure I). At each end of the pipets a portion of the tube was left intact so that teflon sleeves could be attached using epoxy. The pipet plunger consisted of two telfon disks epoxied onto a 3 mm glass tube. Rubber O-ring were fitted to the machined disks to insure they would fit snugly inside the sleeve of the pipet to form a good seal. Two small holes were drilled in the top disk of the plunger to allow the pipet to be filled with a hypodermic syringe.

The heats of opening if the pipets were determined at each operating temperature. These heats varied according to the pipet used and the temperature at which the heats of opening were measured. Average values for the heats of opening are listed in Appendix B. The heats of opening resulted not only from the friction of opening the plunger, but also seemed to be related to a change in the mixing pattern of the solution in the vessel.

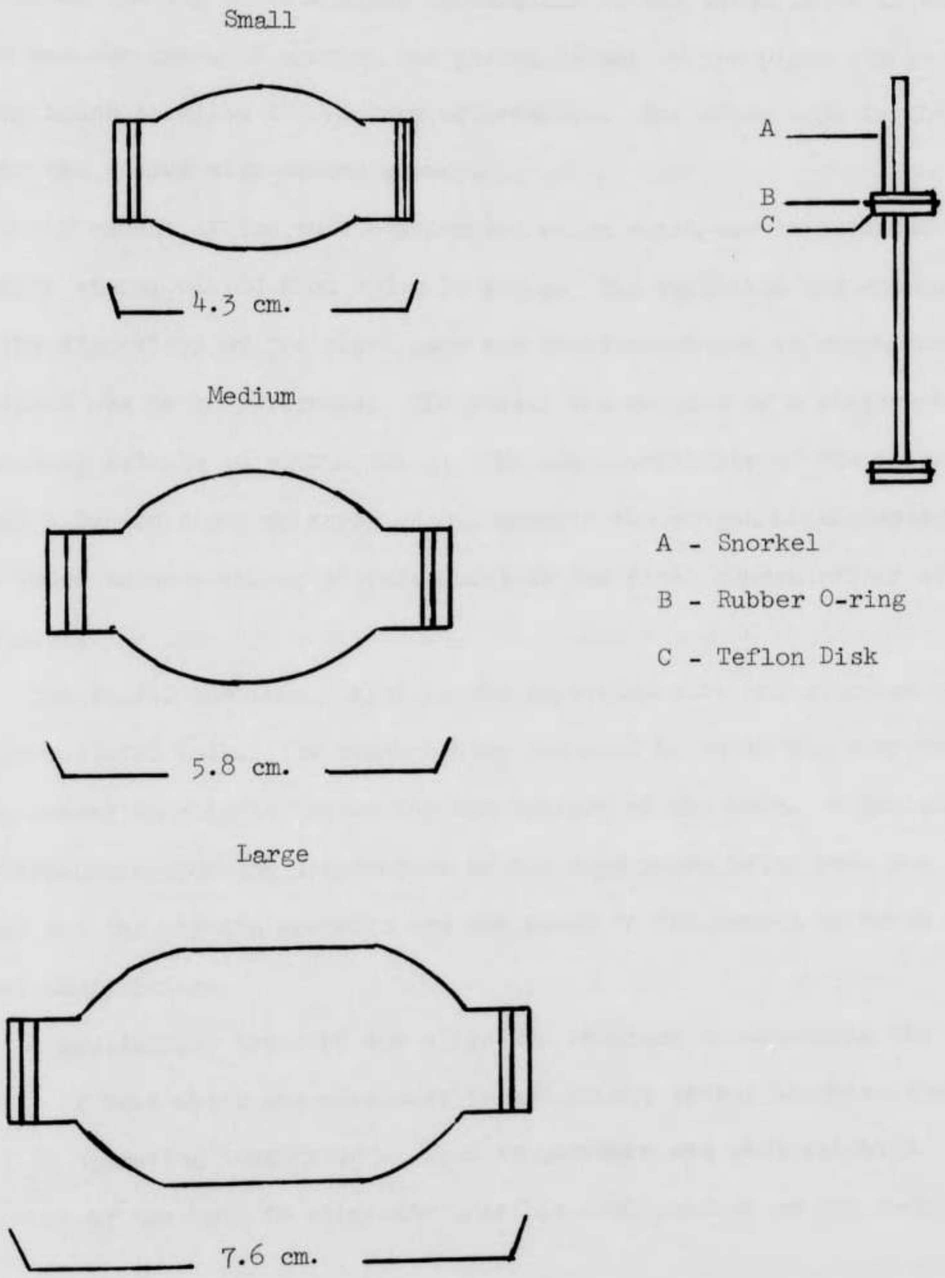
Three different pipets were used in this research (6cc, 10cc, 18cc). The use of different size pipets can be justified as follows: first, by the use of three pipets a more descriptive extrapolation curve was obtained with less experimental work. This will be explained later in greater detail. Secondly, by using the different capacity pipets the experimental heat (Q) was controled so that the calorimeter was operating in its optimun precision range at all times. The smaller the pipet, the smaller the experimental heat obtained; therefore, at dilute concentration where the heat of dilution is small the largest pipet was used, but at high concentration where large experimental heats were expected a smaller pipet was utilized.

Experimental Procedure

The pipet was fitted with the appropriate plunger which was lubricated with silcone vacuum grease to facilitate opening. The empty pipet was weighed using a Mettler analytical balance to within 0.1 mg. A hypodermic syringe was used to fill the pipet with the salt solution to be diluted leaving a small vapor space in the pipet. The filled pipet was reweighed. The pipet plunger was attached to a glass rod with ferrule cement.[58] The glass rod contained a section of precision bore glass which maintained the vessel's seal when fitted into a precision glass bearing located in the superstructure of the calorimeter.

Figure 1

Pipets and Pipet Plunger



The pipet was held in place in the vessel by a basket which hung from the superstructure. The basket was made of a teflon ring and teflon-coated wire. Different baskets were used for each size pipet, so the position of the top of each pipet in relation to the water level in the vessel was the same. A snorkel was placed in one of the pipet plunger's filling holes to allow the venting of pressure. The other hole in the plunger was sealed with vacuum grease.

The amount of the double-deionized water which was to be added to the empty vessel varied from 230 g to 245 g. The variation was dependent upon the dimensions of the pipet used and the temperature at which the experiment was to be performed. The vessel was weighed on a single-pan top-loading balance to within 0.1 g. The low sensitivity of the balance was not a factor since an error of 0.1 gram in the weight of the water would cause an uncertainty of only 0.04% in the final concentration of the vessel.

The vessel was then sealed to the superstructure and situated in the thermostated bath. The rough heater was used to raise the temperature of the vessel to slightly below the temperature of the bath. A period of time, dependent upon the temperature of the experiment being run, was allowed for the pipet's contents and the water in the vessel to reach thermal equilibrium.

A preliminary trace of the slope was obtained to ascertain the quantity of heat which was necessary to add to the vessel to raise the vessel to operating temperature. This temperature was kept slightly below that of the bath to eliminate possible condensation on the vessel lid.

The vessel was assumed to be in thermal equilibrium if an unchanging slope was recorded for at least three minutes. When equilibrium was secured and a suitable foreslope traced, the vessel was ready for the pipet to be opened.

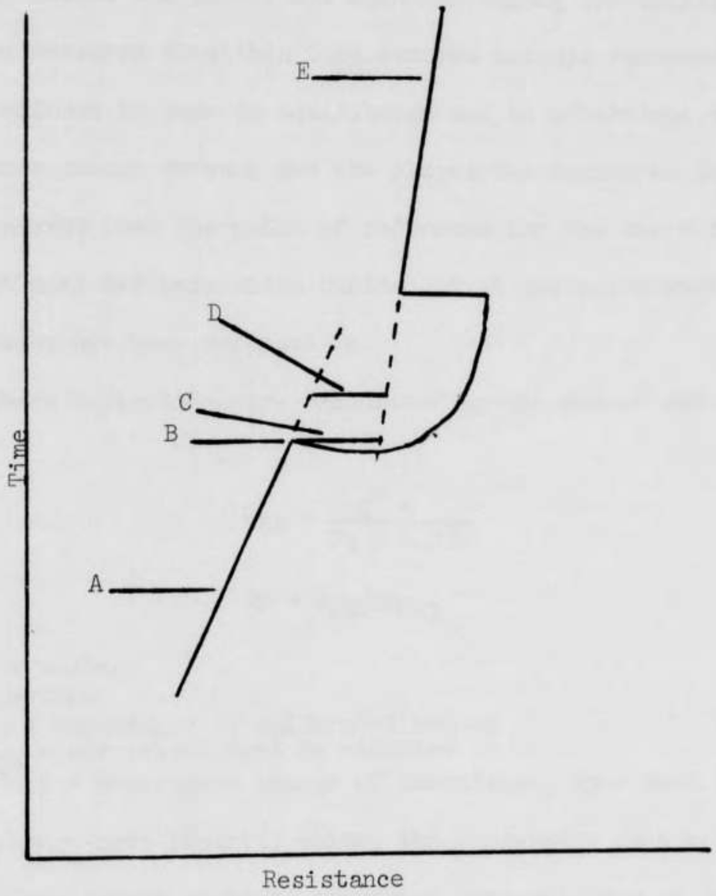
With the recorder on, the glass rod attached to the plunger was pushed down, opening the pipet. A pinch clamp was used to insure the plunger traveled approximately the same distance each time. The heat of dilution was followed by the change in resistance of the thermistor.

Since both endothermic and exothermic reactions were observed, two different methods were used in securing the most accurate experimental heat of dilution value.

Measuring exothermic reactions involved recording the foreslope resistance of the afterslope (see Figure II). The afterslope was adjusted using the decade resistor so that its extrapolation would pass very close to the point of opening on the foreslope. A small resistance change was added or substracted to the resistance change of the two slopes, depending on the size of the gap between the extrapolated slopes and the position of the afterslope in relation to the foreslope. The number of chart divisions contained in the gap were converted to resistance units by multiplying them by the recorder's sensitivity which was expressed in ohms per division. This correction yielded the true resistance change of the dilution experiment.

In an endothermic experiment, the amount of heat to be absorbed was estimated and the time for an equivalent amount of electrical heat was calculated. The foreslope was procured as before, then the amplifier was switched to the 300μ v scale. Electrical heat was introduced into

Figure 2



Experimental Recorder Trace

A. Fore slope

B. Point of Opening

C. Correction For Dilution Experiment

D. Correction For Heat Capacity Experiment

E. After slope

the contents of the vessel for approximately twenty seconds and the voltage drop across the heater was measured during the addition of heat. The time was measured to within 0.01 seconds and was recorded. The vessel was allowed to come to equilibrium and an afterslope was traced. The resistance change between the two slopes was corrected as previously described, except that the point of reference for the correction was after 50% of heat had been added instead of at the point were the electrical heat had been switched on.

The heat capacities were calculated by the use of the following equations:

$$Q_{EH} = \frac{E^2\ t}{R_H \times 4.184} \qquad \text{Eq. 37}$$

$$Cp = Q_{EH}/\Delta R_{Exp} \qquad \text{Eq. 38}$$

E = voltage
t = time
R_H = resistance of calibrated heater
Q_{EH} = electrical heat in calories
ΔR_{Exp} = Resistance change of thermistor, Cp = heat capacity

Using the average heat capacity value, the resistance change caused by the dilution experiment could be converted into calories of heat produced. The heat in calories caused by an exothermic reaction was directly calculated using the following expression:

$$Q_{Exp} = Cp \times \Delta R_{Exp} \qquad \text{Eq. 39}$$

The endothermic resistance change was compared to the resistance change which should have resulted from the electrical heat added to the vessel if no pipet opening had taken place.

$$Q_{elec}/Cp = \Delta R_{pred} \qquad \text{Eq. 40}$$

$$\Delta R_{pred} - \Delta R_{Exp} = \Delta R_{Act}$$

ΔR_{pred} = predicted resistance change
ΔR_{Act} = actual resistance change of experiment

The difference was the resistance change due to the experiment, as shown in equations above. This resistance was then converted into calories using the same equation as the one for exothermic experiments.

Experimental Calculations

The final concentration of the vessel solution was calculated from the following equations:

$$N_2 = \frac{M_{salt} \times Wt_{pipet}}{1000 + M_{sol} \times MW_{salt}} \qquad \text{Eq. 42}$$

$$m_f = \frac{\#N \times 1000}{Wt\ H_2O + Wt_{pipet} - \#N \times MW_{salt}} \qquad \text{Eq. 43}$$

M_{salt} = molality of salt solution
Wt_{pipet} = weight of solution in pipet
N_2 = number of moles of salt
m_f = molality of final solution

The above calculations were performed using a Wang electronic calculator[59] and its card reading attachment.

The heat of each experiment divided by the number of moles of solute in the vessel was equal to the heat of dilution of sodium chloride going from the initial concentration in the pipet to the final concentration of the vessel. This will be referred to as $\Delta\Phi L$.

Since the value of the heat of dilution (ΦL) from the initial concentration to the reference state of infinite dilution was not directly obtainable from the experimental $\Delta\Phi L$ value, it was necessary to use the extended Debye-Hückel equation for 1-1 electrolytes. Guggenhiem and Prue[60] and Owen and Brinkley[69] have shown the equation to be valid for sodium chloride up to 0.1 m, without the C parameter. Recently Jogenburger and Wood[62] have established that the equation is valid for 1-1 electrolytes with a heat of dilution greater than -36 cal/mole.

$$\Phi L = A_H\, m^{\frac{1}{2}}\left[1(1 + Am^{\frac{1}{2}}) - \sigma(Am^{\frac{1}{2}})/3\right] + Bm + Cm^{3/2} \qquad \text{Eq. 21}$$

The valuesof the Debye-Hückel limiting slope at the various temperatures were derived from the dielectric constant measurements of Malmberg and Maryott[63].

Experimental values of $\Delta\Phi L$ at 0.1 m or lower were substituted into the above equation and a least squares computer fit was used to yield the best values of B and C. A complete list of these values are contained in Appendix C. A copy of the Fortran program is in Appendix D.

A weighting process was used so that the more accurate experimental values were given greater consideration in the least squares computer fit. The process arbitrarily assigned a weight of 1.0 to the largest experimental heat value. Each subsequent experimental heat value was weighted as a fraction of the largest value.

To obtain an accurate extrapolation, it was necessary to have data points spread over a major portion of the extrapolation curve. The calorimeter used in the investigation was not capable of accurately detecting the heats evolved from dilution experiments below 0.1 m. This necessitated the use of the three different-sized pipets. Using the same concentration in each pipet, it was possible to obtain three different $\Delta\Phi L$ values for the same concentration going to three different final concentrations. The different $\Delta\Phi L$ values were the results of the different final concentrations reached. It was then possible to calculate the $\Delta\Phi L$ going from one final concentration to another final concentration by the difference in the orginal experimental $\Delta\Phi L$ of the two final concentrations. By this method it was possible to obtain extremely dilute $\Delta\Phi L$ values which were not obtainable by direct calorimetric measurement. An example of this type of experimental method is shown below.

Dilution 1	$m \rightarrow m'$	$\Delta\Phi L\ (m \rightarrow m')$
Dilution 2	$m \rightarrow m''$	$\Delta\Phi L\ (m \rightarrow m'')$
Dilution 3	$m \rightarrow m'''$	$\Delta\Phi L\ (m \rightarrow m''')$

Extrapolation Point From the Above Data

$$\Delta\Phi L(m' \rightarrow m'') = \Delta\Phi L(m \rightarrow m'') - \Delta\Phi L(m - m')$$

$$\Delta\Phi L(m' \rightarrow m''') = \Delta\Phi L(m \rightarrow m''') - \Delta\Phi L(m - m')$$

$$\Delta\Phi L(m'' \rightarrow m''') = \Delta\Phi L(m \rightarrow m''') - \Delta\Phi L(m - m'')$$

In the scheme above m is the initial concentration and m', m'', and m''' are the three different final concentrations reached when m is diluted using the three different pipets. The $\Delta\Phi L$ for one final concentration's, m', being diluted to a second, more dilute final concentration, m'', is the difference of the two experimental dilutions, $\Delta\Phi L$ $m - m''$, and $\Delta\Phi L$ $m - m'$. Each experiment was repeated so that it was possible to generate twelve data points from six dilutions.

To generate a descriptive extrapolation curve, it was necessary to do multiple pipet runs at 0.2 m and 0.8 m, along with two points at 0.1 m. This procedure yielded an extrapolation curve which contained twenty-six data points. The data points were spread over the concentration range of 0.1 m to 0.008 m. Multiple pipet runs were also carried out at 0.1 m at 40°C and 50°C. The heats produced from the dilutions of the solutions in the small and medium pipets were large enough to generate accurate $\Delta\Phi L$ values for the extrapolation.

The ΦL of the initial concentration going to infinite dilution was then calculated using the extended Debye-Hückel equation. The B and C coefficients from the least-squares computer fit of the extrapolation data were used in the Debye-Hückel equation to calculate the value of the experimental final concentration going to infinite dilution. This value (ΦL_f) was then added to the $\Delta\Phi L$ of the experiment and yielded the heat of dilution of the initial concentration going to infinite dilution (ΦL_i). For all experimental data and extrapolation data see Appendix E and F.

RESULTS AND DISCUSSION

Data Treatment

The reliability of the thermodynamic quantities, $\bar{L}_2$, $\bar{J}_2$, $\bar{L}_1$, and φ, which can be derived from experimentally determined ΦL depends largely upon the accuracy with which the slope of the ΦL vs. $\sqrt{m}$ curves ($\partial\Phi L/\partial\sqrt{m}$) can be determined. The dependency of these derived functions on the slopes of ΦL vs. $\sqrt{m}$ curves can be illustrated by examining $\bar{L}_2$ as given by,

$$\bar{L}_2 = \Phi L + \frac{\sqrt{m}}{2} \; \partial\Phi L/\partial\sqrt{m} \qquad \text{Eq. 23}$$[64]

Gulbranson and Robinson[65] evaluated $\bar{L}_2$ from large-scale plots of ΦL vs. $\sqrt{m}$ of NaCl at 25°. The slopes were determined using the differentiated form of the Lagrange interpolation formula. Young and Vogel[66] obtained slopes from plots of ΦL vs. $\sqrt{m}$ curves using a tangentometer. Perhaps the most useful method was the chord-area method developed by Young and coworkers.[67,68,69,70] Parket,[71] in a recent review of thermodynamic data for 1-1 electrolytes, used the chord-area method to obtain $\bar{L}_2$ values from published ΦL data for NaCl at 25°.

The nature of data-collecting in this investigation made the use of large-scale plots undesirable, since the data points were not closely enough spaced. Human prejudice would have been a factor in the drawing of a smoothed curve through the data points. The method of large-scale plots was also tedious and time-consuming, which were two factors undesirable in data treatment. Several hand-plotted ΦL vs. $\sqrt{m}$ curves of Parker's data were made. The slopes were obtained using a mirror to construct tangents to the curve; these slopes were not reproducible and not in good agreement with the published slopes of Parker. The chord-area method was not readily suited to this work because the nature of experimental data would have yielded large chords. The problem of drawing a smoothed curve through the chords would have been the same as with large-scale plots.

A faster method for treating the ΦL vs. $\sqrt{m}$ curves was to fit the data to a polynomial of the type (44),

$$\Phi L = \partial + bm^{\frac{1}{2}} + cm + dm^{3/2} . . .$$

The above equation was easily differentiated to obtain the slope of the ΦL curve. A Fortran computer program for IBM's Scientific Subroutine Package[72] was used to evaluate the coefficients of such a polynomial equation.

The polynomial linear regression program, POLYR, generated successive polynomials of increasing degree until there was no reduction in the residual sum of the squares between two successive polynomials. The polynomial then terminated itself, printing out the successive degree polynomials which has a reduction in the residual sum of the squares. The program also contained a plot subroutine which yielded a plot of the actual data; superimposed on this was the value predicted by the polynomial equation.

The accuracy of the polynomial equation in describing the ΦL vs. $\sqrt{m}$ curve was unknown. An estimate of the precision was necessary, to derive the uncertainty present in the calculated thermodynamic quantities. Already published ΦL for NaCl at 25° was used as a standard to appraise the reliability of the POLYR fit. The ΦL data gathered by Parker[73] was used for this purpose. The curve was constructed using data from eleven different sources. Parker utilized both heats of solution and heats of dilution data. The curve was constructed using twenty-nine data points, giving the more reliable data proper emphasis. The slopes of the ΦL vs. $\sqrt{m}$ curve were obtained using the chord-area method.

Initially, the POLYR program was used to treat fifteen data points over the concentration range of 0.1110 m to 5.8427 m. The other fourteen points not used from Parker's data were not comparable with experimental data in this investigation, since the points were below 0.1 m, the lowest concentration used in the present research. The polynomial equation for the fifteen data points did not yield slopes in good agreement with the published slopes of Parker. It was assumed that the POLYR program was not capable of handling the rapidly changing slopes present in the dilute concentration range.

The next step was to divide the curve into sections and then treat each section with the POLYR program. The coefficients for the most linear portion of the ΦL curve were evaluated first. The slopes generated from this fit were found to be in agreement with those published by Parker. It was possible, by adding data points one or two at a time to the above fit, to derive an equation whose predicted slopes were in agreement within experimental error with the slopes of Parker. The curve constructed in this manner contained twelve data points and covered the concentration range of 0.2775 m to 5.8427 m. Table II contains both published slopes and predicted slopes from the POLYR generated equation. The agreement is not as good at higher concentrations because in that region the slope is changing more rapidly. A plot of Parker's published $\bar{L}_2$, POLYR generated $\bar{L}_2$, and Harned and Owen's[74] $\bar{L}_2$ values from electromotive force data shows agreement over the entire concentration range. (See Figure III)

In this research, ΦL of NaCl was determined at 40°, 50°, 60°, 70°, and 80° over a concentration range of 0.1 m to 6.0 m. The data was fitted to a polynomial using the POLYR program. The only method for checking the apparent consistency of the polynomial to describe the ΦL vs. $\sqrt{m}$ curve was to compare predicted ΦL values, with values interpolated from a hand plotted graph of the experimental ΦL values. Critical areas such as the immediate area around inflection points were checked. Also areas of rapidly changing slope were watched to make sure the predicted ΦL was in agreement within experimental uncertainty.

At 40° and 60° the NaCl ΦL vs. $\sqrt{m}$ curves were adaptable to a single polynomial; however, at the other experimental temperatures (50°, 70°, 80°) it was found that a single polynomial could not describe the curve with the desired accuracy. At these experimental temperatures it was necessary to use two polynomial equations to describe the ΦL vs. $\sqrt{m}$ curve. Each equation defined a portion of the curve with a section of the curve discribed by both equations.

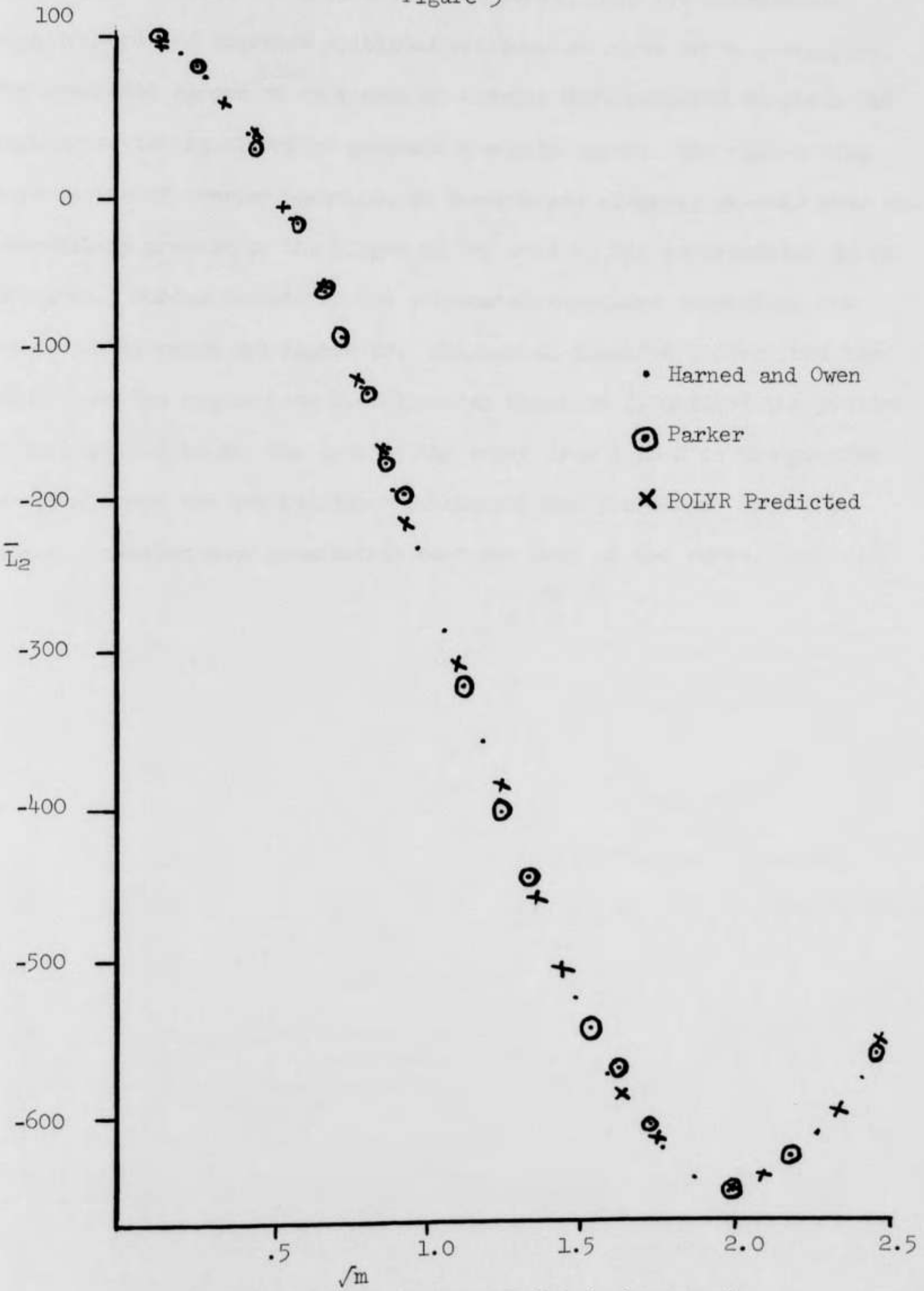
The process for fitting a ΦL vs. $\sqrt{m}$ curve by parts consisted of several steps. First, the complete experimental curve was fitted to a single polynomial equation using the POLYR program. This fit was used to check the consistency of all data points. Next, the curve was divided into parts. Each part contained a section of the more linear portion of the curve with a section that contained some of the rapidly changing slope. At 50°, for example the curve was divided into ten different parts. A polynomial equation was then obtained to describe each section. The precision by which each equation defined its portion of the curve was checked by the method previously described involving a hand-plotted experimental ΦL vs. $\sqrt{m}$ curve. The best-described sections were then pieced

TABLE II

COMPARISON OF ΦL VERSUS $\sqrt{m}$ COMPUTED SLOPES

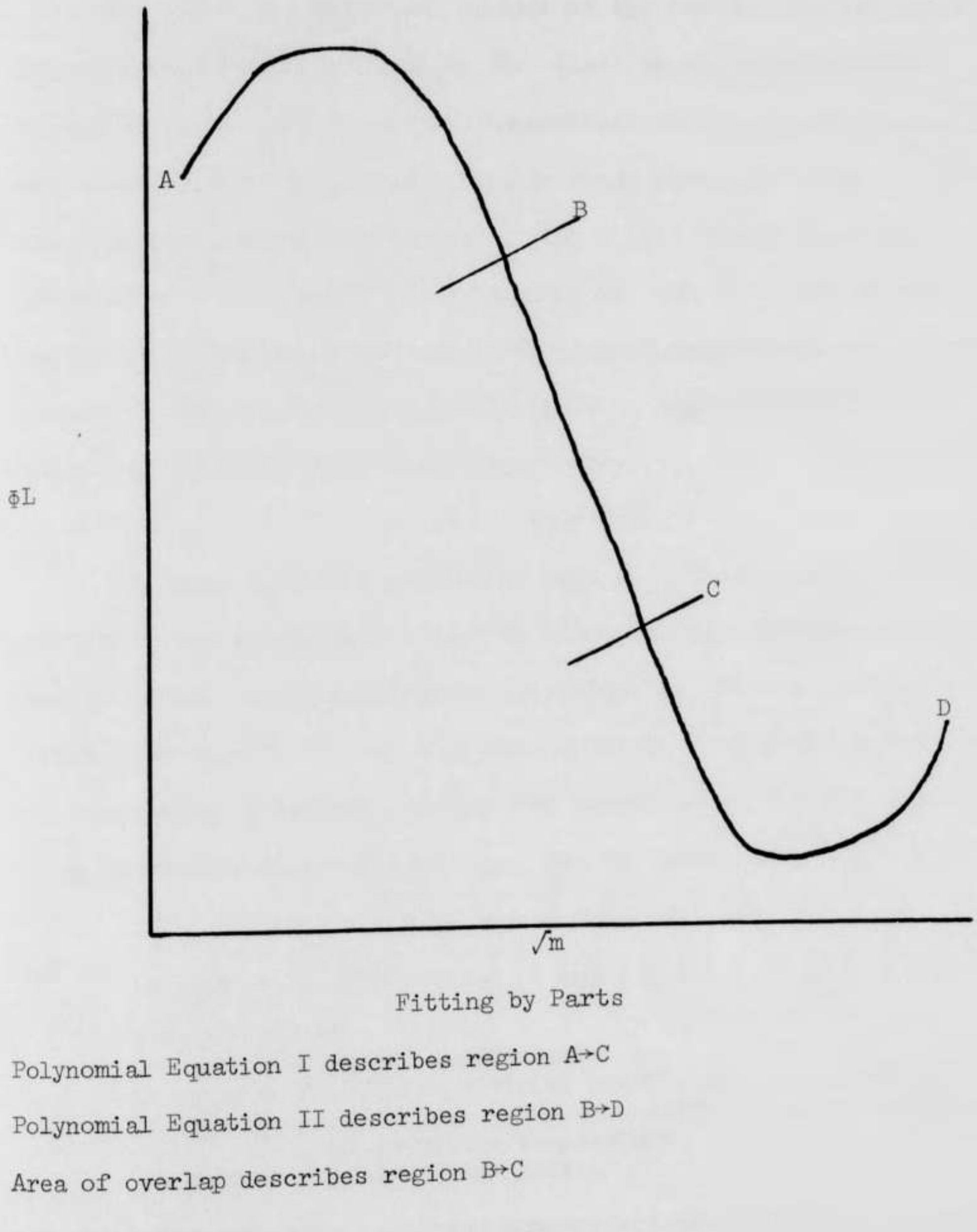
Molality	Parker's $\partial\Phi L/\partial\sqrt{m}$	POLYR $\partial\Phi L/\partial\sqrt{m}$
.2775	-87	-97
.5551	-220	-222
.7401	-275	-273
1.1101	-344	-340
1.3877	-373	-369
1.8502	-394	-392
2.2202	-394	-396
2.7753	-376	-382
3.7004	-321	-323
4.6255	-242	-236
5.5506	-135	-128
5.8427	-93	-89

Figure 3



Partial Molal Heat Content of Solute Agreement together to construct a well-defined ΦL curve. Any two polynomial equations pieced together contained sections of curve which overlapped. The predicted slopes of this area of overlap were compared to check the ability of the equations to generate a smooth curve. The slopes from these areas of overlap contained an uncertainty slightly greater than the uncertainty present in the slopes of the rest of the experimental ΦL vs. $\sqrt{m}$ curve. For an example of two polynomial equations describing one experimental curve see Figure IV. Polynomial Equation I described the curve over the region A to C. Polynomial Equation II defined the portion of the curve B to D. The area of the curve from B to C is the portion of curve where the two equations overlapped and the slopes from this region contained more uncertainty than the rest of the curve.

Figure 4



Fitting by Parts

Polynomial Equation I describes region A→C

Polynomial Equation II describes region B→D

Area of overlap describes region B→C

Derived Thermodynamic Quantities

The relative molal heat content of the solute ($\overline{L}_2$) was derived from the ΦL data, using Equation 22. Since ΦL was experimentally determined as a function of both temperature and concentration, $\overline{L}_2$ values were calculated over the concentration range of 0.1 m to 6.0 m at each experimental operating temperature. For a list of all $\overline{L}_2$ values generated in this research, see Appendix G. The $\overline{L}_2$ values at each concentration were then submitted, as a function of temperature, to the POLYR computer program. This treatment yielded an equation of the form 45 describing $\overline{L}_2$ as a function of temperature.

$$\overline{L}_2 = d + eT + f\,T^2 \qquad \text{Eq. 45}$$

The mean activity coefficient ($\gamma\pm$) is a thermodynamic function describing the solute and is used to calculate the contribution of the salt to the excess free energy of the solution. The existing mean activity coefficient data at 25° for NaCl was corrected to higher temperature using the temperature dependence of $\overline{L}_2$. The extention of 25° data was possible using the relationship of $\gamma\pm$ to $\overline{L}_2$. The integration of Equation 46

$$\int d \ln \gamma\pm = \int -\overline{L}_2/\nu R T^2 \, dT \qquad \text{Eq. 46}$$

$$\ln \gamma\pm(m) = \ln \gamma\pm Tr(m) - \frac{1}{\nu R}\left[d\left(\frac{1}{Tr} - \frac{1}{T}\right) + e \ln \frac{T}{Tr} + f(T - Tr)\right] \qquad \text{Eq. 47}$$

R = gas constant
d, e, f = polynomial coefficients
$\ln \gamma\pm(m)$ = log of mean activity coefficient at concentration
$\ln \gamma\pm Tr(m)$ = log of mean activity coefficient at concentration and reference temperature
ν = number of ions = 2 for NaCl

was performed between a reference temperature (Tr) and the desired higher temperature. In this research, 25° was chosen as a reference temperature because considerable data was available for NaCl. Substituting Equation 45 for $\overline{L}_2$ into Equation 46 and integrating, one obtains Equation 47. Using Equation 47, mean activity coefficient data at 25° was corrected to the temperatures of the present research.

The accuracy of the corrected activity coefficients depends on the reliability of the determination of $\overline{L}_2$ as a function of temperature and the accuracy of the 25° data available in the literature. To check the consistency of the mean activity coefficients calculated from $\overline{L}_2$ temperature dependence, the values for mean activity coefficients published by Harned and Owen[75] were used. The reason for choosing these values was the wide temperature (0° to 100°) and concentration (0.1 m to 4.0 m) ranges published.

The mean activity coefficients in the 0° to 100° temperature range published by Harned and Owen were the resultant of a combination of two experimental methods. The data from 0° to 40° was from electromotive force data. Boiling point elevations were used to calculate the mean activity coefficients at 60° to 100°. A plot of these activity coefficients against temperature showed deviation from smooth curve from 35° to 40° and 60° to 70° above 1.0 m. This error increased in magnitude as concentration increased and was due to the experimental difficulties inherent in the boiling point method and electromotive force method at those temperatures and concentrations. The values published are from a smooth curve drawn through the experimental data taking into account the experimental error present. Good agreement was found between Harned and Owen's values read from the smoothed curve and the mean activity coefficients obtained when Harned and Owen's 25° data was corrected using $\overline{L}_2$ temperature dependence from this research. This comparison is found in Table III.

The corrected mean activity coefficients can be no more accurate than the reference values at 25°. The Harned and Owen data for NaCl at 25° was obtained from electromotive force data and had a concentration range of 0.1 m to 4.0 m. Robinson and Stokes[76] have tabulated mean

TABLE III

COMPARISON OF ACTIVITY COEFFICIENTS

Present Research

conc.	40°	50°	60°	70°	80°
0.1	0.774	0.771	0.767	0.763	0.758
0.2	0.729	0.725	0.721	0.716	0.711
0.5	0.677	0.675	0.670	0.665	0.659
1.0	0.658	0.656	0.652	0.646	0.640
1.5	0.660	0.660	0.656	0.651	0.644
2.0	0.678	0.678	0.674	0.669	0.661
2.5	0.701	0.702	0.698	0.692	0.683
3.0	0.731	0.732	0.728	0.721	0.711
3.5	0.756	0.766	0.762	0.754	0.742
4.0	0.816	0.824	0.827	0.824	0.817

Harned and Owen

conc.	40°	50°	60°	70°	80°
0.1	0.774	0.770	0.766	0.762	0.757
0.2	0.728	0.725	0.721	0.717	0.711
0.5	0.678	0.675	0.671	0.667	0.660
1.0	0.657	0.656	0.654	0.648	0.641
1.5	0.661	0.662	0.659	0.655	0.646
2.0	0.678	0.678	0.676	0.672	0.663
2.5	0.698	0.699	0.696	0.692	0.685
3.0	0.728	0.728	0.726	0.721	0.712
3.5	0.761	0.762	0.760	0.758	0.742
4.0	0.802	0.802	0.799	0.791	0.777

activity coefficients for NaCl at 25° by averaging values from several sources. The data was more extensive than Harned and Owen's data, and reported the mean activity coefficients for NaCl at 25° over a concentration range of 0.1 m to 6.0 m to four significant figures.

Robinson and Stokes used data from four different methods to derive mean activity coefficient values: direct vapor pressure measurements, freezing point depressions, emf data, and isopiestic ratios. At low concentrations (under 1.0 m) freezing point depression data was used along with emf data. At 0.1 m Robinson and Stokes used six different values derived from four different techniques to yield a mean activity coefficient of 0.7784 with a maximum deviation of 0.0005.

Above 1.0 m, data from direct vapor pressure measurements was used. Also, vapor pressure measurements of other salts whose isopiestic ratio with NaCl were accurately known were used to calculate osmotic coefficients which were then converted to mean activity coefficients. This technique was used at higher concentrations, especially at near-saturated solutions. An extensive list of activity coefficients for NaCl over the temperature range of 40° to 80° was calculated by correcting Robinson and Stokes' 25° data using Equation 47. A list of these values is contained in Appendix H.

The partial molal heat content of the solvent ($\overline{L}_1$) is another useful thermodynamic function which can be derived from ΦL data[77],

$$\overline{L}_1 = - MW_1 \, m^{3/2} / \, 2000 \quad \partial \Phi L / \partial \sqrt{m}$$

$\overline{L}_1$ = partial molal heat content of solvent
MW_1 = molecular weight of solvent
m = molality of solution

The $\overline{L}_1$ values were readily calculated since the slope of the ΦL vs. $\sqrt{m}$ curve ($\partial \Phi L / \partial \sqrt{m}$) had previously been evaluated in the calculation of $\overline{L}_2$.

Values of $\overline{L}_1$ as a function of concentration and temperature are listed in Appendix I.

The $\overline{L}_1$ values were then treated by the POLYR program to obtain a polynomial equation describing $\overline{L}_1$ at each concentration as a function of temperature. The treatment was similar to that of $\overline{L}_2$. The polynomial equations were then used to calculate osmotic coefficients.

The relationship by which osmotic coefficients were calculated from $\overline{L}_1$ is found in Equation 48.

$$\int d\varphi = \int \frac{1000\ \overline{L}_1}{MW_1 R T^2 \nu m}\ dT \qquad \text{Eq. 48}$$

φ = osmotic coefficient
$\overline{L}_1$ = partial molal heat content of solvent
MW_1 = molecular weight of solvent
R = gas constant
ν = number of ions
m = molality of solution
e, f, g = coefficients of polynomial equation describing $\overline{L}_1$

$$\varphi = \varphi Tr + \frac{1000}{MW_1 R \nu m}\left[e\left(\frac{1}{Tr} - \frac{1}{T}\right) + f \ln \frac{T}{Tr} + G\,(T - Tr)\right] \qquad \text{Eq. 49}$$

The integrated form (Equation 49) of Equation 48 was obtained using 25° as a reference temperature and the appropriate polynomial equation describing $\overline{L}_1$ as a function of temperature. The osmotic coefficients were then calculated using Equation 49 to correct 25° data to the desired temperature.

Robinson and Stokes[79] published an extensive list of Φ at 25° for NaCl. These values were used as the reference values in Equation 49. A list of osmotic coefficients calculated using $\overline{L}_1$ temperature dependence determined in this investigation is found in Appendix J.

Osmotic coefficients from the literature were used to check the consistency of the calculated values from this research. The boiling point elevation work of Smith[80] and Smith and Hirtle[81] provided osmotic coefficients for NaCl at the temperatures 60°, 70° and 80°. A comparison of these values and osmotic coefficients generated from $\overline{L}_1$ values from this research is found in Table IV. The agreement was good with the deviation ranging from 0.0 to 0.5% with average deviation about 0.15%.

The osmotic coefficients from this investigation were also compared with more recent 75° osmotic coefficients published in a report to the Office of Saline Water by Lindsay and Lui[82]. Their values were derived from measurement of the vapor presure lowering. The agreement between osmotic coefficients from this research and those of Lindsay and Lui is good with a deviation range of 0.00 to 0.45%. This comparison is found in Table V.

The excellent agreement found between existing osmotic coefficient data and data calculated from ΦL curves in this research shows that the experimental ΦL curves are accurate. The osmotic coefficients are calculated from $\overline{L}_1$ values which are directly dependent upon the slope of the ΦL vs. $\sqrt{m}$ curve. The agreement also indicates that the technique of fitting the ΦL vs. $\sqrt{m}$ curves by parts was valid. Accurate results were obtained over the complete concentration range and no deviations are apparent in the regions of overlap where the uncertainty of the slope was expected to be somewhat greater. The agreement with the recent work of Lindsay and Lui and the earlier work of Smith and Hirtle was remarkable since both determined the solvent properties directly and in this investigation solute properties were measured and solvent properties calculated by mathematical relations dependent on accurate determination of the slope of ΦL vs. $\sqrt{m}$ curves.

TABLE IV

COMPARISON OF OSMOTIC COEFFICIENTS

Present Research

m	60°	70°	80°
0.1	0.9296	0.9283	0.9269
0.2	0.9223	0.9208	0.9191
0.4	0.9200	0.9185	0.9166
0.6	0.9250	0.9236	0.9216
0.8	0.9328	0.9317	0.9298
1.0	0.9414	0.9404	0.9386
1.5	0.9686	0.9679	0.9670
2.0	0.9954	0.9946	0.9926
2.5	1.0302	1.0290	1.0262
3.0	1.0584	1.0566	1.0531
3.5	1.0967	1.0943	1.0899
4.0	1.1250	1.1217	1.1165

TABLE IV (contd.)

COMPARISON OF OSMOTIC COEFFICIENTS

Boiling Point Elevation Data[80,81]

m	60°	70°	80°
0.1	0.9291	0.9273	0.9263
0.2	0.9210	0.9190	0.9178
0.4	0.9207	0.9186	0.9170
0.6	0.9267	0.9246	0.9228
0.8	0.9350	0.9339	0.9310
1.0	0.9442	0.9424	0.9402
1.5	0.968	0.968	0.966
2.0	0.999	0.998	0.995
2.5	1.031	1.029	1.026
3.0	1.061	1.059	1.057
3.5	1.092	1.090	1.086
4.0	1.130	1.127	1.120

TABLE V

OSMOTIC COEFFICIENT COMPARISON AT 75°C

m	Liu and Lindsay[82]	Present Research
0.1	0.926	0.9276
0.2	0.918	0.9200
0.4	0.918	0.9176
0.6	0.924	0.9227
0.8	0.934	0.9308
1.0	0.940	0.9396
1.5	0.967	0.9679
2.0	0.996	0.9937
2.5	1.026	1.026
3.0	1.056	1.0551
3.5	1.087	1.0923
4.0	1.119	1.1194
5.0	1.182	1.1838
6.0	1.247	1.2449

An estimate of the reliability of the $\overline{L}_2$ and $\overline{L}_1$ values from this research was possible. Assuming the published values of Harned and Owen to be correct, all uncertainty in calculated osmotic coefficients or activity coefficients was in the determination of $\overline{L}_1$ and $\overline{L}_2$. The correction term in correcting 25° activity coefficient data to higher temperatures ranges from 0.5% to 5% of reference value. The maximum deviation from the published data of Harned and Owen was approximately 0.3% with the average deviation about 0.1%. Based on the maximum deviation in the activity coefficient and considering the correction term to be about 5%, the uncertainty in $\overline{L}_2$ would be about 6%. However, this is a maximum deviation, and in most cases $\overline{L}_2$ would be considerably better. Similar calculations for the osmotic coefficients yield a maximum uncertainty of 10% in $\overline{L}_1$ values when using the maximum deviation present, while an uncertainty of 4% in $\overline{L}_1$ exists when using average values for the deviation and the correction terms.

The relative partial molal heat capacity of the NaCl ($\overline{J}_2$) was calculated from the temperature dependence of $\overline{L}_2$ using relationship 26.

$$\overline{J}_2 = \partial\overline{L}_2/\partial T \qquad \text{Eq. 26}$$

The relative partial molal heat content ($\overline{L}_2$) as given by expression 45 was directly differentiated to give $\overline{L}_2$ in the experimental temperature range. Appendix K contains $\overline{J}_2$ calculated in this research.

The consistency of the $\overline{J}_2$ values determined in this investigation was checked by two different methods. A direct comparison of $\overline{J}_2$ calculated in this research and values derived from the boiling point elevation measurements of Smith[83] and Smith and Hirtle[84] was made in Table IV. Fair agreement is found at concentrations below 2.5 m;

however, the agreement is very poor above that concentration. The failure of Smith and Hirtle's $\bar{J}_2$ values to agree with values from this research at higher concentrations was not surprising since the osmotic coefficients show a rather large deviation from a smooth curve at similar concentrations at 60°. The $\bar{L}_2$ data from which Smith and Hirtle calculate $\bar{J}_2$ has an uncertainty of 17%; therefore, $\bar{J}_2$ values would also contain at least that much uncertainty. No other values for $\bar{J}_2$ at temperatures between 40° and 80° were present in the literature. Therefore, few conclusions, if any, could be drawn about the consistency of $\bar{J}_2$ values of this research.

The second method used to test $\bar{J}_2$ values made use of Equation 27.

$$\bar{J}_2 = \bar{Cp}_2{}^{o} \qquad \text{Eq. 27}$$

$\bar{Cp}_2$ = partial molal heat capacity of solute
$\bar{Cp}_2{}^{o}$= partial molal heat capacity of solute at infinite dilution

Both $\bar{Cp}_2{}^{o}$ and $\bar{Cp}_2$ values were found in the literature for NaCl solutions at elevated temperatures. The $\bar{Cp}_2{}^{o}$ values were published by Criss and Cobble[85] and were obtained using the "integral heat of solution" method. $\bar{Cp}_2$ values used were calculated from apparent molal heat capacities (ϕCp) published by Ackermann[86]; the original heat capacity measurements were made by Eigen and Wicke[87].

A check of the consistency of the $\bar{J}_2$ and $\bar{Cp}_2$ values using Equation 27 was made. The $\bar{Cp}_2$ is concentration independent and therefore should be constant at each temperature. A comparison of the $\bar{Cp}_2{}^{o}$ values from the above procedure was made with published $\bar{Cp}_2$ values of Criss and Cobble. Table VII contains the above comparisons.

At 40° and 60° the $\bar{Cp}_2{}^{o}$ predicted by $\bar{J}_2$ and $\bar{Cp}_2$ was reasonably constant and varied ±0.1 calorie. This consistency was not present at

TABLE VI

COMPARISON OF $\bar{J}_2$

60° Molality	This Research	Smith and Hirtle[81]
0.5	9.06	10
1.0	13.03	12
1.5	15.42	15
2.0	18.85	19
2.5	22.06	21
3.0	24.83	21
3.5	27.10	22
4.0	28.18	24

80° and the predicted $\overline{Cp}_2{}^\circ$ varied ±1.5 calories. A comparison of $\overline{Cp}_2{}^\circ$ from Criss and Cobble showed agreement to about 1 calorie; this exceeded the predicted uncertainty of ±0.5 calorie for the Criss and Cobble value.

The inconsistencies present in the comparisons indicated a closer investigation of the values used was needed. Recalculation of the original data of Eigen and Wicke failed to yield the same values published by Ackermann. The data was treated in the manner described by Ackermann; however, at 60° and 80° the ΦCp values showed large deviation from predicted linearity. A plot (Figure V) of ΦCp vs. $\sqrt{m}$ using values published by Ackermann is superimposed upon a plot of ΦCp values calculated from original heat capacity measurements and illustrates the aforementioned deviations. It seems obvious that in Ackermann's paper some information about the method for calculating ΦCp and the plotting of ΦCp vs. $\sqrt{m}$ has been left out. However, until such time as this inconsistency can be resolved, the use of $\overline{Cp}_2$ data to check the precision of $\overline{J}_2$ values derived in this research cannot be made.

The values of ΦCp for NaCl at 45° have been published by White[88] and Hess and Gramkee[89]. Most of these measurements were made in dilute range below 0.4 m and as previously pointed out, the values are subject to large experimental errors. A plot of ΦCp vs. $\sqrt{m}$ yields rather large deviations from predicted linearity. The measurements yielded no data which could be used to check the consistency of $\overline{J}_2$.

Since the comparison using Equation 27 showed a very little consistency in predicting $\overline{Cp}_2$ at 80°, a study of the polynomial equation to which $\overline{L}_2$ was fitted was indicated. The hand-plotted $\overline{L}_2$ vs. T curve showed an inflection point around 60° with a very rapidly changing slope

TABLE VII

ACKERMANN'S $C\overline{p}_2$

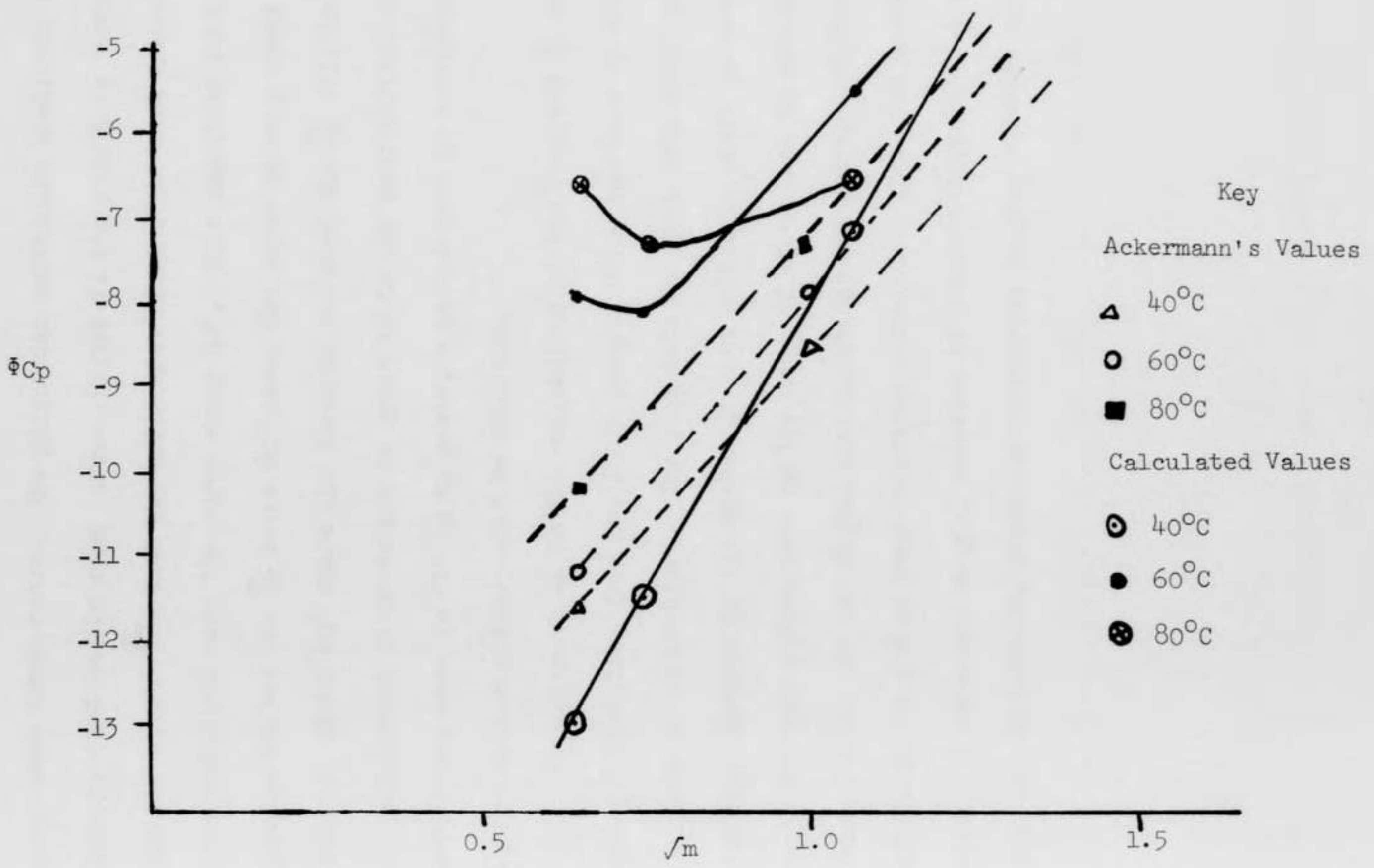
Molality	40°	60°	80°
0.5	-6.9	-6.75	-7.9
1.0	-2.0	-2.66	-3.8
2.0	5.4	3.3	2.3

$C\overline{p}_2{}^{\circ}$ PREDICTED FROM $\overline{J}_2$ and $C\overline{p}_2$

Molality	40°	60°	80°
0.5	-16.4	-15.8	-16.5
1.0	-16.4	-15.7	-15.4
2.0	-16.6	-15.5	-13.4
Avg.	-16.5	-15.7	-15.1
Criss and Cobble	-15.3	-15.2	-16.5

Figure 5

Apparent Molal Heat Capacity Versus $\sqrt{m}$

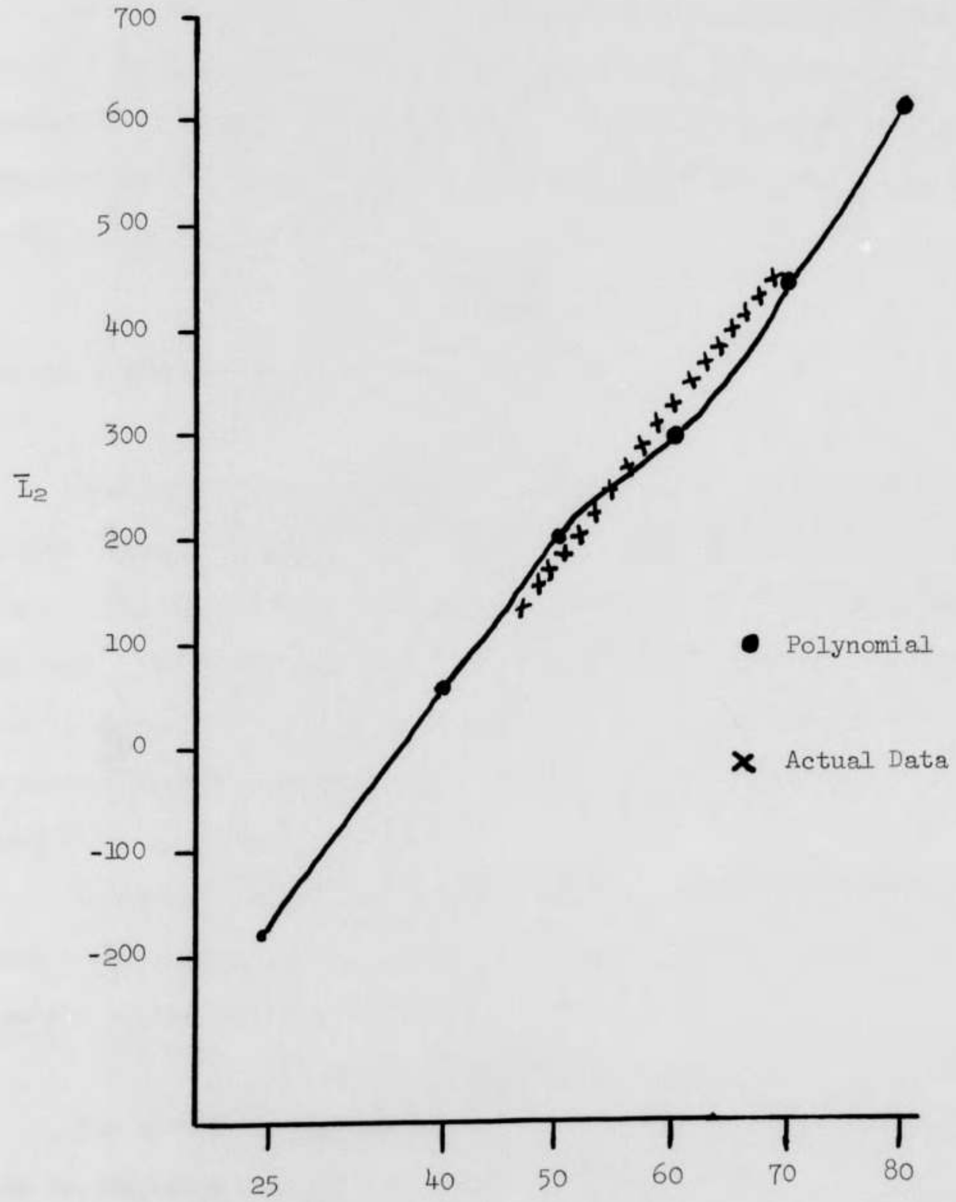


above that temperature. The polynomial equation's predicted values were then plotted on the same curve. Figure VI contains this comparison. It can easily be seen that the polynomial smooths the area around the inflection point and also the curve about 60°. This smoothing would not significantly affect the $\overline{J}_2$ below 60° since the curve is very close to linearity; however, above 60° where the curve is smoothed the $\overline{J}_2$ will be lower since the polynomial slope is not as great as in the hand plotted curve. An effort was made to fit $\overline{L}_2$ by parts, a method used in treatment of ΦL data, but no usable values could be obtained.

An estimate as to the reliability of the reported $\overline{J}_2$ can be made using information from the POLYR program which was used to fit $\overline{L}_2$ as a function of temperature. The residuals for each data point were summed and then divided by the number of data points to yield an average residual. These average values were on the order of 4% or less at concentrations below 2.0 m. At the higher concentrations the average residual gradually increased to 10% at near-saturated solutions. Thus, the present $\overline{J}_2$ values should be accurate to ±0.5 calories at concentrations of 2.0 m or less, with the uncertainty gradually increasing to ±2.0 calories at 6.0 m.

Figure 6

Comparison of Polynomial and Actual Curve



SPECIFIC INTERACTIONS

A comparison of $\overline{L}_2$ vs. $\sqrt{m}$ shows that $\overline{L}_2$ becomes increasingly more positive at increasing temperatures (Figure VII). This behavior can best be explained by considering the effect of temperature on the extended Debye-Hückel equation. The relative partial molal heat content is represented by the relation,

$$\overline{L}_2 = \frac{A_H \sqrt{I}}{1 + A\sqrt{I}} - BI \qquad \text{Eq. 50}$$

The Debye-Hückel limiting law would then be

$$\overline{L}_2 = A_H \sqrt{I} \qquad \text{Eq. 51}$$

The term $A_H \sqrt{I}$ in Equation 57 accounts for the long-range Coulombic interactions. The term $1 + A\sqrt{I}$ takes into consideration the short-range specific interactions resulting from the distance of closest approach of the ions. The value of A is not an experimentally measurable quantity; thus investigators normally set it equal to one (corresponding to a distance of closest approach of about 3 Å). The B term then accounts for all other short range specific interactions.

Using the experimental $\overline{L}_2$ data, the short-range effects, except those corrected for by the distance of closest approach term, can be examined by the relation

$$B = \frac{A_H \sqrt{I}}{1 + \sqrt{I}} - \overline{L}_2 \qquad \text{Eq. 52}$$

The effect of temperature on the B coefficient can be more easily seen by comparing them to a reference temperature,

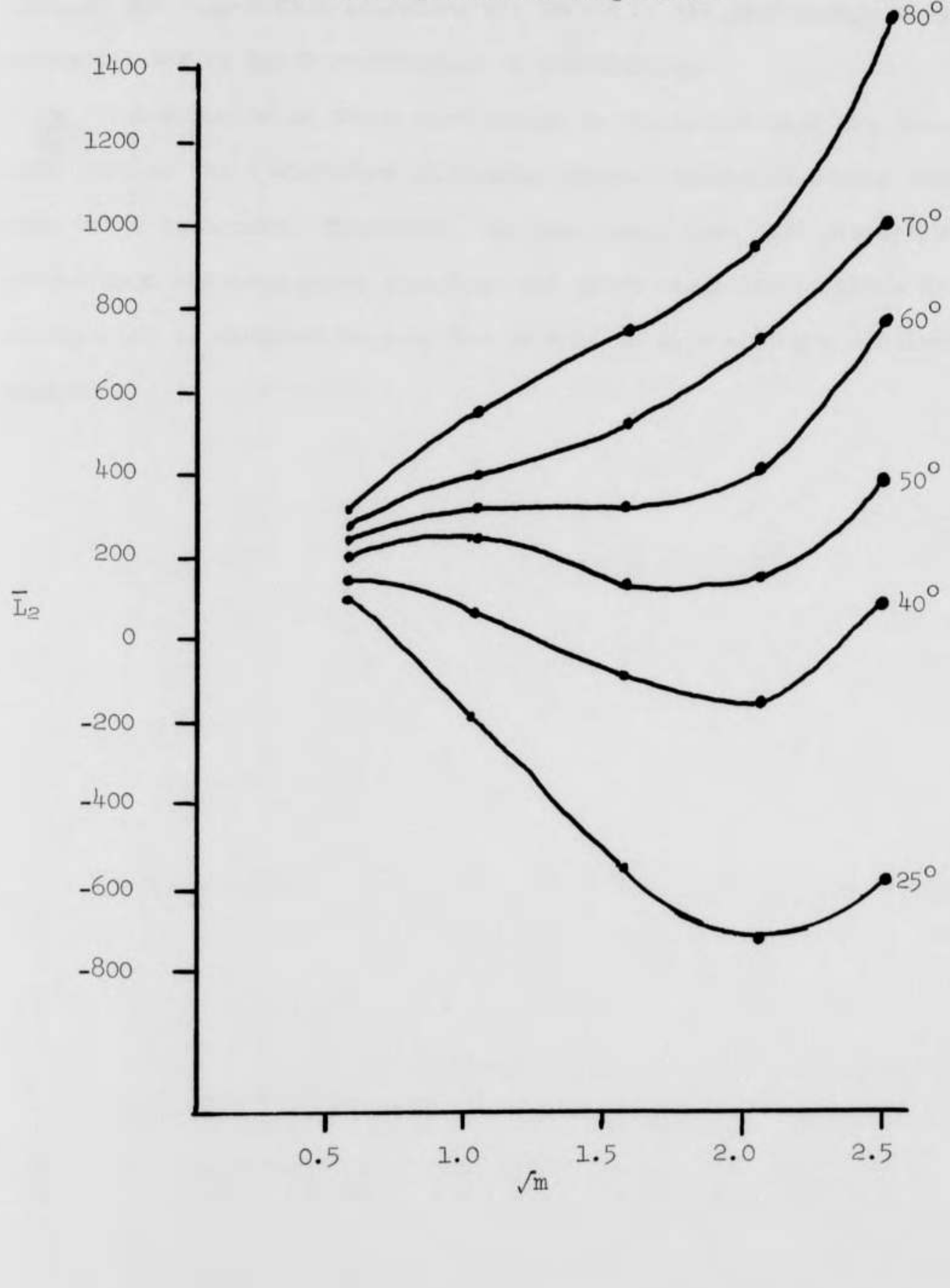
$$\delta = B_{25} - B_T \qquad \text{Eq. 53}$$

Table VIII contains a list of δ's as a function of concentration and

Figure 7

Partial Molal Heat Content of Solute Versus $\sqrt{m}$

At Each Experimental Temperature



temperature. At any given concentration δ increases with increasing temperature; therefore, the B coefficient is decreasing with temperature. Thus, as the temperature increases the effect of the short-range interactions accounted for by the B coefficient is diminishing.

The behavior of the B coefficient is consistent with the observation that as the temperature increases, thermal agitation breaks down the bulk water structure. Therefore, the ions would have less disruptive effect upon the bulk water structure and short range interactions would be expected to decrease because the solvent is approaching a continuous medium.

TABLE VIII

δ/m VALUES

	Temperature				
m	40°	50°	60°	70°	80°
0.5	149	263	309	315	411
1.0	149	236	286	309	381
2.0	126	199	249	297	331
3.0	113	170	223	277	317
4.0	103	149	205	248	288
5.0	95	130	189	213	257

SUMMARY

The heats of dilution of aqueous sodium chloride solutions were measured over the concentration range of 0.1 m to 6.0 m at 40°, 50°, 60°, 70°, and 80°. The partial molal heat content of solute ($\overline{L}_2$) and solvent ($\overline{L}_1$) were calculated from the heat of dilution data using standard thermodynamic relationships.

Existing activity coefficient data at 25° were corrected to higher temperatures using $\overline{L}_2$ as a function of temperature. Excellent agreement was found with previously published activity coefficients from 40° to 80° throughout the entire temperature and concentration range. Similarly, the osmotic coefficients were calculated using $\overline{L}_1$ and good correlation was observed. The values for activity and osmotic coefficients calculated in this research cleared up some uncertainty which existed in previous data between 40° and 60° above 1.0 m.

The partial molal heat content of the solute was also used to calculate the apparent molal heat capacity of the solute ($\overline{J}_2$). The precision of the derived $\overline{J}_2$ values was not readily obtainable since a discrepancy was found in existing high temperature heat capacity data. From the accuracy of the $\overline{L}_2$ values the $\overline{J}_2$ values were estimated to be accurate to at least ± 0.5 calories at concentrations below 2.0 m.

The excellent agreement achieved using partial molal heat contents to correct existing 25° data indicated the validity of the method and that the measurement of heats of dilution is an efficient and accurate method by which high temperature thermodynamic data can be obtained.

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APPENDIX A

RESISTANCE OF CALIBRATED HEATER
AT EXPERIMENTAL TEMPERATURES

	Resistance (ohms)
40°	500.4
50°	501.3
60°	501.2
70°	501.4
80°	501.4

APPENDIX B

HEATS OF OPENING

T ($^{\circ}$C)	Pipet Size	Heat (cal.)
40	small	no detectable slope change
	medium	no detectable slope change
	large	0.0007
50	small	0.002
	medium	0.003
	large	0.002
60	small	0.0035
	medium	0.0025
	large	0.0028
70	small	0.0035
	medium	0.0035
	large	0.0033
80	small	0.0035
	medium	0.0030
	large	0.0035

APPENDIX C

COEFFICIENTS FROM LEAST SQUARES FIT OF $\Delta\Phi L$ FOR DEBYE-HÜCKEL EXTRAPOLATION EQUATION

Temperature (°C)	Debye-Huckel Limiting Slope	B	C	Standard Deviation	No. Data Points
40	856.0	-639.77	1221.10	1.75	46
50	982.0	377.98	-2137.69	1.41	29
60	1122.0	-603.38	1140.31	1.74	30
70	1277.0	-2043.11	5779.84	1.75	26
80	1450.0	-281.23	484.35	1.53	26

APPENDIX D

EXTRAPOLATION PROGRAM FOR HEATS OF DILUTION

```
  IMPLICIT REAL* 8 (A-H,O-Z)
  REAL* 8 DLOG,DSQRT
 ODIMENSION DELH(100),CI(100),CF(100),PHII(100),PHIF(100),F1(100),F2
 1(100),F3(100),W(100),HCALC(100),ERROR(100),CO(100)
 OHSTD(CM)=SLOPE*((DSQRT(CM)/(1.+A*DSQRT(CM)))-((1./(A* A*A*CM))*(1.+
 1A*DSQRT(CM)-1./(1.+A*DSQRT(CM))-2.*DLOG(1.+A*DSQRT(CM)))))
1 READ(1.3) N A.SLOPE
3 FORMAT(25H                         I5,F10.3,F10.1)
4 READ (1,2)  (DELH(K).CI(K).CF(K).W(K),K=1,N)
2 FORMAT(F10.1,2F10.1,F10.2)
5 S11=0.
  S12=0.
  S13=0.
  S22=0.
  S23=0.
  S33=0.
  SWW=0.
  SW=0.
  IW=0.
  DO 9 K=1,N
  PHII(K)=HSTD(CI(K))
  PHIF(K)=HSTD(CF(K))
```

```
      F1(K)=(-PHII(K))+PHIF(K)+DELH(K)
      F2(K)=CI(K)-CF(K)
      F3(K)=CI(K)*DSQRT(CI(K))-CF(K)*DSQRT(CF(K))
      S11=S11+F1(K)*F1(K)*W(K)
      S12=S12+F1(K)*F2(K)*W(K)
      S13=S13+F1(K)*F3(K)* W(K)
      S22=S22+F2(K)*F2(K)*W(K)
      S23=S23+F2(K)*F3(K)*W(K)
      S33=S33+F3(K)*F3(K)* W(K)
      SWW=SWW+W(K)* W(K)
    9 SW=SW+W(K)
      C=(S12/S22-Sle/S23)/(S23/S22-S33/S23)
      B=S13/S23-C*S33/S23
      SEBC=S11-B*S12-C*S13
      WRITE(3,3) N,A,SLOPE
      WRITE(3.7) B,C
    7 FORMAT(4H B= F10.2,4H C= F10.2)
      WRITE(3,8) SEBC
    8 FORMAT(21H SUM ERRORS SQUARED =D10.4)
      WRITE(3,12) S11,S12,S13,S22,S23,S33,SWW,SW
   12 FORMAT(8D10.3)
      DF=N-2
      SYBC=DSQRT(SEBC/DF)
      WRITE(3,110) SYBC
  110 FORMAT(8H SYBC = F10.4)
```

```
 25 WRITE(3,24)
 240FORMAT(78H     CI          CF        PHII       PHIF      HCALC     D
   1ELH     ERROR      W )
   DO 23 K=1,N
   HCALC(K)=(PHII(K))-PHIF(K)+B*F2(K)+C*F3(K)
   ERROR(K)=DELH(K)-HCALC(K)
 230WRITE(3,22) CI(K),CF(K),PHII(K),PHIF(K),HCALC(K),DELH(K),ERROR(K),
   1W(K)
 22 FORMAT(2F10.7,4F10.3,2F10.4)
 20 BO=S12/S22
    SEB=S11-BO*S12
    DF=N-2
    F=(SEB-SEBC)*DF/SEBC
    WRITE(3,26) BO
 26 FORMAT(5H BO= F10.2)
    WRITE(3,8) SEB
    WRITE(3,27) F
 27 FORMAT(13H F(1, N-2) = F12.4)
    SYB=DSQRT(SEB/(DF+1.))
    WRITE(3,111) SYB
111 FORMAT(7H SYB = F10.4)
    GO TO 1
    END
```

APPENDIX E

HEAT OF DILUTION OF NaCl: 40°C

m_i	m_f	Q	$\Delta\Phi_L$	Φ_L^f	Φ_L^i
0.07390	0.005390	0.10215	75.39	36.08	111.47
0.07390	0.00550	0.1035	74.65	37.08	111.73
0.07390	0.00300	0.06265	82.87	28.31	111.18
0.07390	0.00303	0.06066	79.51	29.44	108.95
0.07390	∝			avg.	110.83
0.1086	0.008206	0.1706	82.50	44.08	126.58
0.1086	0.008124	0.1650	80.64	43.89	124.54
0.1086	0.004574	0.10662	92.23	34.19	126.42
0.1086	0.004573	0.10436	90.32	34.19	124.51
0.1086	0.002727	0.06644	96.58	27.11	123.69
0.1086	0.002731	0.06480	94.03	27.13	121.16
0.1086	∝			avg.	124.48
0.2005	0.004877	0.14128	99.2	34.70	133.90
0.2005	0.004840	0.13594	100.35	34.59	134.94
0.2005	0.008314	0.19472	92.77	43.59	136.36
0.2005	0.008239	0.19172	92.21	43.43	135.64
0.2005	0.01458	0.28971	79.09	54.88	133.97
0.2005	0.01475	0.30030	80.95	55.14	136.09
0.2005	∝			avg.	135.2

$\underline{m_i}$	$\underline{m_f}$	$\underline{Q}$	$\underline{\Delta\Phi_L}$	$\underline{\Phi_L^f}$	$\underline{\Phi_L^i}$
0.3995	0.01660	0.39171	91.07	57.80	148.87
0.3995	0.01641	0.3732	90.05	57.54	147.59
0.3995	0.01627	0.35465	86.41	57.34	143.76
0.3995	∝			avg.	146.7
0.5982	0.02429	0.4583	74.12	67.08	141.20
0.5982	0.02470	0.4498	72.05	67.52	139.57
0.5982	0.02326	0.44224	75.51	65.97	141.48
0.5982	∝			avg.	140.8
0.8000	0.05803	0.51579	35.38	93.63	129.01
0.8000	0.05820	0.52570	35.94	93.74	129.68
0.8000	0.03181	0.42774	53.35	74.39	127.74
0.8000	0.03217	0.44399	54.75	74.71	129.46
0.8000	0.01896	0.32513	68.06	60.91	128.97
0.8000	0.01952	0.33966	69.00	61.61	130.61
0.8000	∝			avg.	129.2
0.9503	0.02284	0.29362	51.01	65.50	116.51
0.9503	0.02238	0.28649	50.82	64.99	115.81
0.9503	∝			avg.	116.2
1.505	0.03681	-0.02622	-2.82	78.65	75.83
1.505	0.03532	-0.02399	-2.70	77.42	74.72
1.505	∝			avg.	75.3
2.193	0.05066	-0.81822	-64.14	88.84	24.70

m_i	m_f	Q	$\Delta\Phi L$	ΦL^{f}	ΦL^{i}
2.193	0.04907	-0.7855	-63.61	87.76	24.15
2.193	∝			avg.	24.4
2.948	0.06815	-1.9756	-120.15	99.76	-20.39
2.948	0.06871	-2.0995	-121.31	100.09	-21.22
2.948	∝			avg.	-20.8
4.081	0.09355	-4.2605	-180.89	113.80	-67.09
4.081	0.09151	-4.0993	-178.01	112.71	-65.30
4.081	∝			avg.	-66.2
5.010	0.1161	-5.8175	-198.92	125.53	-73.39
5.010	0.1116	-5.5245	-197.74	123.20	-74.54
5.010	∝			avg.	-74.0
6.078	0.1231	-5.9043	-190.96	129.13	-61.83
6.078	0.1302	-6.3082	-192.67	133.02	-59.65
6.078	∝			avg.	-60.7

TABLE E. II

HEAT OF DILUTION: 50°C

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
0.09979	0.004030	0.09679	95.62	40.64	136.26
0.09979	0.004023	0.09405	93.09	40.61	133.70
0.09979	0.007446	0.16474	88.62	54.40	143.12
0.09979	∝			avg.	137.69
0.1997	0.008596	0.26551	122.47	58.30	180.77
0.1997	0.008160	0.25657	125.13	56.90	182.03
0.1997	0.001484	0.39832	107.57	74.85	182.42
0.1997	0.001486	0.40063	108.02	74.89	182.91
0.1997	0.004873	0.17298	141.34	44.54	185.88
0.1997	0.004764	0.16774	140.27	44.04	184.31
0.1997	∝			avg.	206.83
0.5964	0.01372	0.49321	143.34	72.26	215.60
0.5964	0.01362	0.4961	145.28	72.03	217.31
0.5964	∝			avg.	216.45
0.8025	0.05916	1.3594	91.75	126.49	218.24
0.8025	0.05792	1.3560	93.63	125.77	219.40
0.8025	0.03233	0.9393	115.71	103.63	219.34
0.8025	0.03208	0.93368	115.91	103.31	219.22
0.8025	0.01923	0.64319	133.22	83.85	217.07

TABLE E. II (contd.)

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
0.8025	0.01881	0.64459	136.59	83.06	219.65
0.8025	$\propto$			avg.	218.82
1.125	0.02499	0.79217	126.49	93.59	220.08
1.125	0.02713	0.8116	119.17	96.76	215.93
1.125	$\propto$			avg.	218.00
1.503	0.03615	0.88484	97.49	108.02	205.51
1.503	0.03615	0.88428	97.43	108.02	205.45
1.503	$\propto$			avg.	205.48
1.995	0.04732	0.73554	61.94	118.48	180.42
1.995	0.04564	0.71396	62.39	117.11	179.50
1.995	$\propto$			avg.	179.96
2.996	0.07035	0.41559	23.55	131.81	155.36
2.996	0.06515	0.38921	23.85	129.58	153.43
2.996	$\propto$			avg.	154.40
4.226	0.09209	0.01781	-0.77	137.29	136.52
4.226	0.09131	0.02038	-0.89	137.19	136.30
4.226	$\propto$			avg.	136.41
5.012	0.1126	0.04360	-1.54	137.80	136.26
5.012	0.1114	0.03088	-1.11	137.88	136.77
5.012	$\propto$			avg.	136.51

TABLE E. II (contd.)

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
5.718	0.1237	0.29673	9.61	136.50	146.11
5.718	0.1264	0.39839	12.57	136.04	148.61
5.718	∝			avg.	147.36

TABLE E. III

HEAT OF DILUTION: 60°C

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
0.1023	0.007562	0.2107	111.22	57.25	168.47
0.1023	0.007519	0.2086	110.77	57.10	167.87
0.1023	∝			avg.	168.17
0.2041	0.01510	0.5223	138.11	77.19	215.30
0.2041	0.01458	0.5099	139.98	76.06	216.04
0.2041	0.008312	0.3233	154.85	59.68	214.53
0.2041	0.008327	0.3246	155.25	59.73	214.98
0.2041	0.004717	0.2043	172.71	46.35	219.06
0.2041	0.004791	0.2065	171.81	46.69	218.50
0.2041	∝			avg.	216.40
0.4005	0.01643	0.7028	170.24	80.00	250.24
0.4005	0.01575	0.6749	170.73	78.59	249.32
0.4005	∝			avg.	249.78
0.6035	0.01475	0.7295	196.97	76.44	273.41
0.6035	0.01464	0.7236	196.76	76.19	272.95
0.6035	∝			avg.	273.19
0.8014	0.05926	2.1918	147.63	134.92	282.55
0.8014	0.05812	2.1684	149.15	133.87	283.02
0.8014	0.03234	1.4537	178.96	105.76	284.72
0.8014	0.03233	1.4544	179.09	105.75	284.84

TABLE E. III (contd.)

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
0.8014	0.01956	0.9494	193.28	86.05	279.33
0.8014	0.01789	0.9068	202.24	82.90	285.14
0.8014	∝			avg.	283.27
0.9885	0.02365	1.1836	202.72	93.08	295.80
0.9885	0.02336	1.1806	201.40	92.61	294.01
0.9885	∝			avg.	294.91
1.497	0.03359	1.6439	194.07	107.40	301.47
1.497	0.03607	1.7355	191.63	110.52	302.16
1.497	∝			avg.	301.81
1.998	0.04482	2.0050	178.49	120.61	299.10
1.998	0.04540	2.0299	178.35	121.24	299.59
1.998	∝			avg.	299.34
2.991	0.06920	2.7686	159.51	143.66	303.17
2.991	0.06710	2.7597	162.24	141.83	304.07
2.991	∝			avg.	303.61
3.957	0.09099	3.4475	151.09	160.84	311.93
3.957	0.08601	3.3187	154.07	157.09	311.16
3.957	∝			avg.	311.54
4.873	0.1061	4.6661	175.64	171.73	347.37
4.873	0.1099	4.7190	171.36	174.43	345.79
4.873	∝			avg.	346.57

TABLE E. III (contd.)

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
5.718	0.1222	6.454	210.98	182.77	393.75
5.718	0.1291	6.5376	202.10	187.38	389.48
5.718	$\propto$			avg.	391.62

TABLE E. IV

HEAT OF DILUTION: 70°C

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
0.1002	0.007347	0.25390	138.63	57.21	195.84
0.1002	0.007458	0.25659	137.85	57.54	195.39
0.1002	∝			avg.	195.61
0.1957	0.007944	0.38430	192.59	58.99	251.58
0.1957	0.004676	0.23850	204.03	47.67	251.70
0.1957	0.004707	0.23955	203.56	47.77	251.33
0.1957	0.007824	0.37849	192.69	58.65	251.34
0.1957	0.01424	0.6165	173.77	74.01	247.78
0.1957	0.01415	0.6075	172.39	73.83	246.22
0.1957	∝			avg.	250.00
0.4005	0.01594	0.88225	220.45	77.30	297.75
0.4005	0.01607	0.88530	219.38	77.54	296.92
0.4005	∝			avg.	297.33
0.6035	0.02388	1.4096	236.27	90.51	326.78
0.6035	0.02362	1.3976	236.94	90.12	327.06
0.6035	∝			avg.	326.92
0.7998	0.01884	1.2143	257.92	82.46	340.38
0.7998	0.01847	1.1958	259.27	81.83	341.10
0.7998	0.05843	2.9735	204.19	136.37	340.56
0.7998	0.03187	1.9478	243.54	111.93	345.45

TABLE E. IV (contd.)

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
0.7998	0.03282	1.9721	239.10	103.22	343.32
0.7998	0.05815	2.9756	205.40	136.74	342.14
0.7998	∝			avg.	341.99
0.9997	0.02398	1.6156	269.58	90.67	360.25
0.9997	0.02457	1.6603	240.25	91.55	361.80
0.9997	∝			avg.	366.03
1.432	0.03385	2.2547	269.22	104.61	373.83
1.432	0.03447	2.2987	267.86	105.44	373.30
1.432	∝			avg.	373.57
2.003	0.04876	3.4531	284.32	124.11	408.43
2.003	0.04828	3.3901	282.05	123.49	405.54
2.003	0.04863	3.4567	285.34	123.94	409.28
2.003	∝			avg.	407.75
2.966	0.06896	4.8725	284.16	150.9	435.06
2.966	0.06801	4.9873	295.10	149.60	444.70
2.966	0.06536	4.6671	284.38	146.00	433.38
2.966	∝			avg.	437.68
5.023	0.05548	5.5183	404.86	132.87	537.73
5.023	0.05977	5.9370	404.23	138.52	542.75
5.023	∝			avg.	540.24

TABLE E. IV (contd.)

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
5.718	0.06582	7.0894	438.16	146.62	584.78
5.718	0.06269	6.8516	444.62	142.41	587.03
5.718	$\propto$			avg.	585.91

TABLE E. V

HEAT OF DILUTION: 80°C

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
0.1002	0.007467	0.3092	166.51	76.67	243.18
0.1002	0.007486	0.3084	165.74	76.74	242.48
0.1002	∝			avg.	242.83
0.2017	0.004953	0.3009	243.91	63.39	307.29
0.2017	0.005053	0.3065	243.42	63.99	307.41
0.2017	0.01489	0.7385	199.64	104.81	304.45
0.2017	0.01503	0.7508	200.01	105.24	305.25
0.2017	0.008100	0.4448	224.22	79.58	303.80
0.2017	0.008252	0.4535	221.46	80.26	301.72
0.2017	∝			avg.	304.99
0.4005	0.01630	1.0261	252.66	109.10	361.75
0.4005	0.01662	1.1218	250.69	110.15	360.74
0.4005	∝			avg.	361.25
0.6035	0.02497	1.7165	275.89	131.56	407.45
0.6035	0.02499	1.7155	276.45	131.60	408.05
0.6035	∝			avg.	407.75
0.7991	0.05803	3.7815	262.73	190.00	450.72
0.7991	0.05920	3.8490	266.73	189.56	451.29
0.7991	0.01908	1.5828	333.29	116.97	450.26
0.7991	0.01962	1.6261	332.67	118.42	451.08

TABLE E. V (contd.)

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
0.7991	0.03293	2.4672	301.58	148.19	449.77
0.7991	0.02952	2.2316	306.15	141.41	447.56
0.7991	∝			avg.	450.11
0.9997	0.02488	2.1577	347.99	131.35	479.34
0.9997	0.02444	2.1355	350.55	130.33	481.18
0.9997	∝			avg.	480.26
1.432	0.03510	3.0776	352.01	152.27	504.28
1.432	0.03402	2.9240	345.32	150.26	495.58
1.432	∝			avg.	499.93
2.010	0.04442	3.9890	362.90	168.20	531.09
2.010	0.04505	2.9814	357.05	169.19	526.24
2.010	∝			avg.	528.67
3.965	0.05176	6.1695	486.17	179.29	665.46
5.023	0.04319	6.2309	591.11	166.22	757.33
5.023	0.04273	6.0262	577.82	165.48	743.30
5.023	∝			avg.	750.31
5.718	0.04052	6.3207	640.07	161.82	801.89
5.718	0.03470	5.4889	649.78	151.53	801.31
5.718	∝			avg.	801.60

APPENDIX F

HEAT OF DILUTION OF NaCl: EXTRAPOLATION AT 40°C

Number of data points: 46
Debye-Hückel limiting slope: 856.0
A = 1.000
B = -639.77
C = 1221.10
Standard Deviation: 1.75 cal.

m_i	m_f	$\Delta\Phi L$ calc	$\Delta\Phi L$ exp	Error	Weight
0.1086400	0.0082060	81.373	82.495	1.1222	1.0000
0.1086400	0.0081240	81.561	80.645	-0.9162	0.9670
0.108640	0.0045740	91.261	92.230	0.9690	0.6250
0.1086400	0.0045730	91.264	90.320	-0.9443	0.6120
0.1086400	0.0027270	98.341	96.580	-1.7606	0.3890
0.1086400	0.0027310	98.323	94.030	-4.2925	0.3800
0.0082100	0.0045700	9.911	9.730	-0.1806	0.3750
0.0082100	0.0045700	9.911	7.820	-2.0906	0.3900
0.0082100	0.0027300	16.963	14.080	-2.8834	0.6110
0.0082100	0.0027300	16.963	11.530	-5.4334	0.6200
0.0081200	0.0045700	9.704	11.580	1.8761	0.3420
0.0081200	0.0045700	9.704	9.670	-0.0339	0.3550
0.0081200	0.0027300	16.757	15.930	-0.8226	0.5780
0.0081200	0.0027300	16.757	13.380	-3.3766	0.5870
0.0045700	0.0027300	7.053	4.350	-2.7028	0.2360
0.0045700	0.0027300	7.053	6.260	-.07928	0.2230
0.0739000	0.0053900	69.618	75.390	5.7722	0.5990
0.0739000	0.0055000	69.291	74.650	5.3589	0.6070
0.0739000	0.0030000	78.062	82.870	4.8081	0.3670

TABLE F. I (contd.)

m_i	m_f	ΔΦL calc	ΔΦL exp	Error	Weight
0.0739000	0.0030300	77.934	79.510	1.5757	0.3560
0.0053900	0.0029900	8.487	7.480	-1.0069	0.2340
0.0055000	0.0029900	8.814	8.220	-0.5935	0.2550
0.0145800	0.0082390	11.883	13.120	1.2366	0.5740
0.0145800	0.0083140	11.713	13.680	1.9674	0.5570
0.0145800	0.0048400	20.983	21.240	0.2574	0.9800
0.0145800	0.0048760	20.868	20.110	-0.7579	0.9800
0.0147490	0.0082390	12.148	11.260	-0.8879	0.6360
0.0147490	0.0083140	11.977	11.820	-0.1571	0.6190
0.0147490	0.0048400	21.247	19.400	-1.8471	1.0400
0.0147490	0.0048760	21.132	18.750	-2.3824	1.0500
0.0083140	0.0048760	9.155	6.430	-2.7253	0.4270
0.0082390	0.0048760	8.985	6.990	-1.9945	0.4090
0.0083140	0.0048400	9.270	7.580	-1.6901	0.4240
0.0082390	0.0048400	9.099	8.140	-0.9592	0.4060
0.0321650	0.0189590	14.443	13.310	-1.1333	0.6970
0.0318100	0.0189590	14.113	14.710	0.5974	0.6010
0.0582000	0.0189590	34.356	32.120	-2.2362	1.1760
0.0580300	0.0189590	34.245	32.680	-1.5649	1.1180
0.03216500	0.0195200	13.711	14.250	0.5388	0.6110
0.0318100	0.0195200	13.380	15.650	2.2696	0.5160
0.0582000	0.0195200	33.624	33.060	-0.5641	1.0900
0.0580300	0.0195200	33.513	32.620	-0.8927	1.0320
0.0582000	0.0321650	19.913	18.810	-1.1029	0.4790

TABLE F. I (contd.)

m_i	m_f	ΔΦL calc	ΔΦL exp	Error	Weight
0.0580300	0.0321650	19.802	19.370	-0.4316	0.4210
0.0582000	0.0318100	20.244	17.410	-2.8337	0.5740
0.0580300	0.0318100	20.132	17.970	-2.1623	0.5160

TABLE F. II

HEAT OF DILUTION OF NaCl: EXTRAPOLATION AT 50°C

Number of data points: 29
Debye-Hückel limiting slope: 982.0
A = 1.000
B = 377.98
C = -2137.69
Standard Deviation: 1.41 cal.

m_i	m_f	ΔΦL calc	ΔΦL exp	Error	Weight
0.0591600	0.0323300	22.872	23.960	1.0883	0.5870
0.0591600	0.0320800	23.178	24.160	0.9824	0.5940
0.0591600	0.0192300	42.641	41.470	-1.1711	1.0000
0.0591600	0.0188100	43.434	44.840	1.4056	0.9980
0.0579200	0.0323300	22.157	22.080	-0.0772	0.5820
0.0579200	0.0320800	22.463	22.280	-0.1831	0.5900
0.0579200	0.0192300	41.927	39.590	-2.3366	0.9950
0.0579200	0.0188100	42.720	42.960	0.2402	0.9930
0.0323300	0.0192300	19.769	17.510	-2.2594	0.4130
0.0323300	0.0188100	20.563	20.880	0.3174	0.4110
0.0320800	0.0192300	19.463	17.310	-2.1535	0.4080
0.0320800	0.0188100	20.257	20.680	0.4233	0.4040
0.0997900	0.0040300	97.303	95.620	-1.6829	0.1350
0.0997900	0.0040230	97.337	93.090	-4.2470	0.1310
0.0997900	0.0074460	83.444	88.620	5.1761	0.2300
0.0074460	0.0040300	13.859	7.000	-6.8589	0.0950
0.0074460	0.0040230	13.893	4.470	-9.4231	0.0990
0.0148400	0.0085960	16.542	14.900	-1.6417	0.1850

TABLE F. II (contd.)

m_i	m_f	$\Delta\Phi L$ calc	$\Delta\Phi L$ exp	Error	Weight
0.0148400	0.0081600	17.945	17.560	-0.3851	0.1980
0.0148400	0.0048730	30.306	33.770	3.4643	0.3150
0.0148400	0.0047640	3.787	32.700	1.9128	0.3220
0.0148600	0.0085960	16.587	14.450	-2.1366	0.1900
0.0148600	0.0081600	17.990	17.110	-0.8800	0.2010
0.0148600	0.0048730	30.351	33.320	2.9694	0.3180
0.0148600	0.0047640	30.832	32.250	1.4179	0.3250
0.0085960	0.0048730	13.764	18.870	5.1060	0.1290
0.0085960	0.0047640	14.246	17.800	3.5544	0.1360
0.0081600	0.0048730	12.361	16.210	3.8494	0.1170
0.0081600	0.0047640	12.842	15.140	2.2979	0.1240

TABLE F. III

HEAT OF DILUTION OF NaCl: EXTRAPOLATION AT 60°

Number of data points: 30
Debye-Hückel limiting slope: 1122.0
A = 1.000
B = -603.38
C = 1140.31
Standard Deviation: 1.74 cal.

m_i	m_f	$\Delta\Phi L$ calc	$\Delta\Phi L$ exp	Error	Weight
0.1023000	0.0075190	111.926	110.770	-1.1558	0.1620
0.1023000	0.0075620	111.782	111.220	-0.5620	0.1640
0.0592600	0.0323400	29.162	31.330	2.1678	0.5740
0.0592600	0.032330	29.175	31.460	2.2846	0.5740
0.0592600	0.0195600	48.867	45.650	-3.2172	0.9670
0.0592600	0.0178900	52.012	54.610	2.5976	1.0000
0.0581200	0.0323400	28.111	29.810	1.6990	0.5560
0.0581200	0.0323300	28.124	29.940	1.8157	0.5560
0.0581200	0.0195600	47.816	44.130	-3.6860	0.9490
0.0581200	0.0178900	50.961	53.090	2.1288	0.9820
0.0323400	0.0195600	19.705	14.320	-5.3850	0.3920
0.0323400	0.0178900	22.850	23.280	0.4298	0.4260
0.0323300	0.0195600	19.692	14.190	-5.5017	0.3930
0.0323300	0.0178900	22.837	23.150	0.3130	0.4260
0.0150960	0.0083170	17.483	16.740	-0.7435	0.1540
0.0150960	0.0083220	17.468	17.140	-0.3278	0.1540
0.0150980	0.0047170	30.809	34.600	3.7911	0.2390
0.0150960	0.0047910	30.482	33.700	3.2182	0.2380

TABLE F. III (contd.)

m_i	m_f	ΔΦL calc	ΔΦL exp	Error	Weight
0.0145800	0.0083170	16.355	14.870	-1.4852	0.1450
0.0145800	0.0083220	16.339	15.270	-1.0695	0.1440
0.0145800	0.0047170	29.681	32.730	3.0493	0.2300
0.0145800	0.0047910	29.354	31.830	2.4765	0.2280
0.0083170	0.0047170	13.325	17.860	4.5346	0.0850
0.0083170	0.0047910	12.998	16.960	3.9617	0.0830
0.0083220	0.0047170	13.341	17.460	4.1188	0.0860
0.0083220	0.0047910	13.014	16.560	3.5460	0.0840
0.0148000	0.0082260	17.127	14.910	-2.2168	0.1570
0.0148000	0.0082790	16.959	15.550	-1.4091	0.1540
0.0148400	0.0082260	17.214	15.180	-2.0343	0.1570
0.0148400	0.0082790	17.047	15.820	-1.2267	0.1550

TABLE F. IV

HEAT OF DILUTION OF NaCl: EXTRAPOLATION AT 70°C

Number of data points: 26
Debye-Hückel limiting slope: 1277.0
A = 1.000
B = -2043.11
C = 5779.84
Standard Deviation: 1.75 cal.

m_i	m_f	$\Delta\Phi L$ calc	$\Delta\Phi L$ exp	Error	Weight
0.1002000	0.0073470	139.736	138.630	-1.1063	0.1430
0.1002000	0.0074580	139.395	137.850	-1.5453	0.1440
0.0142400	0.0046760	26.337	30.260	3.9228	0.1930
0.0142400	0.0047070	26.208	29.790	3.5822	0.1930
0.0142400	0.0078240	15.364	18.920	3.5557	0.1150
0.0142400	0.0079440	15.011	18.820	3.8090	0.1120
0.0141500	0.0046760	26.157	31.640	5.4832	0.1910
0.0141500	0.0047070	26.027	31.170	5.1426	0.1910
0.0141500	0.0078240	15.184	20.300	5.1161	0.1130
0.0141500	0.0079440	14.831	20.200	5.3694	0.1090
0.0078240	0.0046760	10.973	11.340	0.3670	0.0790
0.0078240	0.0047070	10.844	10.870	0.0265	0.0780
0.0079440	0.0046760	11.326	11.440	0.1138	0.0820
0.0079440	0.0047070	11.197	10.970	-0.2268	0.0810
0.0584300	0.0318700	34.810	39.520	4.7101	0.5750
0.0584300	0.0328200	33.519	34.910	1.3913	0.5630
0.0584300	0.0184700	54.913	55.080	0.1671	0.9980
0.0584300	0.0188400	54.280	53.730	-0.5502	0.9880

TABLE F. IV (contd.)

m_i	m_f	$\Delta\Phi L$ calc	$\Delta\Phi L$ exp	Error	Weight
0.0581500	0.0318700	34.440	38.310	3.8697	0.5770
0.0581500	0.0328200	33.149	33.700	0.5510	0.5640
0.0581500	0.0184700	54.543	53.870	-0.6732	1.0000
0.0581500	0.0188400	52.911	52.520	-1.3906	0.9890
0.0318700	0.0184700	20.103	15.560	-4.5430	0.4230
0.0318700	0.0188400	19.470	14.210	-5.2603	0.4130
0.0328200	0.0184700	21.394	20.170	-1.2242	0.4360
0.0328200	0.0188400	20.762	18.820	-1.9416	0.4260

TABLE F. V

HEAT DILUTION NaCl EXTRAPOLATION: 80°C

Number of data points: 26
Debye-Hückel limiting slope: 1450.0
B = -281.23
C = 484.35
Standard Deviation: 1.53 cal

Molality Initial	m_f	$\Delta\Phi L$ calc	$\Delta\Phi L$ exp	Error	Weight
0.1002000	0.0074670	158.426	166.510	8.0836	0.1360
0.1002000	0.0074860	158.337	165.740	7.4032	0.1360
0.0148900	0.0049530	41.404	44.270	2.8664	0.1980
0.0148900	0.0050530	40.810	43.780	2.9700	0.1950
0.0148900	0.0081000	25.215	24.580	-0.6352	0.1340
0.0148900	0.0082520	24.535	21.820	-2.7148	0.1310
0.0150300	0.0049530	41.841	44.090	2.2485	0.2000
0.0150300	0.0050530	41.248	43.600	2.3521	0.1970
0.0150300	0.0081000	25.653	25.400	-0.2531	0.1360
0.0150300	0.0082520	24.973	21.640	-3.3327	0.1320
0.0081000	0.0049530	16.188	19.690	3.5016	0.0630
0.0081000	0.0050530	15.595	19.200	3.6052	0.0610
0.0082520	0.0049530	16.869	22.490	5.6212	0.0670
0.0082520	0.0050530	16.275	22.000	5.7248	0.0650
0.0580300	0.0190800	71.027	70.560	-0.4666	0.9700
0.0580300	0.0196200	69.583	69.940	0.3575	0.9510
0.0592000	0.0190800	72.585	71.560	-1.0248	1.0000
0.0592000	0.0196200	71.141	70.940	-0.2007	0.9810
0.0329300	0.0190800	31.214	31.710	0.4962	0.3500

TABLE F. V (contd.)

Molality Initial	m_f	$\Delta\Phi L$ calc	$\Delta\Phi L$ exp	Error	Weight
0.0329300	0.0196200	29.770	31.090	1.3203	0.3400
0.0329300	0.0580300	39.813	38.850	-0.9629	0.6000
0.0329300	0.0592000	41.371	39.850	-1.5210	0.6200
0.0190800	0.0295200	24.439	27.140	2.7010	0.2640
0.0196200	0.0295200	22.995	26.520	3.5251	0.2450
0.0295200	0.0580300	46.588	43.420	-3.1677	0.7000
0.0295200	0.0592000	48.146	44.420	-3.7258	0.7400

APPENDIX G

PARTIAL MOLAL HEAT CONTENT OF THE SOLUTE

m	25°	40°	50°	60°	70°	80°
.1	97.28	148.56	194.58	225.18	262.33	314.47
.2	78.73	159.13	225.36	273.20	318.31	390.13
.3	50.11	154.45	236.85	297.63	349.97	440.03
.4	17.67	143.17	239.50	311.11	370.41	476.57
.5	-16.35	128.47	237.22	318.39	384.55	504.59
.6	-50.86	111.92	231.94	321.82	394.83	526.55
.7	-85.28	94.38	224.22	322.75	402.63	543.92
.8	-119.28	76.41	216.41	322.04	408.83	557.66
.9	-152.63	58.35	207.80	320.26	414.60	568.43
1.0	-185.18	40.46	198.3	317.80	418.60	576.71
1.2	-247.56	5.79	179.79	311.96	427.09	587.19
1.4	-305.95	-26.69	161.16	306.11	435.90	591.18
1.5	-333.59	-41.95	151.5	303.48	440.70	585.00
1.6	-360.16	-56.49	143.66	301.17	444.99	591.00
1.8	-410.11	-83.31	127.75	297.76	460.74	620.91
2.0	-455.78	-106.99	113.0	296.26	481.98	649.78
2.2	-497.21	-127.44	101.81	296.94	501.82	679.46
2.4	-534.44	-144.60	92.11	299.97	522.04	709.83
2.5	-551.50	-151.94	88.13	303.42	532.28	725.25
2.6	-567.53	-158.46	84.73	305.50	542.60	740.82
2.8	-621.54	-169.02	79.73	313.59	563.46	772.35

APPENDIX H

ACTIVITY COEFFICIENTS

m	25°	40°	50°	60°	70°	80°
0.1	0.7784	0.7740	0.7707	0.7669	0.7627	0.7580
0.2	0.7347	0.7305	0.7270	0.7229	0.7181	0.7128
0.3	0.7097	0.7050	0.7017	0.6974	0.6924	0.6867
0.4	0.6928	0.6907	0.6875	0.6833	0.6780	0.6720
0.5	0.6811	0.6795	0.6765	0.6723	0.6670	0.6608
0.6	0.6727	0.6719	0.6693	0.6651	0.6598	0.6535
0.7	0.6668	0.6669	0.6645	0.6604	0.6551	0.6487
0.8	0.6624	0.6628	0.6605	0.6564	0.6505	0.6448
0.9	0.6592	0.6603	0.6583	0.6544	0.6491	0.6424
1.0	0.6569	0.6590	0.6572	0.6535	0.6481	0.6414
1.2	0.6543	0.6526	0.6482	0.6417	0.6337	0.6244
1.4	0.6545	0.6602	0.6596	0.6566	0.6516	0.6451
1.6	0.6574	0.6624	0.6617	0.6583	0.6529	0.6458
1.8	0.6619	0.6675	0.6672	0.6639	0.6583	0.6509
2.0	0.6676	0.6745	0.6745	0.6712	0.6654	0.6576
2.2	0.6747	0.6826	0.6829	0.6797	0.6737	0.6655
2.4	0.6830	0.6926	0.6932	0.6900	0.6838	0.6752
2.6	0.6921	0.7030	0.7039	0.7006	0.6938	0.6843
2.8	0.7024	0.7126	0.7133	0.7101	0.7035	0.6942
3.0	0.7137	0.7308	0.7318	0.7282	0.7209	0.7106

m	25°	40°	50°	60°	70°	80°
3.2	0.7258	0.7377	0.7390	0.7355	0.7281	0.7146
3.4	0.7386	0.7519	0.7530	0.7490	0.7409	0.7295
3.6	0.7527	0.7664	0.7674	0.7632	0.7546	0.7426
3.8	0.7677	0.7816	0.7825	0.7778	0.7687	0.7559
4.0	0.7832	0.7970	0.7977	0.7928	0.7831	0.7697
4.2	0.7996	0.8142	0.8147	0.8093	0.7990	0.7848
4.4	0.8170	0.8311	0.8312	0.8252	0.8142	0.7992
4.6	0.8352	0.8480	0.8476	0.8409	0.8291	0.8133
4.8	0.8541	0.8681	0.8675	0.8604	0.8480	0.8314
5.0	0.8740	0.8878	0.8865	0.8786	0.8653	0.8478
5.2	0.8947	0.9081	0.9064	0.8977	0.8836	0.8652
5.4	0.9162	0.9287	0.9261	0.9165	0.9012	0.8817
5.6	0.9389	0.9510	0.9476	0.9369	0.9206	0.9001
5.8	0.9623	0.9733	0.9691	0.9576	0.9403	0.9189
6.0	0.9863	0.9961	0.9908	0.9780	0.9594	0.9367

APPENDIX I

PARTIAL MOLAL HEAT CONTENT OF THE SOLVENT

$\bar{L}_1$	25°	40°	50°	60°	70°	80°
0.1	-0.013	-0.051	-0.075	-0.105	-0.114	-0.129
0.2	0.039	-0.076	-0.157	-0.229	-0.260	-0.328
0.3	0.169	-0.054	-0.207	-0.337-	-0.400	-0.550
0.4	0.374	0.018	-0.223	-0.421	-0.528	-0.779
0.5	0.650	0.137	-0.204	-0.479	-0.642	-1.005
0.6	0.992	0.302	-0.151	-0.512	-0.743	-1.222
0.7	1.395	0.507	-0.067	-0.523	-0.834	-1.424
0.8	1.854	0.750	0.046	-0.513	-0.918	-1.610
0.9	2.365	1.027	0.186	-0.486	-0.997	-1.774
1.0	2.922	1.333	0.348	-0.444	-1.075	-1.915
1.2	4.157	2.019	0.732	-0.328	-1.244	-2.121
1.4	5.523	2.779	1.173	-0.191	-1.450	-2.213
1.5	6.245	3.178	1.408	-0.122	-1.577	-2.341
1.6	6.987	3.583	1.648	-0.058	-1.723	-2.468
1.8	8.515	4.404	2.134	0.046	-2.150	-3.323
2.0	10.077	5.214	2.600	0.097	-2.881	-4.312
2.2	11.643	5.986	3.040	0.071	-3.750	-5.435
2.4	13.184	6.696	3.432	-0.056	-4.588	-6.693
2.5	13.937	7.020	3.607	-0.164	-5.040	-7.374
2.6	14.673	7.320	3.673	-0.306	-5.514	-8.089

$\bar{L}_1$	25°	40°	50°	60°	70°	80°
2.8	16.083	7.832	4.006	-0.700	-6.529	-9.623
3.0	17.389	8.211	4.141	-1.261	-7.633	-11.296
3.2	18.564	8.433	4.149	-2.010	-8.826	-13.108
3.4	19.585	8.478	4.012	-2.966	-10.110	-15.062
3.5	20.030	8.427	3.884	-3.529	-10.786	-16.091
3.6	20.428	8.323	3.713	-4.151	-11.485	-17.156
3.8	21.071	7.948	3.235	-5.584	-12.950	-19.392
4.0	21.490	7.332	2.559	-7.284	-14.507	-21.771
4.2	21.663	6.457	1.670	-9.270	-16.155	-24.293
4.4	21.570	5.301	0.551	-11.560	-17.894	-26.958
4.6	21.188	3.846	-0.813	-14.173	-19.726	-29.767
4.8	20.498	2.074	-2.439	-17.126	-21.650	-32.721
5.0	19.480	-0.034	-4.341	-20.437	-23.667	-35.819
5.2	18.112	-2.495	-6.536	-24.124	-25.776	-39.062
5.4	16.377	-5.329	-9.037	-28.202	-27.978	-42.451
5.6	14.255	-8.551	-11.860	-32.690	-30.273	-45.986
5.8	11.726	-12.179	-15.019	-37.603	-32.661	-49.667
6.0	8.773	-16.230	-18.528	-42.957	-35.143	-53.494

APPENDIX J

OSMOTIC COEFFICIENTS

m	25°	40°	50°	60°	70°	80°
0.1	0.9324	0.9317	0.9308	0.9296	0.9283	0.9269
0.2	0.9245	0.9243	0.9235	0.9223	0.9208	0.9191
0.3	0.9215	0.9218	0.9212	0.9200	0.9184	0.9165
0.4	0.9203	0.9214	0.9210	0.9200	0.9185	0.9166
0.5	0.9209	0.9226	0.9226	0.9217	0.9202	0.9183
0.6	0.9230	0.9254	0.9256	0.9250	0.9236	0.9216
0.7	0.9257	0.9287	0.9292	0.9287	0.9274	0.9255
0.8	0.9288	0.9324	0.9332	0.9328	0.9317	0.9298
0.9	0.9320	0.9362	0.9372	0.9370	0.9359	0.9341
1.0	0.9355	0.9402	0.9414	0.9414	0.9404	0.9386
1.2	0.9428	0.9486	0.9501	0.9504	0.9495	0.9479
1.4	0.9513	0.9579	0.9598	0.9603	0.9596	0.9581
1.5	0.9590	0.9660	0.9681	0.9686	0.9679	0.9670
1.6	0.9616	0.9690	0.9712	0.9718	0.9711	0.9697
1.8	0.9723	0.9804	0.9828	0.9836	0.9829	0.9812
2.0	0.9833	0.9919	0.9946	0.9954	0.9946	0.9926
2.2	0.9948	1.0039	1.0067	1.0075	1.0065	1.0042
2.4	1.0068	1.0162	1.0191	1.0199	1.0188	1.0161
2.5	1.0170	1.0266	1.0295	1.0302	1.0290	1.0262
2.6	1.0192	1.0288	1.0318	1.0324	1.0311	1.0282

m	25°	40°	50°	60°	70°	80°
2.8	1.0321	1.0419	1.0448	1.0454	1.0439	1.0407
3.0	1.0453	1.0551	1.0580	1.0584	1.0566	1.0531
3.2	1.0587	1.0684	1.0712	1.0714	1.0694	1.0655
3.4	1.0725	1.0820	1.0846	1.0845	1.0823	1.0781
3.5	1.0850	1.0944	1.0969	1.0967	1.0943	1.0899
3.6	1.0867	1.0960	1.0983	1.0980	1.0954	1.0909
3.8	1.1013	1.1100	1.1119	1.1112	1.1082	1.1033
4.0	1.1158	1.1242	1.1259	1.1250	1.1217	1.1165
4.2	1.1306	1.1385	1.1398	1.1384	1.1348	1.1292
4.4	1.1456	1.1529	1.1537	1.1520	1.1479	1.1420
4.6	1.1608	1.1674	1.1679	1.1657	1.1611	1.1544
4.8	1.1761	1.1818	1.1817	1.1790	1.1741	1.1674
5.0	1.1916	1.1964	1.1957	1.1924	1.1871	1.1801
5.2	1.2072	1.2110	1.2095	1.2055	1.1994	1.1916
5.4	1.2229	1.2257	1.2235	1.2188	1.2121	1.2038
5.6	1.2389	1.2405	1.2376	1.2322	1.2249	1.2162
5.8	1.2548	1.2552	1.2515	1.2454	1.2374	1.2282
6.0	1.2706	1.2697	1.2651	1.2583	1.2497	1.2399

APPENDIX K

RELATIVE PARTIAL MOLAL HEAT CAPACITY NaCl (J_2)

CONC.	25°	40°	50°	60°	70°	80°
0.1	3.37	3.65	3.83	4.02	4.20	4.39
0.2	5.55	5.55	5.55	5.55	5.55	5.55
0.3	6.93	6.93	6.93	6.93	6.93	6.93
0.4	8.14	8.14	8.14	8.14	8.14	8.14
0.5	9.8	9.48	9.27	9.06	8.85	8.64
0.6	11.01	10.58	10.30	10.01	9.72	9.43
0.7	12.17	11.61	11.24	10.87	10.50	10.13
0.8	13.28	12.58	12.12	11.66	11.19	10.73
0.9	14.40	13.53	12.95	12.37	11.79	11.21
1.0	15.47	14.43	13.73	13.03	12.34	11.64
1.5	21.00	18.61	17.01	15.42	13.83	12.24
2.0	24.42	22.03	20.44	18.85	17.76	15.67
2.5	27.22	25.01	23.53	22.06	20.59	19.11
3.0	29.64	27.58	24.21	24.83	22.46	22.08
3.5	31.81	29.79	28.45	27.10	25.76	24.41
4.0	33.81	31.70	30.29	28.18	27.47	26.07
4.5	35.69	33.33	31.75	30.18	28.60	27.03
5.0	37.49	34.70	32.84	30.98	29.12	27.26
5.5	39.25	35.85	33.58	31.32	29.05	26.78
6.0	40.93	36.74	33.95	31.15	28.36	25.56

APPENDIX L

GLOSSARY OF SYMBOLS

A_y,A_H	Debye-Hückel limiting slope
A	Distance of closest approach parameter
Cp	Specific heat of solution at constant pressure
Cp^{o}	Specific heat of pure solvent
$\overline{Cp}_2$	Partial molal heat capacity of solute
$\overline{Cp}_2^{o}$	Partial molal heat capacity of solute at infinite dilution
D	Dielectric constant of solvent
H	Total heat content
H^{o}	Total heat content in reference state
$\bar{H}_1,\bar{H}_2$	Partial molal heat content of solvent, solute
$\bar{H}_1^{o},\bar{H}_2^{o}$	Partial molal heat content of solvent, solute in standard state
ΔH_D	Heat of dilution
ΔH_S	Heat of solution
I	Ionic strength
$\bar{J}_2$	Relative partial molal heat capacity of solute
L	Relative heat content of solution
$\bar{L}_1,\bar{L}_2$	Relative partial molal heat content of solvent, solute
m	Molality (concentration in moles per 1000g. of solvent)
n	Number of moles
R	Gas constant in calories per mole degree
T	Absolute temperature
Tr	Reference temperature (298°K in this research)

z^+, z^-	Magnitudes of valences of ions indicated
ν^{+-}	Total number of ions
$\gamma_{\pm}$	Mean activity coefficient of electrolyte
ϕ	Osmotic coefficient
ϕH	Apparent molal heat content
ϕL	Relative apparent molal heat content
ϕC_p	Apparent molal heat capacity