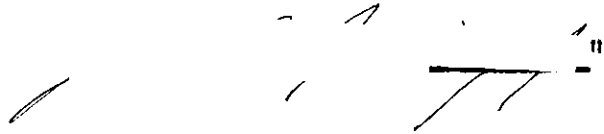


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12 R

THE FREE ENERGY, ENTROPY, AND
ENTHALPY OF TRANSFER OF
SIMPLE SALTS FROM CERTAIN
NON-AQUEOUS SOLVENTS TO WATER

A THESIS

Presented to
the Faculty of the Graduate Division

By

James Collier Fanning

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemistry

Georgia Institute of Technology

August, 1959

Dedicated
to
W. H. Hitechew
a
high school chemistry
teacher who will
long be remembered for his
great interest
in chemistry and for his
ability to pass this
interest over to
many of his students

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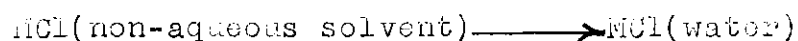
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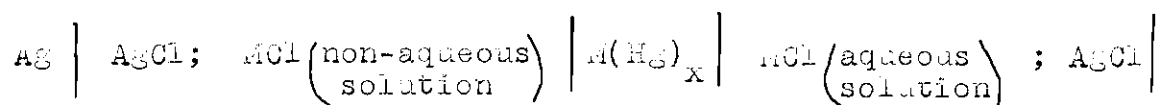
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ABSTRACT

The thermodynamic properties of the transfer



were investigated at several temperatures. A potentiometric method was used to study this reaction, and it employed the cell



Ag.

From potential measurements on this cell the values of the free energy, entropy, and enthalpy of transfer were obtained.

Experimental measurements were made in a type of cell that had been previously used to determine the activity coefficients of various solutes in water. These cells have been referred to as concentration cells. The entire cell consisted of two similar cell units. To perform the measurements each cell unit had placed in it a silver-silver chloride electrode and a long capillary tube through which alkali metal amalgam flowed, forming the alkali metal amalgam electrode.

Both types of electrodes used in this research were prepared by standard procedures. The silver-silver chloride electrode was prepared by first plating silver onto a platinum gauze and then forming silver chloride on top of the silver by anodization. A careful check was made at all times to insure that the potential difference between the silver-silver chloride electrodes themselves was always at a minimum. The amalgam was prepared by the electrolysis of a concentrated alkali metal hydroxide solution with the metal plating out into a pool of mercury. The amalgam was dried and stored in an evacuated glass bulb until ready for use.

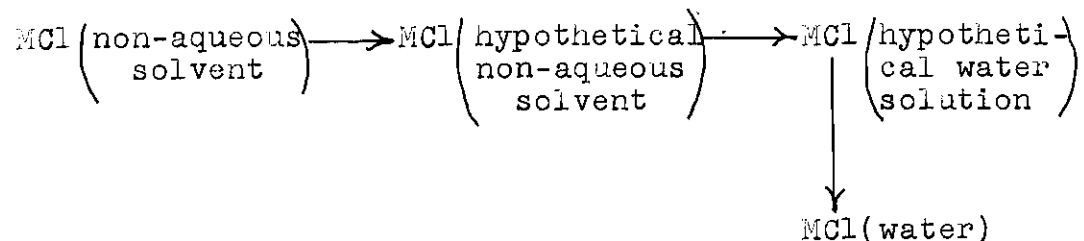
All of the materials used in this research--mercury, sodium chloride, potassium chloride, water, methanol, and ethylene glycol--were purified by methods which had been employed previously by other workers.

Both the non-aqueous solution and the aqueous solution being used in a single measurement had their concentrations in terms of mole fraction units equal. The mole fractions were equal because this equality made available to the solute ion-pair being transferred an identical number of solvent molecules in each solvent. This meant that the solute particles had an equal chance for solvent interaction in both solvents. The solutions were prepared and transferred to their respective cell units with a minimum contact with the atmosphere. The solutions were forced from their

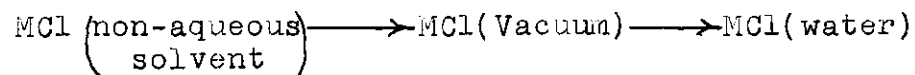
containers to the cell units by the use of solvent-saturated oxygen-free nitrogen.

From the values of the electromotive force of transfer, E_t , the free energy, ΔF_t , the entropy, ΔS_t , and the enthalpy, ΔH_t , of transfer had to be obtained. A fourth degree equation expressing E_t as a function of the mole fraction, N_2 , was obtained for each temperature. For certain chosen values of N_2 , ΔF_t was calculated at several temperatures. At a particular N_2 , a second degree equation with ΔF_t as a function of the temperature was calculated. By the use of this equation, ΔS_t was calculated and, since ΔS_t and ΔF_t for a particular temperature were known, ΔH_t was then available. These thermodynamic quantities were available for various mole fractions for the transfer of potassium and sodium chloride from methanol to water and from ethylene glycol to water. These quantities covered various ranges of concentration; however, the lowest concentration in each case was 0.0005 mole fraction units. This minimum concentration gave about a 0.05 molal water solution. With the type of alkali metal amalgam electrodes used in this research, this is about the minimum concentration that can be measured with any accuracy. The upper limit on the concentration ranges covered was governed by the solubility of the solute in the non-aqueous solvent.

The theoretical study of the transfer can be made by observing the nature of the following reactions:



and



The overall process for both of the reactions above is the transfer process which is to be investigated. The first reaction gives the expression:

$$\Delta F_t = \Delta F_t^{\circ} + RT \ln \frac{f_2}{f_2'}$$

where f_2 and f_2' are the mean rational activity coefficients of the solute in the aqueous and non-aqueous solutions respectively. ΔF_t° is the free energy of transfer from the hypothetical non-aqueous solution where the activity is one to the hypothetical aqueous solution where the activity is one. ΔF_t° is also equal to the free energy of transfer at extreme dilution and is the free energy due only to solvent-solute interaction. Use of the Debye-Huckel theory shows

that ΔF_t in the dilute region is a straight line function with respect to $N_2^{\frac{1}{2}}$. A relation was found to exist between the standard electrode potentials of the electrodes being used and the electromotive force of transfer.

From the second equation the transfer process was investigated from a solvation viewpoint. Born's theory gives an expression for the transfer,

$$\Delta F_t^o = - \frac{Ne^2}{2r} \left(\frac{1}{D} - \frac{1}{D'} \right)$$

where N is Avogadro's number, e is the electronic charge, r is the ionic radius, and D and D' are the dielectric constants of the water and non-aqueous solvent respectively. It had been previously reported that Born's theory did not give the correct results for the transfer of certain alkali metal chlorides from methanol-water mixtures to water. The reason given for this inconsistency was that the ions in the non-aqueous solvent mixture ordered the structure of the solvent more than they ordered the structure of the water. Thus, the experimental results were not explained by the Born theory because it did not consider the order-destroying, order-producing nature of the ions.

The experimental results showed that the Born theory could predict the ΔF_t for the ethylene glycol transfer, but

not for the methanol transfer. The entropy of transfer gives a measure of the order-disorder nature of the ions; it was found to be large for the methanol and smaller for the glycol transfer.

The major points brought out by this research are the following:

(1) The electromotive force of transfer is a function of the activity coefficients of the solutions being used.

(2) The "limiting law" for the transfer process expresses ΔF_t as a function of $N_2^{\frac{1}{2}}$.

(3) The Born theory does not completely describe the transfer process.

(4) The deviations between the experimental values of ΔF_t and those calculated by use of the Born theory are best explained by considering the order-disorder producing nature of the solute's ions on the solvent.

(5) The ordering-disordering nature of ions can be evaluated from the entropy of transfer.

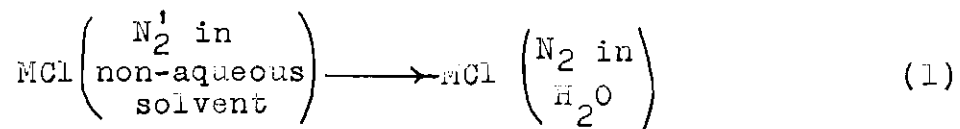
Some work was done on the conductivity of sodium and potassium chloride in methanol and ethylene glycol. The dissociation constants of the solutes were determined by Shedlovsky's method. It was thought that conductivity studies were needed to determine the amount of association

in the solvents, but these studies were inconclusive. More work is needed on both the theory and experimental phases of the conductivity of "strong" electrolytes in non-aqueous solvents before any application can be made.

CHAPTER I

INTRODUCTION

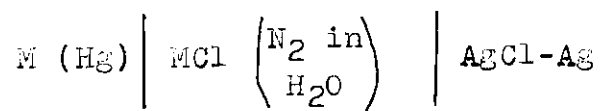
In his recent book Gurney (1) shows how the forces of interactions involved in solutions containing ionic solutes might be studied by investigating the process of transferring a simple 1:1 salt from a non-aqueous solvent to water. The above process might be represented by



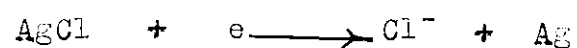
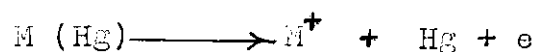
where M is any element with a plus one oxidation state and N_2' and N_2 are the mole fractions of MCl in the non-aqueous solvent and water respectively.

In order to study the process from the viewpoint of the interactions existing between solute and solvent particles the free energy, entropy, and enthalpy for the transfer should be computed at various concentrations of solute in each solvent. These fundamental thermodynamic quantities should be calculated at constant pressure and at various temperatures. Once these quantities are obtained, certain comparisons can be made between the water and the non-aqueous solutions.

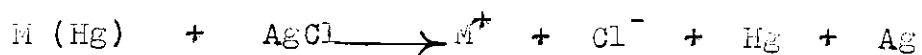
Gurney (1) outlines one method by which the thermodynamic quantities might be acquired. This method is a potentiometric method known as "connecting cells back-to-back." In order to describe this method, one must look at the ordinary chemical cell



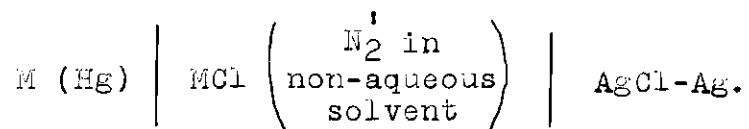
with the following cell reactions taking place:



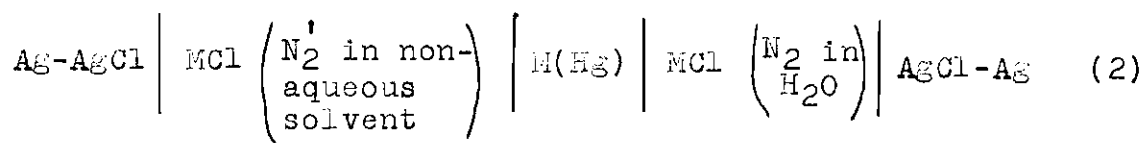
and with



being the total cell reaction. Similarly, for the non-aqueous solution the chemical cell would be



Connecting each of the above cells "back-to-back," the chemical cell formed would be:



which has for its chemical reaction, reaction (1). For statistical reasons which will be shown later, it was found that the mole fractions of MCl on each side of cell (2) should be equal, i. e., $N_2 = N_2'$, for all the measurements of electromotive force. By measuring the electromotive force of cell (2) for various concentrations at several temperatures, the thermodynamic quantities for the transfer are obtained as functions of the mole fraction. Extrapolating these values to the region of extreme dilution, one is then able to obtain the free energy, entropy, and enthalpy of transfer for one mole of MCl from a large quantity of the non-aqueous solvent to a very large quantity of water.

This thesis has as its purpose the investigation of the transfers described by reaction (1) and has employed cell (2) as a means of accomplishing this purpose. As was stated, the investigation is carried out by first measuring the electromotive force of cell (2) under various conditions, then calculating the necessary thermodynamic quantities, and finally interpreting the extrapolated values in order to obtain their exact physical significance.

The interpretation of the quantities involved a comparison between the nature of MCl in the non-aqueous solution and the nature of MCl in the aqueous solution. The thermodynamic properties of transfer are essentially the difference between the solvation properties of water and

those of the non-aqueous solvent. The free energy of transfer would be the sum of the free energy lost by the water when an ion pair has been introduced into the water and the free energy gained by the non-aqueous solvent when the ion pair has been removed from it. The enthalpy of transfer might give the sum of the heat effects which are involved in the transfer. The entropy of transfer should give some idea as to the ability of the ions to break down or build up the structure of the non-aqueous solvent as compared with this same ability in water.

Research concerning thermodynamic quantities of transfer has been very slight. Gurney (1) gives a few graphs showing data which he has accumulated from unpublished research. He does not give any complete experimental details as to how the data were obtained. The data which he presents are those for transferring MCl , NaCl , KCl , and LiCl from water to various water-methanol mixtures and in some cases pure methanol.

This thesis attempts to extend the data and ideas of Gurney and apply his treatment to the transfer of various solutes from ethylene glycol to water. Also, a method is shown whereby certain electromotive force values from the literature might be used to calculate the thermodynamic quantities for HCl and other similar solutes.

CHAPTER II

POTENTIOMETRIC EXPERIMENTAL METHODS

Equipment

As previously stated, the cell needed to measure the thermodynamic quantities of transfer is shown by (2). The actual apparatus used for making these measurements is similar to that described by MacInnes and Parker and Harned (2).

MacInnes and Parker used their apparatus for the measurement of concentration cells where both sides of the cell had the same solvent but the concentration of the solute was different. This type of apparatus has been used often for measuring the electromotive force of concentration cells and thus determining the activity coefficients of various salts in aqueous solutions and, for a small number of cases, in non-aqueous solutions.

The apparatus which was used for these measurements differed only slightly from that of MacInnes and Parker. Two identical units made up the complete cell. Each unit had a chamber for the amalgam electrode and a smaller chamber for the silver-silver chloride electrode. The amalgam chamber was $8 \frac{3}{4}$ inches in length from the top to the narrow constriction, which led to a large bulb. On the other end of

the bulb was a stopcock. A 10 millimeter glass tube led from the side of the amalgam electrode chamber to the bottom of the silver-silver chloride electrode chamber. The silver-silver chloride electrode chamber was $4\frac{1}{4}$ inches in length and had attached to its side a short piece of glass tubing which was knurled for the attachment of plastic tubing. The tubing was used to carry the solution into the cell. The upper ends of both electrode chambers had a 24/40 S glass joint.

Silver-silver chloride electrodes.--The silver-silver chloride electrodes used were of the type described by MacInnes and Beattie (3). The electrodes were held in place in the chamber by means of a 24/40 S glass joint fitted with a 4-inch piece of 8-millimeter glass tubing. A small platinum wire was sealed into the end of the glass tube; a one square centimeter piece of platinum gauze was spot-welded on the end of the platinum wire. Silver was then plated onto the gauze from a 0.1 formal solution of potassium argentocyanide at a current density of 0.5 ampere per square decimeter for eight hours. Silver chloride was deposited on the silver-platinum gauze from a 0.05 formal solution of sodium chloride at a current of 5 to 7 milliamperes for 10 to 20 minutes. Electrical contact was made with the platinum gauze by placing mercury in the glass tube holding the platinum wire and gauze.

The electrodes were compared with one another at various times during the course of this problem. The comparison was made by placing the electrodes into a 0.05 formal sodium chloride solution at constant temperature for about one hour. The potential difference between the electrodes was then measured. The electrode which was used for the non-aqueous solutions was always slightly higher in potential than the one used in the aqueous solution. The value of the potential difference in millivolts was never allowed to be more than 0.2, which was less than the error incurred in the measurements. If the potential difference in millivolts was larger than 0.2, the electrodes were dipped into concentrated ammonium hydroxide solution, washed, and then replated with silver chloride.

The silver-silver chloride electrodes used were sturdy and able to withstand the rather rough treatment which was needed for each measurement; i. e., the electrodes had to be dry before being placed into the various solutions. The electrodes were prepared for the measurement by washing first with distilled water and then with methanol and dried in a stream of nitrogen.

Much time was consumed by using the silver mirror type of electrode described by Purlee and Grunwald (4). It was found to be too fragile to undergo the rigorous drying

procedure without suffering some damage.

Amalgam electrodes.--The amalgam electrodes were formed by flowing the alkali metal amalgam from capillary tubes into the chamber. The amalgam flowed from the capillary through the solution, past the constriction, and into the bulb. The amalgam container was a 500 milliliter Erlenmeyer flask which had been sealed at the top with the exception of two stopcocks--one being vertical at the top of the container and the other being horizontal about one inch below the top. Attached to the bottom of the flask were two capillary stopcocks, and attached to each stopcock was a piece of capillary tubing which had been pulled to a small diameter. Each of these capillary tubes was fitted into the cell units. They were held in place by rubber stoppers. The stoppers were boiled in concentrated sodium hydroxide for one-half hour before being used in the apparatus.

For the preparation of the alkali metal amalgam triply distilled mercury was used, and the amalgam preparation followed basically the procedure given by Harned (5). About 300 milliliters of mercury were placed in a large glass dish which was then covered with one-half liter of a ten formal alkali metal hydroxide solution. The alkali metal was plated into the mercury at a current of one ampere for a period of time long enough to give a 0.01 per cent amalgam. The hydroxide solution was poured off of the amalgam as well as possible,

and the remainder sucked off by using an aspirator pump. The amalgam was washed with methanol quickly and then sucked into a 400 milliliter glass bulb fitted with two stop-cocks--one directly opposite the other. One stopcock was attached to a vacuum pump and the other was used to suck the amalgam into the bulb. After the amalgam was in the bulb the pump was left running for twenty-four hours, and at that time the stopcock was closed and the bulb left standing for at least four days before being opened. When the amalgam was needed it was used within a two-day period. It was drained, as needed, into the amalgam container of the cell, which always contained an atmosphere of nitrogen. A relatively small amount of oxidation was observed to occur in the amalgam, and any residue due to oxidation appeared to float on the surface of the amalgam. The residue did not seem to come into contact with the solutions being studied.

Potentiometer circuit.--A K-2 type Leeds and Northrup potentiometer was used for the measurement of the electromotive force of cell (2). The circuit consisted of a Leeds and Northrup 2430 D-C galvanometer, an Eppley Lab standard cell with a voltage of 1.01860 volts at 20°C, and a six-volt lead storage battery with a resistance box in series with the storage battery and potentiometer. All connections were made with eight B and S gauge insulated copper wire.

The galvanometer rested on a small table which had its feet resting in a box containing one hundred pounds of sand. This arrangement gave a sturdy base for the galvanometer, and little or no vibrations were observed by the galvanometer due to outside disturbances.

Solvents

In this research water and two non-aqueous solvents, methanol and ethylene glycol,* were used. They were purified by methods which seemingly have common acceptance. In Table I data are given for the measured values of the refractive indices and the specific conductivities of the pure solvents at 25°C.

TABLE I
SOLVENT DATA

	Refractive Index for Sodium D Light	Specific Conduc- tivity
Water	1.33228	2.0×10^{-8} ohm ⁻¹ cm ⁻¹
Methanol	1.32650	7.7×10^{-6}
Glycol	1.43031	2.1×10^{-8}

*Ethylene glycol will be referred to as glycol throughout the remainder of this thesis.

Water.--Distilled water was purified by the method described by Glasstone (6). The water was redistilled from an alkaline potassium permanganate solution with nitrogen bubbling through the solution. The water was collected in tared 250 milliliter Erlenmeyer flasks fitted with a glass joint. The flasks were stoppered and set aside until needed.

The nitrogen used in the distillation and in other phases of this research was treated by bubbling it, first through a cuprous chloride--ammonium chloride--ammonium hydroxide solution, then through a concentrated sulfuric acid solution, and finally through a drying tower packed with solid sodium hydroxide and calcium chloride. This treatment was to remove any oxygen which might have been in the nitrogen.

Ethylene glycol.--Technical grade glycol was distilled three times at a pressure of one to two millimeters of mercury. The glycol which was collected for further distillation or use boiled in the range of 60 to 65°C. Nitrogen was bubbled through the glycol during each distillation. The glycol was collected in a 2000 milliliter round bottom flask after the first and second distillations. During the third distillation the glycol was caught in tared 250 milliliter Erlenmeyer flasks similar to those used to receive the water. The flasks of glycol were likewise stoppered and set aside until ready for use. About 130 milliliters of glycol were in each flask. After the first distillation a large amount of anhydrous

sodium sulfate was added to the glycol, and the solution allowed to stand overnight. The glycol was decanted and redistilled a second time.

The purity of the glycol was felt to be very good, especially since water does not form an azeotropic mixture with glycol as it does with monohydric alcohols. The method of purification was that given by Smyth and Walls (7).

Methanol.--The methanol was purified by the method of Vogel (8). This method gave relatively pure methanol, but it was felt that a much more rigorous purification process should be used if one wishes extremely accurate measurements for methanol solutions. A method which might be used for higher purity is one described by Butler and coworkers (9).

For this research methanol was purified by adding 50 milliliters of technical grade methanol to 0.5 grams of iodine and five grams of magnesium in a 2000 milliliter round bottom flask. The flask was fitted with a condenser, and the mixture allowed to react and reflux. When the reaction had subsided and the iodine color had disappeared, approximately one liter of methanol was added to the flask, and the mixture refluxed for one-half hour. After this period the methanol was distilled over into a tared 250 milliliter Erlenmeyer flask and treated in the same manner as were the glycol and water. Only the alcohol which distilled over between 64 to 65°C was used. The distillation was protected from moisture

by using a calcium chloride drying tube connected to the adapter.

Solutes

Sodium chloride and potassium chloride were purified by the recrystallization of J. P. Baker "Analytical Grade" reagents. Sodium chloride and potassium chloride were recrystallized from a water solution. The water used for the recrystallization had been previously treated in the same way as the water used in the measurements. Enough salt was dissolved in the water to give a saturated solution at room temperature; the solution was heated to boiling, filtered, and cooled. The solution was saturated with hydrogen chloride, cooled, and filtered. The salt was dried in a glass dish at 140°C for twenty-four hours and stored in a desiccator until ready for use.

Preparation of Solutions

Why $N_2 = N_2^!$?--In the introduction it was pointed out that the measurements were to be made on solutions having a mole fraction of N_2 and $N_2^!$ in the water and non-aqueous solvent, respectively. It was also stated, without explanation, that the mole fraction of the solute in both the aqueous and non-aqueous solutions should be equal during each individual experiment. Before explaining the reason for using solutions of equal mole fraction, it should be demonstrated why the mole

fraction units of concentration were used instead of other units.

There are three different methods of expressing chemical concentrations: molarity, molality, and mole fraction. One had to be chosen to express the concentrations used in this research. Molarity is dependent on the temperature; and molality, even though independent of temperature, expressed the concentration as a function of the weight of the solvent. The mole fraction method, however, was independent of temperature and expressed the concentration as a function of the moles or molecules of both solute and solvent in the solution.

When the mole fractions of two different solutions (different in the sense that there is present the same solute but different solvents) are equal, equal numbers of solvent molecules will be exposed to each individual solute molecule or ion pair. For example, in the case of hydrogen chloride dissolved in methanol and in water with both solutions having the same molality, one finds $32/18$ times as many solvent molecules for each solute particle present in the water solution as are present in the methanol solution. If the solutions were being measured in a cell similar to (2) but equipped to use the hydrogen electrode instead of the amalgam electrode, one would find that part of the potential difference measured would be due to the fact that the hydrogen ion had more chances for attachment in the water solution than in the

methanol solution. Thus in order to eliminate this additional electromotive force which is due to the unequal number of solvent molecules available to each solute molecule or ion pair, the pair of solutions used in each measurement was prepared with the mole fraction in each solution the same.

The non-aqueous solutions.--In every case the solvent was finally distilled into tared 250 milliliter Erlenmeyer flasks which were sealed with glass stoppers after the proper volume of solvent was distilled into them. The flasks were then reweighed and the exact weight of solvent in each determined. Since the weight of the solvent was known, the correct amount of salt which would give the desired concentration was weighed out. The salt was weighed into a small vial that could be easily and quickly dropped into the flask. After the vial was added, the sealed flask was heated slightly to increase the dissolution of the salt. In all cases, even though the weight of the salt might have been small, the dissolving was very slow unless the flask was heated slightly. The solutions were cooled and reweighed for checking purposes.

The aqueous solutions.--Knowing the exact concentration of a given non-aqueous solution and the weight of the water in the flask, it was an easy matter to calculate the weight of salt necessary to add to the water in order to obtain a solution of the same mole fraction. The weight of salt to be dissolved

in the water, W_2 , was calculated by the equation:

$$W_2 = \left[\frac{M_1'}{18.02} \right] \left[\frac{W_1}{W_1'} \right] \times W_2'$$

where M_1' is the molecular weight of the non-aqueous solvent, W_2' is the weight of salt in the non-aqueous solution, and W_1 and W_1' are the weights of the water and non-aqueous solvent, respectively. The salt was weighed out in a small vial, and salt and vial were added to the solvent.

Measurements

Each pair of solutions was measured at room pressure. The potentials were measured at three different temperatures for each set of solutions. The concentration range covered by the measurements for the alkali metal chlorides extended from 0.0005 mole fraction units to a mole fraction which was very close to that of the saturated non-aqueous solution. This minimum value of the concentration range was chosen since it corresponded to a molality in water of about 0.05. As Robinson and Stokes (10) pointed out, this is about the lowest concentration at which one can obtain reliable results with an alkali metal amalgam electrode.

In order to make the measurements the cell units were cleaned, dried, and filled with nitrogen. They were placed on a special rack which gave the proper separation between units. The amalgam electrode chambers were side by side. The silver-silver chloride electrodes were dried as previously

described and placed into their proper positions. The cell was then placed in the bath and connected by plastic tubing to the solution-dispensing apparatus.

The solution-dispensing apparatus was a special arrangement of glass tubing, plastic tubing, and stopcocks which would lead each solution into its cell unit with a minimum of contact with the atmosphere. Nitrogen gas forced the solution into the proper cell unit. The glass stoppers were removed from the flasks containing the solutions, and a wash-bottle type of apparatus placed in the flask; i. e., one piece of glass tubing extended from the outside to the bottom of the flask and the other provided an opening at the top. The flask with its additional appendage was connected to its appropriate place in the nitrogen train. Nitrogen was first bubbled through pure water which saturated the nitrogen with water vapor. The nitrogen then passed into one of the cell units. After a few minutes a stopcock was turned and the nitrogen forced the aqueous solution over into the cell. After enough solution was in the cell another stopcock was turned to bubble nitrogen through the non-aqueous solvent and then into the other cell unit. While nitrogen was flowing in this manner, the amalgam electrode chamber of the unit with the aqueous solution was closed by using the stopper which had sealed the flask containing the solution. The non-aqueous solution after a few minutes was forced over into its proper cell unit and the unit sealed in a similar manner. The cell units were then

connected to the potentiometer through the silver-silver chloride electrodes. After the cell remained in the constant temperature bath for about an hour, the glass stoppers were removed from the cell units. The amalgam container was placed above the cell units with a capillary tube in each unit. The rubber stoppers on the capillary tubes were seated securely into each of the amalgam chamber openings. The potentiometer was first calibrated with the standard cell; the stopcocks on the amalgam container were opened and measurements were quickly made. At least three measurements were made on each pair of solutions, and only a small amount of variation was noticed unless the amalgam in the container had a large amount of oxide film on its surface. When this occurred, the last measurement was likely to be somewhat lower than the first and second readings. In order to conserve the amalgam the readings were made by opening and closing the stopcocks for each reading.

The constant temperature bath used was made by the American Instrument Company and contained fourteen gallons of water. The temperature was controlled by a "Quick-Set Adjustable" thermoregulator which held the temperature to $\pm 0.05^{\circ}\text{C}$. The thermometer used in the bath had been checked with a National Bureau of Standards thermometer and was found to be correct. During the summer months the bath was cooled with an auxiliary refrigeration unit, and during the winter months with tap water.

CHAPTER III

CONDUCTOMETRIC EXPERIMENTAL METHODS

Conductivity measurements on the non-aqueous solutions used in the potentiometric studies were thought to be desirable because possibly some information should be obtained concerning the extent of ionization which exists in these solutions. By use of the conductivity method, values of dissociation constants of the salts in various solvents could be obtained. In order to calculate the dissociation constants, the resistances of the solutions of varying concentration should be measured at a specific temperature. The literature gives very little data which could be used to calculate dissociation constants; therefore, much of these data had to be obtained by experimental methods.

Equipment

Bridge circuit.--In order to measure the resistance of various solutions a Leeds and Northrup (Jones and Joseph) conductivity bridge was set up. The additional units used in this apparatus were a General Radio Amplifier and Null Detector, a General Radio Filter, an input transformer, an output transformer, a Hewlett-Packard audio-oscillator, and a Dumont cathode ray oscillograph. The bridge circuit was arranged according to

the outline of Dike (11) and the instructions furnished by the Leeds and Northrup Company.

Cell.--The conductivity cell used for the resistance measurements followed the design of Daggett, Bair, and Kraus (12). The cell was especially designed for use in measuring the resistance of solutions which had very high resistance.

A 1000 milliliter Erlenmeyer flask was fitted with a special bulb on the side. This bulb was connected by two large glass tubes to the side of the flask. Two large platinum discs were secured in the bulb. Each disc was spot-welded to a heavy platinum wire which passed through the side of the bulb and into a small glass tube. Electrical contact was made with the disc by placing mercury in the glass tubes and dipping wires into the mercury. The top of the flask had a $3/4/45$ S glass joint. This glass joint provided a good fit for the cap or the special device used for passing solutions into the flask.

The platinum discs were coated with platinum black. The procedure used for platinizing was that given by Jones and Bollinger (13). The platinizing solution used was 0.3 per cent in chloro-platinic acid, 0.025N in hydrochloric acid, and 0.025 per cent in lead (II) acetate. The platinization was carried out at 0.01 ampere for ten minutes, reversing the circuit every ten seconds. The resistance of a 0.00013N HCl solution was measured at different frequencies

in order to detect any variation due to poor platinization.

After platinization and before each measurement, the cell was given a steam-cleaning. The cell was cleaned with steam for thirty minutes, allowed to drain, rinsed with methanol, and dried in a stream of nitrogen.

The cell constant was determined in the following manner. Four 0.01D water solutions of potassium chloride were prepared with extreme accuracy, and the resistance of each solution measured. The average resistance was determined, and using the specific conductance of the 0.01D potassium chloride solutions given by Jones and Bradshaw (14), the cell constant was calculated to be $0.2034_5 \pm 0.0002_0$ at 25°C . Appropriate correction was made for the conductivity of the water used.

Measurements

The cell was cleaned and dried before use each time. In order to place a solution into the flask, a special system of tubing and stopcocks was used which was similar to that used for the potentiometric measurements. Nitrogen was bubbled through pure solvent to saturate the nitrogen with the vapor of the solvent. Nitrogen gas forced the solution into the cell through a special cap. This cap had one long piece of glass tubing extending down into the cell through which the solution passed and another short glass tube opening to the atmosphere. It was a wash-bottle type of arrangement. After

the solution was placed in the flask, the special cap was exchanged quickly for a regular cap, which was completely sealed. The regular cap was attached to the flask by use of wire springs.

With the solution in the cell, the cell was lowered into the bath, and wires from the bridge were connected to the cell. The bath was the same constant temperature bath that had been for the potentiometric measurements. The only difference in the materials being used was that instead of water Gulf Mineral Seal Oil was placed in the bath. The temperature of the bath was held at $25.00 \pm 0.02^{\circ}\text{C}$. After about one hour the resistance of the solution was measured according to the procedures given by Dike (11) and the Leeds and Northrup Company.

CHAPTER IV

METHODS OF CALCULATION

Potentiometric

The potentials of the two cells which were connected back-to-back were measured at three different temperatures and at definite compositions. The mole fraction of the solute was always the same in the two cells. The free energy of transfer, ΔF_t , entropy of transfer, ΔS_t , and enthalpy of transfer, ΔH_t , were calculated from these measured potentials and their temperature differentials. The values in each case are for the transfer of one gram formula weight of solute from the non-aqueous solvent to a water solution at the same mole fraction of solute. The formulas which were used in making the calculations are given below.

Once the electromotive force of transfer, E_t , was measured at several concentrations for a single temperature, a fourth degree equation was fitted to the data expressing E_t as a function of the mole fraction, N_2 . This equation was obtained by using the least square polynomial curve-fitting routine* and the IBM 650 computer. Thus, for each temperature

*In the Georgia Tech Rich Electronic Computer Center this routine is indexed as IPL06. It was devised by the Statistical Laboratory of the University of Florida.

there was an expression giving the electromotive force of transfer as a function of the mole fraction, such as:

$$E_t = a + bN_2 + cN_2^2 + dN_2^3 + eN_2^4. \quad (3)$$

Each solution was prepared with its concentration at or very near some definite composition. Thus at, or very near, this definite composition there were three potential measurements corresponding to each temperature. Using the computed fourth degree equation, the potential values for each of the definite concentrations were calculated. These potential values were converted to free energy of transfer values by multiplying each of potential quantities by -23060, i. e.,

$$\Delta F_t = -23060 E_t. \quad (4)$$

This calculation gave the free energy of transfer in calories per mole.

The calculation of the potentials at each of the definite concentrations and the conversion of the calculated potentials into free energy data were both computed using the Bell General Purpose System* and the IBM 650.

*The Bell General Purpose System is IPL04 in the Georgia Tech Rich Electronic Computer Center. The system was devised by the Bell Telephone Laboratory.

For every one of the concentrations there were three free energy terms corresponding to the three different temperatures. Using these three values and the least square routine, a second degree equation was computed giving the free energy of transfer as a function of the absolute temperature for each mole fraction, i. e.,

$$\Delta F_t = f + gT + hT^2. \quad (5)$$

The second degree equation was differentiated with respect to temperature, thus producing the temperature coefficient of ΔF_t as a function of the temperature,

$$\left[\frac{\partial \Delta F_t}{\partial T} \right]_{P, N_2} = g + 2hT. \quad (6)$$

Since

$$\Delta S_t = - \left[\frac{\partial \Delta F_t}{\partial T} \right]_{P, N_2}, \quad (7)$$

then

$$\Delta S_t = -g - 2hT. \quad (8)$$

The temperature was inserted into the expressions for ΔS_t , and the entropy of transfer was calculated for various

concentrations.

By using the free energy and entropy of transfer and the temperature, the enthalpy of transfer was calculated for the various mole fractions. The fundamental thermodynamic equation

$$\Delta H_t = \Delta F_t + T\Delta S_t \quad (9)$$

was used for this calculation. The Bell General Purpose System was again used; this time, for the calculation of ΔS_t and ΔH_t .

The results obtained were for sodium chloride being transferred from glycol to water, sodium chloride being transferred from methanol to water, potassium chloride being transferred from glycol to water, and potassium chloride being transferred from methanol to water. There were only a very few values for potassium chloride transfer from methanol, because potassium chloride was only very slightly soluble in methanol and, as was previously mentioned, the solubility of the salt in the non-aqueous solvent controlled the concentration range covered.

Tables 2 through 9, Appendix II, contain the tabulated results obtained from the experimental measurements. Figures 1 through 9, Appendix II, contain the experimental results in a graphical form. Graphs of the F_t plotted against the

square root of the mole fraction are also given.

The electromotive force data had an error of about ± 0.3 mv which produced an error in the ΔF_t of about one per cent. The estimated error in the ΔS_t is ± 5 entropy units, and in the ΔH_t , about twenty per cent for the transfer of sodium chloride from glycol to water. The error in the ΔS_t and ΔH_t for the other sets of solutes and solvents is much larger, and the ΔS_t and the ΔH_t values obtained present only an idea as to the order of magnitude. The reason for this inexactness in these cases is probably the small number of experimental measurements made on these systems. The fourth degree equations (3) expressing ΔF_t were not as accurate as those found for the transfer of sodium chloride from glycol to water.

Conductometric

Resistances of various solutions were measured in the conductivity experiments, and from these measurements the dissociation constants of the salts in the non-aqueous solvents was determined. Shedlovsky's method (15) was used to calculate the dissociation constant from the resistances. This method requires that the equivalent conductance, Λ , for the solutions be calculated first from the resistance with appropriate correction for the conductivity of the solvent. Then with various solvent constants obtained from

the literature, the dissociation constant and the equivalent conductance at infinite dilution, Λ° , are obtained by an approximation method. The Bell General Purpose System and the IBM 650 computer were used to carry out this approximation. The Λ° was obtained in the computer program before the dissociation constant, K , was calculated. The absolute difference between the final value of Λ° and the next to the last value in the approximation of Λ° computed was 0.0001. Only the solutions whose concentrations were less than 0.1 molal could be used for this approximation method.

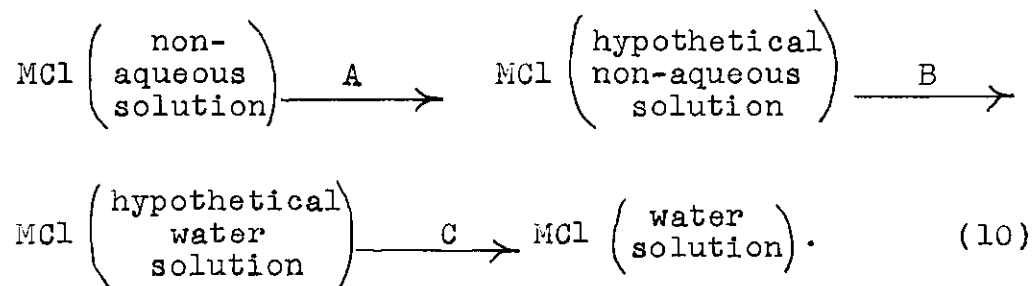
In Tables 11 through 15, Appendix IV, are found the values of the resistances and the equivalent conductances for solutions of various molalities. Also in that section are given the Λ° and K values for various salts in the different solvents. The error in the resistances and the equivalent conductances was about 0.1 per cent. The error in the Λ° is estimated to be 0.5 per cent and that of the dissociation constant about ten per cent.

The data for potassium chloride in methanol and most of the data for sodium chloride in methanol were obtained from the work of Butler, Schiff, and Gordon (9). In their paper no calculation of K was made.

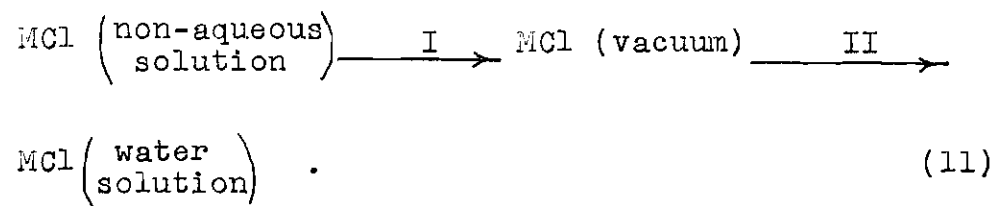
CHAPTER V

THEORETICAL CONSIDERATIONS

The process of transfer described by reaction (1) might be carried out theoretically in two ways. In the first method the ions are removed from the non-aqueous solution and placed successively in the following solutions: a hypothetical non-aqueous solution in which the activity of the solute is equal to one, a hypothetical aqueous solution where the activity of the solute is equal to one, and finally, the real water solution. This process might be illustrated by the following equation:



The second method involves removing the ions from the non-aqueous solution, placing them in a vacuum, and finally plunging them into the aqueous solution. This second method is shown by the following equation:



The over-all equation for both processes is reaction (1).

In order to give some meaning to the values obtained from experiment, these processes will be studied and then possibly some of the ideas presented can be applied to the experimental measurements.

General Thermodynamic Study of the Transfer Process

The first process, which is illustrated by reaction (10), is one which relates the measured quantities with certain other thermodynamic quantities. According to reaction (10), step A, the free energy per mole of solute for this step, ΔF_A , is given by

$$\Delta F_A = -RT \ln a_2'$$

where a_2' is the activity of the solute in the non-aqueous solution and R and T have their usual meaning. (See Appendix I where is given an index for all of the symbols used in this thesis.) For step B, the free energy per mole ΔF_B , is given by the equation,

$$\Delta F_B = F_2^{\circ} - F_2^{\circ}'$$

where F_2° is the chemical potential of the solute in the hypothetical aqueous solution and $F_2^{\circ'}$ is the chemical potential of the solute in the hypothetical non-aqueous solution. In step C the free energy per mole for this phase, ΔF_C , is found to be

$$\Delta F_C = RT \ln a_2$$

where a_2 is the activity of the solute in the aqueous solution. The sum of these free energy values is equal to the free energy of transfer, i. e.,

$$\Delta F_t = \Delta F_A + \Delta F_B + \Delta F_C$$

or

$$\Delta F_t = -RT \ln a_2 + F_2^{\circ} - F_2^{\circ'} + RT \ln a_2$$

or

$$\Delta F_t = F_2^{\circ} - F_2^{\circ'} + RT \ln \frac{a_2}{a_2'} \quad (12)$$

Using equation (12), it is now possible to relate the free energy of transfer to the activity coefficient of each of the two solutions. By definition

$$a_2 = (f_2 N_2)^2 \quad \text{and}$$

$$a_2' = (f_2' N_2')^2$$

where f_2 and f_2' are the mean rational activity coefficients of the solute in the aqueous and non-aqueous solutions, respectively. For each measurement the temperature is constant and

$$N_2 = N_2'. \quad (13)$$

Thus, from equation (12)

$$\Delta F_t = F_2^{\circ} - F_2'^{\circ} + 2 RT \ln \frac{f_2}{f_2'}.$$

Setting

$$F_2^{\circ} - F_2'^{\circ} = \Delta F_t^{\circ},$$

yields the equation

$$\Delta F_t = \Delta F_t^{\circ} + 2 RT \ln \frac{f_2}{f_2'}. \quad (14)$$

Before discussing the activity coefficients, a few statements about the meaning of ΔF_t° should be presented. ΔF_t° is the free energy of transfer for the solute from the hypothetical non-aqueous solution to the hypothetical aqueous solution. In both hypothetical solutions the activity of the solute is equal to one. Since both f_2 and f_2' are one in the extremely dilute region, then

$$\Delta F_t^{\circ} = \Delta F_t^{\circ\circ}$$

where $\Delta F_t^{\circ\circ}$ is the free energy of transfer at extreme dilution. ΔF_t° or $\Delta F_t^{\circ\circ}$ is an important thermodynamic property to evaluate for the transfer process, for it represents the free energy arising from only solvent-ion interaction and is free of any energy terms due to interionic attractions or repulsions. ΔF_t° may be positive, it may be negative, or in some rather unusual cases, it may actually be zero. Also, it should be pointed out that ΔF_t may vary in a positive or negative direction and in some regular or irregular manner as the mole fraction, N_2 , is increased. More will be said about ΔF_t° when the method illustrated by equation (11) is discussed.

Examination of the activity coefficient ratio and the term $2 RT \ln f_2/f_2'$ shows that this term represents a measure of the non-ideality of the transfer. This term might be considered to be due to interionic effects which appear as the concentration is increased. A very happy situation would be to know how this term changes with concentration. A very satisfactory value of ΔF_t° could be obtained by subtracting the value of $RT \ln f_2/f_2'$ from the value of ΔF_t . This situation could be brought about by knowing how the activity coefficients in each solution vary with the mole fraction.

Experimentally, the variation of the activity coefficients with concentration has been measured for only a relatively small group of compounds, and the only solvent which has been studied to any degree is water. The activity coefficients of the alkali metal chlorides in water over a wide concentration range are readily obtainable (16). Experimental determinations of the activity coefficients of electrolytes in non-aqueous solvents are very few, and a large percentage have been made in water--non-aqueous solvent mixtures. Izmailov and Ivanova (17) give several references concerning the activity coefficients in non-aqueous solvents. However, only one of the solvents, methanol, which is covered in these references is of interest in this research. In that particular paper, Akerlof (18) shows how the activity coefficients of the alkali metal chlorides change as the water content of methanol-water mixtures is varied. He makes no measurements in the region of pure methanol; therefore this work is of little aid in getting the activity coefficients for this non-aqueous solvent. Since experimental work is of such small quantity, possibly the activity coefficient might be calculated from theoretical considerations.

In the history of solution theory many theories relating the mean activity coefficient with the concentration of the solution have been developed. The Debye-Huckel theory (19), probably the best known, gives in its treatment the following

expression for a uni-univalent solute:

$$\log f_2 = - \frac{1.8246 \times 10^6}{(DT)^{3/2}} \left(\frac{md}{1 + .001mM_2} \right)^{\frac{1}{2}} \quad (15)$$

where D is the dielectric constant of the pure solvent, d is the density of the solution with m, molality, and M₂ is the formula weight of the solute. For the non-aqueous solution,

$$\log f_2' = - \frac{1.8246 \times 10^6}{(D'T)^{3/2}} \left(\frac{m'd'}{1 + 0.001 m'M_2} \right)^{\frac{1}{2}}. \quad (16)$$

Substituting equations (15) and (16) into equation (14)

$$\Delta F_t = \Delta F_t^{\circ} + \left(\frac{16.70 \times 10^6}{T^{\frac{1}{2}}} \right) \left[\left\{ \frac{m'd'}{(1 + 0.001 m'M_2)D'^3} \right\}^{\frac{1}{2}} - \left\{ \frac{md}{(1 + .001mM_2)D^3} \right\}^{\frac{1}{2}} \right]$$

or using the expression

$$m = \left(\frac{1000}{M_1} \right) \left(\frac{N_2}{1 - N_2} \right),$$

then

$$\Delta F_t = \Delta F_t^0 + \left(\frac{5.280 \times 10^8}{T^{\frac{3}{2}}} \right) \left[\left(\frac{d'/D'^3}{M_1 N_1 + M_2 N_2} \right)^{\frac{1}{2}} - \left(\frac{d/D^3}{M_1 N_1 + M_2 N_2} \right)^{\frac{1}{2}} \right] N_2^{\frac{1}{2}} \quad (17)$$

Equation (17) might be referred to as the "limiting law" for the transfer process since the Debye-Huckel theory is valid only for dilute solutions. In the very dilute region d' and d are approximately equal to the densities of the solvents, and $M_2 N_2$ is very small as compared with the product of $M_1 N_1$. Therefore, in the region of high dilution ΔF_t versus $N_2^{\frac{1}{2}}$ should be a straight line. This function is plotted for the experimental data in Figures 4 through 6, Appendix II.

Even the relatively simple Debye-Huckel theory, which is applicable only in a very dilute region, gives an expression that includes various parameters which are dependent on the concentration. More involved theories concerning the activity coefficients would probably include still more concentration dependent parameters. Thus, in this research only the Debye-Huckel treatment has been applied to the transfer process. Before ΔF_t^0 can be obtained from experimental measurements and activity coefficients, further work will have

to be done on the theoretical and experimental aspects of the activity coefficients in electrolytic solutions.

ΔF_t° can be obtained from experimental work by extrapolation of the ΔF_t values to extreme dilution. Probably the best way to perform such an extrapolation would be to use a plot of ΔF_t versus $N^{\frac{1}{2}}$ and to extrapolate to extreme dilution using the straight line portion of the experimental curve. Measurements such as those obtained from cells being connected "back-to-back" have to be made in rather concentrated solutions, so undoubtedly only an approximate value of ΔF_t° can be obtained from experimental results.

One further word should be said concerning the relationship of E_t , the electromotive force of transfer, with the individual standard potentials of the cells being connected "back-to-back." Since

$$\Delta F_t = -nQE_t$$

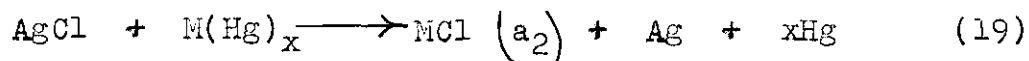
where n is the electrochemical valency (20), then using equation (14),

$$E_t = E_t^{\circ} - \frac{2RT}{nq} \ln \frac{f_2}{f_1}$$

where E_t° is the electromotive force of transfer for the hypothetical solutions. In this research n is equal to one and the reactions which take place in each cell unit are:



for the non-aqueous solution and



for the aqueous solution. In the aqueous solution the electromotive force of the reaction is represented by

$$E = E^\circ - \frac{RT}{Q} \ln a_2(m)$$

where $a_2(m)$ is the activity of the solute based on the molal scale. Similarly for the non-aqueous case

$$-E' = -E^{\circ'} + \frac{RT}{Q} \ln a'_2(m).$$

E° and $E^{\circ'}$ are the molal standard electrode potentials for the aqueous and non-aqueous solutions, respectively. Adding the reactions (18) and (19) produces reaction (1) and the equation

$$E_t = E - E' = E^\circ - E^{\circ'} - \frac{RT}{Q} \ln \frac{a_2(m)}{a'_2(m)}. \quad (20)$$

Since

$$a_2(m) = (m \gamma_{\pm})^2,$$

$$m = \left(\frac{N_2}{1 - N_2} \right) \frac{1000}{M_1}$$

and

$$f_2 = \gamma_{\pm} \left(1 + \frac{kM_1m}{1000} \right) ,$$

then

$$\gamma_{\pm} = f_2 (1 - N_2)$$

when k is equal to one. These equations lead to

$$\ln \frac{a_2(m)}{a_2'(m)} = 2 \ln \frac{M_1'}{M_1} + 2 \ln \frac{f_2}{f_2'} . \quad (21)$$

Substituting equation (21) into equation (20), the following equation is obtained:

$$E_t = E^{\circ} - E^{\circ'} - \frac{2 RT}{Q} \ln \frac{M_1'}{M_1} + \ln \frac{f_2}{f_2'} \quad (22)$$

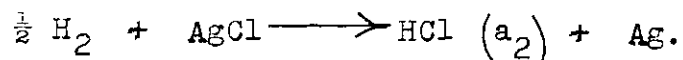
which makes

$$E_t^{\circ} = E^{\circ} - E^{\circ'} - \frac{2 RT}{Q} \ln \frac{M_1'}{M_1} . \quad (23)$$

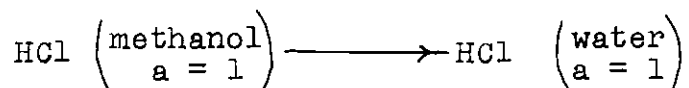
Equation (22) relates the electromotive force of transfer, E_t , for any concentration to the standard electrode potentials. Thus, if the standard electrode potentials are known for a reaction both in water and in a non-aqueous solvent, ΔF_t° can be determined by using equation (23), calculating

the E_t° , and finally multiplying this quantity by -23060 . This final step will produce ΔF_t° in calories per mole.

A large amount of experimental data on the standard electrode potentials of reactions in water have been determined. Only a relatively small amount of data have been gathered for similar reactions in non-aqueous solvents. One of the major reactions which has been studied in non-aqueous solvents is the reaction:



Obtaining the standard electrode potentials of this reaction in methanol and water from Robinson and Stokes (21), ΔF_t° has been calculated for the reaction:



and was found to be -4681 calories per mole at 25°C . The experimental value is given by Gurney (22) and is -4660 calories per mole. Values of ΔF_t° have been calculated for the HCl transfer from methanol to water at several temperatures using the electromotive force data found in the literature. These values are found in Appendix III.

This section was initiated by a brief look at the process illustrated by reaction (10), which gave a pathway for the investigation of the relationship of the free energy of

transfer to certain other quantities. These quantities have included the mean rational activity coefficients and the standard electrode potentials. This section has also provided a "limiting law" expression for the transfer process. A partial look at the nature of ΔF_t^0 was presented. This quantity and the entropy and enthalpy of transfer will be studied in the next section.

The Transfer Process from a Solvation Viewpoint

The second process illustrated by reaction (11) involves removing the ion from the non-aqueous solution, placing it in a vacuum, and finally, plunging the ion into the aqueous solution. The first part of the process, part I, requires energy to be put into the system; the second part, part II, has energy being released. The ions require energy when being removed from a solvent and liberate energy when being placed in a solvent because of their interactions with the solvent molecules. All solvents, being dielectrics, will have a dielectric constant, D , greater than one, the dielectric constant of a vacuum. The energy of the electric field set up by the ion in the solvent is $1/D$ less than the field it produces in a vacuum. This extra energy, which is no longer associated with the solvated ion's field, has been lost to the solvent molecules. Thus, in order to remove the ion from a solvent, extra energy must be supplied to create

a field of greater energy in the vacuum. Similarly, the reverse situation finds the ion as it goes from the vacuum into the solvent losing energy as its field strength is reduced.

The process illustrated by reaction (11) requires two solvation phases. Since solvation is the major factor in the transfer process, the physical nature of the solvation process should be briefly pointed out. As an ion enters a polar solvent--polar solvents are the only type of solvents being used in this research--the ion finds itself surrounded by many associated solvent molecules. These associated molecules have set up throughout the liquid a quasi-crystalline structure. In close proximity to the ion there exists a field of great magnitude; and those solvent molecules that are greatly influenced by this field will reorient themselves in accordance with the nature of the charge on the ion. This reorientation to form ion-dipole bonds will cause the breaking and bending of some dipole-dipole bonds.

Considering the over-all process which is represented either by the sum of reactions I and II in process (11) or by reaction (1), the total energy of the system can be increased or decreased after such a reaction occurs. As Guggenheim (23) points out, the total energy change for a system is a more difficult concept to deal with than is the free energy change for the system. Thus, initially, the free energy of

transfer will be discussed.

It should be pointed out that the primary interest here will be focused on the interaction of the ion with the solvent molecules. The free energy, entropy, and enthalpy of transfer mentioned in this section are the quantities found at extreme dilution.

The free energy change produced in phase I and phase II of reaction (11) can be studied by the application of Born's theory (24). Born's theory gives a mathematical expression with several limitations for the free energy change for the transfer of an ion from a vacuum to a solvent with a dielectric constant, D. The expression for this change is

$$\Delta F_B = - \frac{Nz^2 e^2}{2r} \left(1 - \frac{1}{D} \right)$$

where r is the radius of the ion, ze is the charge on the ion, and N is Avogadro's number. Thus, for the situation shown by part I of equation (11)

$$\Delta F_I = + \frac{Ne^2}{2r} \left(1 - \frac{1}{D} \right)$$

and by II,

$$\Delta F_{II} = - \frac{Ne^2}{2r} \left(1 - \frac{1}{D} \right).$$

The total free energy change would be:

$$\Delta F_I + \Delta F_{II} = \frac{Ne^2}{2r} \left(\frac{1}{D} - \frac{1}{D'} \right). \quad (31)$$

According to equation (31) the free energy of transfer, exclusive of any interionic effects, should be equal to the quantity on the right hand side of the equation. If D is greater than D' , which is normally the case, then the total free energy change represented by equation (31) is a negative quantity. Born's equation also implies that as the radius of the ion is increased the negative free energy of transfer should decrease. This implication as Gurney shows, is not what is found when a study is made of the transfer of the alkali chlorides from water-methanol mixtures to pure water. In Gurney's research the negative free energy of transfer was found to increase as the radius of the metal ion increased in contradiction to what might be predicted from the Born equation.

What is producing this apparent contradiction between experiment and theory? Before this question can be answered, a few brief statements should be made concerning the structure of water and the entropy of solvation.

Several recent authors (25) have used what might be classified as a refined tetrahedral model for the structure of water. Because of its polar nature the water molecule is

considered to be a quadrupole with its four charges residing at the corners of an approximate tetrahedron. This tetrahedral charge arrangement of a central water molecule controls the positions of the four neighboring water molecules. By such arrangements being set up throughout liquid water a liquid structure of some order is produced. What happens to the structure of water when it comes under the influence of a strong ionic field?

When an ion is placed into solution three possible situations concerning the structure of the water can arise: first, the structure can be broken down; second, the structure can be built up or strengthened; and third, the structure can undergo no change. In water at room temperature there are ions which can perform the first two possibilities, i. e., cause the structure of water to be built up or broken down.

Gurney (26) has given a summary of the experimental evidence for the order-producing and order-destroying nature of ions in water. Gurney also presents a model in order to explain this phenomenon. In brief, the model which he presents is the following: An uncharged particle is placed into the water. This particle is able to have a small charge placed on it and then have this charge increased. While the charge is very small, the field which it produces will have only a slight effect on the water molecules; i. e., no

breaking or bending of solvent bonds takes place. The charge on the particle is slowly increased, and at a certain value the solvent molecules which are near the particle find their solvent bonds broken. At this stage the molecules are easily disturbed by thermal motions since neither the ion nor neighboring water molecules have enough control to hold them in place. As the charge is increased further, the solvent molecules orient themselves properly around the charged particle. The first stage, where the charge is so small that it has only a slight influence on the solvent molecules, has not yet been found to occur with ordinary ions. The second situation, where neither the ion nor the neighboring solvent molecules have the dominant influence on a particular solvent molecule, is considered to be the order-destroying ion. In water, large ions, such as the cesium ion and bromide ion, with a single charge, are found to be of the order-destroying type; and small ions, such as the lithium and sodium ions, are of the order-producing type.

The order-producing, order-destroying nature of ions in non-aqueous solvents is not too well-known. An indication of this nature can be obtained from the change in the viscosity of the solvent after dissolving the solute in the solvent. If the viscosity is increased, the solute particles have an over-all order-producing effect; if the viscosity is decreased, the solute particles are considered to have an

over-all order-destroying effect.

In the derivation of Born's equation no consideration was given to the order-producing, order-destroying nature of ions on the solvent. As Gurney points out in his discussion of the transfer of the alkali chlorides from methanol-water mixtures to water, this effect can account for the inconsistency between the experimental values of the free energy of transfer and the values obtained from the Born theory. If the ions in the non-aqueous solution are order-producing and in the aqueous solution are order-destroying, then an increase in entropy will take place during the transfer of ions from the non-aqueous solution to the aqueous solution. Previously it was shown that such a process occurred with a negative free energy change; thus by

$$\Delta F_t^{\circ} = \Delta H_t^{\circ} - T\Delta S_t^{\circ}, \quad (32)$$

an increase in entropy means a corresponding increase in the negative free energy. Therefore, in order to understand fully the transfer process, some knowledge of both the entropy and the free energy of transfer is needed.

Since this research deals with a process that occurs in liquids, there is only a slight change in the volume of the system. This situation makes the total energy release or absorption approximately equal to the enthalpy of transfer.

By equation (32) it is seen that ΔH_t° is a function of ΔF_t° and ΔS_t° or it is a function of the potential energy of the system and the order-producing, order-destroying nature of the system. If the ΔS_t° is a large positive quantity, then ΔH_t° can have a sign opposite to that of ΔF_t° .

This section was presented in order to point out the major features of the transfer process from a point of view which considered only the ion-solvent interaction. The relation between the measured free energy of transfer and the free energy calculated from Born's theory was given along with a possible explanation of the disagreement which can arise between the two. The order-producing, order-destroying nature of ions was related to the entropy of transfer. The total energy of the transfer process was found to be approximately equal to the enthalpy of transfer.

The next chapter will relate the ideas presented in the two sections of this chapter with the experimental data obtained.

CHAPTER VI

DISCUSSION OF RESULTS

In Chapter V, the theoretical aspects of the transfer process were briefly covered. Use of the theoretical ideas presented could possibly provide some evaluation of the experimental data. This chapter will attempt to explain the data given in both tabular and graphical form in Appendix II. Data are given for the transfer of sodium chloride and potassium chloride from methanol to water and from glycol to water. The values of ΔF_t , ΔS_t , and ΔH_t are given in the tables for various mole fractions of solutes.

Initial observation of the data for the transfer of sodium chloride and potassium chloride from methanol to water shows that the free energy of transfer of both is negative. It is observed, also, that the values for potassium chloride have larger negative values than those for sodium chloride. This relationship is similar to the one shown by Gurney (1) for the transfer of alkali chlorides from methanol-water mixtures to water. Even though the entropy data for sodium chloride are only approximate, the entropy is found to be positive and of the order of twenty to thirty entropy units. The entropy data for potassium chloride are too inexact to

make any definite statement about them, other than to observe that the entropy is probably positive. For sodium chloride, ΔH_t is opposite in sign to the ΔF_t , which is to be expected. Table 6 gives the first degree equations for ΔF_t as a function of $N_2^{\frac{1}{2}}$ at various temperatures. From these equations the intercept should give an empirical value of ΔF_t° at the different temperatures. These values of ΔF_t° increase with temperature as would be expected.

The data for the transfer of potassium chloride and sodium chloride from glycol to water cover a wider concentration range than do the data for the transfer of alkali metal chlorides from methanol to water. The negative free energy of transfer for potassium chloride is slightly less than that given for sodium chloride. The entropy of transfer for the sodium chloride is positive and of the order of ten entropy units. Similar data for potassium chloride are also positive, and the magnitude is about the same as for sodium chloride. The ΔH_t for both solutes is opposite in sign to the ΔF_t and larger in absolute value. The ΔF_t° obtained from the ΔF_t versus $N_2^{\frac{1}{2}}$ curve increases with temperature. The first and third curves for the potassium chloride data have the same slope. All of the curves for the sodium chloride have very nearly the same value for their slopes.

Use of the same solute, but for the transfer from different non-aqueous solvents to water, shows that the ΔF_t for methanol is three to four times larger than the same quantity for the glycol transfer. The glycol transfer also gives a much smaller change in entropy. The enthalpy change for the glycol transfer is possibly smaller than for the methanol transfer; however, the data are not accurate enough to make any definite comparison between the two transfers.

One example is given for the calculation of the ΔF_t for the transfer of hydrogen chloride from methanol to water. Only the data at extreme dilution were used for the calculation in this case. The negative free energy is shown to increase with temperature as does the entropy of transfer. $-\Delta H_t^\circ$ decreases with temperature.

All of the differences in the data produced are primarily controlled by the differences in the disorder-order producing nature of the solute. As Gurney (1) pointed out, the ions of the alkali metal chlorides, in going from the methanol to water, produce a rather large amount of entropy. This large amount of entropy makes for a larger value of the free energy of transfer. For the glycol solutions the entropy is less, and, therefore, the free energy is less. The Born theory, however, would predict that the free energy of transfer for both non-aqueous cases should be approximately equal since the dielectric constant of methanol (32.6 at 25°C) and

that of glycol (37.7 at 25°C) are very close.

Potassium chloride has a larger negative free energy of transfer than sodium chloride, whereas the opposite is true for the glycol solutions. This statement might be restated to say that Born's theory holds better for the glycol transfer than for the methanol transfer. Such a statement may be true since the entropy term is smaller for the glycol transfer and this smallness makes the order-disorder influence on Born's theory less than in the methanol case.

Before the discussion can proceed some calculations should be made using Born's theory. For the methanol

$$\Delta F_t^\circ = -2.98 \frac{r_{MCl}}{r_M r_{Cl}} \text{ in kilocalories per mole}$$

at 25°C, where r_{MCl} in Angstrom units is the sum of the radius of the metal ion, r_M , and the radius of the chloride ion, r_{Cl} . Similarly for the glycol

$$\Delta F_t^\circ = -2.29 \frac{r_{MCl}}{r_M r_{Cl}} \text{ in kilocalories per mole at } 25^\circ \text{C.}$$

Assuming that the ionic radii are always constant no matter what solvent the ions are in,

$$\frac{\Delta F_t^\circ \text{ for methanol}}{\Delta F_t^\circ \text{ for glycol}} = \frac{2.98}{2.29} = 1.3.$$

This expression means that for a given solute transfer from methanol to water and from glycol to water, the free energy of transfer of methanol is 1.3 times that of glycol. Data from the sodium chloride experiment show that the value for methanol is 3.2 times that for glycol. From a comparison of different solutes in the same solvent, the following expression is obtained:

$$\frac{\Delta F_t^{\circ} \text{ for KCl}}{\Delta F_t^{\circ} \text{ for NaCl}} = \frac{r_{\text{KCl}}}{r_{\text{K}}} \times \frac{r_{\text{Na}}}{r_{\text{NaCl}}} .$$

Substitution of the values of the radii given by Latimer (27) for water gives the ratio of 0.91, whereas for glycol the experimental value is 0.95 and for methanol it is greater than one.

Consideration of the applicability of Born's equation to the experimental values of ΔF_t° shows that Born's theory applies to some degree to the glycol transfer; but, as has been pointed out, the theory does not fully explain the values obtained in the methanol transfer. This fact is partially evident from the calculations presented above since, for the glycol, the ratio of the free energy of transfer for potassium chloride and for sodium chloride is very near to the theoretical value. The ratio could be even closer to or farther away from the theoretical value; for it is assumed that the radius of each ion is the same no matter which solvent it is in.

This assumption would probably be invalid if ratios were not involved see Amis and Stern (28) . Since ratios are being used, only a major change in r , which would not be expected, would affect the theoretical ratio to any great extent.

An explanation for the difference between the glycol and the methanol transfers is based on the order-disorder nature of the solute ions. Glycol and water at room temperature are both not too far above their respective melting points. (The melting point of glycol is -12°C .) However, for methanol and water at room temperature, methanol is about five times higher above its melting point than is water. (The melting point of methanol is -98°C .) Thus, an ion in methanol is in a solvent that is considerably more disordered, so practically the only thing the ion can do is produce order. In glycol the ion is surrounded with a solvent which has considerably more order than is the situation in methanol. For this situation the ion can either produce a small amount of order or even destroy some of the order which still exists. The ion in water would find a similar situation to that found in the glycol. Since the glycol and water are similar, the order-producing nature of the ions would have a smaller influence on the transfer process, and the Born theory might apply. The methanol transfer would be just the opposite and Born's theory would not apply. By the use of such compounds as lithium chloride, cesium, and rubidium chloride in these

solvents more could evidently be learned about the nature of the transfer process. The lithium, cesium, and rubidium ions would be the extreme cases for consideration of size and possibly of order-disorder producing effects.

The thallium (I) chloride transfer from glycol to water, in preliminary studies, was found to give a positive value for the free energy of transfer in the concentration region of 1×10^{-5} mole fraction units. Only a few values were obtained for thallium (I) chloride and these with rather poor precision. However, a positive value for ΔF_t was observed, and this value is in direct disagreement with Born's theory. This disagreement might be explained by noticing that Born's theory was derived on the assumption that only Coulombic forces were important in a structureless dielectric medium. When an ion, such as the thallium (I) ion, is investigated, quantum-mechanical forces must be considered since thallium (I) is an ion with a non-inert gas type structure. The existence of these forces may lead to some rather unexpected values of the free energy of transfer. More work on this solute is planned.

Some statements should be made concerning the extrapolation of the curve, ΔF_t versus $N_2^{\frac{1}{2}}$. This extrapolation, as was shown previously, is what might be expected from the Debye-Huckel theory. It appears from the experimental measurements that the Debye-Huckel theory is valid over a

wider concentration range for this type of measurement than is normally the case. This fact could only be proved by making very accurate measurements in the very dilute region and extending these measurements out to the more concentrated region. However, this validity of this long-range concentration might be expected. Since the term $\ln f_2/f_2'$ is the expression that is causing the variation in ΔF_t with concentration, and since the Debye-Huckel theory is being used to calculate the value of two activity coefficients, possibly some of the assumptions involved in the use of the Debye-Hickel equation are partially removed in the subtraction of various quantities.

A brief look at the conductance measurements made on potassium chloride and sodium chloride in methanol and glycol indicates that the dissociation constants obtained by Shedlovsky's method are of the order of 0.2 to 0.3. Also, the values of Λ_0 for the methanol solutions are slightly less than the values obtained by Schiff and co-workers. This latter statement is to be expected when Shedlovsky's method is used, as Fuoss (29) points out. The dissociation constants may be considerably in error. Further study and calculations are needed to give a better picture of the dissociation of the solutes in the non-aqueous solvents. One unusual feature is the fact that both methanol and glycol give about the same

dissociation constant, but sodium chloride, for example, is approximately eight times more soluble in glycol than in methanol. Until more research has been done in this area it is assumed that none of the ΔF_t is due to a difference in the nature of ionization of the solute in the water and the non-aqueous solvent.

The assumption that ionization is nearly complete in all the solvents used is probably valid for the region where the "limiting law" appears to hold. At the higher concentrations ΔF_t varies only slightly with concentration. In this latter region ΔF_t includes a large amount of interionic effects. Possibly to understand more fully what is happening in this concentrated region, some knowledge of the dissociation constant is needed.

Basically in this chapter an attempt has been made to coordinate the theoretical ideas of the previous chapter with the experimental values obtained. The experimental values have been compared with the values which might be obtained from Born's theory. Any disagreement which resulted between the calculated and experimental values has been resolved by use of the ordering and disordering nature of the ions on the solvent.

CHAPTER VII

SUMMARY OF RESULTS

A brief outline of some of the major items which have been covered by this research should be given. The major objective of this research was to study reaction (1). Some of the major points which have been brought out by this research are the following:

(1) The electromotive force of transfer is a function of the activity coefficients of the solutions being used.

(2) The "limiting law" for the transfer process expresses ΔF_t as a function of $N_2^{\frac{1}{2}}$.

(3) The Born theory does not completely describe the transfer process.

(4) The deviations between the experimental values of ΔF_t and those calculated by use of the Born theory are best explained by considering the order-disorder producing nature of the solute's ions on the solvent.

(5) The ordering-disordering nature of ions can be evaluated from the entropy of transfer.

CHAPTER VIII

RECOMMENDATIONS

Only a beginning in the study of the transfer process has been presented in this thesis. There are two specific points of interest which should be investigated if further study on the transfer process is to be carried out. The first point is to investigate the preparation of an alkali metal electrode that can operate accurately at low concentrations in aqueous and non-aqueous solutions.

The second point is the measurement of the transfer potential of a solute transferring from a non-aqueous solution to an aqueous solution when both solutions are at different temperatures. The difference between the temperature of each solution and the melting point of its respective solvent should be equal. Possibly from a study such as this the nature of the entropy of transfer could be investigated further. In this situation the entropy would possibly be small since the amount of order to be destroyed by an ion in each solvent is equal. That is, the entire transfer process would gain as much entropy in the removal of the ion from the non-aqueous solution as it loses when the ion enters the aqueous solution.

More research should be carried out on various solvents, especially acidic and basic ones. Many different solute-solvent combinations might be studied by application of the technique of the transfer process. The transfer of a solute from a non-aqueous solvent to water offers another method which, when sufficient experimental data are accumulated, may add immeasurably to the knowledge of electrolytic solutions.

APPENDICES

APPENDIX I

SYMBOLS USED

The following is a list of the symbols used in this thesis:

D	dielectric constant
E_t	electromotive force of transfer
E_t°	electromotive force of transfer for the solute from the hypothetical non-aqueous solution to the hypothetical aqueous solution
ΔF_t	free energy of transfer
$\Delta F_A, \Delta F_B, \Delta F_C$	free energy terms (p. 30) (p. 31)
ΔF_t°	free energy of transfer for the solute from the hypothetical non-aqueous solution to the hypothetical aqueous solution
$\Delta F_t^{\circ\circ}$	free energy of transfer at extreme dilution
F_2°	free energy of a hypothetical solution
ΔH_t	enthalpy of transfer
ΔH_t°	enthalpy of transfer at extreme dilution
K	dissociation constant
M_1	molecular weight of solvent
M_2	formula weight of the solute
N_2	mole fraction
N	Avogadro's number
P	pressure
Q	Faraday's constant

R	gas constant
ΔS_t	entropy of transfer
ΔS_t°	entropy of transfer at extreme dilution
T	absolute Temperature
W_1	weight of solvent
W_2	weight of solute
Y_0	actual value of E_t at a mole N_2
Y^*	value of E_t calculated at N_2 by using the fourth degree equation
a =	activity of the solvent
a_2	activity of the solute
a, b, c, d, e	constants (p. 24)
d	density of solution
f_2	mean rational activity coefficient
f, g, h	constant (p. 25)
m	molality
n	electrochemical valency
r	radius of the ion
r_M, r_{Cl}, r_{MCl}	r_{MCl} is the sum in Angstrom units of the radius of the metal ion, r_M , and the radius of chloride ion, r_{Cl}
Ze	charge on an ion
γ_{\pm}	molal activity coefficient
\wedge	equivalent conductance
\wedge°	equivalent conductance at inf. diln.

All the symbols which have a prime notation are for the non-aqueous solutions.

APPENDIX II

EXPERIMENTAL POTENTIOMETRIC DATA

In this section are found all of the experimental data obtained for the transfer process. In tables 2, 4, and 5, is given, for each temperature at which measurements were made, a fourth degree equation with the electromotive force of transfer, E_t , as a function of the mole fraction, N_2 . With each equation is given its standard deviation, $\sum (Y_0 - Y^*)^2$, where Y_0 is the actual value of E_t at a mole fraction, N_2 , and Y^* is the value of E_t calculated at N_2 by using the fourth degree equation.

In tables 6, 8, and 9, are presented the free energy, entropy, and enthalpy of transfer at various mole fractions. In these tables is shown, for each temperature, an equation expressing ΔF_t as a function of $N_2^{\frac{1}{2}}$. This equation was derived using only those values of ΔF_t which appeared in Figures 4, 5, and 6, to lie along a straight line.

Table 2. Electromotive Force Data for the Transfer of Sodium Chloride from Methanol to Water.

T = 25°C		T = 30°C		T = 35°C	
N ₂ x 10 ³	E _t in volts	N ₂ x 10 ³	E _t in volts	N ₂ x 10 ³	E _t in volts
0.5011	0.1941	0.5033	0.1965	0.5027	0.2036
.9984	.1676	1.007	.1895	1.004	.1936
1.003	.1861	2.997	.1789	2.989	.1838
2.494	.1749	3.006	.1797	4.799	.1779
3.015	.1733	5.020	.1742	5.930	.1764
5.005	.1691	6.023	.1721		
5.991	.1667				

$$\sum (y_o - y^*)^2$$

25°C E_t = 0.2039 - 22.36N₂ + 5.933 x 10³N₂² - 7.229 x 10⁵N₂³ + 3.041 x 10⁷N₂⁴; 1.08 x 10⁻⁶
 30°C E_t = 0.2070 - 25.04N₂ + 9.083 x 10³N₂² - 1.563 x 10⁶N₂³ + 9.719 x 10⁷N₂⁴; 3.36 x 10⁻⁷
 35°C E_t = 0.2204 - 41.89N₂ + 1.848 x 10⁴N₂² - 3.605 x 10⁶N₂³ + 2.477 x 10⁹N₂⁴; 0.0

Table 3. Electromotive Force Data for the Transfer of Potassium Chloride from Methanol to Water.

T = 25°C		T = 30°C		T = 35°C	
$N_2 \times 10^3$	E_t in volts	$N_2 \times 10^3$	E_t in volts	$N_2 \times 10^3$	E_t in volts
0.4958	0.2411	0.5044	0.2429	0.5024	0.2424
.9922	.2175	1.004	.2197	1.006	.2321

Table 4. Electromotive Force Data for the Transfer of Sodium Chloride from Ethylene Glycol to Water.

T = 25°C		T = 30°C		T = 35°C	
N ₂ x 10 ²	E _t in milli-volts	N ₂ x 10 ²	E _t in milli-volts	N ₂ x 10 ²	E _t in milli-volts
0.05060	56.92	0.05012	59.31	0.05008	61.87
.1020	50.80	.05016	58.16	.05022	60.41
.2550	46.70	.09972	54.63	.1001	55.10
.3037	46.52	.1009	52.57	.1011	56.28
.5019	43.44	.3000	48.32	.3001	50.46
.7543	41.55	.5002	45.19	.5020	48.27
1.001	40.53	.5043	45.90	.5083	48.38
1.018	41.11	.7537	44.00	.7532	45.88
1.303	40.00	1.025	42.69	1.003	44.37
1.501	39.27	1.309	41.32	1.307	43.34
1.880	37.50	1.503	40.03	1.509	42.49
2.504	36.53	1.879	38.94	1.870	40.16
4.005	34.53	2.523	37.10	2.506	38.96
		4.045	35.90	2.518	39.77
				4.001	37.70

Table 4 (Continued).

	$\sum (Y_o - Y^*)^2$
$25^\circ\text{C } E_t = 0.05611 - 3.866N_2 + 331.1N_2^2 - 1.195 \times 10^4 N_2^3 + 1.437 \times 10^5 N_2^4$	$: 1.71 \times 10^{-5}$
$30^\circ\text{C } E_t = 0.05807 - 3.973N_2 + 327.2N_2^2 - 1.161 \times 10^4 N_2^3 + 1.365 \times 10^5 N_2^4$	$: 2.05 \times 10^{-5}$
$35^\circ\text{C } E_t = 0.06101 - 3.788N_2 + 294.5N_2^2 - 1.006 \times 10^4 N_2^3 + 1.175 \times 10^5 N_2^4$	$: 2.28 \times 10^{-5}$

Table 5. Electromotive Force Data for the Transfer of Potassium Chloride from Ethylene Glycol to Water.

T = 20°C		T = 25°C		T = 30°C	
N ₂ x 10 ²	E _t in milli-volts	N ₂ x 10 ²	E _t in milli-volts	N ₂ x 10 ²	E _t in milli-volts
0.05041	50.17	0.05150	53.45	0.05106	54.55
.1017	46.76	.09991	48.20	.09989	50.43
.2995	42.49	.3001	43.89	.3010	46.65
.7013	38.54	.6951	41.16	.6951	43.40
1.089	37.76	.7058	41.40	1.089	41.17
1.090	37.88	1.087	38.52	1.977	38.60
2.018	35.00	1.969	37.72		

$$\sum (Y_o - Y^*)^2$$

$$20^\circ\text{C } E_t = 0.05200 - 5.042N_2 + 708.0N_2^2 - 4.370 \times 10^4 N_2^3 + 9.382 \times 10^5 N_2^4 : 1.06 \times 10^{-6}$$

$$25^\circ\text{C } E_t = 0.05598 - 7.626N_2 + 1447N_2^2 - 1.143 \times 10^5 N_2^3 + 2.948 \times 10^6 N_2^4 : 3.73 \times 10^{-6}$$

$$30^\circ\text{C } E_t = 0.05645 - 5.792N_2 + 998.1N_2^2 - 7.517 \times 10^4 N_2^3 + 1.881 \times 10^6 N_2^4 : 2.26 \times 10^{-6}$$

Table 6. Free Energy, Entropy, and Enthalpy of Transfer for Sodium Chloride from Methanol to Water.

		T = 25°C			T = 30°C			T = 35°C		
$N_2 \times 10^3$	$N_2^{\frac{1}{2}}$	ΔF_t	ΔS_t	ΔH_t	ΔF_t	ΔS_t	ΔH_t	ΔF_t	ΔS_t	ΔH_t
0.5	0.02236	-4476	+0.1	-4400	-4531	22	2100	-4695	44	8800
1.0	.03162	-4307	10	-1500	-4370	16	400	-4464	22	2300
3.0	.05477	-3993	32	5430	-4133	24	3300	-4237	17	1100
5.0	.07071	-3899	65	15000	-4017	30	5200	-4083	-4	-5300
6.0	.07746	-3842	67	17000	-3968	37	7200	-4072	5	-2600

$$25^\circ\text{C}: \Delta F_t = -4599 + 10010 N_2^{\frac{1}{2}}$$

$$30^\circ\text{C}: \Delta F_t = -4636 + 8763 N_2^{\frac{1}{2}}$$

$$35^\circ\text{C}: \Delta F_t = -4736 + 8914 N_2^{\frac{1}{2}}$$

Table 7. Free Energy, Entropy, and Enthalpy of Transfer for Potassium Chloride from Methanol to Water.

		T = 25°C			T = 30°C			T = 35°C		
$N_2 \times 10^3$	$N_2^{\frac{1}{2}}$	ΔF_t	ΔS_t	ΔH_t	ΔF_t	ΔS_t	ΔH_t	ΔF_t	ΔS_t	ΔH_t
0.5	0.02236	-5560	18	-200	-5610	2	-5000	-5580	-14	-9900
1.0	.03162	-5010	-14	-9200	-5580	34	+5200	-5350	82	20000

Table 8. Free Energy, Entropy, and Enthalpy of Transfer for Sodium Chloride from Ethylene Glycol to Water.

		T = 25°C			T = 30°C			T = 35°C		
$N_2 \times 10^2$	$N_2^{\frac{1}{2}}$	ΔF_t	ΔS_t	ΔH_t	ΔF_t	ΔS_t	ΔH_t	ΔF_t	ΔS_t	ΔH_t
0.05	0.02236	-1251	+14	2800	-1313	11	2100	-1364	9	1400
.1	.03162	-1212	13	2700	-1273	11	2200	-1326	10	1700
.3	.05477	-1038	11	2100	-1143	11	2300	-1200	12	2400
.5	.07071	-1006	9	1800	-1056	11	2200	-1112	12	2500
.75	.08660	- 949	7	1200	- 991	10	1900	-1044	12	2600
1.0	.1000	- 923	6	1000	- 960	8	1600	-1007	10	2200
1.3	.1140	- 914	5	500	- 944	7	1300	- 987	10	2100
1.5	.1225	- 912	4	200	- 938	7	1100	- 979	10	2000
1.8	.1342	- 904	3	-100	- 926	6	900	- 966	10	2100
2.5	.1581	- 826	0.4	-700	- 846	7	1500	- 902	15	3700
4.0	.2000	- 795	-3	-1600	- 807	7	1500	- 870	18	1400

$$25^\circ\text{C}: \Delta F_t = -1369 + 5131 N_2^{\frac{1}{2}}$$

$$30^\circ\text{C}: \Delta F_t = -1430 + 5155 N_2^{\frac{1}{2}}$$

$$35^\circ\text{C}: \Delta F_t = -1481 + 5113 N_2^{\frac{1}{2}}$$

Table 9. Free Energy, Entropy, and Enthalpy of Transfer for Potassium Chloride from Ethylene Glycol to Water.

$N_2 \times 10^2$	$N_2^{\frac{1}{2}}$	$T = 20^\circ\text{C}$			$T = 25^\circ\text{C}$			$T = 30^\circ\text{C}$		
		ΔF_t	ΔS_t	ΔH_t	ΔF_t	ΔS_t	ΔH_t	ΔF_t	ΔS_t	ΔH_t
0.05	0.02236	-1145	17	3800	-1211	10	1600	-1240	2	-600
.1	.03162	-1098	10	1700	-1145	9	1600	-1189	9	1400
.3	.05477	- 971	27	6800	- 998	18	4300	-1065	9	1700
.7	.08367	- 891	14	3200	- 954	11	2400	-1004	9	1600
1.09	.1044	- 871	-2	-1400	- 886	8	1400	- 948	17	4200
2.0	.1414	- 803	+8	1500	- 850	11	2400	- 911	14	3200

$$20^\circ\text{C}: \Delta F_t = -1267 + 5391 N_2^{\frac{1}{2}}$$

$$25^\circ\text{C}: \Delta F_t = -1354 + 6529 N_2^{\frac{1}{2}}$$

$$30^\circ\text{C}: \Delta F_t = -1360 + 5391 N_2^{\frac{1}{2}}$$

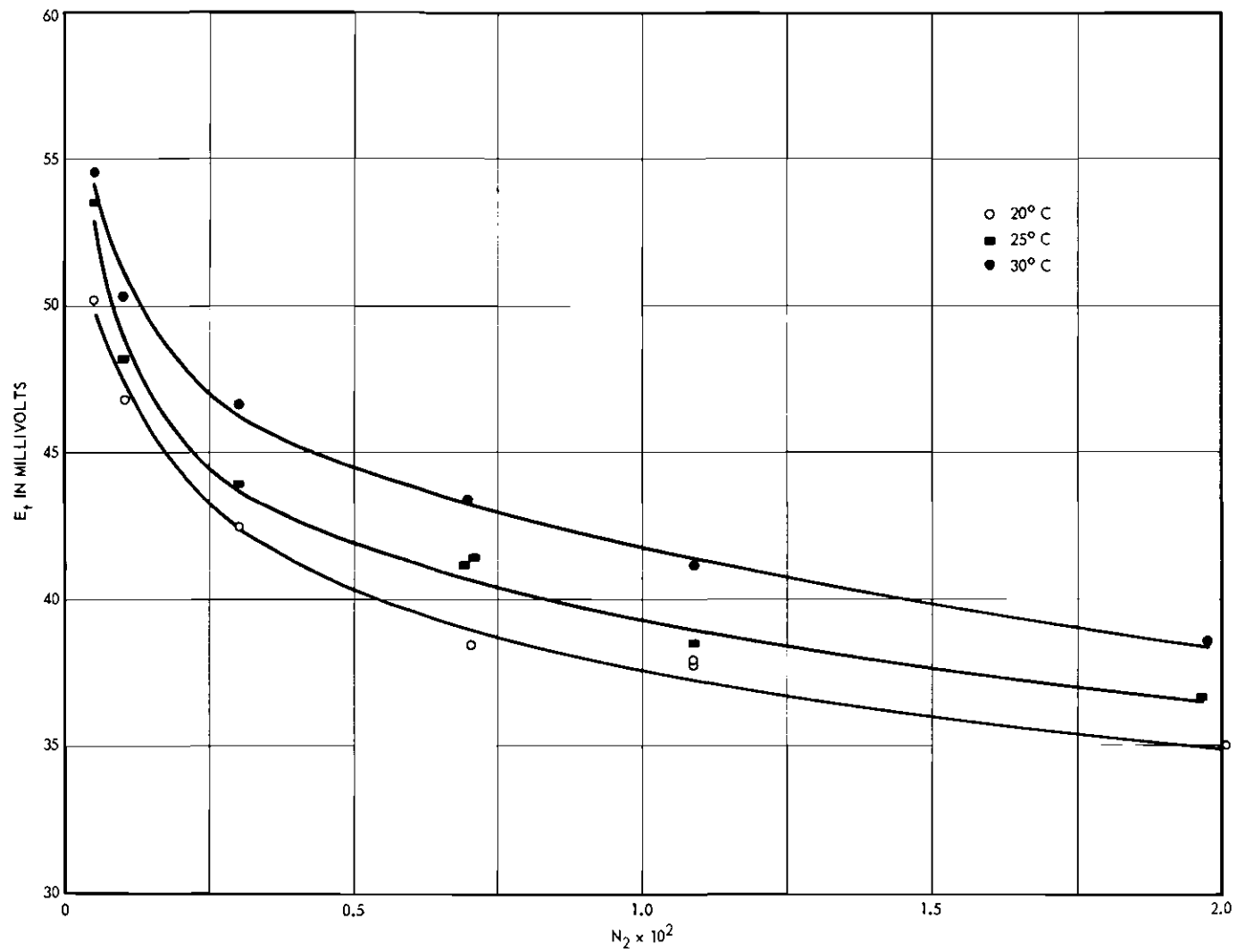


Figure 1. Electromotive Force Data for the Transfer of Potassium Chloride from Ethylene Glycol to Water.

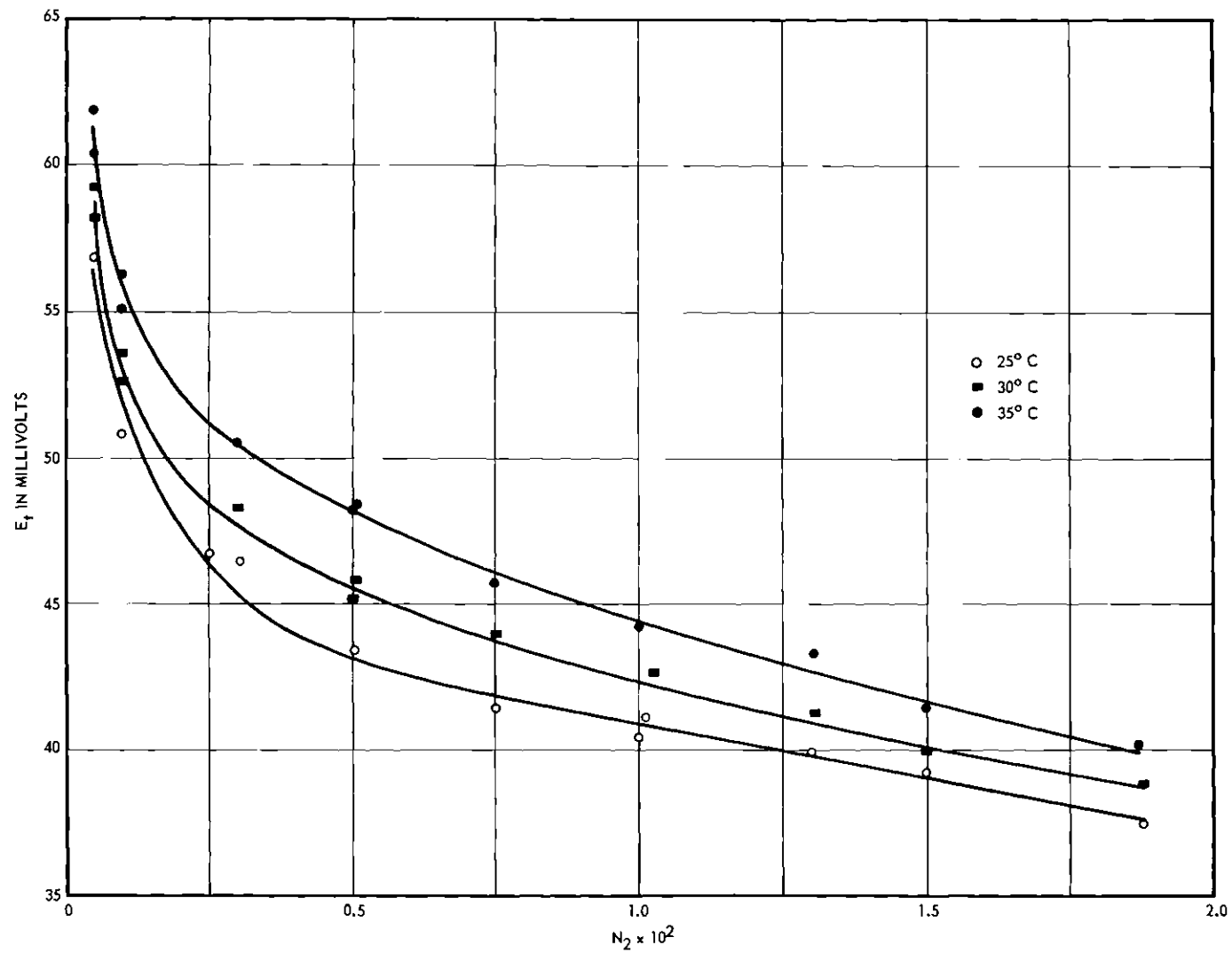


Figure 2. Electromotive Force Data for the Transfer of Sodium Chloride from Ethylene Glycol to Water.

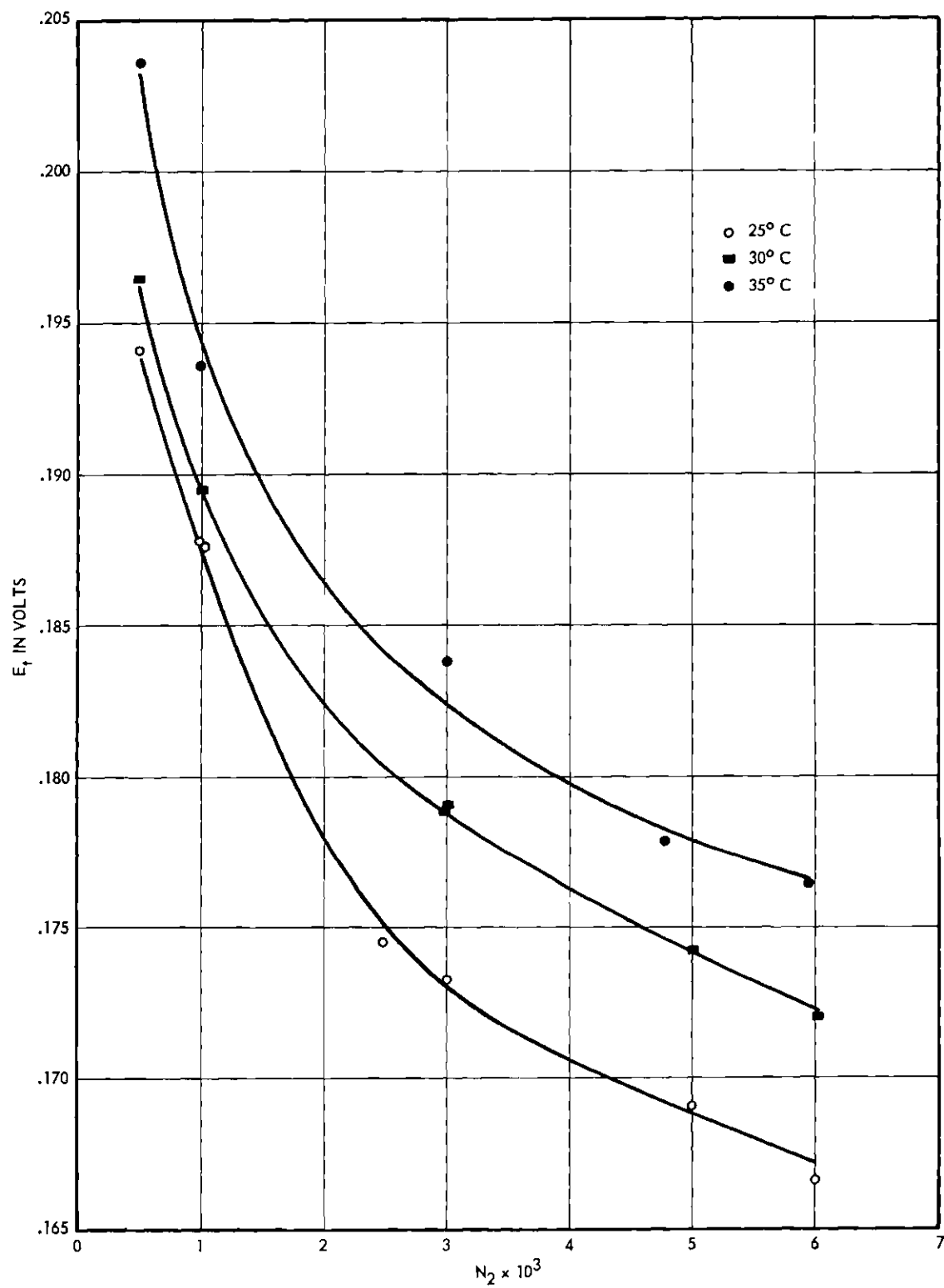


Figure 3. Electromotive Force Data for the Transfer of Sodium Chloride from Methanol to Water.

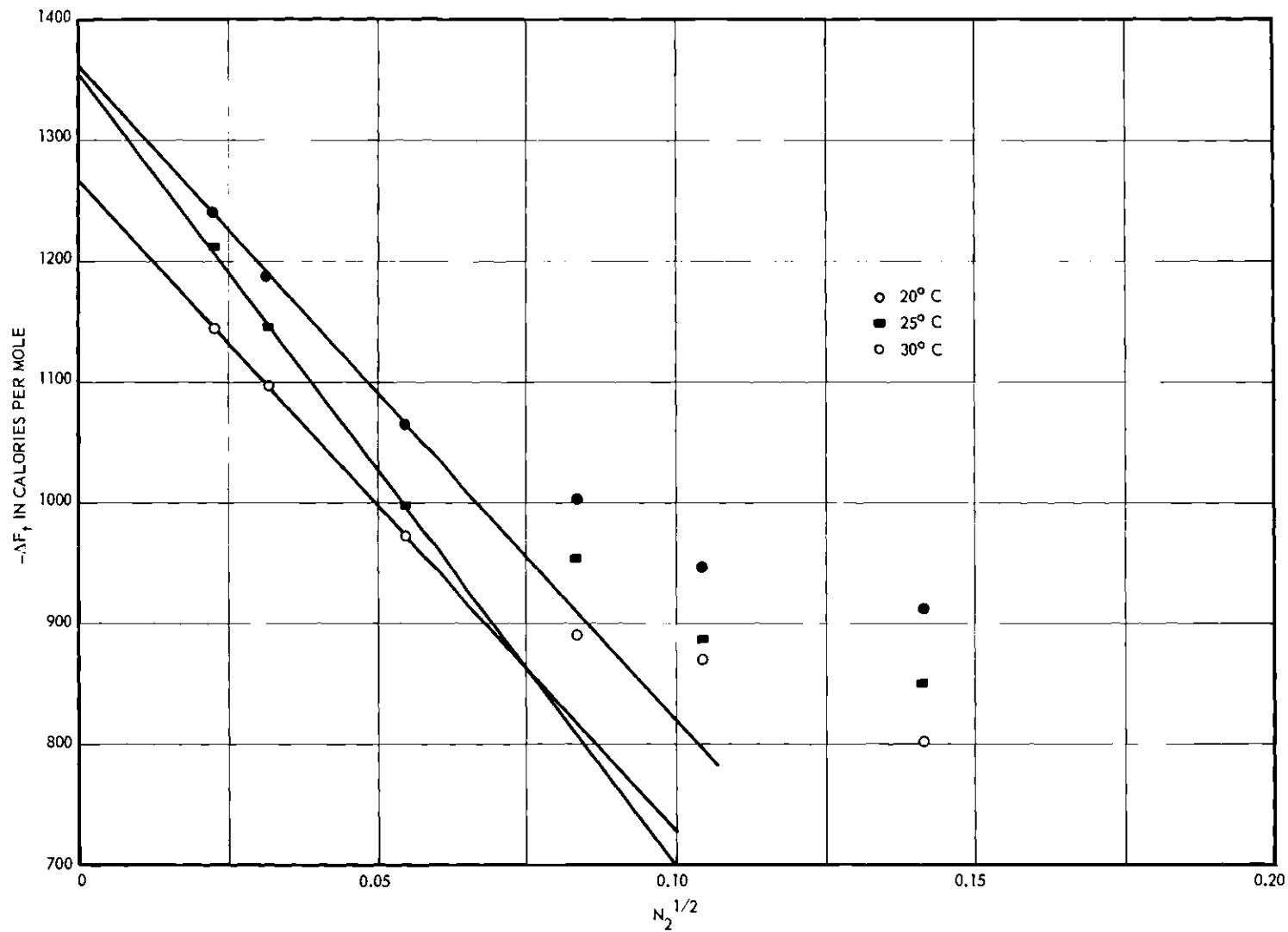


Figure 4. Free Energy of Transfer Versus $N_2^{1/2}$ for the Transfer of Potassium Chloride from Glycol to Water.

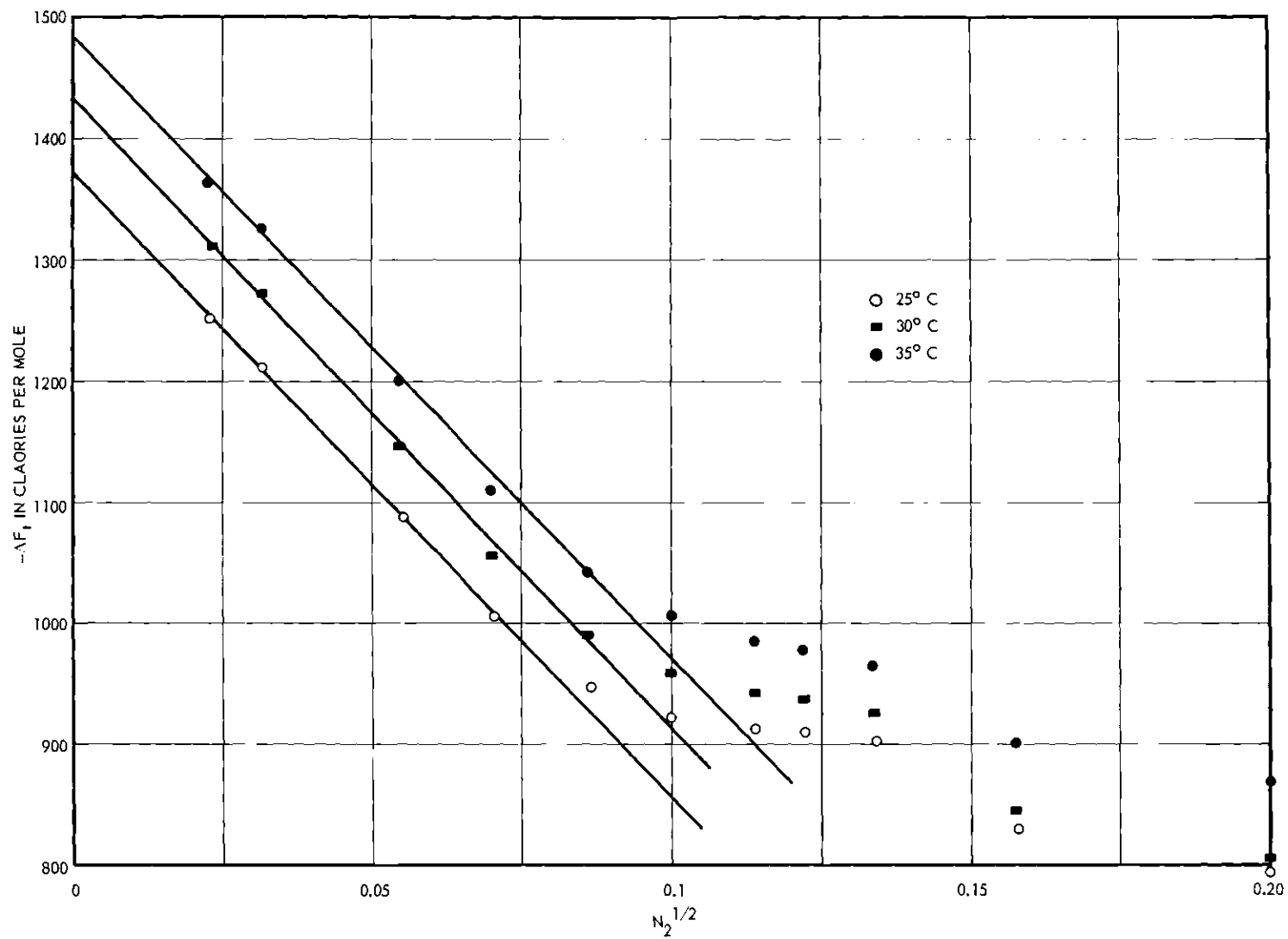


Figure 5. Free Energy of Transfer Versus $N_2^{1/2}$ for the Transfer of Sodium Chloride from Glycol to Water.

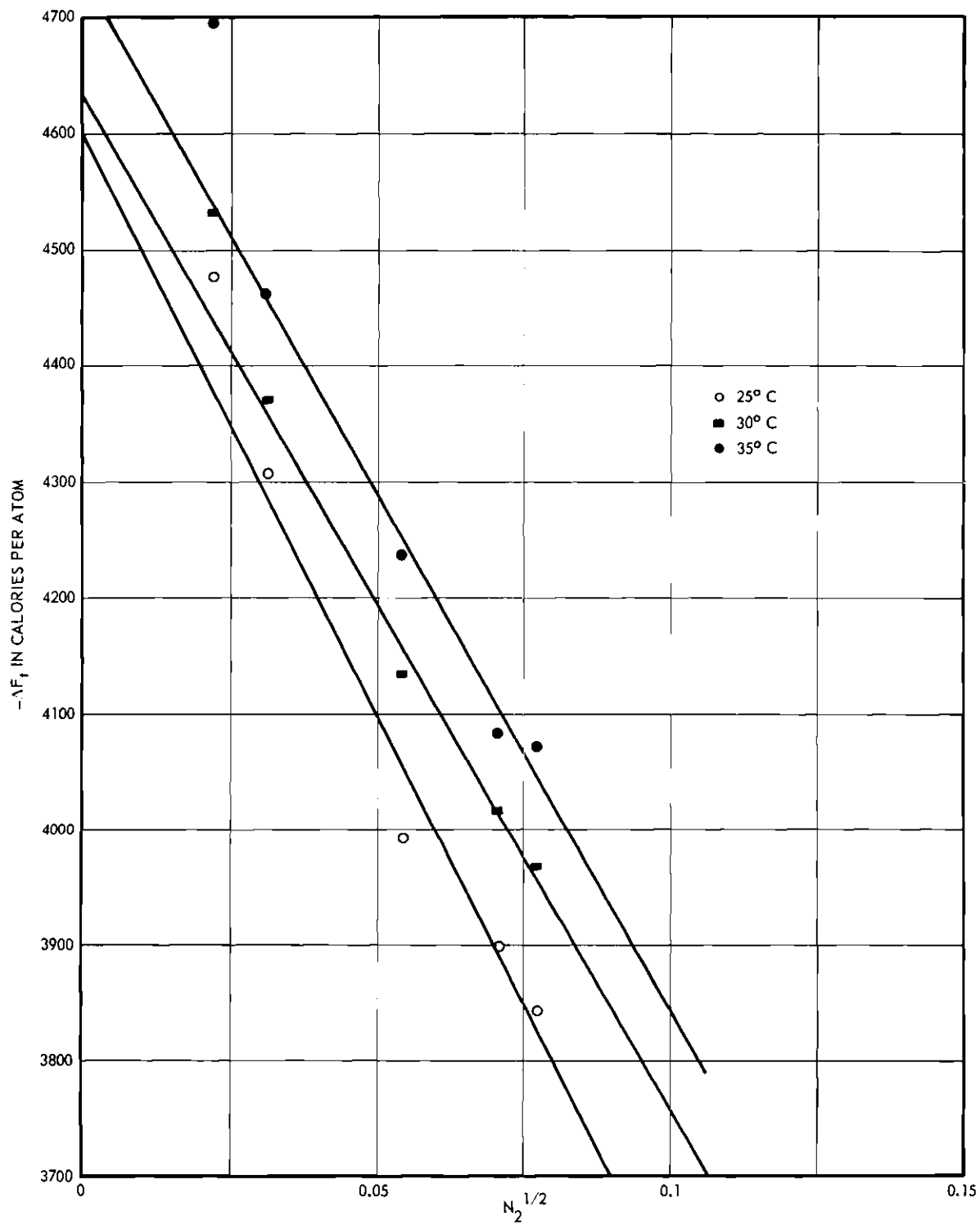


Figure 6. Free Energy of Transfer Versus $N_2^{1/2}$ for the Transfer of Sodium Chloride from Methanol to Water.

APPENDIX III

CALCULATED THERMODYNAMIC QUANTITIES OF TRANSFER

Table 10. Free Energy, Entropy, and Enthalpy of Transfer at Extreme Dilution for Hydrogen Chloride Transferring from Methanol to Water.

t in $^{\circ}\text{C}$	ΔF_t° in cals/mole	ΔS_t° in e. u.	ΔH_t° in cals/mole
15	-4578	10.9	-1446
20	-4631	10.2	-1630
25	-4681	10.4	-1589
30	-4734	10.9	-1426
35	-4792	11.5	-1248
40	-4849	11.8	-1162
45	-4908	11.4	-1290

APPENDIX IV

CONDUCTANCE DATA

The data assembled in this section cover the conductivity measurements made on several non-aqueous solutions. Only the data actually obtained by the methods given in Chapter IV are presented in this section. The K and Λ_0 were calculated using conductance data which were obtained at concentrations of 0.012 molar or less. Data used to calculate the K and Λ_0 for sodium chloride and potassium chloride in methanol were found in the work of Schiff, Butler, and Gordon. The values of Λ_0 in parentheses were the values obtained for these alkali metal chloride solutions by Schiff and co-workers.

Table 11. Conductance Data for Potassium Chloride in Ethylene Glycol

$C \times 10^2$	$N_2 \times 10^3$	R	Λ
0.07630	0.04261	28475	9.337
.1943	.1085	11449	9.110
.8926	.4982	2625.0	8.683
1.598	.8918	1500.8	8.486
4.284	2.387	593.86	7.997
10.05	5.580	264.36	7.658
18.29	10.12	150.29	7.403
34.34	18.82	84.157	7.041

$$K = 0.188; \Lambda_0 = 9.51$$

Table 12. Conductance Data for Sodium Chloride in Ethylene Glycol.

$C \times 10^2$	$N_2 \times 10^3$	R	Λ
0.07905	0.04416	33146	7.756
.2179	.1215	12224	7.627
1.058	.5904	2671.7	7.198
1.867	1.042	1556.3	7.001
3.978	2.217	763.63	6.697
9.785	5.434	331.59	6.270
17.34	9.588	197.51	5.940
47.08	25.62	83.32	5.187
74.36	39.88	58.61	4.068

$$\kappa = 0.208; \Lambda_0 = 7.94$$

Table 13. Conductance Data for Sodium Chloride in Methanol

$C \times 10^2$	$N_2 \times 10^3$	R	\wedge
1.230	0.5009	220.58	74.98
2.460	1.001	120.58	68.25
12.32	4.993	32.08	51.50

$$K = 0.289; \quad \wedge_o = 97.24 \\ (97.61)$$

Table 14. Conductance Data for Potassium Chloride in Methanol.

$$K = 0.177; \quad \wedge_o = 104.45 \\ (104.78)$$

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VITA

The author was born in Atlanta, Georgia, on November 8, 1931, the son of James and Lois (nee Collier) Fanning. He attended public schools in Oglethorpe, Georgia, Spartanburg, South Carolina, and Atlanta, Georgia. In the spring of 1949 he graduated from Grady High School in Atlanta, Georgia, and the following fall he entered the Citadel. He received the degree of B. S. in Chemistry from that institution in June, 1953. In the fall of 1953 he entered the Georgia Institute of Technology as a graduate assistant. He obtained a master's degree in Chemistry from Georgia Tech in June, 1956. The author spent the summers of 1954, 1956, and 1957, working in Savannah, Georgia, as a research chemist (GS-7) for the United States Public Health Service. Research for the Ph D. degree was begun in September, 1956, and was supported for six months during the academic year 1957-1958 by a Departmental Fellowship awarded by the Graduate Division. On August 10, 1957, the author was married to Sybil Rebecca Smith. He was an instructor in the School of Chemistry at Georgia Tech from September, 1958, until December, 1959. A daughter, Elizabeth Rebecca, was born on March 6, 1959. After completing his work at Georgia Tech, the author will enter the Army for a six-month period of active duty as a first lieutenant in the Chemical Corps.