STUDY OF CONCENTRATED AQUEOUS ELECTROLYTE SOLUTIONS

By a Static Vapor Pressure Method

By

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ABSTRACT

A new apparatus for static vapor pressure measurements has been built and used to make vapor-liquid equilibrium measurements on the systems sodium chloride, water (1-6 molal) and lithium chloride, water (4-18 molal), over the range 25°-100°. The precision of the temperature measurement is ± 0.002°, and that of the pressure measurement is about 0.005 mm. Osmotic coefficients have been computed from the measurements, and comparisons with literature values have been made for sodium chloride. An analytical expression for the osmotic coefficients of sodium chloride has been developed and used to fit the results to within the estimated experimental error of ± 0.002 in the osmotic coefficient.

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I. INTRODUCTION

This thesis describes the construction of a new apparatus for static vapor pressure measurements and the use of the apparatus to study the systems sodium chloride, water and lithium chloride, water. The primary purpose of this research was to obtain results useful in understanding the properties of concentrated electrolyte solutions.

At present there is no satisfactory molecular theory of concentrated electrolyte solutions. Most treatments of electrolyte solutions at concentrations above the Debye-Huckel range are phenomenological treatments involving ion association (chemical reaction between ions) or ion hydration (chemical reaction between ions and solvent molecules.) However, several workers are presently investigating short range ion-ion and ion-solvent interactions in attempts to build better models for electrolyte solutions. In addition to the striving for better models, progress in the statistical mechanical treatment of these models is being made, notably along the lines of the Mayer cluster theory (1, 2). A survey of current progress in electrolyte theory has been given by the recent symposium on the chemical physics of ionic solutions held by the Electrochemical Society in Toronto in 1964 (3).
The most stringent tests of a theory of concentrated electrolyte solutions will be comparisons with precise experimental results over wide ranges of concentration and temperature, i.e., just the kind of results reported here. Such comparisons will be facilitated by the analytical expressions of the results, described in Chapter IV.

The measurement of vapor pressures is one of the most widely applicable techniques for studying the thermodynamic properties of liquid mixtures. Previous workers in this laboratory have used dynamic (4-12) and static (13-15) vapor pressure methods for studying systems of non-electrolytes. The static method is equally well suited for investigating the properties of aqueous electrolyte solutions: but few precise, direct vapor pressure measurements have been made on electrolytes (16-20).

Few direct measurements have been made because of the convenience of the "isopiestic" or isotonic method invented by Bousfield (21) and improved by later workers (22-24). In this method two solutions containing non-volatile solutes are maintained at the same temperature, and solvent distils from one to the other until the solutions are isotonic, i.e., have equal water activity. Since the activity of the solvent is the same for both solutions at equilibrium, the vapor pressure of a solution can be determined by comparing it isotonically with a standard solution
whose vapor pressure is previously known as a function of composition. The results of isotonic measurements are usually expressed in terms of the osmotic coefficient, \( \Phi \), which is defined by

\[
\nu m \Phi = -(1000/w_1) \ln a_1
\]

where

\( \nu \) is the number of moles of particles produced by the ionization of one formula weight of solute,

\( m \) is the weight molality,

\( w_1 \) is the molecular weight of the solvent, and

\( a_1 \) is the activity of the solvent.

The accuracy of the osmotic coefficients obtained by the isotonic method is limited by the accuracy of the values for the standard. Scatchard, Hamer, and Wood (24) chose sodium chloride as their standard electrolyte at 25\(^\circ\), and their choice has been accepted by other workers in this field (25, 26). However, Robinson (25), considering results unavailable to Scatchard, Hamer, and Wood, arrived at somewhat different values for the osmotic coefficients of sodium chloride solutions. The difference between the two sets of standard values increases with concentration above four molal and reaches 0.015 at six molal.

Most of the measurements on electrolytes reported in the literature have been made at 25\(^\circ\) or slightly below. Because of current interest in the properties of electrolyte solutions at
moderate (60°-100°) and high (100°-374°) temperatures (see the recent review by Cobble, Ref. 27), it would be desirable to make measurements on concentrated as well as dilute electrolyte solutions in these temperature ranges. Already Soldano (28-32) and his coworkers have made isotonic measurements on several salts, relative to sodium chloride, in the range 99.6-165°. Below 100° two sets of measurements have been reported, from which the osmotic coefficients of sodium chloride solutions up to four molal can be computed over a range of temperatures. The electromotive force measurements of Harned and Nims (33) cover the range 0°-40° and the boiling point elevation studies of Smith and Hirtle (34, 35) the range 60°-100°. Unfortunately, it is by no means clear how these two sets of measurements should be connected. ¹ Recently Gardner, Jones, and de Nordwall (36) have made static vapor pressure measurements on sodium chloride solutions as concentrated as three molal over the range 125°-275°. Above 25° there are no precise sodium chloride measurements above four molal.

Because of the remaining uncertainty in the osmotic coefficients of sodium chloride solutions at 25° and the discrepancies in the temperature variation, the system sodium chloride, water was the first chosen to be studied with the new vapor pressure apparatus.

¹See Fig. 1 of Ref. 35 or Fig. 7 of this thesis.
For the second solute to be studied we wanted a salt with interesting differences from sodium chloride. Lithium chloride was chosen for several reasons: it is soluble up to 20 molal, giving water activities much lower than the 0.76 attainable with sodium chloride. Soldano (29-32) has found that the difference between the osmotic coefficients for LiCl and NaCl solutions increases markedly with increasing temperature, in contrast to the nearly constant differences for NaCl and alkali halides other than LiCl.

Once solvent vapor pressure has been measured as a function of temperature and composition, other thermodynamic properties of the solution (partial molal enthalpy, heat capacity, entropy, etc. of the solvent or of the solute) may be computed.
II. EXPERIMENTAL

The advantages and disadvantages of the static method of studying vapor-liquid equilibria have been discussed by Scatchard, Wilson, and Satkiewicz (13, 38, 39.) For binary solutions containing a non-volatile component, there is the additional advantage that the calculation of the liquid phase composition is very easy.

The Apparatus

The vapor pressure apparatus constructed by Dr. R. A. Rousseau with the aid of the author is, in principle, a descendant of the static vapor pressure apparatus built by Wilson and Satkiewicz (written WS hereafter) (13.) However, in the details of its construction, it bears little resemblance to its ancestor.

The most troublesome feature of the WS apparatus was the bellows null manometer. It was sensitive to building vibrations, and its zero point had to be determined for each pressure measurement. In place of this instrument a mercury null manometer is used in the present apparatus. It is the only null device known to the author which satisfies each of the following conditions:

1) It can be read to 0.001 mm of Hg.

2) Its zero point does not shift with temperature.
3) It is relatively insensitive to vibrations.

4) It is rugged (can withstand moderately large pressure changes without damage.)

The use of a mercury null manometer places only one limitation on the design of a vapor pressure apparatus -- there must be a clear optical path from a cathetometer to the null manometer. Thus, the apparatus cannot be completely enclosed in a windowless tank, nor can a turbid fluid be used in the thermostat bath surrounding the null manometer.

Another aspect of the WS apparatus which was not a serious problem in their measurements but would have been in the present measurements was the length of time required for degassing. Their system contained metal parts which were slow to degas and sometimes caused leaks. WS never opened their system to atmospheric pressure except for repairs, because their components could be removed from the cell by distillation. With the non-volatile components used in the present research the system must be opened for introduction of the non-volatile component and for analysis of the solution. An all glass system has been used, in order to decrease to about a day and a half the degassing time after exposure to atmospheric pressure, in contrast to the "several days" mentioned by WS.

WS used an air thermostat, which had an appreciable (0.1°) temperature gradient from the top to the bottom. The low heat
capacity of air may have been responsible for this (38.) The present apparatus has an oil thermostat, in which the temperature gradients in the working area of the bath are less than 0.01°.

In the following sections the apparatus and its operation are described in detail.

(a) The Thermostat

Fig. 1 shows the thermostat bath. Its walls are 1/2 " aluminum plate; its outside dimensions are: height, 15"; width, 16"; front to back, 16 1/2". The walls and base are held tightly together by machine screws; rubber-impregnated cork gaskets prevent leakage of the bath oil. The front is held on by capscrews, which fit into the threads of steel Helicoil inserts. Steel rather than aluminum threads are needed for the front, because it is removed and replaced whenever repairs are necessary.

The bath is divided into three sections. The left part contains the equilibrium cell and its stirrer; the right front holds the mercury null manometer; and the right rear compartment contains the horizontally diffuse light source recommended by Beattie for illuminating manometer tubes. There are three 1/2" thick glass windows; two permit the null manometer to be observed during the measurements, and one is used only to view the cell when no measurements are being made.
Figure 1. The Thermostat
The right front compartment is filled with a Conoco white mineral oil. This oil has remained transparent during nearly a year of use. General Electric silicone oil used earlier was discarded because it became cloudy after a few tests of the apparatus. Several oils were tested for use in the left (cell) compartment. Here turbidity is of no importance, but good stirring (to give adequate temperature control) requires low viscosity. 10W motor oil was chosen for the cell compartment, because it appeared to flow freely at 100° but did not vaporize excessively at 100°. Each compartment is fitted with a drain opening at the bottom, by which the oil may be rapidly drained into a tank by opening a valve. To fill the thermostat the storage tanks are pressurized with about 3 lb. of compressed air.

A powerful stirrer S located at the rear of the cell compartment provides good oil circulation in this chamber. The outside of the stirrer is a 15" length of 3" steel pipe. Oil enters the intake I (which must be 1/2" or more below the oil surface to prevent frothing) and is forced out the open lower end by two three-blade propellers attached to the shaft S'. The shaft is held in place by ball bearings at the upper and lower ends of the stirrer and is driven at 1750 RPM by a 1/6 HP electric motor and V-belt drive. Inside the outer case of the stirrer is mounted a concentric steel cylinder on which two 50 ohm resistance heaters are
wound. These were made by wrapping the inner cylinder with Fiberglas tape and coating the tape with glyptal; then the Nichrome resistance wire was wound around the tape and coated with glyptal to hold it in place. Binding posts for the heaters are located at the top of the stirrer. After leaving the stirrer the oil flows toward the front of the bath beneath a transite baffle located about four inches above the bottom and occupying the whole width of the cell compartment. The baffle ends about five inches from the front of the thermostat, and here the oil rises and flows again to the stirrer intake. The stirring is quite vigorous, and even at low temperatures the only "dead spots" noticed are small areas near the corners of the bath. At 25°C and above there are no "dead spots."

The stirrer for the null manometer compartment (not shown in Fig. 1) is like the cell compartment stirrer described above, except that its diameter is 2 1/2", and it has no built-in heater. It is located at the right front corner of the null manometer compartment. The two oil stirrers do not touch the thermostat or the table on which the thermostat rests. They are held by heavy I beam supports bolted to the floor. This arrangement decreases the vibration which could interfere with sighting on the null manometer. Further decrease in vibration was achieved by placing a pad of 1/2" sponge rubber between the null manometer
stirrer support and the floor, then tightening the bolts until the rubber was compressed by about one-third.

For temperature control at 25° and below cooling is necessary. This is provided by coils of 3/8" copper tubing in the bottom of each compartment; the length in each compartment is roughly proportional to the volume of oil contained. A mixture of ethylene glycol and water is pumped through these coils from a large reservoir maintained at 8.0±0.1°. A bypass system permits the rate of circulation of coolant to be varied from zero to the full speed of the mechanical pump with constant speed of the motor driving the pump. At 25° the 8° coolant provides too much cooling even at a minimal flow rate, so before entering the thermostat the coolant is passed through a 20' copper coil immersed in a small water thermostat set at 24°.

The outside walls of the thermostat are covered by a layer of 1/2" Fiberglas "aircraft" insulation, then by 1/4" plywood. The thermostat rests on a sturdy 3/4" hardwood table, which is bolted to the floor. A sheetmetal tray with a drain is provided in case of oil leakage from the bath, but no oil has collected in a year of operation.

(b) Temperature Control.

The thyratron temperature control system used by Scatchard, Hamer, and Wood (21) was renovated and used to control the cell
compartment temperature. The selenium phototube was worn out, and the manufacturer was unable to supply a replacement. A Clai- rex Co. cadmium sulfide photocell was tried and found to give excellent sensitivity. The old Wheatstone bridge was replaced by a better one designed by Beattie (40). A remote control unit was set up so that the photocell could be moved very precisely to compensate for zero shifts of the control circuit galvanometer. An ammeter was added to the heating circuit so that the heat output at galvanometer zero could be reproduced exactly.

The resistance thermometer in the control circuit is placed vertically in the cell compartment, equidistant from the sides and about three inches from the front. The end of the blade containing the platinum resistance element is about five inches above the bottom of the bath. One of the heaters contained in the stirrer is the control heater in the thyratron plate circuit of the regulator. The other heater is connected to a Variac, the setting of which depends on the temperature being maintained in the bath (see section on Procedure). Two blade-type immersion heaters rated at 250 watts each are used only when the temperature of the bath is being raised.

The temperature of the null manometer compartment is maintained 0.5° higher than that of the cell compartment. This prevents condensation when water is used in the cell during calibration runs. The same temperature difference is maintained for the measure-
ments on salt solutions so that the operating conditions are as nearly the same as possible. The temperature in the null manometer compartment is regulated by a Sargent Thermomonitor Model SV. The temperature sensitive element in this unit is a thermistor probe. One probe is used up to 37.5°, another from 50° to 100°. Three immersion blade heaters are used in the null manometer compartment: a 125 watt heater which is the regulating heater of the SV, a 125 watt heater connected to a Variac (see Procedure section), and a 250 watt heater which is engaged by a pushbutton on the SV and is automatically disconnected when the bath reaches the set temperature.

The temperature control of the compartments is quite satisfactory: ±0.001° for the thyatron regulator and ±0.01° for the commercial unit over a period of several hours. The long-term regulation has never been tested, because the static vapor pressure apparatus reaches equilibrium quickly.

(c) The Equilibrium Cell

The cell (see Fig. 2) is of the same type as that of Wilson and Satkiewicz (13). The thermocouple well W extends from the top of the cell to within about one cm of the bottom. It is filled to the top of the cell with white mineral oil. This provides good thermal contact for the thermocouple. Above the cell the thermocouple wires are enclosed by an air-filled glass tube which extends
Figure 2. Vapor Pressure System
to degassing
and transfer
manifold (Fig. 3)
above the oil surface of the bath. In addition to holding the thermocouple, the well helps to center the stirrer in the cell.

The stirrer S is a soft iron ring sealed in glass; two Alnico magnets outside the cell move it up and down about once every six seconds. On each cycle the stirrer breaks the surface of the liquid twice and forces most of the liquid in the cell through the spaces between the stirrer and the walls of the cell and between the inside of the stirrer and the thermocouple well.

The cell is permanently connected to one arm of the null manometer N. It may be opened to the vacuum manifold system for degassing or transport of water by lowering the mercury in the tube U. The mercury, glass float seals described by Wilson and Satkiewicz (13, 38, 39) work well in many parts of this apparatus, but they are not satisfactory when used in the thermostat as seal U must be. Large temperature changes caused these seals to stick so tightly that they could not be opened with a magnet. One seal cracked during a measurement; oil flowed into the vacuum system, and a several weeks' cleanup was necessary. These difficulties were solved by the use of the U-tube, which must be pressurized at high temperatures (see Procedure section).

The ground glass vacuum seal G is opened to add salt samples, to remove solutions for analysis, and to clean the
cell.

(d) The Null Manometer

The null manometer N is shown schematically in Fig. 2. The arms are made of 22 mm O. D. (19 mm I. D.) Pyrex glass tubing chosen for its uniformity. One arm $A_1$ is connected permanently to the vapor pressure cell. The other arm $A_2$ is normally pressurized with helium with stopcock $S_2$ open to the pressure control system. For pressures less than 25 mm there is a distinct advantage in using N as an absolute manometer by opening $S_1$ and making $A_2$ the vacuum arm. This procedure makes it unnecessary to read the large manometer (see section e), which decreases the probable error of the measurement. Another manometer tube (not shown in Fig. 2) is connected in parallel with $A_2$. It was intended to be used in an automatic pressure control system to be used during temperature changes. The tungsten contacts in this tube proved to be troublesome leak sources; so they were removed, and the auxiliary manometer tube was not used.

The null manometer is held in place by a heavy steel framework, which is bolted to the table on which the thermostat rests. Each arm is held at its upper and lower ends by set screws which tighten against Teflon split collars.

The null manometer N was positioned so that when the
comparator telescope was focussed on the invar scale (see section e) and then rotated to look at N, the crowns of the mercury menisci were also in focus. In the positioning of the null manometer the effect of the refractive index of the oil on the focal length of the telescope lenses was neglected, and when oil was put in the bath the telescope was badly out of focus. Moving the null manometer would have meant practically rebuilding a large portion of the apparatus, so for a while measurements were made by focussing the comparator telescope once for the null manometer and again for the large manometer. But sighting through nearly four inches of swirling oil was not very satisfactory, because small pieces of debris and occasional bubbles were distracting.

The problems with the null manometer were very nearly solved by installing an air-filled brass box with glass ends against the glass front plate of the null manometer compartment. With this arrangement the null manometer could be read with about the same precision as the large manometer. The air-filled box leaked oil and occasionally clouded up; a metal capillary added to maintain atmospheric pressure in the box cured these troubles. By this time the telescope was only slightly out of focus with the null manometer, when it was in focus with the scale. Exact focus was obtained by gently clamping a piece of 1/2" thick plate glass onto the scale. The glass was tested thoroughly to make sure that the same scale reading was obtained, no matter what part of the glass was sighted through.
The modifications described in the previous paragraph made the apparatus more precise for two reasons: (1) the null manometer menisci could be seen much better, and (2) the manometer N could now be used as an absolute manometer at $25^\circ$ and below.

(e) Manometer and Pressure Control Systems

The manometer is the same one set up by Raymond (41) and Gilman and modified for reading pressered less than 100 mm by Kavanagh (42). It is shown in Fig. 3. One tube is always kept evacuated, and the pressure in the vacuum arm is checked frequently with the McLeod gauge. If the gauge registers other than a "sticking vacuum" the vacuum arm is pumped down by the vacuum pump. The pressure arm of the manometer is connected to the 90 liter helium-filled tank. For pressures above 100 mm the mercury level is adjusted so that the meniscus of the pressure arm lies directly below that of the vacuum arm. For lower pressures (the case illustrated by Fig. 3) the two side tubes serve as duplicate pressure arms.

Earlier workers used "equilibrium stills" and needed the manostat tank to smooth out pressure fluctuations caused by boiling the solutions. For static measurements the manostat is not essential, but is has been found very useful in decreasing the time required for each pressure measurement (see Procedure section). The pressure in the manostat may be varied by opening
Figure 3. Manometer and Pressure Control Systems
one of the metal bellows valves to the helium line or to the vacuum line. By observing the differential manometer DM the manostat pressure is adjusted to within one mm of the pressure in the helium arm of the null manometer. Then the stopcock $S_1$ is opened, and final pressure adjustments are made through the solenoid and needle valves of the pressure control system.

(f) Degassing and Water Transfer System

The manifold used for degassing and transport of water is shown in Fig. 4. A degassing apparatus similar to the ones used by Wilson and Satkiewicz was used to degas the water. It consists of a reservoir, at the top of which are a fractionating column, a condenser, and a volume filled with water vapor. Heat from a small resistance heater at the point H causes water to be pumped up the tube beside the reservoir and spatter against the opposite wall. The water drains down the sides of the reservoir and continuously renews the surface of the bulk liquid. Periodically the seal $S$ is opened, and the water vapor is expanded into the manifold. This unit was operated for more than a year before the first measurements were made.

The residual gas in the water vapor is measured by the McLeod gauge $G$. The mercury level in the gauge is raised above the reference line by an amount equal to the vapor pressure of pure water at room temperature. The water vapor condenses
Figure 4. Degassing and Transfer Manifold
in the capillary, and the reading obtained is taken as the pressure of residual gas. After a few weeks of operation the residual gas pressure was always less than 0.0001 mm. Immediately before water was transferred to the cell, the vapor was expanded off several times until the reading of residual gas pressure was zero.

Water to be transferred to the vapor pressure cell was first collected and measured in the centrifuge tube GT, which is graduated in tenths of a cc. Transfer to the cell was very slow, partly because of evaporative cooling of the top layer of water in the narrow tube GT. A magnetic stirrer was provided, and this decreased the transfer time considerably. This device is a soft iron rod sealed in glass and attached to a glass stirring rod. The solenoid coil C is energized and turned off at three-second intervals, which causes the stirrer to rise and fall several cm.

In water transport the receiving container was cooled with an ice bath, but heating the source container even slightly above room temperature always caused water to bump and spatter into the manifold.

**Temperature Measurement**

The temperature in the cell is measured with a 20-junction copper-constantan thermocouple. The working junctions are in the cell (see section c above), and the reference junctions are immersed in an ice bath in a one liter Dewar flask. For good
thermal contact the thermocouple well for the reference junctions is filled with oil to the same height as the one in the cell.

The electromotive force of the thermocouple is measured with a Leeds and Northrup Type K-3 potentiometer with a high sensitivity reflecting galvanometer as null instrument. The potentiometer is read to 0.001 mv; at 10° one mv corresponds to 1.28° and at 100° to 1.08°. The thermocouple was calibrated over the range 10°-100° by measuring the vapor pressure of pure water and obtaining the temperature from the equation of Keyes (43). Details of the calibration are given in Appendix I. The precision of the temperature measurement is ± 0.002°.

A regular variation of ± 0.001° was observed to be correlated with the motion of the stirrer. Wilson and Satkiewicz noticed this same variation and attributed it to the effect of the movement of the stirrer magnets upon the thermocouple. The present author found that when the stirrer was operated with no liquid in the cell, there was no cyclic variation of the temperature. This observation prevents any magnetic explanation for the effect. The period of the fluctuations is the same as that of the stirrer; this probably rules out Joule heating, which ought to give half the stirrer period. The fluctuations may be caused by vaporization of small quantities of water as the stirrer breaks the liquid surface.
Pressure Measurement

The comparator and invar scale are the same ones used by previous workers. Before use they were carefully made vertical by the use of fine plumb lines. The comparator telescopes each have a fixed vertical cross hair and a horizontal cross hair which is moved by a micrometer screw. The position of the horizontal cross hair may be estimated to about 0.001 mm. The height of a column of mercury is determined by obtaining a reading of the micrometer, then rotating the telescope to calibrate the screw in terms of the millimeter divisions of the scale.

For pressures above 160 mm both telescopes are used, and the comparator is rotated only once from the manometer to the scale. For lower pressures only the lower telescope is used, and the comparator is rotated twice from manometer to scale. The telescope is always rotated clockwise before a reading of the null manometer, large manometer, and scale. This makes it necessary to rotate the comparator about 220° from the null manometer to the scale, but the reproducibility is ± 0.004 mm.

The observed pressure readings are corrected for capillary depression of mercury in the null and large manometers. Static head corrections are made for water vapor and helium, and the scale readings are corrected for thermal expansion and ruling error. The corrected pressures are reduced to pressures in mm of Hg at 0° and standard gravity. The static head corrections were computed for each measurement, and the correction
to $0^\circ$ was computed by the author at $25^\circ$ and $12.5^\circ$; the other corrections were taken from tables constructed by earlier workers.

**Materials**

Before the degassing procedure described in section f, the water was distilled twice and boiled for several minutes to expel dissolved gases.

Mallinckrodt analytical reagent grade sodium chloride was precipitated from a nearly saturated solution by passing hydrogen chloride gas through the solution in an all glass apparatus. The precipitate was packed in a glass funnel and washed with a small amount of doubly distilled water. The washed precipitate was fused in a platinum crucible, then cooled and ground to a fine powder in an agate mortar. It was stored in a drying oven at $130^\circ$.

Fisher Certified Reagent lithium chloride, lot No. 783230, was twice recrystallized from water and dried in a vacuum oven at $130^\circ$. It also was stored in the drying oven at $130^\circ$.

The degassing of solutions of sodium chloride and lithium chloride is described in the Procedure section.

**Analysis of Solutions**

After completion of a run the solution in the cell is removed at room temperature with a hypodermic syringe. Samples are weighed out directly from the syringe and analyzed gravimetrically for chloride. The analytical procedure described by Kolthoff and
Sandell (44) is followed. All weights are corrected to vacuum; densities of the solutions are obtained by interpolation in the I. C. T.

The concentration \( m' \) obtained from the analysis is in the units of moles of solute/kg of solution. It is converted to weight molality by the equation

\[
m = m'/(1 - 0.001Wm')
\]

where \( W \) is the formula weight of the solute. The precision of the determination of \( m \) is \( \pm 0.05 \) percent.

Procedure

This section gives a detailed description of the procedure followed during one run, i. e., measurements at one composition and several temperatures.

In order to transfer salt to the cell the vacuum seal \( G \) (see Fig. 2) is opened, before which the pressure in the cell must be raised to one atmosphere. This is done by opening stopcock \( S_2 \) and seal \( S_3 \) and bleeding in helium from the pressure control system. The vacuum seal \( G \) is opened, and a weighed amount of finely powdered salt is deposited at the bottom of the cell through a long-stemmed metal funnel. Lithium chloride must be transferred very rapidly, because it is hygroscopic and would stick in the funnel if wet. When the salt has been transferred to the cell the seal \( G \) is closed, and the degassing process begins.

Because of the importance of degassing to static vapor
pressure measurements, several methods were tried. The "freeze, pump, and thaw" method was not considered because of the danger of breaking the cell. In one approach the salt was dissolved in degassed water, heated to 100°, cooled to room temperature, and the vapor expanded off repeatedly. An improvement of this method was to expand off the vapor at 100°, but this required a careful balance of helium pressure and water vapor pressure in the tube U. This method was used on several of the early sodium chloride runs but was replaced by a technique which gives as good results but runs no risk of exposing the solution to helium contamination.

In the adopted degassing method the dry salt is pumped on overnight; then the cell and its contents are heated to 105° with pumping. The apparatus is maintained at this temperature for about six hours. Periodically the cell is exposed to about 20 mm Hg of water vapor by opening seal S4 (Fig. 2) and seal S1 (Fig. 4). After exposure to water vapor for a few minutes the cell is again evacuated. In this way the gases adsorbed on the solid salt surfaces are displaced by adsorbed water. After five or six exposures to water vapor the apparatus is allowed to cool slowly to room temperature with continued pumping. The last traces of foreign gases are not removed by the treatment and do not come off until the salt is dissolved in water. Thus some degassing of the solution is necessary.
Six cc of water is collected in the tube GT (Fig. 4) as described in part f. Transfer to the cell is accomplished by opening the tube U and seal $S_4$ (Fig. 2) with the cell compartment cooled to about $10^\circ$. Initially the water condenses in the tube leading to the cell, but it all condenses in the cell when some dissolved salt lowers the vapor pressure. The solution is degassed by expanding off water vapor into the manifold with the cell stirrer operating continuously. The residual gas pressure after each expansion is measured as described in part f.

At the beginning of the solution degassing procedure the residual gas pressure in the cell is usually less than 0.010 mm. Degassing continues until the residual gas pressure in the cell is 0.0001 mm or less; then the water vapor is expanded off once more immediately before the first measurement is made.

After the degassing is finished the temperature is set at $25^\circ$ and the measurements are begun. The cell stirrer and both bath stirrers operate throughout the run. The temperature controller for the null manometer compartment is set for $25.5^\circ$. The filament circuit of the thyatron controller for the cell compartment is turned on and allowed ten minutes to warm up. Then the plate circuit is switched on; this may give a plate current of from zero to 0.75 amperes, depending on the zero point shift of the control galvanometer. The remote control photocell is moved
until the current through the plate circuit is half the maximum current obtained with the light beam directly on the photocell. A rheostat in series with the plate circuit is adjusted until the current is 0.35 amperes. The control bridge is set to the value corresponding to 25°C; and after a coarse galvanometer shows near balance, the reflecting galvanometer ordinarily used to measure thermocouple emf is switched into the control bridge circuit. The spot of light on the frosted glass scale one meter from the galvanometer moves from left to right as the bath temperature increases.

Refrigerant is circulated through the cooling coils at an approximate valve opening determined by experience. With the use of the Variac connected to the auxiliary stirrer heater (see section b) the temperature is raised a few hundredths of a degree above the desired temperature. The refrigerant flow rate is adjusted until the temperature in the bath drops at the rate of about a hundredth of a degree per minute. When the desired temperature is reached (at galvanometer zero), the reading galvanometer is switched out of the bridge circuit and is replaced by the control galvanometer. The controller begins operating immediately, and usually no further adjustments are necessary.

The thermocouple emf is read frequently with the K-3
potentiometer; after the reading becomes constant (±0.001 mv) a period of 30 minutes is allowed to ensure equilibrium before the pressure is read. First the reading for the left tube of the manometer is compared with the scale, then the right. Thermo-couple readings are taken after the reading of each tube; the pressure reading is rejected if the emf difference is greater than 0.001 mv. Infrequently building vibrations prevent reading the manometer N with the desired precision; on these occasions measurements cease until the vibrations subside. This is always only a matter of minutes.

During a run the seal S₄ (see Fig. 2) remains closed. At 25⁰ the manometer N is isolated from the pressure control system by closing stopcock S₂ and evacuated by opening S₁. After the measurements at 25⁰ have been completed, S₁ is closed and S₂ is opened to the pressure control system. All the heaters in both baths are turned on full and the pressure in the helium side of N is increased to match the increasing water vapor pressure. Seal S₃ is opened to keep the same difference in mercury levels in U as in the tubes of N.

The same procedure used to set the temperature at 25⁰ is used at higher temperatures, except for minor differences. No cooling is necessary above 25⁰, but heating in addition to that supplied by the controllers is necessary above 37.5⁰. A summary
of the approximate settings used at each temperature is given in Table I. The first column gives the temperature in the cell compartment, the second the setting of the control bridge, the third the setting of the Variac for the auxiliary cell compartment heater, the fourth the Variac setting for the null manometer compartment, and the last column the setting of the "coarse" control of the Sargent Thermomonitor Model SV. The letters L and M in the fourth column refer to the use of the "low" and "medium" thermister probes. (See also section b.)

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Once the temperature is set the pressure in the helium arm of the null manometer is varied until the difference between the two arms is less than one millimeter. Then the manostat pressure (Fig. 3) is adjusted until the same condition obtains in
the manometer DM. The stopcock $S_1$ is opened, and final pressure adjustments are made by sighting on each meniscus of the null manometer and varying the pressure to null out the difference. (It should be mentioned that the pushbutton controls for the solenoid valves of the pressure control system are mounted on a hand-held box on a flexible cable, so that they may be operated from various parts of the room.) The pressure difference in the null manometer is brought to 0.010 mm or less in the final adjustments. Especially at high temperatures it is necessary to wait several minutes between pressure adjustments; evaporation and condensation of water vapor involve considerable amounts of heat, which can perturb the temperature by several hundredths of a degree.

When the temperature of the apparatus is raised, it takes a certain amount of time for the cell temperature to "catch up" to the bath temperature. As much as 15 or 20 minutes can be saved at the higher temperatures by simply raising the temperature of the bath about a degree higher than the desired final temperature and maintaining this temperature for a few minutes.

When the temperature has been set and equilibrium reached in the cell, the null manometer is read with no need to refer to the scale. Then the stopcock $S_1$ and the bellows valve leading from the manostat to the pressure control system are shut, and the process of raising the temperature another $12.5^\circ$ is begun.
This is where the manostat becomes useful; it maintains the pressure which was in the helium arm of the null manometer to be read at the same time the temperature is being raised. This roughly halves the time required per measurement.

Measurements are made every 12.5° from 25° to 100°. Some of the early sodium chloride measurements were at 25° intervals. For sodium chloride measurements were also made at 12.5° (and a few at 10°), but these gave poor results which cannot be even nearly explained by the lower water activity and the fixed uncertainty in the pressure measurement. In order to find the cause of the erratic low temperature results several experiments were performed to find whether there were large temperature gradients in the bath.

The reference junctions of the thermocouple were removed from the Dewar flask well and slipped into a movable glass tube. By using this tube as a probe the temperature difference between the cell and any point in the bath could be measured. At 12.5° differences of a few hundredths of a degree were found over even the small vertical distance spanned by the cell. The gradients depended somewhat on the rate of coolant through the coils in the bottom of the bath but could not be greatly reduced by adjustments of the flow rate or by minor changes in the geometry of the baffle above the coils. It was concluded that the oil was simply too viscous
to stir well enough to prevent temperature gradients at 12.5° and below. The same kind of experiment performed at 25° revealed no gradients greater than one or two thousandths of a degree in the vicinity of the cell, provided that the flow rate of coolant was kept at the lowest level consistent with the steady thyatron heating.

After the measurement at 100° the apparatus is cooled to room temperature by circulating coolant rapidly through the coils. The temperature is set again at 25°, and the build-up of residual gas pressure is checked by referring to the first 25° measurement. The increase in pressure is usually less than 0.020 mm and never much greater than 0.030 mm. The increase is attributed to the highest temperatures measured, where it is only of the same magnitude as the pressure fluctuations from the temperature control.

In order to remove solution for analysis the cell is brought to atmospheric pressure. The mercury in the tube U (Fig. 2) is lowered to about one cm above the U. Helium is bubbled through the seal, which prevents water vapor from escaping from the cell. The vacuum seal G is opened, and solution is removed with a syringe equipped with a long needle. A dimple at the bottom of the cell permits the last drop to be removed. The solution is analyzed as described previously in this chapter.
A run as described in this section requires 12 to 14 hours. One man can operate the apparatus, owing to the automatic, dependable temperature control and the convenience and accessibility of all controls and instruments.
III. RESULTS

Each measured "point" consists of a value of the pressure $p$ and a value of the temperature $t$. The vapor pressure $p_0$ of pure water at $t$ is obtained by interpolation in the table of vapor pressures constructed from the equation of Keyes (43). The water activity is the ratio of the fugacity of the water in the solution to the fugacity of pure water at the same temperature and pressure. It may be evaluated by considering the four step process

$$H_2O(\text{liquid, } p, T) = H_2O(\text{liquid, } p_0, T) = H_2O(\text{gas, } p_0, T) = H_2O(\text{solution, } p, T).$$

The change $\Delta G_1$ in the molar free energy of the water is

$$\Delta G_1 = \overline{G}_1 - \overline{G}_1^0 = \int_{p_0}^{p} \overline{V}_1 \, dp + \int_{p_0}^{p} \overline{V}_g \, dp$$

$$\Delta G_1 = RT \ln \frac{p}{p_0} + \overline{V}_1 (p_0 - p) + \int_{p_0}^{p} (\overline{V}_g - RT/p) \, dp$$

where $\overline{V}_1$ and $\overline{V}_g$ are the molar volumes of liquid water and water vapor, $R$ is the gas constant, and $T$ is the absolute temperature. The term $\overline{V}_1(p_0 - p)$ is negligibly small for aqueous solutions below $100^\circ$, so the water activity is given by

$$\ln a_1 = \ln \frac{p}{p_0} + 1/RT \int_{p_0}^{p} (\overline{V}_g - RT/p) \, dp$$

and the osmotic coefficient by

$$\phi = -55.506/\gamma_m \left[ \ln \frac{p}{p_0} + 1/RT \int_{p_0}^{p} (\overline{V}_g - RT/p) \, dp \right]$$

An adequate equation of state for water vapor up to pressures of one atmosphere is

$$p = RT/(\overline{V}_g - b)$$

When equation 3.5 is expanded in virial form,
p\bar{V}g = RT (1+b/V+b^2/V^2+. . . ), \hspace{1cm} (3.6)

it is seen that \(b\) is the second virial coefficient. Inserting the expression for \(\bar{V}g\) from equation 3.5 into equation 3.4 gives

\[ \bar{\phi} = -55.506/\gamma m \ln\frac{p}{p_0} + \frac{b}{RT} (p-p_0) \] \hspace{1cm} (3.7)

The value of \(b\) at each temperature has been computed using the expression of Keyes, et al. (45),

\[ b = 18[1.89 - 2641.62/T + 10^{80870/T^2}] \] \hspace{1cm} (3.8)

and osmotic coefficients have been computed using equation 3.7. The osmotic coefficients for sodium chloride and lithium chloride solutions are listed in Tables I and II, respectively. \(\bar{\phi}(\text{calc.})\) is the value of \(\bar{\phi}\) computed from equation 4.31.

It should be mentioned that most previous workers in electrolyte chemistry have ignored the "\(b\)" term in equation 3.7, because it is small at 25\(^{\circ}\). The correction to \(\bar{\phi}\) does not change much with concentration at constant temperature, because \((p-p_0)/m\) is nearly constant. However, the size of the correction to \(\bar{\phi}\) increases rapidly with temperature, from about -0.0016 at 25\(^{\circ}\) to about -0.016 at 100\(^{\circ}\). For consistency the correction has been applied to the present results at all temperatures.

The molality of the solution varies slightly with temperature owing to the evaporation of some water from the solution as the temperature is raised. The concentration \(m^l\) in moles of solute/kg of solution is computed using the equation
### TABLE I.

**Osmotic Coefficients for Sodium Chloride Solutions**

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TABLE II.

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\[ m' = \frac{m_o}{1 - \frac{\Delta w}{w_s}} \approx m_o (1 + \frac{\Delta w}{w_s}) \] (3.9)

where \( m_o \) is the concentration measured at room temperature \( (25^\circ) \) and \( w_s \) is the weight of the solution at \( 25^\circ \). \( \Delta w \) is the weight of water vapor above the solution less the weight of the vapor at \( 25^\circ \); it is computed using the perfect gas law. In order to calculate the weight of water vapor the volume of the vapor space in the cell, null manometer, and tube U (Fig. 2) must be known. This was determined to be 37.2 cc by expanding helium at a known pressure into an evacuated bulb of known volume, connected to the cell at the vacuum seal C. The value obtained depends on the height of the mercury in the null manometer and tube U, so these levels are set the same before each run. The conversion from \( m' \) to the weight molality \( m \) is given by equation 2.1.
IV. ANALYTICAL EXPRESSION OF THE RESULTS

In this section an analytical expression is described, by which the experimental results have been smoothed simultaneously with respect to concentration and temperature. The expression is consistent with the Debye-Huckel theory at low concentrations. The parameters of the equation have been chosen so that agreement with the calorimetric values of the apparent molal heat contents and heat capacities (46) is obtained at $25^\circ$.

We begin the representation of the thermodynamic properties of aqueous electrolyte solutions by considering the total free energy. The total free energy of mixing $G^m$ is defined by

$$G^m = G - \sum_i n_i \bar{G}_i^o$$

where $G$ is the total free energy of the solution, $n_i$ the number of moles of component $i$ and $\bar{G}_i^o$ the chemical potential in the standard state. Scatchard (47) has defined useful total excess functions by subtracting the ideal solution values from the thermodynamic properties of mixing. The excess free energy $G^E$ of an electrolyte solution of ionic strength $I$ is given by the Debye-Huckel theory in terms of the variable $x = \chi a$, where $1/\chi$ is the "thickness of the ion atmosphere," and $a$ is the distance of closest approach to the central ion (48)

$$G^E_{DH}/RT = -2(1/x) I^{3/2} X(n_1 W_1/1000) \tag{4.1}$$
where
\[ X = \frac{x(x - 2) + 2 \ln(1 + x)}{x^2} \quad (4.2) \]
\[ Y = \frac{x}{1 + x} \quad (4.3) \]
\[ Z = Y - X \quad (4.4) \]

\( \mathcal{A} \) is a function of the dielectric constant \( D \) and density of the solvent, \( d_1 \),
\[ \mathcal{A} = N_0^2 e^3 (d_1 \pi / 500)^{1/2} / (RTD)^{3/2} \quad (4.5) \]

where \( N_0 \) is Avogadro's number, and \( e \) is the protonic charge.

The activity coefficient of the \( k^{th} \) type of ion is given by
\[ \frac{1}{RT} \theta_n E_k^{1/2} \theta_n \left[ \frac{1}{1 + x} \right] \quad (4.6) \]

where \( z_k \) e is the charge on ion \( k \). If an electrolyte dissolves to give \( \mathcal{Y}_+ \) ions of charge \( z_+ \) and \( \mathcal{Y}_- \) ions of charge \( z_- \), the mean activity coefficient of the ions is given by
\[ \gamma_+ (\mathcal{Y}_+ + \mathcal{Y}_-) = \gamma_+ \gamma_- \quad (4.7) \]

Equations 4.6 and 4.7, together with the condition of electroneutrality,
\[ \gamma_+ z_+ + \gamma_- z_- = 0 \quad (4.8) \]
give the following expression for the Debye-Hückel mean activity coefficient
\[ (\ln \gamma_+)_{DH} = \mathcal{A} \left| z_+ z_- \right| \frac{1}{1 + x}^{1/2} \quad (4.9) \]

If it is assumed that the ions behave like regions of very low dielectric constant, then \( D \) is proportional to the volume
concentration of solvent, and $\chi$ is proportional to the square root of the ionic strength:

$$\chi = (8\pi N_0 e^2 d_1 l / 1000RTD)^{1/2}$$  \hspace{1cm} (4.10)

Scatchard and Epstein (48) assumed that $x$ is independent of pressure and temperature at constant ionic strength, which requires that a decrease about six percent from $0^\circ$ to $100^\circ$. Thus equation 4.9 becomes

$$(\ln x)_{DH} = -d \frac{Y}{\gamma + 2 - 1} \frac{\gamma Y}{1 + \gamma Y} = -\frac{d}{A} \frac{Z + 2 - 1}{Y}$$  \hspace{1cm} (4.11)

where $A$ is a constant. The assumption of Scatchard and Epstein seems reasonable, because ions might be expected to approach each other more closely at higher temperatures. However, the great advantage of this proposal is the practical one that any partial molal excess property of the solute is proportional to $Y$, any partial molal excess property of the solvent to $Z$, and any total excess property to $Y - Z$. Any excess property is thus a product of a function of composition alone and the appropriate derivative of $\chi$.

The Debye-Huckel osmotic coefficient is given by

$$\Phi_{DH} = 1 - \frac{1000}{W_1 MRT} \frac{\partial G^E_{DH}}{\partial W_1} = 1 - \frac{Z + 2 - 1}{A M}$$  \hspace{1cm} (4.12)

where $M$ is the sum of the molalities of the ions.

In order to fit the results at high concentrations, further terms may be added to equation 4.1

$$\frac{G^F}{Rf} = \frac{G^F_{DH}}{Rf} + \sum b_{ij} \ln \left( \frac{W_{ij}}{M_i W_j} \right) + \sum c_{ij} \ln \ln \left( \frac{W_{ij}}{M_i W_j} \right) \frac{1000}{M_i W_j} + \ldots$$  \hspace{1cm} (4.13)
where the b's and d's are functions of temperature and \( n_i \) is the number of moles of species i, and the sums are taken over the solute species present. It is assumed that the use of the Debye-Hückel theory with the distance of closest approach obviates the use of terms in \( I^{1/2} \). Equations 4.12 and 4.13 give for the osmotic coefficient

\[
\Phi = \Phi_{DH} + \frac{1}{m} (\sum_{ij} b_{ij} m_i m_j + \sum_{ijk} d_{ijk} m_i m_j m_k + \ldots ) \tag{4.14}
\]

where \( m_i \) is the molality of the \( i^{th} \) species. For a solution containing one solute with two kinds of ions, equation 4.14 is considerably simplified by defining coefficients \( B_i \), as follows:

\[
B_1 = 2(\sum_{ij} b_{ij} x_i x_j) m^2 / IM \tag{4.15a}
\]

\[
B_2 = 2(\sum_{ijk} d_{ijk} x_i x_j x_k) m^3 / MI^2 \tag{4.15b}
\]

... ...

In terms of the B's equation 4.14 becomes

\[
\Phi = \Phi_{DH} + \sum_{i=1}^{n} B_i I^i \tag{4.16}
\]

and equation 4.13 becomes

\[
\frac{G^E}{RT} = \frac{G^E}{RT} + \frac{n_i w_i}{1000} \sum_{i} B_i I^i \tag{4.17}
\]

Equations 4.6 and 4.13 give for the activity coefficient \( \gamma_k \)

\[
\ln \gamma_k = (\ln \gamma_k)_{DH} + 2 \sum_j b_{pj} m_j + 3 \sum_{jkl} d_{jkl} m_j m_k \ldots \tag{4.18}
\]

The equation for \( \ln \gamma_k \) is also much simpler for a single solute when it is written in terms of the B's defined above

\[
\ln \gamma_k = (\ln \gamma_k)_{DH} + \sum_{i=1}^{n} B_i \left( \frac{i+1}{i} \right) I^i \tag{4.19}
\]
If equation 4.16 is used to fit osmotic coefficients by varying the parameter A the the B's, then equation 4.18 immediately gives the corresponding activity coefficients. This "integration of the Gibbs-Duhem equation" may be performed equally well by fitting solute activity results to equation 4.18 and computing osmotic coefficients from equation 4.16. Guggenheim and Stokes (49) used equations 4.16 and 4.18 with \( n = 1 \) to compute activity coefficients for 0.1 molal solutions of 1:2 and 2:1 electrolytes from isopiestic results. Lietzke and Stoughton (50) used \( n = 3 \) and computed \( A, B_1, B_2, \) and \( B_3 \) for a variety of electrolytes by means of a non-linear least squares computer program. They found that at \( 25^\circ \) "osmotic coefficients in the range 1-3 molal can be used to calculate values of both osmotic and activity coefficients at lower concentrations with good accuracy." The technique may fail when used on an electrolyte which shows evidence of association (49, 50) or when the equations are extrapolated to concentrations higher than those used in determining the parameters (50).

In order to consider the temperature variation of the thermodynamic properties of the system, we begin with the Gibbs-Helmholtz equation,

\[
\frac{\partial (\frac{E^E}{T})}{\partial T} = -\frac{H^E}{T^2} \tag{4.20}
\]

The excess enthalpy \( H^E \) corresponding to equations 4.1 and 4.16 for \( G^E \) is
\[ H^E = -RT^2 \left[ -2T^{3/2} \frac{\partial^3}{\partial T^3} + M \frac{\partial}{\partial i} \left( \frac{1}{\zeta} \right) \frac{\partial B}{\partial T} \right] \frac{\eta_i w_i}{1000} \]  

(4.21)

It is convenient to define a shorthand notation for differentiation of \( H^E \) as follows: the order of a partial derivative of \( H^E \) with respect to temperature at constant pressure and composition is given by the number of primes used as a superscript to \( H^E \). Expanding \( H^E \) in a Taylor series in the temperature around a standard reference temperature \( T_s \), we obtain

\[ H^E = H^E(T_s) + H^E_p(T_s)(T-T_s) + \frac{1}{2} H^{E''}(T_s)(T-T_s)^2 + \ldots \]

\[ H^E = \sum_{j=0}^{\infty} \frac{H^E_j(T_s)}{j!} (T-T_s)^j \]  

(4.22)

Now we express \( H^E \) and each of its derivatives, evaluated at the reference temperature \( T_s \), as a Debye-Huckel term plus a power series in the ionic strength

\[ H^{(i)}_p(T_s) = H^{(i)}_{DH}(T_s) + \frac{\eta_i w_i M}{1000 \bar{V}} \sum_{i=1}^{\infty} \frac{c_i^{(i)}}{i} \left( \frac{1}{\bar{V}} \right)^i \]  

(4.23)

where the \( c_i^{(j)} \) are constants. Substituting equations 4.23 into equation 4.22, we obtain \( H^E \) in terms of power series expansions in both temperature and ionic strength,

\[ H^E = \sum_{j=0}^{\infty} \frac{H^E_j(T_s)}{j!} \left[ H^{(i)}_{DH}(T_s) + \frac{\eta_i w_i M}{1000 \bar{V}} \sum_{i=1}^{\infty} \frac{c_i^{(i)}}{i} \left( \frac{1}{\bar{V}} \right)^i \right] (T-T_s)^j \]  

(4.24)

In principle there is no upper limit to the summation indices; in practice \( p \) and \( n \) will be chosen as the smallest integers which will provide a sufficiently precise representation of the experimental results. Comparison of equation 4.24 with equation 4.21 gives the functional form for the derivative of \( B \) with respect to temperature,

\[ \frac{dB}{dT} = -\frac{1}{\gamma} \frac{V}{RT^2} \sum_{j=0}^{p} \frac{c_i^{(j)}}{j!} (T-T_s)^j \]  

(4.25)
Equation 4.25 may be integrated to give

\[
B_i = \frac{-1}{\frac{1}{\Delta R}} \left\{ B_i^0 - \left[ \sum_{j=0}^{p} \frac{C_i^{(j)}}{j!} (-T_0)^j \right] / T + \left[ \sum_{j=1}^{p} \frac{C_i^{(j)}}{(-T_0)^{j-1}} \right] \right. \\
+ \left. \sum_{j=2}^{p} \frac{C_i^{(j)}}{j-2} \frac{T^{j-k-1}}{k} \frac{1}{(j-k)!} (j-k-1)! \right\} (-T_0)^k \right\} (4.26)
\]

Knowing the functional form of the \( B_i \), we need only choose the coefficients of the temperature terms of 4.26 to fit the results for \( \phi \) (or for \( \ln \psi \)), and from equation 4.17 we may derive any thermodynamic property of the solution.

Equation 4.26 is complicated, but it is only the coefficients of the temperature terms that make it so. The temperature terms themselves are simple: a term in \( 1/T \), one in \( \ln T \), and a power series in \( T \) whose upper bound is chosen as the highest term required to fit the results. Stoughton and Lietzke (51) used equation 4.16 with \( n = 2 \) and the equivalent of the equation 4.26 with \( p = 1 \) to fit osmotic coefficients for sodium chloride over a wide temperature range. They lumped together the sums involving the \( C_i^{(j)} \) of equation 4.26 into a single coefficient for each temperature term. The coefficients were determined by least squaring literature values of \( \phi \) to fit equation 4.16. Stoughton and Lietzke's method of fitting \( \phi \), which does not take account of the identity of the \( C_i^{(j)} \), will be called a "non-calorimetric" method in contrast to the "calorimetric" method described below.

Calorimetric measurements of heats of dilution yield a
quantity $\Phi_L$ called the "relative apparent molal heat content." $\Phi_L$ is the negative of the heat absorbed when a solution containing one mole of solute is diluted to infinite dilution. A simple relation exists between $\Phi_L$ and $H^E$:

$$n_2 \Phi_L = H^E$$

(4.27)

where $n_2$ is the number of moles of solute. From equation 4.23 it is seen immediately that if the values of $\Phi_L$ are at the reference temperature $T_s$, then $\Phi_L$ is given by

$$\Phi_L = \Phi_L^{DH} + \sum_{i=1}^{n} \frac{c_i^i}{i} T^i$$

(4.28)

Calorimetric measurements of specific heats yield a quantity $\Phi_{C_p}$, which is the value the partial molal heat capacity of the solute would have if the partial molal heat capacity of the solvent were the same in the solution as at infinite dilution. An equation analogous to 4.27 holds for $\Phi_{C_p}$ and $H^E$ (or $C_p^E$):

$$\Phi_{C_p} = \Phi_{C_p}^o + \frac{H^E}{n_2}$$

(4.29)

and from equation 4.23

$$\Phi_{C_p} = \Phi_{C_p}^o + \frac{H^E_T(\tau_s)}{n_2} + \sum_{i=1}^{n} \frac{c_i^i}{i} T^i$$

(4.30)

Having found the relations between experimental thermochemical quantities and $\Phi$ through equations 4.16, 4.26, 4.28, and 4.30, we now have several different ways of considering the temperature variation of $\Phi$. First we note that if specific heat measurements are made over a range of temperatures then the second order and even higher derivatives of $H^E$ may be computed.
Therefore, given sufficient calorimetric data, it is only necessary to measure $\phi$ at one temperature and to determine it at any other temperature using the thermal results and the equations developed above. Unfortunately, the precise measurement of specific heats of electrolyte solutions is very difficult. For sodium chloride results are lacking at high concentrations above $25^\circ$, and the only workers currently equipped to make such measurements have no immediate plans to do so (52).

Lacking sufficient calorimetric results to compute the temperature variation of $\phi$, we may consider a second method, which is exactly the reverse of the first. We may make measurements of $\phi$ over a range of temperatures and either ignore the thermal properties, as Stoughton and Lietzke (51) did; or we may attempt to determine the thermal properties from the experimental results, and compare with calorimetric results in the regions they are available. The second course was followed by Harned and Cook (53) and by Smith and Hirtle (35) in the treatment of sodium chloride results from emf and boiling point elevation measurements.

To obtain $H^E_s(T_s)$ of equation 4.23 would require one differentiation of the experimental osmotic coefficients with respect to temperature. Another would be required to obtain $H'_E(T_s)$. Probably no one would expect to be able to differentiate
the results meaningfully a third time, and some critics would even question whether accurate enthalpies can be obtained from vapor pressures. However, the primary purpose of the present measurements is to obtain accurate values of the osmotic coefficients. The method used by Stoughton and Lietzke and earlier, at a single concentration, by Robinson and Harned (54) might have been used to treat the present results, except for considerations described below.

The most important results from the standpoint of establishing isotonic standards are those at 25°, for it is there that most isotonic measurements have been made. Unfortunately, it is just at this temperature that the precision of the measured pressure is less than that of the temperature; at higher temperatures the precision of the pressure is better. We should then like to weight the 25° values somehow with the presumably more accurate values at higher temperatures. The way to do this is obvious from the equations developed in this chapter.

We choose the reference temperature $T_s$ as 25°; accurate values of $\Phi_L$ and $\Phi_{C_P}$ are available (46). These values permit the evaluation of the $C_i$ and $C_i'$ of equations 4.28 and 4.30. $C_i''$ and higher coefficients, as well as the coefficients $B_i^o$, are treated as parameters to be determined by the method of least squares.
For the uni-univalent salts on which the present measurements have been made, equations 4.16 and 4.26 give for the osmotic coefficient

\[ \Phi = 1 - \frac{1}{A} \left[ \frac{1}{A} - \frac{1}{A_{m}} \right] \left[ 1 + A_{m} b_{2} - 2 \ln \left( 1 + A_{m} b_{2} \right) - \frac{1}{1 + A_{m} b_{2}} \right] \\
- \frac{1}{2} \sum_{i=1}^{r} \left\{ \frac{B_{i}^{o}}{C_{i}^{(1)}} \left[ \sum_{j=0}^{p} \frac{C_{i}^{(j)}}{j!} \left( -T_{S} \right)^{j} \right] \ln T \right\} \left( \frac{1}{T} \right) \\
+ \left[ \frac{1}{T} \sum_{j=1}^{p} \frac{C_{i}^{(j)}}{j!} \left( -T_{S} \right)^{j-1} \ln T \right] \\
+ \left[ \frac{1}{T} \sum_{j=2}^{p} \frac{C_{i}^{(j)}}{j!} \left( -T_{S} \right)^{j-1} \ln T \right] \right\} \left( \frac{1}{T} \right) \}

All the \( C_{i}^{(j)} \) and the \( B_{i}^{o} \) parameters were determined by the method of least squares on the IBM 7044 computer of the M. I. T. Laboratory for Nuclear Science. The values of the coefficients are listed in Appendix II. For sodium chloride the upper limits \( n \) and \( p \) of the summations were both chosen as three. \( A \) was chosen as 1.5. The analytical representation of the LiCl results has not yet been accomplished, and it is thought that a different functional form than a power series in the molality may be necessary to express the results over the large range of compositions.

Equation 4.31 gives a term in \( 1/T \), one in \( \ln T \), one in \( T \), and one in \( T^2 \) for sodium chloride. Thus the Debye function \( \Delta \) was expressed in the form

\[ \Delta = S_{1}/T + S_{2} \ln T + S_{3} T + S_{4} T^2 + S_{5} \]

The dielectric constants of Owen, et al. (55), and of Åkerlöf and Oshry (56) and the water densities of the I. C. T. were used in the least squaring of \( \Delta \).
V. DISCUSSION

The apparatus and techniques used in the research described here differ significantly from other precise measurements of water vapor pressure of electrolyte solutions. First it seems to the author that one of the primary advantages of static vapor pressure measurements is the capability of making measurements over a wide range of temperatures. This possibility seems to have been largely ignored by other workers, except for the recent high temperature work of Gardner, Jones, and de Nordwall (36). The only other technique which has a temperature range comparable to that of the vapor pressure method is the study of electromotive force cells. This method has the advantage that it is applicable to dilute solutions, but it requires reversible electrodes and may fail because of electrode solubility at high electrolyte concentrations or high temperatures.

The results reported here are the first attempt to measure precisely vapor-liquid equilibria for electrolyte solutions over a $75^\circ\text{C}$ temperature range and over the widest possible range of compositions. The error in the osmotic coefficient for a given error in the pressure is inversely proportional to the molality, so that it is not profitable to make vapor pressure measurements below
one molal. The upper limit of concentration is determined only by the solubility at the lowest temperature at which measurements are made.

The present apparatus differs from the ones used by Gibson and Adams (16) and Gordon (19, 20) in two respects, in addition to the temperature range mentioned above. The first is the fluid used in the manometer. The other workers used n-butyl phthalate or vacuum pump oil because of their low density; the author used a mercury manometer. The reason for the choice of a low density fluid is that it gives a greater difference in height between pressure and vacuum arms, thus supposedly decreasing the error of the measurement. However, these fluids wet the manometer walls and give a concave meniscus, which can be located at best to 0.01 mm. A mercury meniscus is convex, and its crown can be estimated to 0.001 mm. Therefore, given a sufficiently precise thermometer, there is no advantage in precision in the use of low density manometer fluid in place of mercury. In fact, there is a considerable disadvantage in the use of these liquids, because they must be distilled into the manometer and must be replaced occasionally by fresh liquid.
The other respect in which the present apparatus differs from others is the use of only one cell containing the electrolyte. Other workers (16, 19, 20) have used two vessels, one containing the electrolyte, and one pure water. With the two cells the vapor pressure of water is measured in each: then the difference between the two cells is measured. With one cell the measurement of the vapor pressure of pure water and that of electrolyte involves two separate experiments. This method relies heavily on the precision of the temperature control and measurement. In practice the temperature control and measurement of the apparatus have been so satisfactory ($\pm 0.002^\circ$) that the author considers having one cell no disadvantage in precision. The possibility must also be considered with two cells, no matter how carefully placed with respect to the geometry of the thermostat, that temperature differences may exist between the two cells.

For sodium chloride many comparisons of the results with those of other workers are possible. In addition to results obtained by measurements on sodium chloride (vapor pressure, electromagnetic force cells, freezing point depression, boiling point elevation, etc.), one may also compare the results for any other salt whose
isopiestic ratios with respect to sodium chloride have been measured. Here we will compare only with precise measurements on sodium chloride itself.

Figure 5 shows the deviations of the experimental osmotic coefficients from the values calculated using equation 4.31. Included for comparison are the static vapor pressure measurements of Frazer and Negus (17) and Olynyk and Gordon (20). Figure 6 shows the deviations at all temperatures. It may be seen from these figures that two expectations have been realized: 1) the magnitude of the deviations shows that the present apparatus is capable of precision comparable with the best previous work in this field, and 2) the deviations from the analytical expression are not much larger than the deviations would be from any smooth curve, except at 25°. The hope expressed in Chapter IV, that the somewhat more precise values at higher temperatures would weight the values at 25°, appears to have been realized. Though all of the author's points but two lie below the curve, still the agreement of the calculated values with those of Gordon is excellent. The agreement with Frazer and Negus is very good above three molal and is poor only near one molal, which is near the limit below which vapor pressure measurements scatter too widely to be useful.
Figure 5. Deviations of Osmotic Coefficients at 25°C
Figure 6. Deviations of Osmotic Coefficients
The values established by Scatchard, Hamer, and Wood (SHW) (24) and Robinson (25) for isotonic standards are shown as broken and solid lines, respectively, in Figure 5. The agreement with Robinson is very good and within the apparent error of any of the three series of measurements. That the SHW values are too high at high concentrations is not too surprising, because they are based largely on the emf results of Harned and Hamer (57, 58), which later work (19, 59, 60) has shown are too high. However, the SHW curve fits the results in the region 1-3 molal better than either Robinson's or the author's. The SHW and Robinson curves have both been lowered by about 0.0016 from the published values to be consistent with the author's values, corrected for imperfection of water vapor. However, this is not strictly correct at the lowest concentrations because their values below one molal are based on freezing point and emf results, for which no such correction is necessary. The difference is not very significant, but it should be noted that with no correction their values would agree even better with the present results at one molal.

Inspection of Figure 6 shows that the precision of the results is better at higher temperatures, with the exception of the 100° results. The reason for the large deviations at 100° is not known.
It is not a question of temperature control, because the thermo-couple emf readings indicate fluctuations of only a thousandth of a degree, or something half that amount. Possibly the trouble is the same as that encountered at 12.5°, i.e., temperature gradients. There is a 75° difference in the oil bath and room temperatures, and several metal supports enter the bath through the oil surface.

Figures 7a and 7b give a comparison with the emf measurements of Ham and Nims (0°-40°) and the boiling point elevation measurements of Smith and Hirtz (60°-100°). The agreement of the curves calculated from equation 4.31 with the experimental points is good at low concentrations but becomes poorer with increasing concentration. This is not too surprising for the emf results, because electrode solubility or other phenomena might affect the results at high salt concentrations. That the boiling point results also appear high is reasonable at 60°-70°, because here the technique is operating at the lowest temperature limit for water solutions. The disagreement at 100° is harder to understand; if a choice must be made, the author prefers his own measurements because of the known agreement with other workers at lower temperatures. It is an interesting fact that when the boiling point results are extrapolated linearly from 60° to higher temperatures, the extrapolated
Figure 7a. Osmotic Coefficients of Sodium Chloride
Figure 7b. Osmotic Coefficients of Sodium Chloride (cont.)
values at $100^\circ$ agree with the vapor pressure results within about 0.002. This is probably only an accident, because one would expect the boiling point results to be better, the closer to $100^\circ$.

The method of expressing osmotic coefficients described in Chapter IV is valid to at least $275^\circ$. Figure 8 shows the results of Gardner, Jones, and de Nordwall and curves calculated using the author's results and including their results in the least squaring. The agreement is seen to be within their experimental error. Similar agreement is obtained with their revised results at 0.5 and 1.0 molal (61). The inclusion of their results in the least squaring does not change the values computed in the range $25^\circ$-$100^\circ$ by more than 0.003.

For lithium chloride a comparison of the $25^\circ$ results can be made with the isotonic measurements listed by Robinson and Stokes (26). The 3.940 m value agrees very well with the RS value obtained from a large scale plot of $\Phi$-0.15 m. At higher concentrations the author's results are consistently 0.006 to 0.012 lower than Robinson and Stokes's. This may be evidence that the osmotic coefficients of sulfuric acid, the standard for the LiCl isotonic measurements at high concentration, are also too high. However, the static vapor pressure results of Kangro and Groeneveld (57) are in
Figure 8. Osmotic Coefficients of Sodium Chloride to $275^\circ$
quite good agreement with the RS LiCl osmotic coefficients. A better comparison could be made if Kangro and Groenewold had published the experimental results in addition to a smoothed curve. The present LiCl results substantiate the reports of Soldano that from $25^\circ$ to $100^\circ$ the osmotic coefficients of LiCl decrease nearly an order of magnitude more than those for NaCl at the same concentration.
APPENDIX I. THERMOCOUPLE CALIBRATION

The 20-junction copper-constantan thermocouple was calibrated \textit{in situ} by measuring the vapor pressure of water as a function of thermocouple emf. The temperature was found by interpolation in a table of the vapor pressure of water every 0.01° from 0° to 100°. The table was printed out by the LNS IBM 7040 computer, using the equation of Keyes (45),

\[
\log P = A/T + B \log T + CT + DT^2 + ET^3 + FT^4 + G
\]

where

\[A = -2892.3693\]
\[B = -2.892736\]
\[C = -4.9369728 \times 10^{-3}\]
\[D = 5.60695 \times 10^{-6}\]
\[E = 4.645869 \times 10^{-9}\]
\[F = 3.7874 \times 10^{-12}\]
\[G = 19.3011421\]

The temperature was converted from the thermodynamic to the International scale by the relation

\[T - t = 273.16 + \left( t/100 - 1 \right) \times (0.04217 - 0.00007481t)(t/100)\]

The deviations of thermocouple emf from the quadratic expression \((0.7673777)(t/100) + 0.0815375 (t/100)^2\) were plotted and a
smooth curve drawn through the points. The curve was read to 0.001 mv, which corresponds to 0.0013° at 10° and to 0.0011° at 100°. Several calibrations were performed, but the deviation curve was established on the basis of two calibration runs which agreed within 0.003 mv at every temperature. The mean values of these two runs are given in the following table, in which δ is the experimental emf less the value calculated by the quadratic expression given above.

<table>
<thead>
<tr>
<th>t</th>
<th>emf (mv)</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.500</td>
<td>9.695</td>
<td>-0.025</td>
</tr>
<tr>
<td>25.000</td>
<td>19.441</td>
<td>-0.033</td>
</tr>
<tr>
<td>37.500</td>
<td>29.900</td>
<td>0.023</td>
</tr>
<tr>
<td>37.500</td>
<td>29.900</td>
<td>-0.023</td>
</tr>
<tr>
<td>50.000</td>
<td>40.407</td>
<td>+0.000</td>
</tr>
<tr>
<td>62.500</td>
<td>51.162</td>
<td>0.016</td>
</tr>
<tr>
<td>75.000</td>
<td>62.162</td>
<td>0.018</td>
</tr>
<tr>
<td>87.500</td>
<td>73.400</td>
<td>0.012</td>
</tr>
<tr>
<td>100.000</td>
<td>84.878</td>
<td>-0.013</td>
</tr>
</tbody>
</table>
APPENDIX II.

For the evaluation by the method of least squares of the parameters appearing in equation 4.31, a Fortran IV computer program has been written for the IBM 7044 computer. A listing of the Fortran source program is included in this appendix. The following values were obtained for the parameters for sodium chloride.

\[ C_1 = -0.2838563 \times 10^3 \]
\[ C_2 = 0.6519849 \times 10^2 \]
\[ C_3 = -0.3883116 \times 10^1 \]
\[ C_1' = 0.855878 \times 10^1 \]
\[ C_2' = -0.2444508 \times 10^1 \]
\[ C_3' = 0.2506253 \times 10^0 \]
\[ C_1'' = -0.2471982 \]
\[ C_2'' = 0.8816691 \times 10^{-1} \]
\[ C_3'' = -0.9612983 \times 10^{-2} \]
\[ C_1''' = 0.5613594 \times 10^{-2} \]
\[ C_2''' = -0.1552979 \times 10^{-2} \]
\[ C_3''' = 0.1657625 \times 10^{-3} \]
\[ B_1^o = -0.1821411 \times 10^4 \]
\[ B_2^o = 0.5217242 \times 10^3 \]
\[ B_3^o = -0.5613675 \times 10^2 \]

For the least squaring of the Debye slope, the following parameters were obtained:

\[ S_1 = 0.6202357 \times 10^4 \]
\[ S_2 = 0.5442507 \times 10^2 \]
\[ S_3 = -0.1619930 \times 10^0 \]
\[ S_4 = 0.8596094 \times 10^{-4} \]
\[ S_5 = -0.2890653 \times 10^3 \]
C THIS PROGRAM ACCEPTS AS INPUT VALUES OF THE APPARENT MOLAL
C HEAT CONTENTS AND HEAT CAPACITIES AND VALUES OF THE MOLALITY,
C TEMPERATURE, AND OSMOTIC COEFFICIENT. THE OSMOTIC COEFFICIENT
C IS LEAST SQUARED AS A FUNCTION OF M AND T USING AN EXTENDED
C DEBYE-HUCKEL EXPRESSION. OUTPUT IS THE OSMOTIC COEFFICIENT,
C ACTIVITY COEFFICIENT, AND APPARENT MOLAR ENTHALPY AND HEAT
C CAPACITY, OVER SPECIFIED RANGES OF TEMPERATURE AND MOLALITY.

10 FORMAT(11,F8.3,18,I5,15)
20 FORMAT(F7.4,F10.2)
25 FORMAT(1H1,3X,1HM,10X,4HPHIL,11X,4HCALC,11X,5HDELTA)
30 FORMAT(F6.4,3E15.5)
35 FORMAT(1H1,3X,1HM,9X,5PHICP,11X,4HCALC,11X,5HDELTA)
40 FORMAT(F6.4,F9.1,F10.4)
45 FORMAT(5H1 M,8X,1HT,7X,6HPHIOBS,10H PHICALC,4X,5HDELTA)
50 FORMAT(F8.4,F9.1,3E10.4)
55 FORMAT(1H1,3X,1HM,8X,1HT,9X,3PHI,15H 1+LOG GAMMA,4X,4PHIL,11LX,5PHICP)
60 FORMAT(F8.4,F9.1,2F10.4,2E15.4)
65 FORMAT(1H1,10HPARAMETERS)
70 FORMAT(E15.7)
100 DOUBLE PRECISION SUM2,SUM3,SUM4,TS(3),F,DA,COF,DELTA,T,DELT,
101 GAMMA,SL(12,13),X(12),A,T,TEE,LOGS,LOGM,LOGE,LOX,Y,Z,D1,D2,D3,
102 L,DO,SLOPE,EM,PHIL,PHICP,PHI,TS,TS2,TS3,F1,F2,BL(4),BJ(4),B(4),
110 BPHI(4),TI,TF,EM,EMF
105 DIMENSION STORE(3,100)
20 READ(5,10)NO,A,N1,N2,N3
25 READ(5,15)TI,TF,EM,EMF,DELTA,DELT
26 NOO=NO+1
27 DO 120 I=1,NO
30 DO 110 J=1,NOO
31 S(I,J)=0.0D0
32 110 CONTINUE
34 120 CONTINUE
36 S1=-0.2890653D3
37 S2=-0.6202357D4
40 S3=-0.5442050D2
41 S4=-0.1619930D0
42 S5=-0.8596094D-4
43 TEE=25.0D0
44 T=298.16D0
45 D1=3.97440D0*(-S2+S3*T+(S4*T)*T+(2.0D0*(S5*T)*T)*T)
46 D2=3.97440D0*(S3+(2.0D0*S4)*T+(6.0D0*S5*T)*T)
47 DO 150 I=1,N1
50 READ(5,20)EM,PHIL
51 STORE(I,11)=EM
52 STORE(1,11)=PHIL
53 CALL DEBYE(TEE,EM,4,SLOPE,Y,Z)
54 X(1)=EM
55 NOO=NO-1
56 DO 140 I2=1,NO0
57 140 X(I2+1)=X(I2)*EM
F = PHI(I) - (D1/A) * (Y - Z)

CALL SUMS(S,X,F,NO)

CONTINUE

CALL GROUT(S,NO)

DO 160 I = 1,NO

C = I

160 BL(I) = C * S(I,NO + 1)

WRITE(6,25)

C
C LEAST SQUAREING OF HEAT CONTENTS COMPLETE.
C PARAMETERS STORED IN MATRIX BL.
C

DO 190 I1 = 1, N1

EM = STORE(I1, I1)

CALL DEBYE(TEE, EM, A, SLOPE, Y, Z)

X(I1) = EM

NO0 = NO - 1

DO 170 I2 = 1, NO0

170 X(I2 + 1) = X(I2) * EM

SUM = 0.000

DO 180 I2 = 1, NO

180 SUM = SUM + X(I2) * S(I2, NC + 1)

PHIL = SUM + (D1/A) * (Y - Z)

DELTA = STORE(2, I1) - PHIL

WRITE(6,30) EM, STORE(2, I1), PHIL, DELTA

C
C BEGINNING LEAST SQUAREING OF HEAT CAPACITIES.
C

NO0 = NO + 1

NO0 = NO + 2

DO 210 I = 1, NO0

DO 200 J = 1, NO00

S(I, J) = 0.000

200 CONTINUE

210 CONTINUE

DO 230 I1 = 1, N2

READ(5, 20) EM, PHICP

STORE(I1, I1) = EM

STORE(2, I1) = PHICP

CALL DEBYE(TEE, EM, A, SLOPE, Y, Z)

X(1) = 1.000

DO 220 I2 = 1, NO

220 X(I2 + 1) = X(I2) * EM

F = PHICP - (D2/A) * (Y - Z)

CALL SUMS(S, X, F, NO + 1)

CONTINUE

230 CONTINUE

CALL GROUT(S, NO + 1)

DO 240 I = 1, NO

C = I

240 BJ(I) = C * S(I + 1, NO + 2)

WRITE(6,35)

C
C LEAST SQUAREING OF HEAT CAPACITIES COMPLETE.
C PARAMETERS STORED IN MATRIX BJ.

C

151 DO 270 I1=1,N2
152 EM=STORE(1,I1)
153 CALL DEBYE(TEE,EM,A,SLOPE,Y,Z)
154 X(1)=1.000
155 DO 250 I2=1,NO
156 250 X(I2+1)=X(I2)*EM
160 SUM=0.000
161 NOO=NO+1
162 DO 260 I2=1,NOO
163 260 SUM=SUM+(X(I2)*S(I2,NO+2))
165 PHICP=SUM+(D2/A)*(Y-Z)
166 DELTA=STORE(2,I1)-PHICP
167 270 WRITE(6,30) EM,STORE(2,I1),PHICP,DELTA
C
C BEGINNING LEAST SQUAREING OF OSMOTIC COEFFICIENTS.
C

171 N02=2*N0
172 N03=3*N0
173 N04=N03+1
174 DO 290 I=1,N03
175 DO 280 J=1,N04
176 S(I,J)=0.000
177 280 CONTINUE
201 290 CONTINUE
203 TS=298.1600
204 TS2=TS*TS
205 TS3=TS2*TS
206 DO 340 I1=1,N3
207 READ(5,40)EM,TEE,PHI
210 STORE(1,I1)=EM
211 STORE(2,I1)=TEE
212 STORE(3,I1)=PHI
213 T=TEE+273.1600
214 TLOG=DLOG(T)
215 F1=-(TS2)/(2.000*T)-(TS*TLOG)+0.500*T
216 F2=(1.000/6.000)*(TS3/T+(3.000*TS2)*TLOG-(3.000*TS)*T+(0.500*T)*T)
217 X(1)=EM
220 NOO=NO-1
221 DO 300 I2=1,NOO
222 300 X(I2+1)=X(I2)*EM
224 NOO=NO+1
225 DO 310 I2=NOO,N02
226 I3=I2-N0
227 310 X(I2)=X(I3)*F1
231 N00=N02+1
232 DO 320 I2=NOO,N03
233 I3=I2-N02
234 320 X(I2)=X(I3)*F2
236 CALL DEBYE(TEE,EM,A,SLOPE,Y,Z)
237 SUM=0.000
240 DO 330 I2=1,N0
241 330 SUM=SUM+((-BL(I2)+TS*BJ(I2))/T+BJ(I2)*TLOG)*X(I2)
243 PHIDH=1.000-(SLOPE/A)*Z
F = -3.974400*(PHI - PHIDH) - SUM
CALL SUMS(S, X, F, NO3)
CONTINUE
340  CONTINUE
CALL CROUT(S, N03)
WRITE(6, 45)
C
LEAST SQUARING OF OSMOTIC COEFFICIENTS IS COMPLETE.
C
I = 1
DO 400 I1 = 1, N3
EM = STORE(I, I1)
TEE = STORE(I2, I1)
355  T = TEE + 273.1600
CALL DEBYE(TEE, EM, A, SLOPE, Y, Z)
TLOG = DLOG(T)
DO 360 I2 = 1, N0
I4 = I2 + NO
I5 = I2 + NO2
360  BPHI(I2) = -0.2516103D0*((-BL(I2) + TS*BJ(I2) - 0.5D0*TS*I4, N03 + 1)*TS2)
* (1.0D0/6.0D0)*(S(I5, N03 + 1)*TS3) / T + BJ(I2) - TS*I4, N03 + 1)
* 1 - 0.5D0*(TS2*S(I5, N03 + 1)) + TLOG*(0.5D0*S(I4, N03 + 1))
* 1 - 0.5D0*(TS*X(I2, N03 + 1)) + T*((1.0D0/I2)*S(I2, N03 + 1))
PHIDH = 1.0D0 - (SLOPE/A)*7
X(I) = EM
I6 = NO - 1
DO 370 I2 = 1, I6
370  X(I2 + 1) = X(I2) + EM
SUM = 0.0D0
DO 380 I2 = 1, N0
380  SUM = SUM + X(I2) * BPHI(I2)
PHI = PHIDH + SUM
GO TO (390, 410), I
390  DELTA = STORE(3, I1) - PHI
WRITE(6, 50) EM, TEE, STORE(3, I1), PHI, DELTA
400  CONTINUE
WRITE(6, 55)
EM = EMI
TEE = TI
I = 2
GO TO 355
410  SUM = 0.0D0
DO 420 I2 = 1, N0
420  C = I2
SUM = SUM + BPHI(I2)*(((C + 1.0D0)/C)*X(I2))
GAMMA = -SLOPE*(Y/A) + SUM
DAGOF = 1.0D0 + (GAMMA/2.302585)
C1 = 3.974400*(-S2 + S3*T + S4*(T*T) + ((2.0D0*S5)*(T*T)) + T)
D2 = 3.974400*(S3 + (2.0D0*S4)*T + (6.0D0*S5)*T) + T)
D3 = 3.974400*(2.0D0*S4 + 12.0D0*S5*T)
D4 = 3.974400*(12.0D0*S5)
TTS(1) = T - TS
TTS(2) = TTS(1) + TTS(1)
TTS(3) = TTS(2) + TTS(1)
ISN

SUM=0.000
SUM2=0.000
SUM3=0.000
SUM4=0.000
DO 430 I2=1,NO
C=I2
SUM=SUM+(BL(I2)/C)*X(I2)
SUM2=SUM2+(BJ(I2)/C)*X(I2)
I4=I2+NO
15=I2+NO2
SUM3=SUM3+(SI4,N03+1)/C)*X(I2)
SUM4=SUM4+(SI5,N03+1)/C)*X(I2)
SUM=SUM+(D1/A)*(Y-Z)
SUM2=SUM2+(D2/A)*(Y-Z)
SUM3=SUM3+(D3/A)*(Y-Z)
SUM4=SUM4+(D4/A)*(Y-Z)
PHIL=SUM+TTS(1)*SUM2+((0.5D0)*TTS(2))*SUM3+((1.0D0/6.0D0)
1*TTS(3))*SUM4
PHICP=SUM2+TTS(1)*SUM3+((0.5D0)*TTS(2))*SUM4
WRITE(6,60)EM,TEE,PHI,DACOF,PHIL,PHICP
IF(EM.GE.EMF)GO TO 440
EM=EM+DELTAM
GO TO 355
IF(TEE.GE.TF)GO TO 460
TEE=TEE+DELTAT
EM=EMI
GO TO 355
WRITE(6,65)
WRITE(6,70)(BL(I),I=1,NO)
WRITE(6,70)(BJ(I),I=1,NO)
N031=N03+1
WRITE(6,70)(SI,N031),I=1,N03)
STOP
END
SUBROUTINE CROUT(S,NO)

C THIS SUBROUTINE SOLVES AN NO BY NO SET OF SIMULTANEOUS LINEAR EQUATIONS.

DOUBLE PRECISION S(12,13)

NOO=NO+1

DO 22 I=1,NO

DO 20 J=1,NOO

K=1

16 IF(K.GE.I .OR. K.GE.J) GO TO 18

S(I,J)=S(I,J)-(S(I,K)*S(K,J))

K=K+1

GO TO 16

18 IF(I.GE.J) GO TO 20

S(I,J)=S(I,J)/S(I,I)

20 CONTINUE

22 CONTINUE

I=NO-1

K=NO

J=K

26 IF(J.EQ.NO+1) GO TO 28

S(I,NO+1)=S(I,NO+1)-(S(I,J)*S(J,NO+1))

J=J+1

GO TO 26

28 IF(I.EQ.1) GO TO 30

I=I-1

K=K-1

GO TO 24

30 CONTINUE

RETURN

END
SUBROUTINE DEBYE (TEE, EM, A, SLOPE, Y, Z)

THIS SUBROUTINE COMPUTES THE DEBYE LIMITING SLOPE AND THE
FUNCTIONS Y AND Z, GIVEN VALUES OF TEMPERATURE, MOALITY,
AND THE ION SIZE PARAMETER.

DOUBLE PRECISION T, TEE, EM, A, SLOPE, Y, Z, SQR, X

S1 = -0.2890653E3
S2 = 0.6202357E4
S3 = 0.5442507E2
S4 = -0.161930
S5 = 0.8596694E-4
T = TEE + 273.1600
TLOG = DLOG(T)
SLOPE = S1 + S2/T + (S3*TLOG) + S4*T + S5*(T*T)
SQR = DSQRT(EM)
X = 1.000 + (A*SQR)
Y = A*SQR/X
ZLOG = DLOG(X)
Z = (X - 1.000 * ZLOG) - (1.000/X) / ((A*A)*EM)
RETURN
END
SUBROUTINE SUMS(S,X,F,NO)

C THIS SUBROUTINE COMPOSES LEAST SQUARES SUMS AND
C STORES THEM IN MATRIX S.

C

DOUBLE PRECISION S(12,13),X(12),F

DO 10 I=1,NO

10 S(I,J)=S(I,J)+(X(I)*X(J))

RETURN

END
REFERENCES


52. Th. Ackermann, personal communication.
The author is the son of Frank and Veva Jean Gibbard and was born in Norman, Oklahoma on December 27, 1940. He attended public schools in Oklahoma and Colorado and U.S. Army schools in Tokyo, Japan and Frankfort, Germany. He entered the University of Oklahoma in 1958 and received the B.S. degree in Chemistry in June, 1962. In September, 1962 he entered the graduate school of the Massachusetts Institute of Technology and received the S.M. degree in February, 1964. While at M.I.T. he held appointments as a teaching assistant, research assistant, and predoctoral fellow.

He is a member of Phi Eta Sigma, Phi Lambda Upsilon, and Phi Beta Kappa honorary societies and of the Society of the Sigma Xi and the American Chemical Society.

The author is married to the former Linda Louise Scott and has three sons: Franklin, five; John Scott, three; and Mark, three months.