# The Vapour Pressures of Concentrated Solutions of Lithium Nitrate at various temperatures.

By

Lyman Ross

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## Abstract

The vapour pressures of solutions of lithium nitrate for concentrations varying from ten to approximately sixty-five weight per cent, (the limiting solubility), were determined over a range of temperatures varying from thirty to about one hundred and five degrees centigrade. The two types of apparatus used to measure the vapour pressures were the differential and the absolute manometers.

From the vapour pressures, the enthalpies of evaporation of water have been calculated by a modification of the Clapeyron-Clausius equation, together with the differential heats of dilution, the activities of water (as compared with the mole fraction of the solvent) and the osmotic pressures. From the results it was concluded that the water of hydration of the lithium ion is strongly bound, as compared to the water of hydration of the ammonium and silver ions (if, indeed, these ions are hydrated at all).

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# THEORETICAL INTRODUCTION

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## Ionic Solvation:

An accurate knowledge of ion-solvent interaction that occurs in ionic solvation has become of great importance for the following reasons, firstly, in order to develop further the model of ionic solutions, secondly, in the development of the theory of concentrated electrolytic solutions and thirdly, in the calculation of solvation numbers as an aid in the theory of reaction of solutions.

The term "solvation number" represents the number of solvent molecules that coordinate with the ion in solution in polar solvents. The number of solvent molecules would, of course, vary from ion to ion. Various experimental methods have been employed in order to estimate the solvation numbers but the numerical values obtained are not in good agreement. Therefore, the meaning of the term "solvation number" remains indefinite.

Recent workers have overcome this difficulty by attacking the problem from a different direction. They have directed their efforts principally to the calculation of heats of solvation (or solvation energies) because this quantity infers a total interaction and is open to less ambiguity than are the solvation numbers.

In the beginning when the idea of ionic solvation was introduced, the ions were thought of as being chemically bound to the water molecules. This was confirmed at that time by S. Asckenazi's (3) observations. He found sudden changes in conductivity, cryoscopic constants etc. with change in composition which he thought corresponded to the formation of various definite hydrates, but this was not so, because there was difficulty in confirming the existence of these hydrates in solution. Morever, K. Fajans (21) after studying the polarizability of water molecules and the field about the ion, came to the conclusion that the interaction energy in solvation did not involve covalent linkage but was entirely coulombic. He also pointed out that he believed that the water molecules did not adhere to the ion at all times but remained in an hydration sheath in such a position that they were continuously interchanging with those in the bulk of the solution.

This picture of ionic hydration was substantiated by M. Born (9). He showed that the solvation energy which arose from the interpretation of Fajans' concept of ionic hydration was in close agreement with experiment for univalent electrolytes. When the existence of a definite structure for liquids was realized it became apparent that the steric properties of the ion became important in determining its solvation. This accounts for the different ionic velocities found for a series of ions in various solvents.

From the Fajans-Born concept of simple coulombic interaction, it follows that there are a number of solvent molecules attached firmly to the ion. Outside this hydration sheath the ion-dipole interaction that occurs involves other solvent molecules. It has been suggested by J. Bockris (7) that the term primary hydration or primary solvation be used when referring to the attachment of solvent molecules to those ions in solution for which the ion and its attached solvent molecules move together as one entity during electrolytic transport and for which the solvent ions have completely lost their own separate translational degrees of freedom. The term "secondary solvation" involves all interactions which are not included in the definition of primary solvation and the "total solvation" would therefore be the sum of these two types.

The electrostatic theory of solvation seems to apply only to the simpler ions of Group IA and IIA of the Periodic Table and to the halogens because the ion-solvent interaction is considered to be almost completely electrostatic in nature. Of course, this conclusion is not certain for the more complicated ions, for example the ones in Group VIII, where strong coordinating power tends to favour covalent linkages between ion and solvent, but although these ions tend to favour this type of attachment, there still exists a little quantitative evidence of solvation.

Lindemann (31) proposed quite a different theory of ionic solvation from that of Fajans. He suggested that no permanent solvation sheath exists in solution. The solvent transport during movement of an ion is caused by the transfer of momentum from the ion to the solvent molecules with which it collides. Thus smaller ions on the basis of this theory, would be expected to transfer more momentum than the larger ones. On this basis, it was possible to explain the dependence of temperature coefficient of conductance upon ion size. Due to the lack of evidence to support this theory there is little advantage in considering it any further.

R.H. Stokes and R.A. Robinson (43) proposed a hydration model for highly concentrated solutions. They suggested that at high concentrations the ion-solvent forces are the dominant factor and that solutions containing these ions are in various stages of hydration, some with a complete hydration shell forming a monomolecular layer round the ion, others with incomplete shells and some others containing more than one layer. The outer layers of solvent molecules are less strongly bound to the ion than the inner-most layer of the hydration sheath. Now, this model bears a resemblance to that from which the adsorption isotherm of Brunauer, Emmett and Teller (13) was derived. Stokes and Robinson modified the notation of these authors to suit the situation and obtained this equation.

$$\frac{ma_w}{55.51\,(1-a_w)} = \frac{1}{Cr} + \frac{C-1}{Cr} \cdot a_w \qquad (1)$$

where $a_w$ = activity of water

$m$ = molality

$r$ = the number of water molecules in a monomolecular hydration sheath when complete

$C = \exp (E-E_1) \ / \ RT$

$(E-E_L)$ = excess of energy of adsorption in the first layer over the latent heat of vaporization of water

Anderson (1) also modified the B-E-T equation so that the subsequent layers (up to about the tenth) have a heat of adsorption less by a value "d" than that of water. This has the effect of multiplying $a_w$, wherever it occurs in equation (1) by a factor $K=\exp-d/RT$. Table 1 compares the values of r obtained for a number of electrolytes from Anderson's modified equation to those obtained by using the equation of Stokes and Robinson.

## TABLE 1

Comparison of r (the number of water molecules in a monomolecular hydration sheath) from the modified equation of Anderson and from the equation of Stokes and Robinson

| Electrolyte | Values of r obtained from: | |
|---|---|---|
| | Anderson's Equation | S and R equation |
| LiCl | 4* | 3.64 |
| LiBr | 4 | 3.82 |
| HCl | 4 | 3.50 |
| $HClO_4$ | 4 | 3.93 |
| $Ca(NO_3)_2$ | 4 | 3.86 |
| $ZnCl_2$ | 4 | 3.69 |
| $ZnBr_2$ | 4 | 4.01 |
| $CaCl_2$ | 8 | 6.73 |
| $CaBr_2$ | 8 | 7.06 |

* rounded of to whole numbers by Anderson

Anderson rounded off his numerical values to whole numbers. The first four electrolytes with univalent cations require four molecules of water to complete the first layer; the last two electrolytes with bivalent cations require eight water molecules. Calcium nitrate, zinc chloride, and zinc bromide also have bivalent cations but there is evidence, as in the case of zinc salts that they are more correctly represented by the formula $Zn^{++}[ZnY_4]^{--}$ and only half the zinc ions are therefore available for hydration and in calcium nitrate solution the calcium nitrate is subject to ion pair formation and therefore in more concentrated solutions the predominant ion is univalent $[CaNO_3]^+$.

Much of the more recent work has been done on the problem of solvation energies rather than on solvation numbers; we will therefore direct our attention to the heat of solvation.

It is argued from the point of view of the theory of salt dissolution, that the large solubility of many salts in suitable solvents, in which the essential steps are the breaking down of the crystal lattice and the creation of free ions, can only be explained if some special process occurs upon dissolution of a crystal which produces an amount of energy of the same order as that of the crystal lattice. The amount of energy required in this process will be of considerable magnitude because of the large lattice energies themselves. This "special process" refers to the hydration of ions in aqueous solutions and signifies the attachment of solvent molecules to the ions in solution. The forces causing this attachment are principally electrostatic. If the heat of solvation is sufficiently exothermic, it will compensate for the energy used in breaking up the lattice and the salt will dissolve. Thus using the first law of thermodynamics one can obtain an equation in which the algebraic sum of the heat of solvation and the lattice energy is equal to the heat of solution.

$$\Delta H = -U + (Q_{+} + Q_{-}) \qquad (2)$$

where $\Delta H$ = the heat of solution
$U$ = the lattice energy
$(Q_{+} + Q_{-})$ = the heat of solvation

Now, if one knows the lattice energy and the heat of solution, one can place these values into equation (2) and find the heat of solvation. This value contains both the interaction energy of the ion and dipole and the work of breaking up the solvent caused by the dissolution of the ion.

Table 11 shows the heat of hydration of the alkali halides calculated from lattice energies and heats of solution in water.

Salts, such as LiF, LiCl, and NaF, that possess large solubilities, are observed to have high heat of solvation $(Q_{+} + Q_{-})$ values in this table.

## TABLE 11

### Lattice Energies, Initial Heats of Solution, and Heats of Hydration of the Alkali Halides in Kilocalories

| Salt | U<br>T=291°K | $\Delta$ H<br>T=291°K | $Q_+ + Q_-$<br>T=291°K |
|---|---|---|---|
| LiF | -247.0 | 1.1 | -245.9 |
| LiCl | -202.7 | -8.6 | -211.3 |
| LiBr | -191.4 | -11.1 | -202.5 |
| LiI | -177.6 | -14.8 | -192.4 |
| | | | |
| NaF | -218.2 | 0.6 | -217.6 |
| NaCl | -185.5 | 1.3 | -184.2 |
| NaBr | -177.8 | 0.2 | -177.6 |
| NaI | -165.6 | -1.4 | -167.0 |
| | | | |
| KF | -194.7 | -4.1 | -198.8 |
| KCI | -169.6 | 4.4 | -165.2 |
| KBr | -162.8 | 5.1 | -157.7 |
| KI | -153.9 | 5.1 | -148.8 |

Hydration energies of individual ions have been determined but with much difficulty. In order to obtain these individual values, some non-thermodynamic facts such as the properties of the ions and solvent have to be taken into account.

Born (9) calculated the heat of hydration from the properties of the ion and solvent. He regarded the heat of hydration of an ion as the difference in its electrostatic energy in vacuo and that in a medium of dielectric constant $\epsilon$.

The energy of an ion, regarded as a sphere of radius "a", in vacuo is

$$\frac{Z_i^2 e^2}{2a}$$

where $Z_i$ = the valence of the ion

$e$ = the electronic charge

If the medium of dielectric constant $\epsilon$ is considered as a continuum the corresponding energy in it is $\frac{1}{\epsilon}$ times that in a vacuum. Therefore the change in free energy per mol accompanying the transfer of the ion from vacuum into a medium of dielectric constant $\epsilon$ is

$$F = -N_a \left[ \frac{Z_i^2 e^2}{2a} - \frac{Z_i^2 e^2}{2\epsilon a} \right]$$

$$= \frac{-N_a Z_i^2 e^2}{2a} \left[ 1 - \frac{1}{\epsilon} \right] \qquad (3)$$

where $N_a$ = number of moles of species A. The heat of hydration $Q_i$ can be obtained from the Gibbs-Helmholtz equation as

$$Q_i = \Delta F - T\left(\frac{\partial \Delta F}{\Delta T}\right)_P$$

and replacing $\Delta F$ with that obtained in equation (3)

$$Q = \frac{-N_a Z_i^2 e^2}{2a}\left[1 - \frac{1}{\epsilon} - \frac{T}{\epsilon^2}\left(\frac{\partial E}{\partial T}\right)_P\right] \quad (4)$$

Two main difficulties arise in the use of this equation. One is the difficulty of ascertaining the radius of the ion. From X-ray measurements, the internuclear distances in the crystal are obtained on the assumption of course, that cation and anion are in close contact. The main ambiguity is encountered in the division of these internuclear distances into the individual ionic radii. Then another uncertainty lies in assuming that the radii of the ions in a crystal are the same as they are in the solvent medium. The second difficulty in this treatment arises because Born's equation infers that the heat of solvation of a monovalent ion should depend on the temperature and on the dielectric constant of the medium. This would imply that all ions whether cations or anions having the same radius would yield the same solvation energy. Also the use of macroscopic dielectric constant is in serious error since near the vicinity of the ion, at least, the dielectric constant is considerably reduced, due to the influence of the field of the ion.

The ion-dipole interaction, the orientation, the polarization of the water molecules by the ionic fields, and the work of disturbing the structure of the solvent caused by the presence of the ions, were taken into account in order to improve the values of the heat of solvation. In Table 111 the heat of hydration of some individual ions are calculated from Born's equation and compared to the more recent values corrected in accordance with the factors mentioned above.

## TABLE 111

Heats of Hydration in Individual Ions
in Kilocalories at 291°K

| Ion | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $F^-$ | $Cl^-$ | $Br^-$ | $I^-$ |
|---|---|---|---|---|---|---|---|---|
| Radius Å | 0.68 | 0.98 | 1.33 | 1.48 | 1.33 | 1.81 | 1.96 | 2.19 |
| $Q_i$(Born's equation) | 240 | 166 | 123 | 110 | 123 | 90 | 83 | 74 |
| $Q^i$(Corrected) | 131 | 116 | 92 | 87 | 94 | 67 | 63 | 49 |

Although much work has been done on ionic solvation the theoretical concept has been found to be inadequate to a greater or lesser degree. The reason for this difficulty lies greatly in the lack of knowledge of the type of binding, that exists between the ions and solvent molecules and the difficulty in getting some accurate measurement of solvation numbers and energies of ions from reliable experiments.

Many different physical properties have been studied in order to determine the solvation numbers, viz: freezing and boiling points, refractivity, vapour pressure, density, surface tension, specific heat, compressibility of ionic solutions, transport numbers of ions and solubility of non-electrolytes in the presence of electrolytes. The results seem to indicate that ion-solvent interactions have an influence on the behaviour of solutions.

A difficulty common to most of these methods is that of dividing up the solvation of the salt between its ions. Some workers (38) have assumed that large organic ions such as $PhNH_3^+$ possess a zero solvation number. Some have extended this to include such ions as $NO_3^-$ (10) and $I^-$ (17). The most logical method appears to be division in the ratio of the ion sizes, based upon some salt such as Potassium fluoride whose ionic radii are nearly equal.

Until recently the principal way of estimating ionic hydration was Washburn's modification (49) of the Hittorf method of ionic or solvent transport using an inert reference substance. The inert substances employed by Washburn were raffinose, sucrose or arsenious acid. The reference substance is actually used to determine if there is a change in concentration of inert material when the ions move under an applied difference in potential.

Now the fundamental assumption is that the reference substance does not move under the influence of the applied field. If one refers the changes in the content of water and of the salt to the non-electrolyte as a reference substance then for a series of measurements with various electrolytes, hydration numbers can be allotted to each ion provided that one ion, say the chloride ion, is assumed. A great deal of work was done by Bockris (7) on this principle. The method always led to this order of hydration values for the monovalent cations $Li^+ > Na^+ > K^+ > Cs^+ > H^+$ but as for the actual numerical values there was considerable disagreement, which is in part due to the different assumptions about the hydration of the chloride ion.

Washburn used the following equation to calculate the numbers of moles of water carried per equivalent of cation and anion.

$$\Delta n = T_c N_w^c - T_a N_w^a \qquad (5)$$

where $\Delta n$ = number of moles of water transferred from anode to cathode per faraday of electricity

$T_c$ = the true transference number of the cation

$T_a$ = the true transference number of the anion

$N_w^c$ & $N_w^a$ = the number of moles of water combined with one equivalent of cation and anion respectively.

$N_w^c$ or $N_w^a$ must be assumed since both of these quantities are unknown.

P.Z. Fischer and T.E. Koval (22) have since shown that the inert reference substance raffinose, which was used by Washburn, is transported under these conditions. Also L.G. Longsworth (32) showed that a non-electrolyte in presence of electrolyte does migrate. As a result the calculated water transport per faraday of electricity passed depends on the particular non-electrolyte employed. This method is therefore open to considerable objection and the results obtained are quite uncertain.

Other workers have employed the water-transfer method without the use of inert reference substances. For instance, in the Remy (36)-Baborovsky (4) method of water transport the liquid is allowed to pass through a thin membrane between cathode and anode compartments and this indicates the net volume change arising from the different extent of solvation of the cation and anion. The principal objection is in the measurement of water transport because it may have included in it the water which is transported by a transfer of momentum from ions to molecules in the manner suggested by Lindemann. This, of course, would result in hydration numbers that were too high. Another objection is in the considerable volume change in the anode and cathode compartments caused by reactions at the electrodes. Also, the effect of electroendosmosis at the membrane is considerable below a concentration of 1 N. Thus the Remy-Babarovsky method must measure some part of the total rather than the primary solvation, a conclusion which also holds true for Jander's diffusion method (26) and the dialysis method of Brintzinger (12).

Ulich employed an ionic-mobility method (45) which appears to measure a more definite quantity than did the previous method. He obtained directly the volume of the solvated ions from an application of Stoke's law to ionic mobilities at very low concentrations, thus obtaining primary solvation numbers. This method gave low results for some ions in aqueous solutions (29). The appropriate volume of the solvent molecule to use in the evaluation of the solvation number is somewhat indefinite because the high pressure in the vicinity of the ion and the inhibition of rotational degrees of freedom of the dipoles attached to the ion make the molecular volume, calculated in the usual way, too large. Thus Ulich's solvation numbers were too small and probably represent a lower limit. He also calculated an upper limit assuming the molecular volume was diminished, to one half its original value, hence his final values were an average of the upper and lower solvation limits.

In the opinion of the author, ionic mobility should be used with great caution in the estimation of the water sheaths of the ions, because of the very large differences between the water sheaths calculated by a number of investigators such as Riesenfeld (39) Ulich (45) and Remy (37) from ionic mobilities.

A number of methods involve activity determinations based on cryoscopic, vapour pressure, and the salting-out methods. These give high results and therefore seems to give a total interaction effect.

The cryoscopic method of E. Rouyer, F. Bourion, and Hun (11) appears to be of doubtful validity because the results depend upon the use of a non-electrolyte. These workers used such non-electrolytes as acetone, paraldehyde and resorcinol. They measured the cryoscopic or ebullioscopic constants of non-electrolytes in electrolytic solutions or in pure water. Using the following relationships they obtained the hydration of the electrolyte.

$$X = \frac{100\ (K' - K)}{K'} \qquad (6)$$

where X = the per cent of water of hydration of the electrolyte

K = the cryoscopic constant of the non-electrolyte in water

K'= the cryoscopic constant of the non-electrolyte in the electrolytic solution.

The results obtained for the first two non-electrolytes were unreasonable but resorcinol appeared to function satisfactorily. The theory from which the results are evaluated is inadequate and therefore had to be abandoned.

The estimation of the hydration numbers by the use of vapour pressure measurements was carried out by B.H. Van Ruyven (47), (48). He proposed that a hydrated ion has several water molecules bound to it, and that strong electrolytes are not wholly ionized. With the use of Arrhenius law of Electrolytic dissociation and Raoult's law he deduced this expression:

$$\alpha p = \frac{1000\ (S - S_1) \quad - 18\ N_W S_1}{18\ N_W S_1} \qquad (7)$$

where $\alpha p$ = the degree of ionization calculated from vapour pressure

$N_W$= the number of moles of the dissolved substance in 1000 grams of solvent.

$S$ = the vapour pressure of pure solvent

$S_1$= the vapour pressure of solution at the same temperature as $S$

This equation breaks down at high concentrations because of the decrease in the amount of free water present as a consequence of the binding of water molecules to the ions. He therefore rewrites the equation as:

$$\alpha Pa = \frac{1000\ (\ S - S_1\ ) \ - 18\ N_W S_1}{18\ N_W S_1 \quad + \ 18\ aN_W (S - S_1)} \qquad (8)$$

where a = the number of firmly bound water molecules

$\alpha Pa$ = the degree of ionization of the electrolyte binding a molecule of water.

The hydration numbers obtained for individual ions by Van Ruyven are shown in the Table IV.

## TABLE IV

Ionic Hydration Numbers

| Positive Ions | | Negative Ions | |
|---|---|---|---|
| Li | 13 | $NO_3$ | 0 |
| Na | 8 | $NO_2$ | 1 |
| K | 4 | CNS | 2 |
| Rb | 2 | Cl | 3 |
| | | Br | 3 |
| | | I | 3 |

Unfortunately Van Ruyven's results apply to dilute solutions. When applied to more concentrated solutions the relationship does not seem to hold. The theoretical treatment must therefore fail for the more concentrated solutions due to the different interionic attraction that takes place.

Kosakewick and Ismailov (30) have utilized the salting-out effect in order to estimate the hydration number of ions. The solubility of a non-electrolyte decreases upon the addition of an electrolyte and this change in solubility is used to gain a measure of the hydration on the assumption that the decrease in solubility is due to the reduction of the activity coefficient in water. This method does not take account of the effect of the non-electrolytic solute on the dielectric constant of the medium. Values calculated from this method also depend upon the nature of the non-electrolyte and therefore cannot be considered as valid for the determination of ionic solvation.

However, it is sometimes possible to make qualitative inferences regarding solvation from salting-out studies. For example, J.O.M. Bockris and H.Egan (8) found that for concentration range between N/1000 to 1 N for sodium chloride solutions using benzoic acid as non-electrolyte the salting-out decreases anomalously with decreasing dielectric constant in alcohol-water mixtures containing an excess of water. This fact can be explained if it assumed that sodium chloride is preferentially solvated with water.

The determination of solvation numbers by the measurement of partial molal volumes of electrolytes at infinite dilution was carried out by J.D. Bernal and R. H. Fowler (5). They refer to their method and its results as being particularly satisfactory and Darmois (19) describes the procedure and results of this method for a large number of simple aqueous electrolytic solutions. This method measures the primary hydration since it is concerned with the volume of the ion-solvent complex only and not with the surrounding water molecules which are not firmly attached to the ion. But the values of the solvation numbers obtained were much lower than those obtained from similar experiments. The reason for this is not yet quite clear.

Primary solvation was calculated by Ulich (46) by employing entropy determinations. This method is due to the decrease in entropy occuring when gaseous ions undergo solution in water at infinite dilution. It also depends upon the "freezing up" of the degrees of freedom of the water molecules near the ion. The assumption is made that the entropy decrease when water is transferred from the bulk of the solution to the primary solvation sheath is the same as that on freezing water. The entropy method may also be employed to calculate the solvation of non-electrolytes. (28).

Some other methods such as the compressibility of ionic solutions, the variation of the distribution of an electrolyte between two immiscible solvents, the use of supersonic emf's and polarimetry, all involve the measurement of reaction velocities.

The compressibility method gave results which agreed quite well with those obtained from the ionic mobility method. Thus, it seems highly probable that this method also yields primary solvation numbers. This assumption is supported by the concept that the solvent sheath in primary solvation is under very large pressure, owing to the field near the ion and therefore reaches a limiting value beyond which further compressibility is due to that of the solvent.

The distribution method used recently by Cordier (18) gave very high values for the solvation numbers (of the order of $10^2$). These values sometimes imply that more water is used up in the hydration sheath than exists in the solution. There are several unsolved difficulties that exists in the distribution method. The results obtained by J.N. Sugden (44) and E. Angelescu, and O. Dutchieviu (2) are discrepant. Sugden even obtained negative solvation numbers for anions. The reason for these negative values is that the anions were supposed to exert a "depolymerizing effect" upon the water as $(H_2O)_3$ in the liquid state.

Lastly, Debye's (20) theoretical treatment of the potential difference produced in an electrolytic solution when it is subjected to supersonic vibrations appears to be a method that is acceptable in principle. It yields individual solvation numbers because the emfs produced are a function of the ratio of both positive and negative ion-solvent complexes in the electrolyte. Measurements attempted by this method are difficult because the emf's recorded are of the order of $10^{-6}$ volts.

Bjerrum (6) calculated solvation numbers by using the activity of water in aqueous electrolytic solutions. His method was considered by Ulich to yield primary solvation numbers. Since Bjerrum's method has not been applied to many ions no definite conclusion can be made about it. The water that is held by the ion is taken into account by Bjerrum's treatment and the concentrations are expressed as x, the mole fraction of solute. The mole fraction of ions which are hydrated will be larger than the mole fraction of unhydrated ions. In measuring the activity as defined by emf measurements the activity of water-free ions is obtained. Now if the ion binds m molecules of water the activity of the water-free ions should be multiplied by the activity of the water raised to the $m^{th}$ power. From this line of argument Bjerrum derived this equation.

$$\ln Fa = \ln f_a - \frac{2M-2C}{55.5} \qquad (9)$$

$F_a$ = the apparent activity coefficient of the salt

$f_a$ = the corresponding true activity coefficient

$M = m + m'$ = the number moles of water carried by anion plus the number of moles carried by cation.

E. Schreiner (42) used this method to calculate the hydration numbers of several ions and found the improbable result of 11 obtained for hydrogen chloride. Even though this particular method is quite an improvement over the majority of methods discussed so far the results are still not too reliable.

Stokes and Robinson, (43) working on ionic hydration with regard to its effect on activity in electrolytic solutions came to a result equivalent to that of Bjerrum, though the treatment was by a somewhat different route. The authors discuss a modified form of the famous Debye-Hückel equation in which they introduce the effect of ion-solvent interaction in terms of "hydration" which is considered applicable up to ionic strength of about 4. (The other equation of Stokes and Robinson which was presented on page 4 is used for concentrations above the ionic strength of 4.) They consider 1 molecule giving rise in the solution to $\nu$ ions. The total interaction between these ions and the surrounding solvent can be allowed for as a "binding" of n molecules in their "hydration shells". In a solution of molality m, there are nm molecules of "bound" water to (55.51-nm) molecules of free water. The true molality m' (in moles of hydrated solute 1000 g. of"free" water) is therefore.

$$m' = \frac{55.51m}{55.51-nm} = \frac{m}{1-0.018\ nm} \qquad (10)$$

then if a'=the activity of the hydrated solute, and $a_w$=that of the water, then the Gibbs-Duhem relation becomes

$$\ln a' = -\frac{55.51}{m'}\, d \ln a_w \qquad (11)$$

If no hydration occurs then this equation is equally valid as the ordinary form using the stoichiometric molality and activity.

$$d \ln a = -\frac{55.51}{m}\, d \ln a_w \qquad (12)$$

Introducing the mean molal activity coefficients $\gamma'$

and $\gamma$ we obtain these two equations:

$$d \ln \gamma' = \frac{-55.51}{\nu m'} (d \ln a_W - d \ln m') \qquad (13)$$

and

$$d \ln \gamma = \frac{-55.51}{\nu m} ( d \ln a_W - d \ln m) \qquad (14)$$

Next substituting for m' from equation (10) into equation (13) we have

$$d \ln \gamma' = d \ln \gamma + \frac{n}{\nu} d\ln a_W + d \ln (1-0.018\ nm) \qquad (15)$$

Upon integrating between molalities zero and m we obtain,

$$\ln \gamma' = \ln \gamma + \frac{n}{\nu} \ln a_W + \ln (1-0.018\ nm) \qquad (16)$$

The mean rational activity coefficient of the hydration solute f' is related to $\gamma'$ by this relationship:

$$\mathrm{In}\ f' = \ln \gamma' + \ln (1+0.018\nu m') \qquad (17)$$

Combining equation (16) and (17) and simplifying with equation (10) we obtain,

$$\ln \gamma = \ln f' - \frac{n}{\nu} \ln a_W - \ln \left[ 1-0.018\ (n-\nu)m \right] \qquad (18)$$

This expression gives a relation between the observed stoichiometric activity coefficient and the rational activity coefficient of the hydrated solute.

Now replacing the term ln f' by the Debye-Hückel expression

$$\ln f = \frac{-A\sqrt{C}}{1 + B\overset{\circ}{a}\sqrt{c}}$$

equation (18) becomes

$$\ln \gamma = \frac{-A\,ZZ'\sqrt{\mu}}{1+B\overset{\circ}{a}\sqrt{\mu}} - \frac{n}{\nu}\ln a_w - \ln\left[1-0.018\,(n-\nu)m\right] \quad (19)$$

where A and B = the Debye-Hückel constants that vary with temperature,

Z and Z' = the valences of cation and anion respectively

$\mu$ = the ionic strength,

$\overset{\circ}{a}$ = the mean distance of closest approach in Angstrom units.

Fischer and Koval (22) found that this equation gave good results up to the point where the product of nm did not exceed 10 or 15. Above this nm value, the competition for water molecules became noticeable. In order to proceed at higher concentrations an n which was more suitable would have to be used i.e. a decreasing function of concentration.

Table V shows the type of agreement obtained from the different methods. Therefore, at best it can be said, after such a long and intensive literature survey, that the values give only an approximate measure of primary solvation.

## TABLE V

Results of Experimental Methods giving
Primary Hydration Numbers at Infinite Dilution

| | Methods | | | | |
|---|---|---|---|---|---|
| Ion | Mobility (1) | Entropy (2) | Compressibility (3) | Density (4) | Mean (1,2,3,4) |
| $Li^+$ | 5 | 5 | 3 | 2 | 4 |
| $Na^+$ | 4 | 4 | 4 | 1 | 3 |
| $K^+$ | 4 | 2 | 3 | 0 | 2 |
| $Rb^+$ | | 2 | | 0 | 1 |
| $F^-$ | | 5 | 5 | | 3 |
| $Ce^-$ | 4 | 2 | 3 | 0 | 2 |
| $I^-$ | 0.7 | 0.5 | 2 | 0 | 0.7 |

# STATEMENT OF SPECIFIC PROBLEM

## Statement of Specific Problem

This work was undertaken because it was thought that a knowledge of vapour pressures of solutions of different concentrations at a series of temperatures would yield the heats of evaporation of water from these solutions and hence might throw some light, if only of a qualitative nature, on the firmness with which the different ions held their water of hydration.

The soundest theoretical treatment so far advanced is that of Stokes and Robinson. Their hydration model bears a resemblance to the Brunauer, Emmett and Teller theory of adsorption, in that the solvent molecules are considered to be held in layers about the ion. As the concentration of aqueous electrolytic solutions is increased the number of layers about the ion decreases until finally all the remaining water molecules are tightly bound to the ions. This picture is valid only, of course, if no other forces come into play, to neutralize the ion-solvent interaction. If these layers do occur, then, the amount of energy required to strip the outer layer will be less than the amount of energy required to strip the inner layer. Also, as the concentration is increased it becomes increasingly difficult for the water molecule to overcome the strong ion-solvent forces and escape the solution.

According to our concept we can write the following equations for the reactions taking place;

$$(\text{Ion} + (n-1)\ H_2O_{(l)}) + H_2O_{(l)} \rightleftharpoons (\text{Ion} + n\ H_2O_{(l)}) \qquad (1)$$

$$(\text{Ion} + n\ H_2O_{(l)}) \rightleftharpoons (\text{Ion} + (n-1)\ H_2O_{(l)}) + H_2O_{(v)} \qquad (2)$$

$$H_2O(l) \rightleftharpoons H_2O(v) \qquad (3)$$

where the subscripts (l) and (v) refer to liquid and vapour phase respectively and the letter n represents the number of water molecules that are bound around the ion. Each of the reactions (1), (2), and (3) will have a corresponding heat of reaction $\Delta H_1$ and $\Delta H_2$ and $\Delta H_3$ respectively. Since equation (3) is the sum of equations (1) and (2),

$$\Delta H_3 = \Delta H_1 + \Delta H_2 \qquad (4)$$

or

$$\Delta H_1 = \Delta H_3 - \Delta H_2 \qquad (5)$$

Here $\Delta H_3$ is the heat of vaporization of pure water, $\Delta H_2$ the heat of vaporization of water from the solution and $\Delta H_1$ can be shown to be equivalent to the differential heat of dilution of the solution because it is the difference between the molar heat of vaporization of water from pure water and of water from solution. If there were no ion-solvent interaction $\Delta H_1$ would be expected to be zero. A positive value for $\Delta H_1$ means that heat is absorbed and it is our belief that no hydration occurs under this condition, or as in the case of dilute solutions, that hydration of the ions cannot be detected because there are other forces that predominate over the ion-solvent forces. Now if $\Delta H_1$ is a negative value which increases with increasing concentration heat is evolved, the effect of ionic hydration.

In order to evaluate $\Delta H_1$ , it was decided to apply the Clausius-Clapeyron equation to the vapour pressures of progressively more concentrated solutions at various temperatures. One form of this equation is written as:

$$\frac{dP}{dT} = \frac{\Delta HP}{RT^2} \qquad (6)$$

where $\Delta H$= the molar heat of vaporization

T= the absolute temperature

P= the pressure

R= the universal gas constant.

Equation 6 may be written as

$$\log_{10}P = -\frac{\Delta H}{2.3\ R}\ \frac{1}{T} + C \qquad (7)$$

where C is the constant of integration. If $\log_{10} P$ is plotted against $\frac{1}{T}$ for a small temperature gradient a straight line with slope equal to $-\frac{\Delta H}{2.3R}$ is obtained.

From the slope it is then possible to determine $\Delta H_3$ and $\Delta H_2$ for each solution in turn; $\Delta H_1$ can be evaluated by means of equation (5). The use of equation (7) is limited to small ranges of temperature over which $\Delta H$ may be regarded as constant. Since we have worked over a large range of temperature this method had to be abandoned in favour of a more suitable form of the Clausius-Clapeyron equation.

A very useful application of this equation in the correlating of vapour pressure and latent heat data is described in a paper by D.F. Othmer (35). This author rearranged equation (6) so that one can obtain a much more suitable expression for the evaluation of latent heats of vaporization especially applicable over a large temperature range.

Rearranging equation (6) and introducing the subscript 2 we get,

$$\frac{I}{\Delta H_2} \times \frac{d\,P_2}{P_2} = \frac{dT}{RT^2}, \qquad (8)$$

an equation obeyed by any material consistent with the assumption of the ideal gas law and such that the volume of the condensed phase is insignificant compared to the vapour volume. The same equation may be written for any other like material at the same temperature giving,

$$\frac{I}{\Delta H_3} \times \frac{dP}{P_3} = \frac{d\ T}{RT^2} \qquad (9)$$

where $P_2$ = the vapour pressure of another substance at temperature T

$P_3$ = the vapour pressure of pure water at the same temperature T

$\Delta H_2$ = the latent heat per mole of this other substance also at the temperature T

$\Delta H_3$ = the latent heat per mole of pure water at the temperature T.

Then equating equations (8) and (9) gives

$$\frac{I}{\Delta H_2} \frac{dP_2}{P_2} = \frac{I}{\Delta H_3} \frac{dP_3}{P_3}$$

or

$$\frac{dP_2}{P_2} = \frac{\Delta H_2}{\Delta H_3} \frac{dP_3}{P_3} \qquad (10)$$

If $\Delta H_2/\Delta H_3$ is considered constant, equation (10) may be integrated to give

$$\log P_2 = \frac{\Delta H_2}{\Delta H_3} \log P_3 + C \qquad (11)$$

where C is a constant of integration and $P_2$, $P_3$, $\Delta H_3$ are always taken at the same temperatures.

If the logarithm of the vapour pressure, $P_2$ of a solution is plotted against the logarithm of the vapour pressure, $P_3$ , of pure water at the same temperature, a straight line results which has for its slope the ratio of the molar enthalpies of evaporation. This line is straight if the ratio $\frac{\Delta H_2}{\Delta H_3}$ is constant over the temperature range in question and this is reasonably near the truth for water and aqueous solutions. From the value of the ratio, and that of the latent heat of evaporation of pure water, $\Delta H_3$, the latent heat of evaporation of water from solutions, $\Delta H_2$ , is obtained. From equation (5), $\Delta H_1$ the differential heat of dilution, may be calculated.

The best available data on the latent heats of vaporization and vapour pressures of pure water are contained in a paper by J.A. Goff and S. Grotch (23). These authors calculated the vapour pressures of pure water from the following equation:

$$\log_{10} P_s = -7.90298 \left(\frac{T_s}{T} - 1\right) + 5.02808 \log_{10}\left(\frac{T_s}{T}\right)$$
$$- 1.3816 \times 10^{-7}\, 10^{11.344\,(1-T/T_s)} - 1$$
$$+ 8.1328 \times 10^{-3}\, 10^{3.49149\,(T_s/T-1)} - 1 \qquad (12)$$

where $P_s$ = the pressure in atmospheres

$T$ = the absolute temperature

$T_s$ = 373.16°K, the normal boiling point of pure water

Using this equation (12) the vapour pressures of pure water were calculated. The slopes of log $P_2$ versus log $P_3$ were calculated analytically by the method of moments instead of by the more inaccurate graphical method.

Little experimental work has been done on the vapour pressures of aqueous electrolytic solutions especially over a range of temperature, except for isopiestic measurements of vapour pressures for the determination of activity coefficients at 25°C. Johnson and Molstad (27) have determined the vapour pressures of lithium chloride solutions by employing the gas saturation method. They also calculated the latent heat of vaporization of water from the solutions and the differential heats of dilution.

In addition the vapour pressure measurements were utilized in the calculation of the activity of the water given by the ratio $\frac{P}{P_o}$

where P = the vapour pressure of solutions at temperature T

$P_o$ = the vapour pressure of pure water at same temperature ,

The osmotic pressures were also calculated by means of the expression:

$$\Pi = \frac{RT}{\bar{v}} \cdot \ln \frac{P}{P_o}$$

where $\bar{v}$, the partial molal volume of the solvent, was approximated by v, the molar volume of water.

# EXPERIMENTAL PROCEDURE

## Experimental Procedure

### 1. Purification of Material

The lithium nitrate was supplied by the Fisher Scientific Company (Catalogue Number L-132). The salt was pure enough for research purposes but hygroscopic, therefore, it had to be heated in a platinum crucible over a Meker Burner for about an hour in order to drive off all the water. When this process was over, it was stored in the platinum crucible, over sulfuric acid in a dessicator.

### 2. Preparation of Solutions

Solutions were made up by weighing and recorded as weight percent. In order to transfer the salt from the platinum crucible into the weighing bottle, the solid mass had to be broken into small pieces by means of agate mortar. It was then poured into the weighing bottle and tightly capped. The pure dry salt was weighed on an analytical balance in a tall weighing bottle using a weighing bottle of similar size and shape as counterpoise. The necessary amount of water was added to the salt in order to obtain the desired weight percent.

### 3. Apparatus and Procedure

Throughout the whole research work only two types of apparatus were employed; one was used for the more dilute solutions of lithium nitrate and the other for the more concentrated solutions. The apparatus used to measure the vapour pressure of solutions up to and including 30 percent by weight of lithium nitrate was the differential manometer of E.J. Hartung (24), illustrated in figure (1) and in figure (2). Figure (3) and figure (4) illustrate the absolute manometer which was used for lithium nitrate solutions above 30 percent by weight.

## The Differential Manometer

Figure (1) and figure (2) represent the differential apparatus employed. The upper part of manometer is shown in figure (1) and continued in figure (2) on the left hand side of the page. The bottom half is on the right hand side of the page of figure (2). The differential manometer consists of two bulbs of approximately 50 ml. capacity labelled A and B in figure (1) each connected to an arm of the manometer tube F, 25 cms. long. Just below the U tube of the top part of the apparatus was a glass tube of wide bore, G, which served the purpose of holding the apparatus in the thermostat by means of a neoprene rubber stopper as shown in figure (5). H. represents a ball joint which was conveniently connected to the socket I of the bottom part of the apparatus. This ball and socket joint made it easy for the experimentor to remove the apparatus between runs. The ball and socket joint were lubricated with silicone grease to prevent the leakage of mercury and clamped together as shown in figure (5).

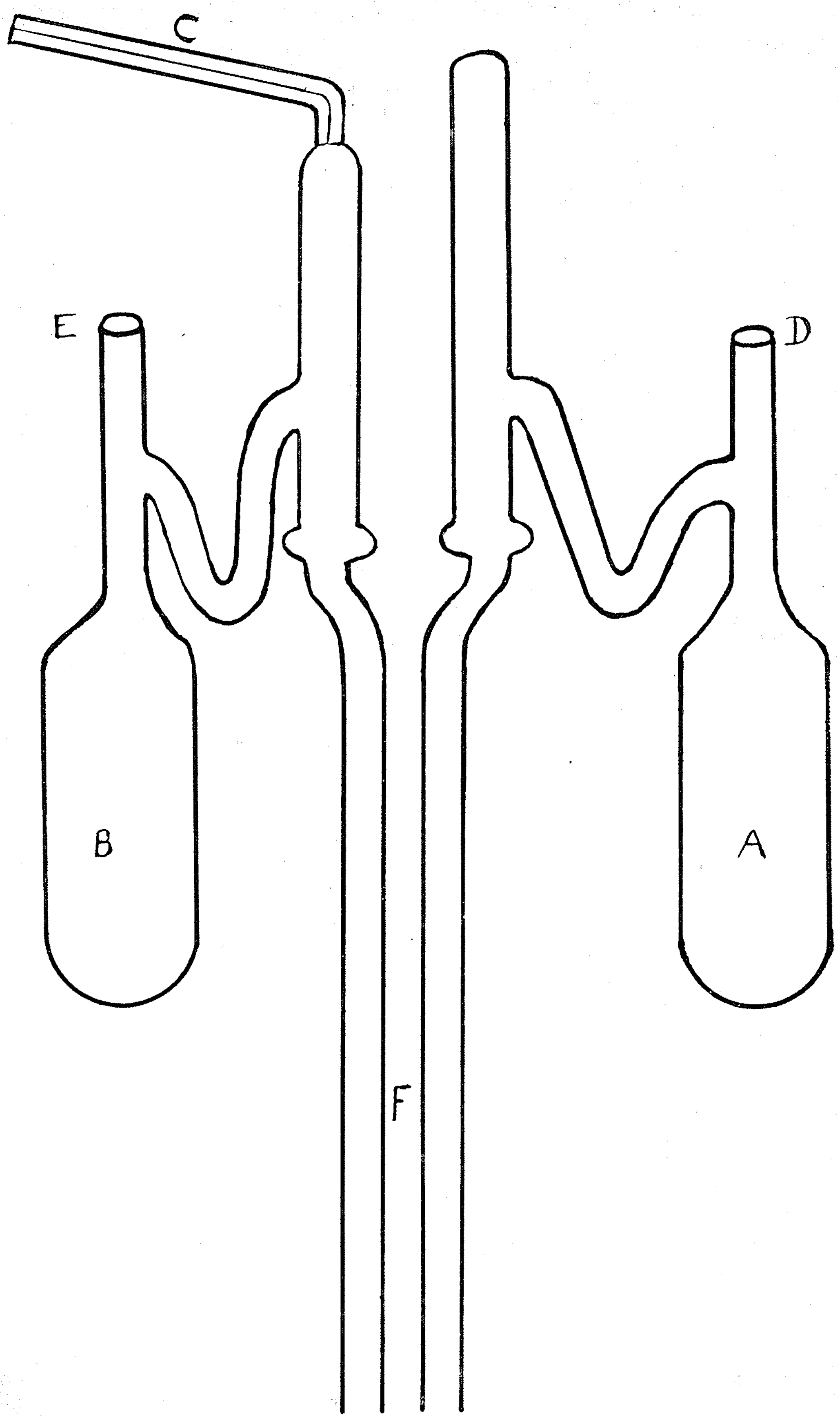

Figure (1)

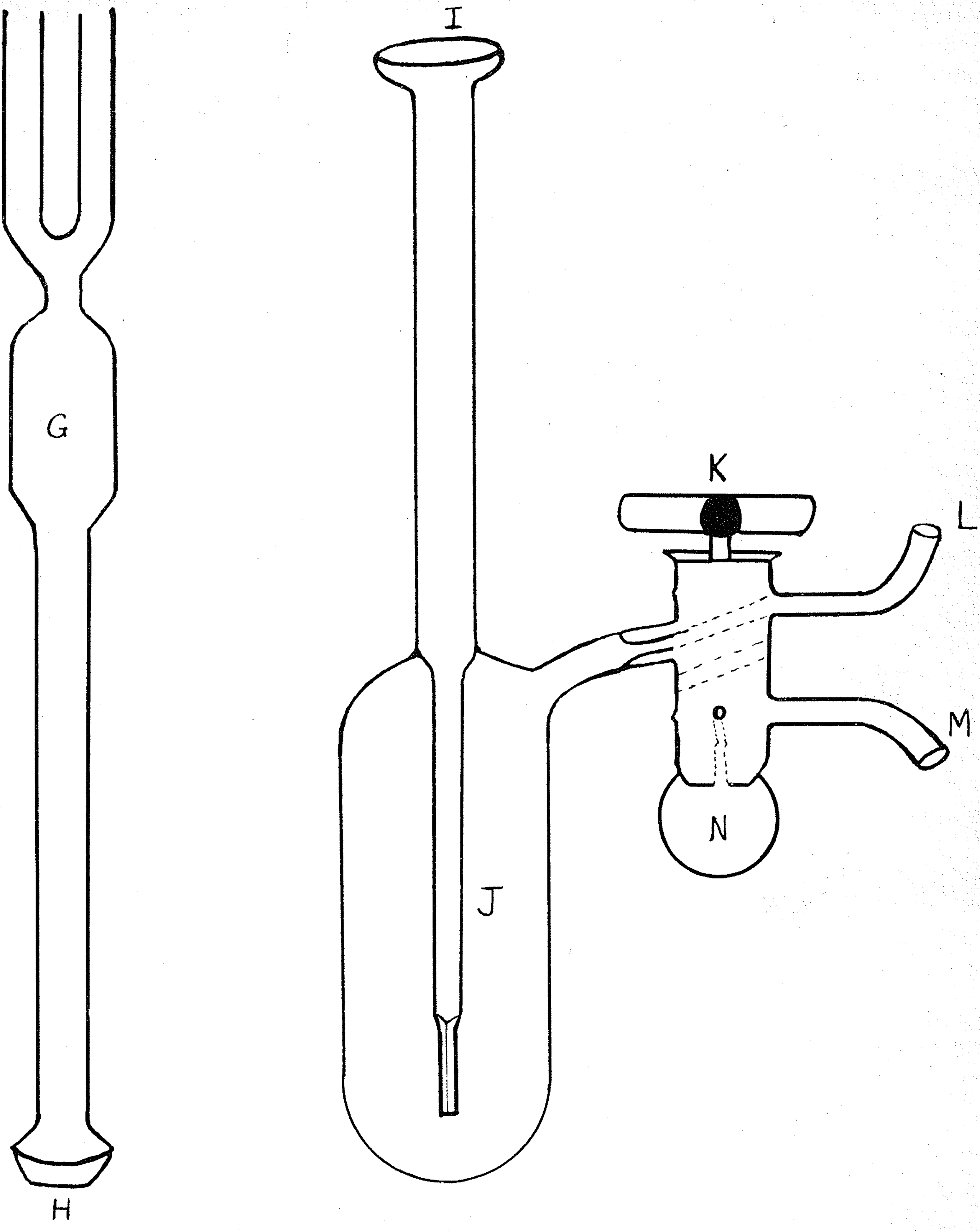

Figure (2)

K represents a three-way vacuum stop-cock, With the stop-cock in one position, the small bulb N is connected through outlet M and through pressure tubing to a vacuum pump by means of which N can be evacuated. A turn of the stop-cock to the left disconnects M from the small bulb N, the stop-cock being held firmly in place due to the atmospheric pressure. An auxiliary mercury reservoir is connected to outlet L and clamped into position as shwon in figure (5).

Mercury was added by means of the auxiliary bulb until the tube, reservoir J, and rubber tubing were filled and the auxiliary bulb about half-full. The level of the mercury was raised by manipulation of the stop-cock until it was 3 cms. from the top of the socket I. The capillary termination in reservoir J prevented violent rushings of the mercury which might have led to an accident. Next about 1cc. of silicone oil was placed on top of the mercury just below the socket I. The purpose of the silicone oil was to prevent the condensation of small amounts of water on the mercury meniscus which would lead to distortion in the field of vision of the cathetometer and also to minimize the possibility of the mercury vapour contaminating the lithium nitrate solutions. Silicone oil was chosen because of its very low vapour pressure at the temperatures concerned.

When this part of the apparatus was set up as described above, the bulbs B and A were filled with distilled water and the lithium nitrate solution respectively through the wide-diameter tubes E and D by means of a thistle tube. About 30 ccs. of distilled water and of solution were used. Then the wide tubes E and D were sealed off by means of a torch. The apparatus was then lowered into the thermostat and set up as shown in figure (5) with the necessary clamps to keep the apparatus vertical and to hold the ball and socket tightly together.

After the ball and socket joint had been closed and clipped firmly in place, the mercury was allowed to rise up the manometer tube to a height a little above the U of the tube. The rubber vacuum tubing was then joined to capillary C and a stop-cock which was located between the apparatus and the air pump was closed. Next, a freezing mixture of dry ice-acetone was prepared in an insulated metal container large enough to accomodate both bulbs at the same time. The container was placed in such a position in the thermostat that both bulbs were well immersed. After ten minutes time the mercury was lowered below the U so that both sides of the manometer were open to the evacuation outlet. The stop-cock between the apparatus and the air pumps was opened and evacuation begun. The pumping down continued for a half hour. During this time the apparatus was checked for leaks with a tesla coil. When the half hour terminated the stop-cock was closed and the mercury again allowed to rise above the U of the manometer, the freezing mixture removed and the contents of the bulbs allowed to thaw. Since the thawing was very slow the bulbs were immersed in luke warm water, and tapped to make sure that all the salt returned into solution. Bumping sometimes resulted on thawing, and in order to prevent either the distilled water or the solutions from being thrown over into the manometer tubes, traps in the form of wide U shaped tubes were constructed in the apparatus between bulbs B and A and the tubes.

Repetition of the above procedure was carried out at least ten times or until no air bubbles were observed to evolve from the water and the solution.

After having finally evacuated all the air out of the system, the capillary tube C was sealed off from the air pump with a torch. Then the mercury was allowed to rise up into the manometer tubes well above the U and the freezing mixture removed. When the solution had thawed out completely it was agitated in order to insure complete homogeneity.

The Barometric Manometer

With the more concentrated solutions (i.e. over 30 percent by weight for lithium nitrate solutions) it was impossible to use the differential manometer, since the limbs of the U-tubes were only 25 cms. long, and the difference in vapour pressure of these solutions from that of water became greater than 25 cms. of mercury. Therefore a direct barometric apparatus was employed.

To obtain a picture of the whole apparatus place the apparatus in figure (3) at right angles to the one in figure (4). The manometer consists of a barometer tube F, which is just a continuation of E, of 6 cms. internal diameter and 90 cms. long connected at its lower end to a mercury reservoir C. Fused to the upper end of the barometer tube was a short piece of coarse capillary tubing G which connected to a vacuum pump. Another piece of short capillary D was connected to the same vacuum pump. Between both capillaries and the vacuum pump were stop-cocks, joined through vacuum tubing and a glass T joint to the vacuum pump. B was a wide diameter tubing leading into bulb A which held the solution.

Mercury was added to the system by pouring it through a funnel into the capillary D until the reservoir C was approximately three quarters filled. The opening B was sealed off with a torch. The air pump was then turned on in order to evacute the system. Meanwhile the mercury was heated and agitated vigorously to expel the air from the body of the mercury and from the walls of the reservoir. When all the air was removed from the mercury the pressure tubing behind the stop-cock from the main line was disconnected so that air could seep into both sides of the T joint at the same time.
Very little air was found in the body of the mercury and only slight amounts along the walls of the reservoir close

to the mercury surface.

B was reopened and the solution was placed in the bulb by a thistle tube passing through B. The tube was quickly sealed off to insure minimum loss of water vapour and the stop-cocks were closed. The bulb containing the solution was lowered into a freezing mixture of acetone-dry ice for at least 10 minutes. Then the stop-cocks were reopened and evacuation of the air was begun. After 30 minutes the stop-cocks were closed and the freezing mixture removed.The thawing of the solution was so slow that the bulb A had to be immersed in a beaker of warm water until the solution dissolved. If this did not help, the whole apparatus was lowered into a large beaker filled with water and heated as necessary. In order to make sure that no air was trapped at the bottom of the bulb by a few crystals of salt the bulb A was tapped with a rubber policeman. The tapping of the bulb also dissolved any salt which might have remained out of solution. As the solutions became more concentrated the number of times the above procedure had to be repeated became fewer, that is, only six times of freezing and thawing, before finally sealing off the two capillaries.

The apparatus was then clamped to a stand with a flat metal base to give it stability and placed in the thermostat between the two windows. The thermostat was deep enough to cover only about 40 cms. of the barometer tube; the rest protruded above the oil surface. Therefore a stem correction had to be applied to the mercury height above the oil. The experimental results where this occurs have this symbol (*) to indicate that the correction has been applied. The correction was made by the use of another thermometer clamped to the barometer with its bulb at a point half-way between the surface of the oil bath and the mercury meniscus. This means that for these (*) readings there was a loss of accuracy in the measurements since the stem correction was only approximate. However, the percent error was not large at these high vapour pressures.

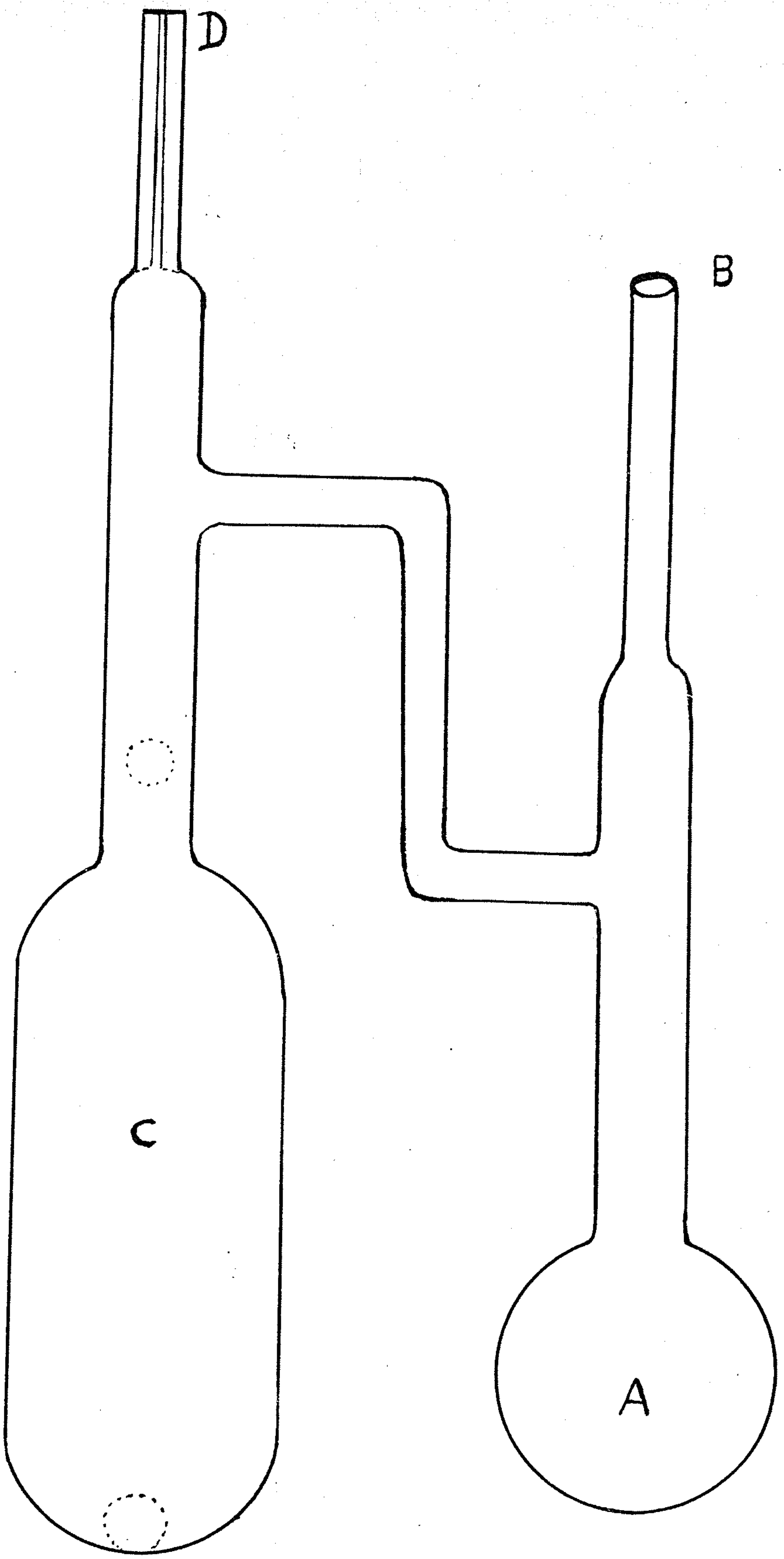

Figure (3)

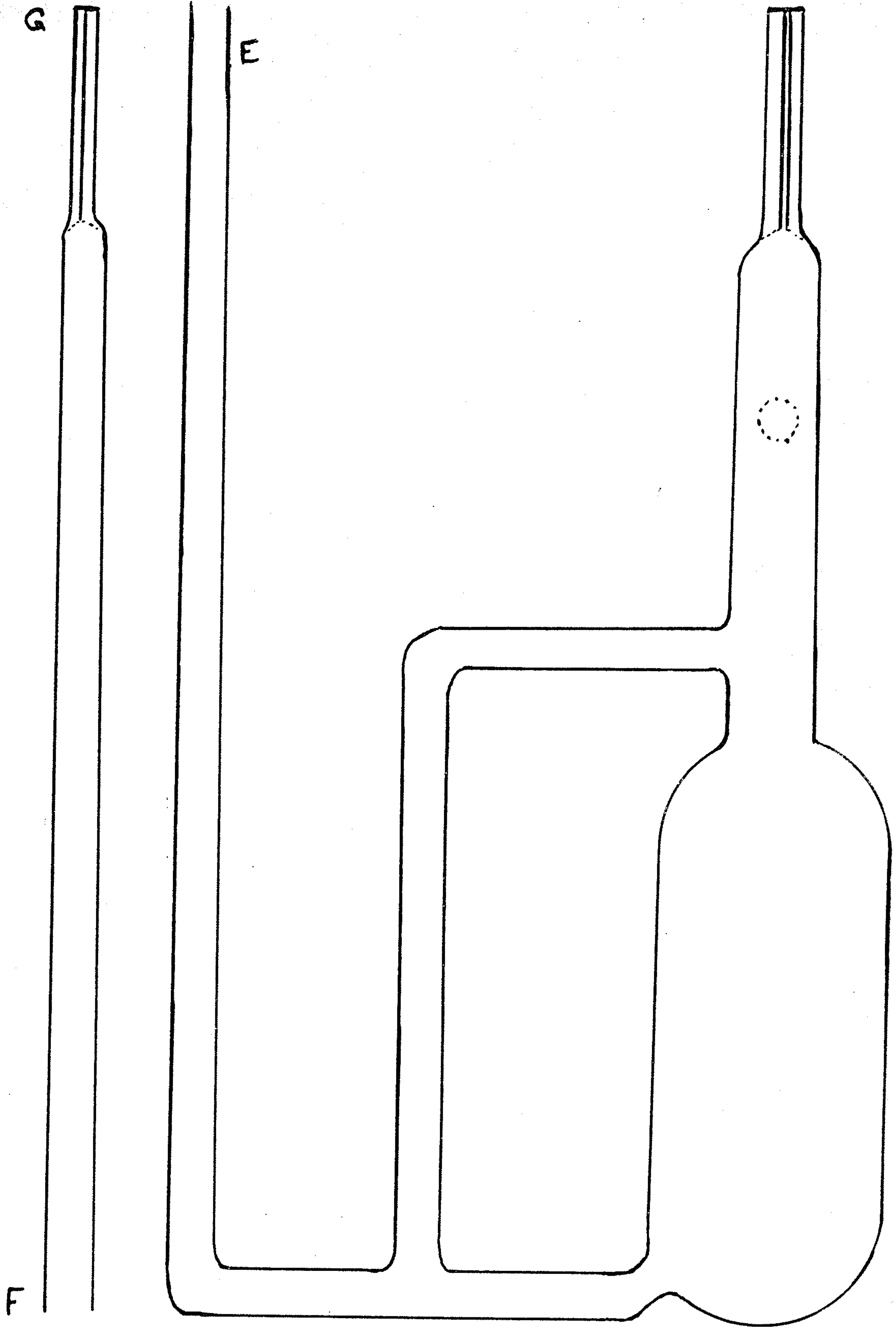

Figure (4)

## Thermostat and Temperature Control

The thermostat consisted of a tall rectangular copper tank of approximately 65 liters capacity ( or 15 gallons) and furnished with two glass windows. Since the thermostatic fluid was mineral oil ( Marcol G X) it was necessary to use Buna-N rubber as gasket material for the glass panes. These windows were held in place with set screws. The tank was well insulated by a surrounding wooden box lined with rock wool and powdered asbestos.

After each run the oil was filtered through Kieselguhr in order to remove the suspended foreign matter. The oil itself changed from a clear solution to a green colour, likely due to the copper of the tank. With clear oil the manometer tubes could be seen distinctly.

The oil was heated with three heating coils and three light bulbs. E is a 300 watt heater connected through a rheostat, supplying constant heat at all temperatures above 50°C. Two 500 watt heaters D and D' were used only in bringing the thermostat to the desired temperature and were not required when the bath was on control. The 60 and 150 watt light bulbs G and H were employed to control the temperature when needed. The other 150 watt light bulb I was used as the temperature control heater and was connected through a relay to the thermoregulator. The use of the light bulb as a source of heat was advantageous on two counts. Firstly, the time lag of a lamp filament is much shorter than an ordinary resistance heater so that a finer temperature control is possible. Second, the operation of the relay was rendered visible so that any relay failures could be immediately detected and corrected before the bath deviated greatly from its set temperature.

The thermoregulator used was of Swedish design and manufacture.* Essentially it was a mercury-in-glass Beckmann thermometer graduated in degrees over the range 0-105°C. It has an upper and lower scale identical to each other. The mercury height i.e. the temperature was indicated by the lower scale. The upper scale was used in setting the regulator at desired temperature. This was done by rotating a magnet on top of the regulator which raised or lowered a fine metal wire running downward through the thermometer capillary to the mercury meniscus. There was a small indicator bar attached to the wire which was set at the desired temperature on the upper scale by rotation of the magnet. Fused through the glass was a wire which led to a screw contact in the head of the regulator.The other lead was attached to the movable wire in the thermometer capillary. Finally the thermoregulator was connected by means of two fine copper wires to the relay.

* Made by Labora, in Stockholm, Serial No. 1252.

Using the three stirrers, I obtained very good control with this type of regulator. The regulator was checked against a Beckmann thermometer and control was within ±.01° and ±.02° over the whole range. The thermometer used was a mercury in glass thermometer graduated in tenths and calibrated against a Platinum resistance thermometer available in one of the laboratories.

The oil bath was stirred by means of two propeller type mechanical stirrers J and J' with three inch blades and one Archimedean screw type stirrer F. The stirrers J and J' were connected to Powerstats. In this way the stirrers were adjusted so that the stirring of the bath was maintained just below turbulence.

## The Measurement of Vapour Pressure

Two cathetometers were used to measure differences in mercury levels, one a short range instrument which could be read to 0.01 mm. and estimated to 0.001mm., and another of greater range which could be read to 0.1 mm, and estimated to 0.01 mm. The short range cathetometer could only take readings for differences of levels less than 2.5 cms. and for anything greater one had to employ the 100 cm. range cathetometer.

The cathetometer, properly levelled, was mounted on a table opposite the window M of the thermostat. Extra light was provided by either a 60 watt light bulb or 150 watt light bulb depending on the clearness of the oil. The bulb was mounted behind the rear window in order that a very clear view of the mercury meniscus in the manometer tubes could be seen at all times.

After the temperature of the bath had been set and was under control successive readings showed that it required about an hour to an hour and a half to obtain equilibrium at lower temperatures while half an hour was sufficient at higher temperatures. On all the runs as many as fifteen readings were taken. The readings were averaged and corrected to 0°C. The probable error does not exceed 0.2 percent and this makes the data good enough for most purposes.

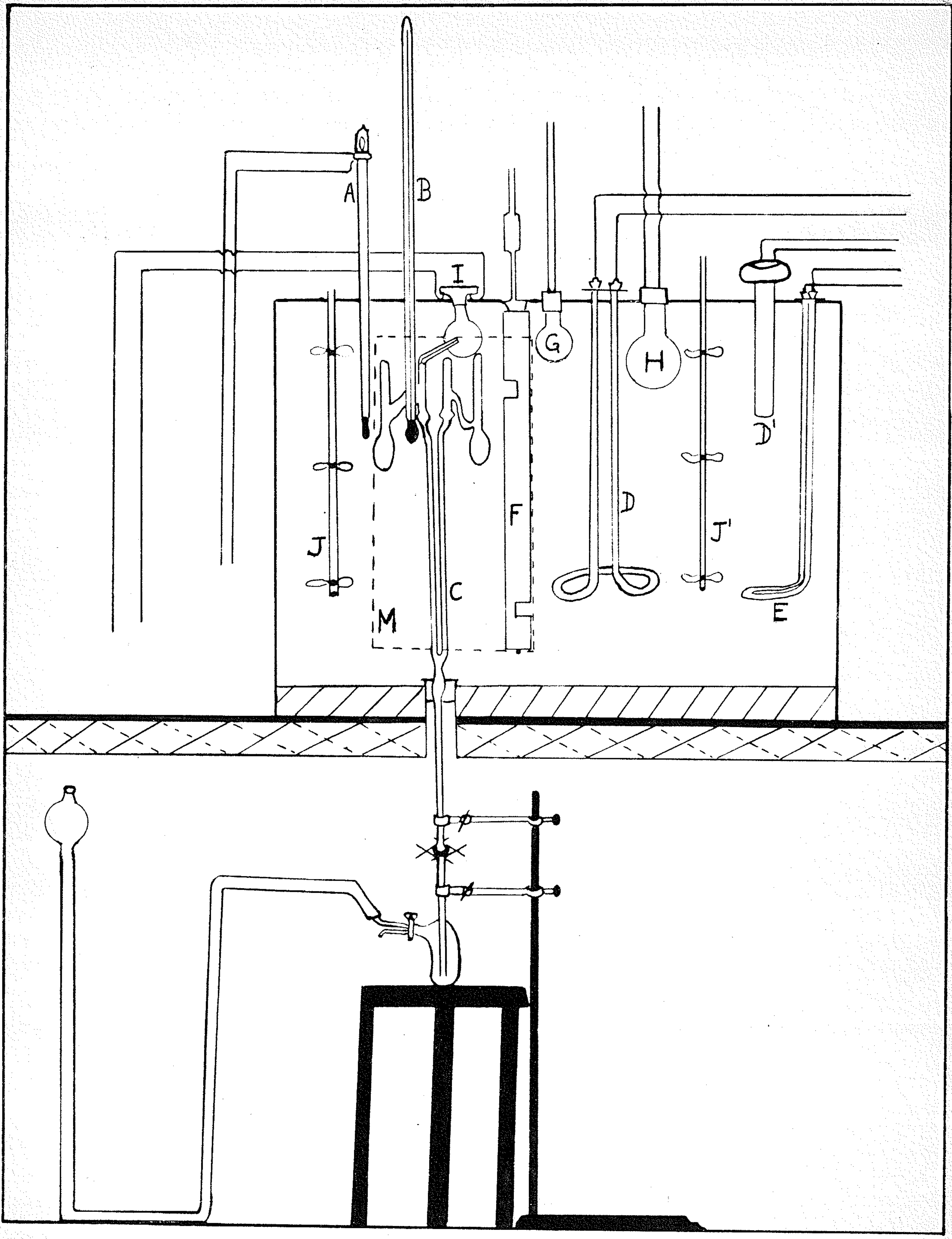

Figure (5)

# EXPERIMENTAL RESULTS

## Table VI

The Vapour Pressures of Lithium Nitrate Solutions, $P_2$, at Various Temperatures and the Corresponding Vapour Pressures of Pure Water, $P_3$.

| Concentration | | Temperature | $P_2$ | $P_3$ |
|---|---|---|---|---|
| Weight % | Molality | (K°) | (mms. of $H_g$) | (mms. of $H_g$ ) |
| 10.00 | 1.612 | 303.16 | 30.479 | 31.83 |
| | | 313.16 | 52.571 | 55.34 |
| | | 323.16 | 87.83 | 92.56 |
| | | 333.16 | 141.76 | 149.5 |
| | | 343.16 | 221.40 | 233.8 |
| | | 353.16 | 335.90 | 355.3 |
| | | 363.16 | 497.20 | 525.8 |
| | | 373.16 | 718.35 | 760.0 |
| | | 375.16 | 771.08 | 815.9 |
| 20.00 | 3.626 | 303.16 | 27.826 | 31.83 |
| | | 313.16 | 48.349 | 55.34 |
| | | 323.16 | 80.67 | 92.56 |
| | | 333.16 | 130.60 | 149.5 |
| | | 343.16 | 203.93 | 233.8 |
| | | 353.16 | 309.12 | 355.3 |
| | | 363.16 | 456.21 | 525.8 |
| | | 373.16 | 658.05 | 760.0 |
| | | 378.16 | 784.04 | 906.1 |

Table VI (continued)

| Concentration | | Temperature | $P_2$ | $P_3$ |
|---|---|---|---|---|
| Weight % | Molality | (°K) | (mms. of $H_g$) | (mms. of $H_g$) |
| 30.00 | 6.214 | 303.16 | 23.078 | 31.83 |
| | | 313.16 | 40.223 | 55.34 |
| | | 323.16 | 66.79 | 92.56 |
| | | 333.16 | 109.42 | 149.5 |
| | | 343.16 | 171.32 | 233.8 |
| | | 353.16 | 261.16 | 355.3 |
| | | 363.16 | 388.41 | 525.8 |
| | | 373.16 | 562.25 | 760.0 |
| 40.00 | 9.657 | 303.16 | 19.182 | 31.83 |
| | | 313.16 | 33.106 | 55.34 |
| | | 323.16 | 55.73 | 92.56 |
| | | 333.16 | 89.34 | 149.5 |
| | | 343.16 | 140.45 | 233.8 |
| | | 353.16 | 215.06 | 355.3 |
| | | *363.16 | 320.30 | 525.8 |
| | | *373.16 | 463.97 | 760.0 |
| | | *378.16 | 556.78 | 906.1 |

Table VI (continued)

| Concentration | | Temperature | $P_2$ | $P_3$ |
|---|---|---|---|---|
| Weight % | Molality | (°K) | (mms. of $H_g$) | (mms. of $H_g$) |
| 50.00 | 14.504 | 303.16 | 13.586 | 31.83 |
| | | 313.16 | 23.373 | 55.34 |
| | | 323.16 | 39.93 | 92.56 |
| | | 333.16 | 64.66 | 149.5 |
| | | 343.16 | 102.21 | 233.8 |
| | | 353.16 | 157.20 | 355.3 |
| | | 363.16 | 236.10 | 525.8 |
| | | *377.16 | 400.57 | 875.1 |
| 57.28 | 19.447 | 303.16 | 9.208 | 31.83 |
| | | 313.16 | 16.606 | 55.34 |
| | | 323.16 | 28.49 | 92.56 |
| | | 333.16 | 46.86 | 149.5 |
| | | 343.16 | 75.77 | 233.8 |
| | | 353.16 | 118.25 | 355.3 |
| | | 363.16 | 179.31 | 525.8 |
| | | 373.16 | 264.20 | 760.0 |
| | | 378.16 | 319.87 | 906.1 |

Table VI (continued)

| Concentration | | Temperature | $P_2$ | $P_3$ |
|---|---|---|---|---|
| Weight % | Molality | (°K) | (mms. of $H_g$) | (mms. of $H_g$) |
| 64.95 | 26.880 | 313.16 | 11.141 | 55.34 |
| | | 323.16 | 19.011 | 92.56 |
| | | 333.16 | 31.74 | 149.5 |
| | | 343.16 | 50.77 | 233.8 |
| | | 353.16 | 79.77 | 355.3 |
| | | 363.16 | 122.22 | 525.8 |
| | | 373.16 | 182.06 | 760.0 |
| | | 378.16 | 221.34 | 906.1 |

## TABLE VII

The slopes $\frac{\Delta H_2}{\Delta H_3}$ of log $P_2$ VS log $P_3$ for Lithium Nitrate Solutions and the Resulting Values of $\Delta H_2$ and $\Delta H_1$ at 50°C ($\Delta H_3$= 10,245 Cals/mole)

| Concentration | | Slope | $\Delta H_2$ | $\Delta H_1$ |
|---|---|---|---|---|
| Weight % | Molality | $\Delta H_2/\Delta H_3$ | (Cals/mole) | (Cals/mole) |
| 0 | 0 | 1.00 | 10,245 | 0 |
| 10.00 | 1.612 | 0.9967 | 10,211 | 34 |
| 20.00 | 3.626 | 0.9969 | 10,213 | 32 |
| 30.00 | 6.214 | 1.0078 | 10,325 | -80 |
| 40.00 | 9.657 | 1.0063 | 10,310 | -65 |
| 50.00 | 14.504 | 1.0225 | 10,475 | -230 |
| 57.28 | 19.447 | 1.0585 | 10,844 | -599 |
| 64.95 | 26.880 | 1.0700 | 10,962 | -717 |

## TABLE VIII*

The $\Delta H_2$ and $\Delta H_1$ values for ammonium nitrate and silver nitrate solutions at 50°C ($\Delta H_3$ = 10,245 cals/mole)

| Ammonium Nitrate | | | Silver Nitrate | | |
|---|---|---|---|---|---|
| Concentration Weight % | $\Delta H_2$ | $\Delta H_1$ ($\Delta H_3$-$\Delta H_2$) | Concentration Weight % | $\Delta H_2$ | $\Delta H_1$ ($\Delta H_3$-$\Delta H_2$) |
| 10.00 | 10158 | 87 | 9.98 | 10227 | 18 |
| 20.00 | 10047 | 198 | 19.98 | 10172 | 73 |
| 30.00 | 9948 | 297 | 30.00 | 10204 | 41 |
| 40.00 | 10130 | 115 | 40.00 | 10202 | 43 |
| 50.00 | 9832 | 413 | 50.00 | 10192 | 53 |
| 60.00 | 10044 | 191 | 59.29 | 10192 | 53 |
| 70.00 | 9999 | 246 | 69.99 | 10138 | 107 |
| 80.00 | 9834 | 411 | 80.05 | 10135 | 110 |
| 90.00 | 9759 | 486 | 85.07 | 10039 | 206 |

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* Table taken from the publication of Dr. A.N. Campbell et al (15)

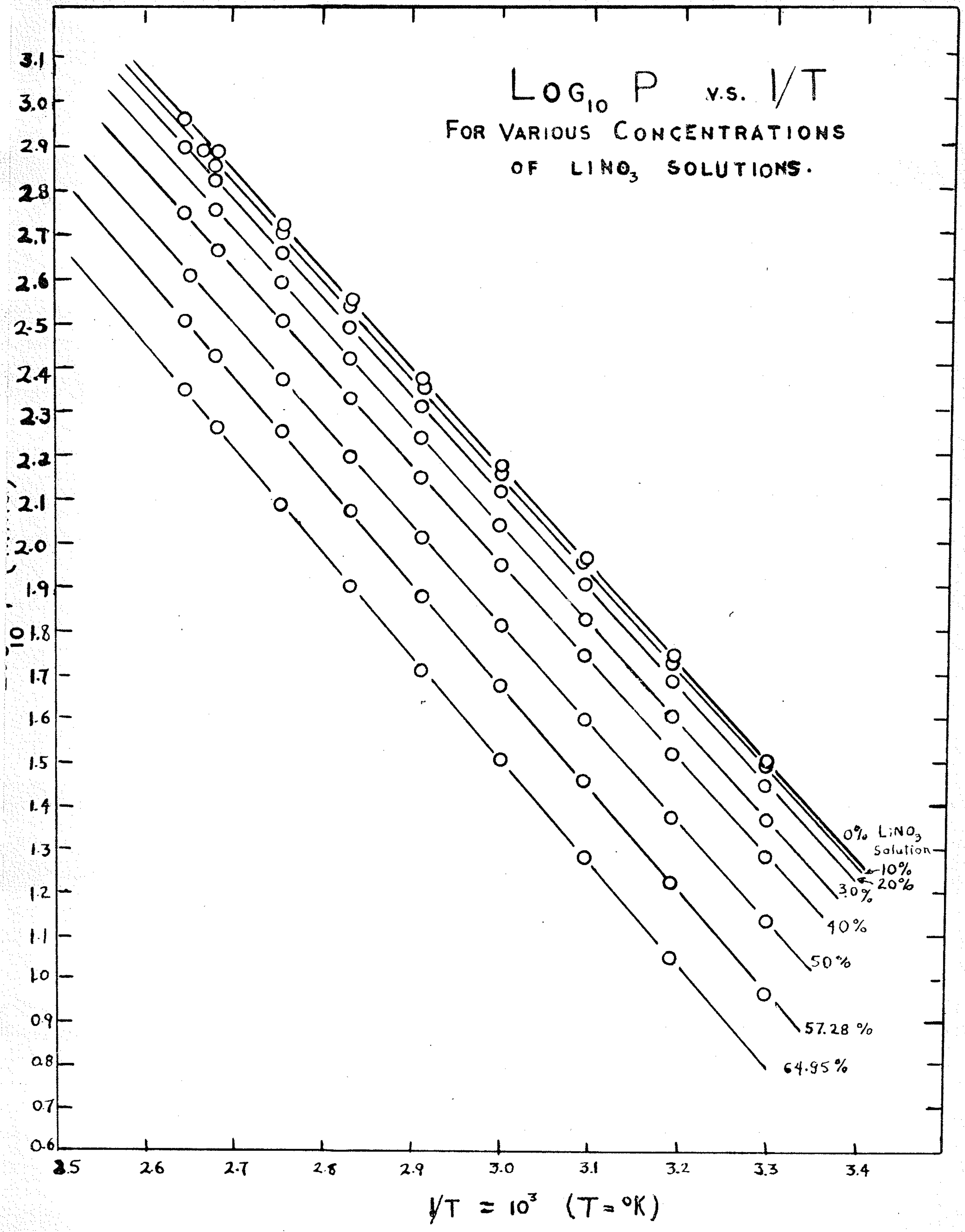
LOG₁₀ P v.s. 1/T
FOR VARIOUS CONCENTRATIONS
OF LINO₃ SOLUTIONS.
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
10
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
0% LiNO₃ Solution
10%
20%
30%
40%
50%
57.28 %
64.95 %
1/T = 10³ (T = °K)

Figure (6)

## TABLE IX

### The Activity of Water $P/P_o$ , in Lithium Nitrate Solutions at Various Concentrations and Temperatures

| Concentration (Mole fraction water*) | Temperature | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| 0.9719 | .9577 | .9500 | .9490 | .9485 | .9470 | .9455 | .9455 | .9452 |
| 0.9387 | .8743 | .8737 | .8716 | .8738 | .8723 | .8701 | .8675 | .8659 |
| 0.8993 | .7251 | .7269 | .7216 | .7321 | .7328 | .7351 | .7386 | .7398 |
| 0.8518 | .6021 | .5983 | .6021 | .5977 | .6007 | .6053 | .6091 | .6105 |
| 0.7928 | .4269 | .4224 | .4314 | .4326 | .4372 | .4425 | .4490 | ..... |
| 0.7406 | .2893 | .3009 | .3078 | .3135 | .3241 | .3328 | .3410 | .3476 |
| 0.6737 | ..... | .2013 | .2054 | .2123 | .2172 | .2245 | .2324 | .2396 |

* Calculated on the assumption of no ionization.

## TABLE X

### The Osmotic Pressure II of Solutions of Lithium Nitrate at 50°C and 70°C.

| Concentration | | II (atms) | |
|---|---|---|---|
| Weight % | Molality | (50°C) | (70°C) |
| 10.00 | 1.612 | 76.07 | 89.1 |
| 20.00 | 3.626 | 199.00 | 208.7 |
| 30.00 | 6.214 | 473.00 | 474.9 |
| 40.00 | 9.657 | 735.00 | 778.7 |
| 50.00 | 14.504 | 1205.00 | 1260.9 |
| 57.28 | 19.447 | 1704.00 | 1721.6 |
| 64.95 | 26.880 | 2296.00 | 2333.3 |

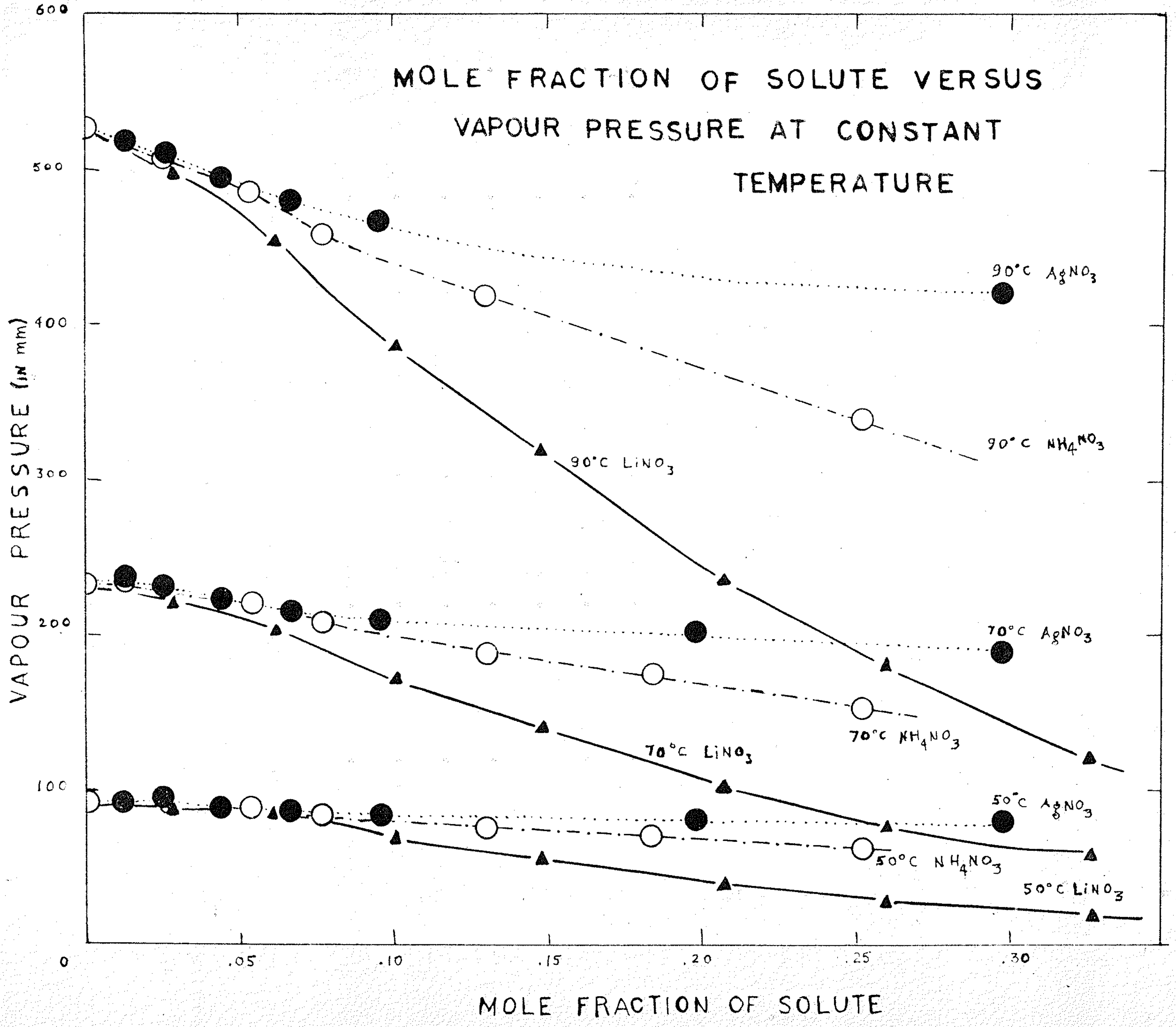
MOLE FRACTION OF SOLUTE VERSUS
VAPOUR PRESSURE AT CONSTANT
TEMPERATURE
VAPOUR PRESSURE (IN mm)
MOLE FRACTION OF SOLUTE
600
500
400
300
200
100
0
.05
.10
.15
.20
.25
.30
90°C $AgNO_3$
90°C $NH_4NO_3$
90°C $LiNO_3$
70°C $AgNO_3$
70°C $NH_4NO_3$
70°C $LiNO_3$
50°C $AgNO_3$
50°C $NH_4NO_3$
50°C $LiNO_3$

Figure (7)

# DISCUSSION OF RESULTS

## Discussion of Results

In the opinion of this author, no lengthy discussion about the pure experimental data, shown in Table VI on page 52-55, is necessary. It is, of course, interesting to note that if one compares the vapour pressures of solutions of lithium nitrate, ammonium nitrate, or silver nitrate, shown in Table II of Campbell et al's publication (15), he will find that lithium nitrate solutions have a much lower vapour pressure than those of the other two salts at the same concentration and at the same temperature. Also as the concentration or the temperature of the solutions is increased the vapour pressure of lithium nitrate is observed to become very much lower than those of the other two salts. An attempt to explain this phenomenon will be considered later in this discussion. The probable error in the measurements of the vapour pressure does not exceed 0.2% and this makes the data good enough for most purposes.

Table VII, on page 56, gives the latent heat of vaporization of water from solutions of various concentrations of lithium nitrate ($\Delta H_2$) at 50°C. The $\Delta H_2$ values were calculated using the method of Othmer, equation 11 on page 32 and the experimental data from Table VI, instead of using the slope $-\frac{\Delta H}{2.3\ R}$ from the plot of log P v.s. $\frac{1}{T}$ shown in figure (6) on page 58. $\Delta H_3$ is 10,245 cals/mole, the value calculated for the latent heat of vaporization of pure water from an average of several measured calorimetric determinations of Johnson and Molstad (27). The latent heat of vaporization of water from lithium nitrate solutions ( $\Delta H_2$) at 50°C increases with increasing concentrations and is always greater than that of pure water, $\Delta H_3$, in the more concentrated solutions, i.e. above the concentrations of 20 weight per cent. Now, the $\Delta H_2$ values of ammonium nitrate and silver nitrate given in Table VIII on page 57 decrease for increasing concentrations and at no concentration is the $\Delta H_2$ value greater than $\Delta H_3$.

The reason that more heat is required to liberate a water molecule from lithium nitrate solutions to the vapour state than is required from pure water, or even from the ammonium and silver nitrate solution must be due to a greater force of attraction between the water molecules and the lithium ion. This force is called the ion-solvent attractive force according to the model proposed for concentrated solutions by Stokes and Robinson (43). It will exist in all electrolytic solutions to a greater or lesser degree, depending on the ions present.

Table VII on page 56 gives also the differential heat of dilution ( $\Delta H_1$) for various concentrations of lithium nitrate solutions at 50°C. The $\Delta H_1$ values were calculated using equation 5 on page 29, i.e. the latent heat of vaporization of pure water minus the latent heat of vaporization of water from solutions of lithium nitrate ( $\Delta H_3 - \Delta H_2$). $\Delta H_1$ was found to have positive numerical values for such salts as ammonium nitrate and silver nitrate at 50°C by Campbell et al's (15), for aqueous solutions of sodium chloride by Roehl (40), and also for dilute solutions of lithium nitrate at 50°C, i.e. for 10 and 20 weight per cent in Table VII. This indicates that heat is absorbed when one mole of water is added to a large amount of solution. Therefore, the dilution effect must be the predominant factor. This effect, causing an absorption of heat in these electrolytic solutions, is just the energy required to separate the ions which are held close together by their electrostatic force of attraction. The $\Delta H_1$ values in Table VII are negative for the concentrated solutions of lithium nitrate, i.e. above 20 weight per cent, at 50°C. This means that heat is evolved when a concentrated solution of lithium nitrate is diluted. Since heat is evolved instead of absorbed, there must be some other reaction taking place that is greater than and opposite in character to the dilution effect. This other reaction is thought to be due to the ion-solvent attractive forces in lithium nitrate solutions. Now the question that arises is why are the differential heat of dilution values ( $\Delta H_1$) for 10 and 20 weight percent for lithium nitrate solutions not negative also, if the lithium ions are hydrated. One can explain this by saying that the lithium ions in these solutions are hydrated but the dilution effect must be greater than the hydration, therefore heat is absorbed instead of evolved in these dilute solutions. The lower vapour pressures obtained for lithium nitrate solutions (shown in Table VI) also suggest that the ion-solvent attractive force is much stronger in this solution than in the silver nitrate and ammonium nitrate solutions. Van Ruyven (48), studying many electrolytic solutions, stated that the electric forces of the silver and nitrate ions are too feeble to bind any water molecules. His observations were based on the degree of ionization calculated from the elevation of the boiling point and those calculated from conductivity measurements. Buchboch, (14) also was unable to detect any evidence of hydration of the ions of silver nitrate. This must also be the case for the ions of ammonium nitrate.

In Table IX on page 59, the activity of the water in solution, equal to $\frac{P}{P_o}$, the ratio of the vapour pressure of solution to the corresponding vapour pressure of pure water is compared to the mole fraction of water (calculated on the assumption of a non-ionized salt). On examination it is noticed that there exists no agreement between the mole fraction and activity for lithium nitrate solutions i.e. Raoult's law is not obeyed at all in this concentration range. On the other hand Campbell et al (15) found the agreement to be suprisingly good and independent of temperature for silver nitrate solutions i.e. Raoult's law is obeyed over this range, far more closely than it should be obeyed by an electrolytic solution. Campbell and Kartzmark (16) have calculated the extent of ion-pair formation in silver nitrate solutions. It is far from complete at concentrations for which the activity calculation is valid and therefore it is impossible to account for the above observations on the assumption that silver nitrate is only slightly ionized. The activity of ammonium nitrate (15) drops markedly and is much lower than the mole fraction but the differences is not as remarkable as for lithium nitrate. These results can be accounted for on the assumption that the silver ion is not (or is very feebly) hydrated, the ammonium ion a little more so while the lithium ion is very strongly hydrated.

The osmotic pressures calculated from equation II $= \frac{RT}{\bar{V}} . \ln \frac{P}{P_o}$ on page 34 of lithium nitrate solutions at 50°C and at 70°C are presented in Table X, on page 60. A detailed discussion of the results is not thought necessary. It is sufficient to say that the high osmotic pressures calculated in Table X, shows that the lithium ions have very strong ion-solvent attractive forces as compared to say, the electrostatic forces of silver nitrate, where the osmotic pressures calculated by G. Rutherford (41) are much lower at the same temperature.

Finally, in figure (7) on page 61 the vapour pressures of all three electrolytes, at different temperatures, have been plotted against mole fraction of solute. This figure shows very clearly that at corresponding mole fraction and temperature, the vapour pressures of lithium nitrate solutions are much lower than those of silver nitrate and of ammonium nitrate solutions. The obvious explanation of this is that lithium ion holds its water of hydration much more firmly than do the silver and ammonium ions. The high viscosity obtained for lithium nitrate solutions also points in this direction.

# CONCLUSION

## Conclusions

1. The vapour pressures of lithium nitrate solutions for concentrations varying from 10 to approximately 65 weight per cent were determined over a range of temperatures varying from 30° to 105°C.
2. The latent heat of vaporization of water from lithium nitrate solutions ($\Delta H_2$) at 50°C was calculated over the concentration range of 10 to 65 weight per cent.
3. The differential heat of dilution ($\Delta H_1$) at 50°C was calculated over the concentration range of 10 to 65 weight per cent of lithium nitrate solutions.
4. The activity of the water $\frac{P}{P_o}$, in lithium nitrate solutions from 10 to 65 weight per cent and over the temperature range from 30°C to 100°C, was calculated.
5. The osmotic pressures, over the concentration range of 10 to 65 weight per cent and at temperatures 50°C and 70°C, were calculated using this equation

   $$\Pi = \frac{RT}{\overline{V}} \cdot \ln \frac{P}{P_o} .$$
6. From the results, it was concluded that the lithium ion binds the water molecules very strongly.
7. Also, from the results, it was concluded that the water of hydration of the lithium ion is strongly bound, as compared to the water of hydration of the ammonium and silver ions.

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