

THE VAPOUR PRESSURES OF
CONCENTRATED SOLUTIONS
OF SILVER NITRATE AT
VARIOUS TEMPERATURES.

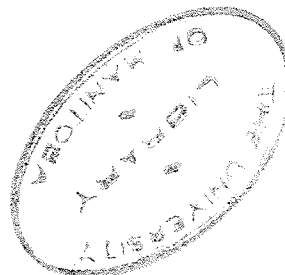
By

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Abstract.

The vapour pressures of solutions of silver nitrate from zero concentration to eighty-five weight percent were determined over a range of temperature from 30° to about 100°C. (for solutions up to seventy percent) and over a more narrow range for the more concentrated solutions. A differential manometer and an absolute barometric apparatus were used to measure the vapour pressures.

By an application of the Clausius-Clapeyron equation it was hoped to detect evidence of layer hydration of ions as postulated by Stokes and Robinson. Within the limits of experimental error no evidence of hydration was found and it was concluded that the Clausius-Clapeyron equation as applied in this research was not suitable for the estimation of the extent of ionic hydration. Water activities, osmotic pressures, and osmotic coefficients were also calculated.

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THEORETICAL INTRODUCTION.

THEORETICAL INTRODUCTION

Ionic Solvation:

The concept of ionic solvation has become an important part of the theory of electrolytic solutions. Ions in solution in polar solvents are thought of as being coordinated with a certain number of solvent molecules. The number varies from ion to ion and is referred to as the solvation number of the ion, but, in spite of much experimental work, the significance of the term "solvation number" has remained in doubt. The various experimental methods used to estimate the solvation number give large differences in numerical values. Thus, partly because of the unreliability of the experimental methods, the meaning of the term "solvation number" remains indefinite.

In order to get around the difficulty of assigning a solvation number to an ion more recent workers on ionic solvation have attacked the problem from a different direction. In this regard efforts have been directed 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.

A more accurate knowledge of ion-solvent interaction is of great importance in several ways, firstly, to further the model of an ionic solution, secondly in the development of the theory of concentrated electrolytic solutions and lastly, the calculation of solvation

numbers as an aid in the theory of reactions in solution.

Early in the development of the idea of ionic solvation the ions were regarded as being chemically bound to the water molecules. The observations of S. Aschkenazi (1) seemed to support this concept. He quoted sudden changes in conductivity, cryoscopic constants, etc. with solution composition which he thought corresponded to the formation and composition of various definite hydrates. There was difficulty, however, in confirming the existence of definite hydrates in solution. Therefore consideration of the polarizability of water molecules and the field about the ion led K. Fajans (19) to the conclusion that the interaction energy in solvation was entirely coulombic and did not involve covalent linkages. The water molecules did not adhere to the ion at all times but rather it was believed that the molecules in the hydration sheath were continually interchanging with those in the bulk of the solution.

This picture of ionic hydration was substantiated by M. Born (8) who showed that the solvation energy arising from a very simple interpretation of Fajans concept 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 since ions having a radius greater than some critical value would have difficulty "fitting in" to the structure of

certain solvents.

It would seem that the electrostatic theory of solvation energy applies as long as the simpler ions of groups IA and IIA of the Periodic Table and the halogens are considered. This type of ion-solvent interaction is almost entirely coulombic, other types of interaction being unimportant in this connection.

This conclusion cannot be assumed for certain in the case of the more complicated ions e.g. for those of group VIII where strong coordinating power tends to favor covalent attachment between ion and solvent. For many of these ions there exists little quantitative evidence of solvation.

If we are willing to accept the Fajans-Born concept of simple coulombic interaction it follows logically that a certain number of solvent molecules would be attached firmly to the ion and further ion-dipole interaction would involve other solvent molecules outside the inner solvation sheath. It has been suggested (6) that the term primary hydration or more generally primary solvation be used when referring to the attachment of solvent molecules to those ions in solution for which (i) the ion and its attachment of solvent molecules move together as one entity during electrolytic transport and (ii) the solvent ions have completely lost their own separate translational degrees of freedom.

"Secondary solvation" then involves all interactions which are not included in the definition of primary solvation. The term

total solvation would therefore be the sum of these two types. It may be said here that the measurement of solvation energies involves the estimation of the energies involved in the total effect.

Investigations (4) into the structure of water have been a great aid in accounting for the properties of ionic solutions especially those relating to solvation. Since the internal field of water is determined by the electrostatic field of the dipoles the introduction of charged ions will obviously modify the field considerably. This effect on the basis of coulombic forces will be roughly proportional to the polarizing power of the ion, that is, its charge divided by the ionic radius. It follows that large monovalent ions will have comparably small polarizing power because of their low charge density. Small, highly charged ions on the other hand will have a much greater effect. According to J. D. Bernal and R. H. Fowler (4) the hydration of an ion will occur when the potential energy of a water molecule forming part of the coordination shell about an ion is less than that of a molecule in free water. The charge of the ion would be expected to attract the two H-nuclei or the two vacant spaces in the water molecule symmetrically, that is, from the point of view of further coordination to occupy them both. Therefore it follows in free water every molecule has four neighbors and a single molecule coordinated to an ion has three, the ion and two water molecules on either side. On this basis it would seem that except for F^- and OH^- the potential energy of coordination is so small

that there is no true hydration of anions.

F. A. Lindemann (30) has proposed a different theory of ionic solvation. He suggests that there is no permanent hydration sheath existing in solution. The observed solvent transport during movement of an ion is caused by the transfer of momentum from ion to solvent molecules on collision. Smaller ions, on the basis of this theory, would be expected to transfer more momentum than the larger ions. Also the theory explains the dependence of the temperature coefficient of conductance on ion size, but this theory suffers from lack of evidence and will not be considered further.

R. H. Stokes and R. A. Robinson (39) have advanced a hydration model for concentrated solutions from studies made on the highly concentrated solutions and gels of calcium nitrate. They picture the system as an adsorbent (calcium nitrate) - adsorbate (water) system. At high concentrations it is their belief that ion-solvent forces are the dominant factor and they develop a treatment which to a first approximation ignores ion-ion forces or rather assumes that they are little affected by concentration in this range. The concentrated solutions contain ions in different stages of hydration, some with complete monomolecular layers, some incomplete and others with more than one layer. The outer layer of solvent molecules would be held much less firmly than the innermost solvation sheath. This hydration model bears a close resemblance to the adsorption isotherm of Brunauer, Emmett and Teller (12) with the result that Stokes and

Robinson presented their equation as

$$\frac{m a_w}{55.51 (1-a_w)} = \frac{1}{Cr} \left/ \frac{C-1}{Cr} a_w \right. \quad (1)$$

where a_w = the activity of water,

m = the molality,

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

C = a constant related to the heat of adsorption E of the molecules in the layer by the approximate relation

$C = \exp. (E - E_L) / RT$, E_L being the heat of liquifaction of pure water.

On the whole this theory seems to be one of the best advanced to date although until more theoretical and practical work is done on the basis of this theory no really reliable estimate of its possibilities can be stipulated.

Since a great deal of the more recent work on the problem of solvation has to do with solvation energies rather than with solvation numbers a closer examination of the pertinent theory regarding energies of solvation is in order.

On the basis of the theory of salt dissolution it is argued 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. Since the

lattice energies are of considerable magnitude even for salts containing univalent ions it follows that the amount of energy required in the process must also be considerable. This process is termed the solvation or in aqueous solution the hydration of ions and signifies the attachment of solvent molecules to ions in solution, caused principally by the coulombic attraction forces of the ions for the polar molecules of the solvent. If the heat change which occurs during solvation (the heat of solvation) is sufficiently exothermic, it compensates for the energy used in breaking up the lattice and the salt dissolves. As a consequence of the first law of thermodynamics the algebraic sum of the heats of solvation and the lattice energy is the heat of solution thus:

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

where ΔH = the heat of solution,

U = the lattice energy,

$(Q_s + Q_{-})$ = the heat of solvation.

The heat of solvation therefore can be calculated by this equation it being borne in mind that the value found contains both the interaction energy of the ion and dipole and the work of breaking up the solvent (hole formation) caused by the dissolution of the ion.

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

TABLE I.

Lattice Energies, Initial Heats of Solution, and Heats of
Hydration of the Alkali Halides in Kilocalcs.

Salt	U T = 291°K	ΔH T = 291°K	$Q_f \neq Q_-$ T = 291°K
LiF	- 247.0	1.1	- 245.9
LiA	- 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
KCl	- 169.6	4.4	- 165.2
KBr	- 162.8	5.1	- 157.7
KI	- 153.9	5.1	- 148.8
RbF	- 184.9	- 5.8	- 190.7
RbCl	- 163.4	4.5	- 158.9
RbBr	- 157.4	6.4	- 151.0
RbI	- 149.2	6.5	- 142.7

The problem of obtaining values for hydration energies of individual ions is frequently encountered but generally it is very difficult to solve. These individual values cannot be obtained directly from experimental results without resorting to the use of some non-thermodynamic facts such as the properties of the ions and solvent.

The best known attempt to calculate the heats of hydration from the properties of ion and solvent is that of Born (8) who 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 ϵ .

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

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

where Z_i = the valence of the ion,

e_o = the electronic charge.

If the medium of dielectric constant ϵ 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 vacuo into a medium of dielectric constant ϵ is

$$\begin{aligned} F &= -N_A \left[\frac{Z_i^2 e_o^2}{2a} - \frac{Z_i^2 e_o^2}{2\epsilon a} \right] \\ &= \frac{-N_A Z_i^2 e_o^2}{2a} \left[1 - \frac{1}{\epsilon} \right] \end{aligned} \quad (2)$$

The heat of hydration Q_i can be obtained from the Gibbs Helmholtz equation as

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

from which

$$Q_i = - \frac{N_A Z_i^2 e_o^2}{2a} \left[1 - \frac{1}{\epsilon} - \frac{T}{\epsilon^2} \left(\frac{\partial \epsilon}{\partial T} \right)_P \right] \quad (3)$$

Two main difficulties are immediately confronted in the application of this equation. Firstly there is the difficulty of ascertaining the radius of the ion. X-ray measurements of crystals give internuclear distances in the crystal on the assumption that the cation and anion are in close contact in the crystal. The main ambiguity is encountered in the division of these internuclear distances into the individual ionic radii. Also it is not certain that the ionic radii of the crystal are the same as that in the solvent medium. Secondly the Born equation infers that the heat of solvation of a monovalent ion should depend only on the dielectric constant of the medium and the temperature, apart from the ionic radius. This would mean that all ions whether cation or anion of the same radius would yield the same solvation energy. The use of the macroscopic dielectric constant is also 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 simple theory of Born has been extensively improved by taking into account ion-dipole interaction, the orientation and 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. In Table II the heats of hydration of some individual ions calculated by the Born equation are compared with more recent values corrected in accordance with the factors mentioned above.

TABLE II

Heats of Hydration of Individual Ions in
Kilocals at 291°K.

Ion	Li ⁺	Na ⁺	K ⁺	Rb ⁺	F ⁻	Cl ⁻	Br ⁻	I ⁻
Radius A°	0.68	0.98	1.33	1.48	1.33	1.81	1.96	2.19
Q _i (Born Equation)	240	166	123	110	123	90	83	74
Q _i (Corrected)	131	116	92	87	94	67	63	49

Although a great deal of work has been done on the problem of ionic solvation there is still no acceptable theory at present. All of the theoretical concepts advanced to date have been found to be inadequate to a greater or lesser degree. Much of the difficulty lies in

the lack of knowledge of the type of binding that exists between the ions and the solvent molecules and the dearth of reliable experimental methods available for the measurement of both the solvation numbers and energies of the ions. Until such time as these inadequacies are removed the entire problem of electrolytic solutions will remain unsettled.

Experimental:

A wide range of experimental phenomena have been studied in attempts to determine solvation numbers experimentally. This fact alone would seem to indicate that ion-solvent interactions have a widespread influence on solution behavior. Included among the phenomena studied are: refractivity, freezing and boiling points, vapor pressure, surface tension, density, specific heat, compressibility of ionic solutions, transport numbers of ions, and solubility of non-electrolytes in the presence of electrolytes.

Most of these methods have a common difficulty; the dividing up of the solvation of the salt between its ions. Some workers (34) in the field have assumed that large organic ions such as $C_6H_5NO_3^+$ have zero solvation. Some have extended this to include such ions as NO_3^- (9) and I^- (15). The most sensible method appears to be division in the ratio of the ion sizes based upon some salt such as potassium fluoride where the ionic radii are close to being equal.

One of the first methods used in attempting to estimate ionic hydration is the method of ionic or solvent transport using an inert

reference substance. The reference substance is used to determine if there is a concentration change when the ions move due to an applied difference in potential. If the ions are hydrated water will be transported with the ions and an increase in the concentration of the reference substance should be observed. The fundamental assumption of course is that the reference substance does not move under the influence of the applied field. Buchbock (13) and Washburn (44) were the first to use this method successfully. They used raffinose as their inert reference solute. By referring the changes in the content of water and of the salt to the non-electrolyte as a reference substance a relation between the degrees of hydration of the ions was derived. Using the following equation Washburn was able (as he thought) to calculate the number of moles of water carried per equivalent of cation and anion:

$$\Delta n = \tau_c N_w^c - \tau_a N_w^a \quad (4)$$

where Δn = the change in the number of moles of water in a given electrode portion,

τ_c = the true transference number of the cation,

τ_a = the true transference number of the anion

N_w^c and N_w^a = the number of moles of water carried per equivalent of cation and anion respectively. It is necessary to assume either N_w^c or N_w^a since both of these quantities are unknown.

P. Z. Fischer and T. E. Koval (20) have since shown that raffinose, the inert reference substance, used by Washburn is transported during electrolysis. Also it has been shown by L. G. Longworth (31) that the non-electrolyte used has an effect on the displacement per Faraday of the ions. Therefore it would seem that this method is open to considerable objection and that the results obtained are quite uncertain.

In the Remy (35)-Babarovsky (3) method of water transport which overcame the necessity of adding an inert non-electrolyte the liquid is allowed to pass through a thin membrane between cathode and anode compartments and thus indicate the net volume change arising from the different extent of solvation of the cation and anion. This method too is open to adverse criticism. Probably included in the measured water transport is the water which is transported by a transfer of momentum from ions to molecules much in the same way as that suggested by Lindemann. This would result in hydration numbers that were too high. Another objection is the considerable volume change in the anode and cathode compartments caused by reactions at the electrodes. Also, below a concentration of 1 N the effect of electroendosmosis at the membrane is considerable. In conclusion the Remy-Babarovsky method measures some part of the total rather than the primary hydration.

The same conclusions and criticism also holds true for the Jander's diffusion method (26) and the dialysis method of Brintzinger (11).

Ionic mobilities constitute another phenomenon which has been studied as an aid in determining the solvation of ions. In this regard the method of Ulich (41) is probably the best known. This method seems to measure a more definite quantity than the methods so far discussed since it obtains directly the volume of the solvated ions from an application of Stoke's law to ionic mobilities at low concentrations, so that an estimate of primary solvation is obtained. Several objections have been leveled against this method. The non applicability of Stoke's law to some ions in solution (28) seems to be the most serious one. Also the calculation of the molecular volume of the water molecules about the ion is open to doubt. The high pressures in the vicinity of the ions and the inhibition of rotational degrees of freedom of the dipoles attached to the ion tend to constrict the normal molecular volume of the water. Therefore the molecular volume so calculated would be too large and the resulting solvation numbers would be too small, giving therefore a lower limit.

Ulich calculated an upper limit by assuming that the molecular volume was diminished to one half its original value. Ulich's final value is an average taken of the upper and lower solvation limits.

Methods based upon activity determinations such as the cryoscopic, vapor pressure, and salting-out methods all give high results and therefore seem to give a total interaction effect.

The cryoscopic method employed by E. Rouyer, F. Bourion and Hun (10) seems to be open to doubt since the results depend upon the

non-electrolyte employed. In this method the cryoscopic or ebullioscopic constants of a non-electrolyte is measured in an electrolytic solution and in pure water. Using the following relation the hydration of the electrolyte may be found

$$x = \frac{100 (k' - k)}{k'} \quad (5)$$

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.

These workers used such non-electrolytes as paraldehyde, acetone and resorcinol. The first two act unreasonably while resorcinol appears to be a suitable non-electrolyte. This method suffers to a great extent by the absence of a satisfactory theoretical basis and it would appear that the advancement of an adequate treatment would be extremely difficult.

The measurement of vapor pressures to estimate hydration numbers was carried out by B. H. Van Ruyven (43). He pictures the ion as having a definite number of water molecules bound to it in solution. The strong electrolyte is not considered to be in general wholly ionized but there exists a degree of ionization.

From considerations of the Arrhenius law of electrolytic dissociation and Raoult's law he deduces the expression:

$$\alpha_p = \frac{1000 (S-S_2) - 18 N_w S_2}{18 N_w S_2} \quad (6)$$

where α_p = the degree of ionization calculated from vapor pressures,
 S = the vapor pressure of solvent,
 S_2 = the vapor pressure of the electrolyte,
 N_w = the concentration in gram molecules of solute per 1000 grams of solvent.

The above equation breaks down at higher concentrations because of the lowering of the amount of free water present as a consequence of the binding of water molecules to the ions. He therefore rewrites the equation as:

$$\alpha_{px} = \frac{1000 (S-S_2) - 18 N_w S_2}{18 N_w S_2 + 18x N_w (S-S_2)} \quad (7)$$

where α_{px} = the degree of ionization of the electrolyte binding x molecules of water. By the use of proper values of x in this equation the discrepancies which arise at the higher concentrations are removed and the resulting hydration number assumed correct. Van Ruyven's values are quite high and as a result it would seem that his measurements include more than just the firmly held molecules. Also his theoretical treatment leaves much to be desired.

The salting-out effect (29) has been utilized in an attempt to deduce 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 a reduction of the activity coefficient of water. This method takes no account of the effect of the non-electrolyte solute on the dielectric constant of the medium. Secondly, values calculated depend upon the nature of the non-electrolyte employed. Therefore it appears that values calculated by this method do not give valid results.

One can however obtain qualitative inferences regarding solvation from salting-out studies. J. O'M. Bockris and H. Egan (7) found that for solutions of sodium chloride in the concentration range $\frac{N}{1000}$ to 1 N using benzoic acid as the non-electrolyte the salting-out decreases anomalously with decreasing dielectric constant in alcohol-water mixtures containing an excess of water. This observed anomaly can be explained if it is assumed that the sodium chloride is preferentially solvated with water.

The activity of water in aqueous electrolytic solutions was utilized by N. Bjerrum (5) to calculate solvation numbers. Ulich considers this method yields primary solvation numbers, but since this method has been applied to so few ions no definite conclusions can be made. In Bjerrum's treatment the water held by the ion is taken into account in calculations and the concentrations are expressed as a mole fraction solute x . If the ions are hydrated then it follows that the mole fraction will be larger than without hydration. In measuring the activity as defined by e.m.f. measurements the activity of water free

ions is obtained. If the ion binds m molecules of water then the activity of the water free ion should be multiplied by the activity of the water raised to the m^{th} power. Following this line of argument Bjerrum derives the expressions:

$$F_a C (p/p_0)^m = x_{55.5} f_a \quad (8)$$

$$F_a' C (p/p_0)^{m'} = \frac{C}{55.5 + 2C - (m' + m'')} C_{55.5} f_a' \quad (9a)$$

$$\text{and } F_a'' C (p/p_0)^{m''} = \frac{C}{55.5 + 2C - (m' + m'')} C_{55.5} f_a'' \quad (9b)$$

where F_a, F_a', F_a'' = the apparent activity coefficients of the salt,
the anion and the cation respectively,

f_a, f_a', f_a'' = the corresponding true activity coefficients,

m and m'' = the moles of water carried by the anion and
cation respectively.

Substituting into equations (9a) and (9b) the relationships

$$F_a = \sqrt{F_a' F_a''}$$

$$f_a = \sqrt{f_a' f_a''}$$

$$m = m' + m''$$

and converting to logarithm and adding we get

$$\ln F_a = \ln f_a - \frac{2m - 2C}{55.5} \quad (10)$$

E. Schreiner (38) using this method calculated the hydration numbers of several ions including hydrogen chloride and obtained the improbable result of 11. Although this method is a great improvement over the majority of them so far discussed the results obtained are still not too reliable.

Stokes and Robinson (39) have recently arrived at a result equivalent to that of Bjerrum though by a somewhat different approach. These authors derive an empirical relation between the activity coefficient and concentration for electrolytes in relatively concentrated solution. They consider one molecule of solute as giving rise to ν ions. The total interaction between these ν ions and surrounding solvent can be allowed for as a "binding" of n molecules of water in their hydration shells. In a solution of molality m , there are $n m$ molecules of bound water to $(55.51 - n m)$ molecules of free water. The true molality (in moles of hydrated solute per 1000 grams of free water) m' is therefore

$$m' = \frac{55.51}{55.51 - n m} = \frac{m}{1 - 0.018 n m} \quad (11)$$

Letting a' be the activity of the hydrated solute and a that of water the Gibbs-Duhem relation becomes

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

If hydration is neglected the form of the Duhem relation remains the same except that the stoichiometric molality and activity are used.

Thus:

$$d \ln a = - \frac{55.51}{m} d \ln a_w \quad (13)$$

On introducing the mean molal activity coefficients γ' and γ we have

$$d \ln \gamma' = - \frac{55.51}{m'} d \ln a_w - d \ln m' \quad (14)$$

and

$$d \ln \gamma = - \frac{55.51}{m} d \ln a_w - d \ln m \quad (15)$$

On substituting the value for m' from equation 11 we have

$$d \ln \gamma' = d \ln \gamma \not\frac{n}{\gamma} d \ln a_w \not d \ln (1-0.018 n m) \quad (16)$$

Integrating between molalities zero and m we have

$$\ln \gamma' = \ln \not\frac{n}{\gamma} \ln a_w \not \ln (1-0.018 n m) \quad (17)$$

Using the mean rational activity coefficient of the hydrated solute f' which is related to γ' by the relation

$$\ln f' = \ln \gamma' \not \ln (1 \not 0.018 m') \quad (18)$$

and combining (18) and (17) and simplifying with the aid of (11) we obtain

$$\ln \gamma = \ln f' - \frac{n}{\gamma} \ln a_w - \ln [1 - 0.018 (n - \gamma)m] \quad (19)$$

Now replacing the term $\ln f'$ by the Debye-Huckel expression

$$\ln f = \frac{-A \sqrt{C}}{1 + B a^0 \sqrt{C}} \quad \text{the relation becomes}$$

$$\ln \gamma = \frac{-A \sqrt{\mu}}{1 + B a^0 \sqrt{\mu}} - \frac{n}{\gamma} \ln a_w - \ln [1 - 0.018 (n - \gamma)m] \quad (20)$$

where $\sqrt{\mu}$ = the ionic strength,

a^0 = the mean distance of closest approach in Angstrom units.

This equation (20) was found to give very good results up to the point where product $n m$ exceeded 10 or 15. Above this, competition for water molecules became noticeable. To proceed to higher concentrations an n which was a suitably decreasing function of concentration would have to be used.

H. Ulich (42) has employed entropy determinations to calculate primary solvation. The method is based upon the entropy decrease accompanying the act of solution of gaseous ions in water at infinite dilution. The measurement would seem to depend on the "freezing up" of the degrees of freedom of the water molecules near the ion. It is assumed 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. This method may be employed to calculate the solution of non-electrolytes as well.

The measurement of partial molal volumes of electrolytes at infinite dilution has been applied to the calculation of solvation numbers by J. D. Bernal and R. H. Fowler (4). They refer to this method as being a particularly good one and Darmois (17) describes the procedure and results of this method for a large number of simple aqueous electrolytic solutions. This method is concerned with the volume of the ion-solvent complex only and not with the more loosely held surrounding water molecules. It follows then that the resulting solvation numbers would represent primary hydration but, the values obtained seem much lower than other similar methods. Just why this should be the case is not yet clear.

Other methods which have been utilized involve the measurement of reaction velocity, the variation of the distribution of an electrolyte between two immiscible solvents, the compressibility of ionic solutions, the use of supersonic emf's and polarimetry.

Cordier (16) recently employed the reaction velocity method which yielded very high values for the solvation number (of the order of 10^2). Values such as these often imply that more water is bound to the hydration sheath than exists in the solution. The distribution method is hampered considerably by several unsolved difficulties. Discrepancies exist between the results of J. N. Sugden (40) and E. Angelescu and O. Dutchieviu (2) and negative solvation numbers for anions result from Sugden's values. In this connection the anions were supposed to exert a depolarizing effect upon the water regarded by Sugden as $(H_2O)_3$ in the liquid state.

Compressibility measurements (32) yield results consistent with those of the ionic mobility and entropy methods. It seems logical therefore that this method measures primary hydration numbers. Support for this assumption may be derived from the concept that the hydration sheath about the ion in primary solvation has large pressures exerted on it due to the field near the ion and therefore attains a limiting value beyond which further compressibility is due to that of the bulk of the solvent.

Lastly Debye (18) has given a theoretical treatment of the potential difference produced in an electrolytic solution when it is subjected to supersonic vibrations. This method seems acceptable in principle and yields individual solvation numbers, as the emf's produced are a function of the ratio both positive and negative of ion-solvent complexes in the electrolyte. Any measurements which are attempted by means of this method would involve the difficulty of measuring emf's of the order of 10^{-6} volts.

As a whole the results from the various methods are highly discrepant mainly because many methods measure not only the primary hydration but also different amounts of secondary hydration. There are reasons for believing, however, that methods based upon measurements of mobility, entropy, compressibility and possibly also partial molal volume (i.e. density) all give approximate measures of primary hydration and it can be seen from Table III that some degree of agreement is obtained among the results of these methods.

TABLE III

Results of Experimental Methods Giving
Primary Hydration Numbers at Infinite Dilution.

Ion	Mobility	Entropy	Compressibility	Density	Mean
	(1)	(2)	(3)	(4)	(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
Cl ⁻	4	2	3	0	2
I ⁻	0.7	0.5	2	0	0.7

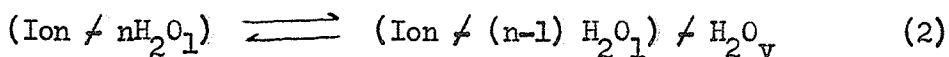
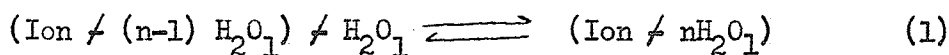
STATEMENT OF SPECIFIC PROBLEM.

STATEMENT OF SPECIFIC PROBLEM

Up to the present time there exists no really satisfactory theory on ionic solvation, but it is generally agreed that ions are solvated on undergoing solution by the attachment of solvent molecules to the ions. Furthermore, the effect of the ionic field extends beyond the solvent molecules immediately surrounding the ion and in reality the binding involves to a greater or lesser extent many of the solvent molecules outside the primary solvation sheath.

In the opinion of this author the soundest theoretical treatment so far advanced is that of Bjerrum and Stokes and Robinson. Applying their picture to aqueous electrolytic solutions it is clear that the concentration of the solution increases the competition for water molecules becomes increasingly keen until finally all the water molecules are tightly bound to the ions. This picture is valid only, of course, if no other forces come into play, to neutralize this ion-solvent interaction. Now if one visualizes the reverse procedure of stripping away the water molecules from the ions it can readily be seen that as the concentration increases it would become increasingly difficult for the water molecules to overcome the strong ion-solvent forces and escape the solution.

According to our concept we can write the following equations for the reaction taking place:



where the subscripts l and v refer to liquid and vapour phase respectively. Each one of the reactions (1), (2), (3) will have a corresponding heat of reaction ΔH_1 , ΔH_2 and ΔH_3 respectively. Since equation (3) is the sum of equation (1) and (2) then

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

or

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

ΔH_3 is the heat of vaporization of pure water and ΔH_2 may be interpreted as the heat of vaporization of water from the solution. Finally ΔH_1 is the difference between the molar heat of vaporization of water from pure water and of water from the solution which can be shown to be equivalent to the differential heat of dilution of the solution. In the terms of ionic solvation ΔH_1 represents the heat of reaction associated with the addition of a relatively infinitesimal amount of water to the solvent-ion complex leaving the concentration of the solution essentially unchanged. That is to say ΔH_1 is the change of solvation energy with concentration. If there was no ion-solvent inter-

action then ΔH_1 would be expected to be zero. As the number of ions increase and the competition for water molecules becomes strong the negative values of ΔH_1 should increase progressively up to the point where there is just enough water molecules to go around among the ions.

In order to evaluate ΔH_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:

$$\frac{dP}{dT} = \frac{\Delta H}{RT^2} \quad (6)$$

where ΔH = the molar heat of vaporization,

T = the absolute temperature,

P = the pressure,

R = the universal gas constant.

Equation 6 may be rewritten as

$$\ln P = - \frac{\Delta H}{R} \frac{1}{T} + C \quad (7)$$

where C is the constant of integration. If $\ln P$ is plotted against

$\frac{1}{T}$ for a small temperature gradient the result should give a straight line of slope equal to $-\frac{\Delta H}{R}$. Knowing the slope it is then possible

to determine ΔH_3 for pure water and ΔH_2 for each solution in turn. Therefore ΔH_1 could be evaluated by means of equation (5), but, the use of equation (7) is limited to small ranges of temperature over which ΔH may be regarded as constant. Consequently one must confine the vapour pressure readings to a narrow range of temperature in order to obviate the introduction of significant error. Since in this present work vapour pressure measurements were made over a large temperature range the use of equation (7) was abandoned in favor 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 (33). This author shows how equation (6) may be rearranged to give an expression better suited to the evaluation of latent heats of vaporization especially when using vapour pressure measurements made over a large temperature range.

Thus rearranging equation (6) and introducing the subscript 2 we get

$$\frac{1}{\Delta H_2} \times \frac{dP_2}{P_2} = \frac{dT}{RT^2} \quad (8)$$

where this equation refers to any material consistent with the assumptions that the ideal gas law is followed and the volume of condensed phase is insignificant to the vapour volume. The same equation may be written for any other consistent material at the same temperature

giving

$$\frac{1}{\Delta H_3} \times \frac{dP_3}{P_3} = \frac{dT}{RT^2} \quad (9)$$

where P_3 = the vapour pressure of the second substance at temperature T ,

ΔH_3 = the latent heat per mole of the second substance, also at the temperature T .

Thus equating equations (8) and (9) gives

$$\frac{1}{\Delta H_2} \frac{dP_2}{P_2} = \frac{1}{\Delta H_3} \times \frac{dP_3}{P_3}$$

or

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

Since $\frac{dP}{P} = d \log P$ equation (10) may be rearranged to give

$$\frac{d \log P_2}{d \log P_3} = \frac{\Delta H_2}{\Delta H_3} \quad (11)$$

If $\frac{\Delta H_2}{\Delta H_3}$ is considered constant then equation (11) may be integrated to give

$$\log P_2 = \frac{\Delta H_2}{\Delta H_3} \log P_3 + C \quad (12)$$

where C is a constant and P_2 , P_3 , ΔH_2 and ΔH_3 are always taken at the same temperatures.

Equation (12) states that, if the log of the pressure of any substance P_2 is plotted against the log of the pressure of any other substance P_3 at the same temperature, a straight line results which will have for its slope the ratio of the molal latent heats. This line is straight if the ratio $\frac{\Delta H_2}{\Delta H_3}$ is constant over the temperature range in question which is reasonably near the truth for most compounds over wide ranges. That is the term $\frac{\Delta H_2}{\Delta H_3}$ will be substantially unchanged (especially for related compounds) over a much wider range than either ΔH_2 or ΔH_3 , since the variation of both will follow the same law and the quotient will therefore be comparatively unchanged.

In applying equation (12) to aqueous solutions of non-volatile solutes we let P_2 and ΔH_2 refer to the vapour pressure and latent heat of vaporization respectively of the solution and P_3 and ΔH_3 to that of water at the same temperature. The best available data on the latent heats of vaporization and vapour pressures of water are contained in a paper by J. A. Goff and S. Gratch (23). These authors calculated the vapour pressures of pure water from the following equation

$$\log_{10} p_s = -7.90298 \left(\frac{T_s}{T} - 1 \right) + 5.02808 \log_{10} \left(\frac{T_s}{T} \right) - 1.3816 \times 10^{-7} \left[10^{11.344(1-T/T_s)} - 1 \right] + 8.1328 \times 10^{-3} \left[10^{-3.49149(T_s/T-1)} - 1 \right] \quad (13)$$

where p_s = the pressure in atmospheres,

T = the absolute temperature,

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

In this present work the vapour pressures of pure water were calculated by means of equation (13) in every case. The slopes of $\log P_2$ against $\log P_3$ were calculated analytically by the method of moments instead of attempting the more inaccurate graphical evaluation.

There has been surprisingly little experimental work done on the vapour pressures of aqueous electrolytic solutions especially over a range of temperature. Most of that which has been done is confined to the isopiestic measurement of vapour pressures for the determination of activity coefficients at 25°C. Johnson and Molstad (27) have applied the gas saturation method to the determination of the vapour pressures of lithium chloride solutions at 30, 50 and 70°C. up to saturation. They also calculated the latent heat of vaporization of water from the solutions and the differential heats of dilution.

This present work was undertaken with silver nitrate solutions in the belief that the measurement of vapour pressures instead of the determination of boiling points, as was carried out by J. B. Fishman (21), afforded a more reliable method of estimating the change of solvation energy with concentration. In addition the vapour pressure measurements were utilized in the calculation of the activity of water given by the ratio $\frac{p}{p_0}$, the van't Hoff factor i and the osmotic coefficient g . The osmotic pressures were also calculated by means of the expression

$$\text{II} = \frac{RT}{\bar{v}} \ln \frac{p}{p_0} \quad (14)$$

where \bar{v} , the partial molal volume of the solvent, was approximated by v , the molar volume of water. This approximation was thought to be justified since the partial molar volume of water in silver nitrate solutions has been found (14) to vary only slightly from the molar volume even at high concentrations.

EXPERIMENTAL PROCEDURE.

EXPERIMENTAL PROCEDURE

1. Purification of Material.

The silver nitrate was supplied by the Johnson Matthey and Mallock Company and was adequately pure for the present research. The large crystals were ground up in an agate mortar and stored over sulphuric acid in a darkened space. The resulting finely divided salt was pure white in appearance and did not show any visible evidence of decomposition.

2. Preparation of Solution.

The pure dry salt was weighed out on an analytical balance in a weighing bottle using a weighing bottle of similar size and shape as counterpoise. The salt was then transferred to a volumetric flask and the solution made up to weight by the addition of distilled water. The solutions were kept in a darkened space until ready for use.

3. Apparatus and Procedure.

In this research two types of vapor pressure apparatus were employed; one for the measurements in the more dilute range of concentrations and the other for the more concentrated solutions. A differential manometer fashioned after that of E. J. Hartung (24) was employed for the vapor pressure measurements of solutions up to 60 weight percent. This apparatus is shown in figure (1). For solutions above 60 weight percent an absolute apparatus was used and is illustrated in figure (2).

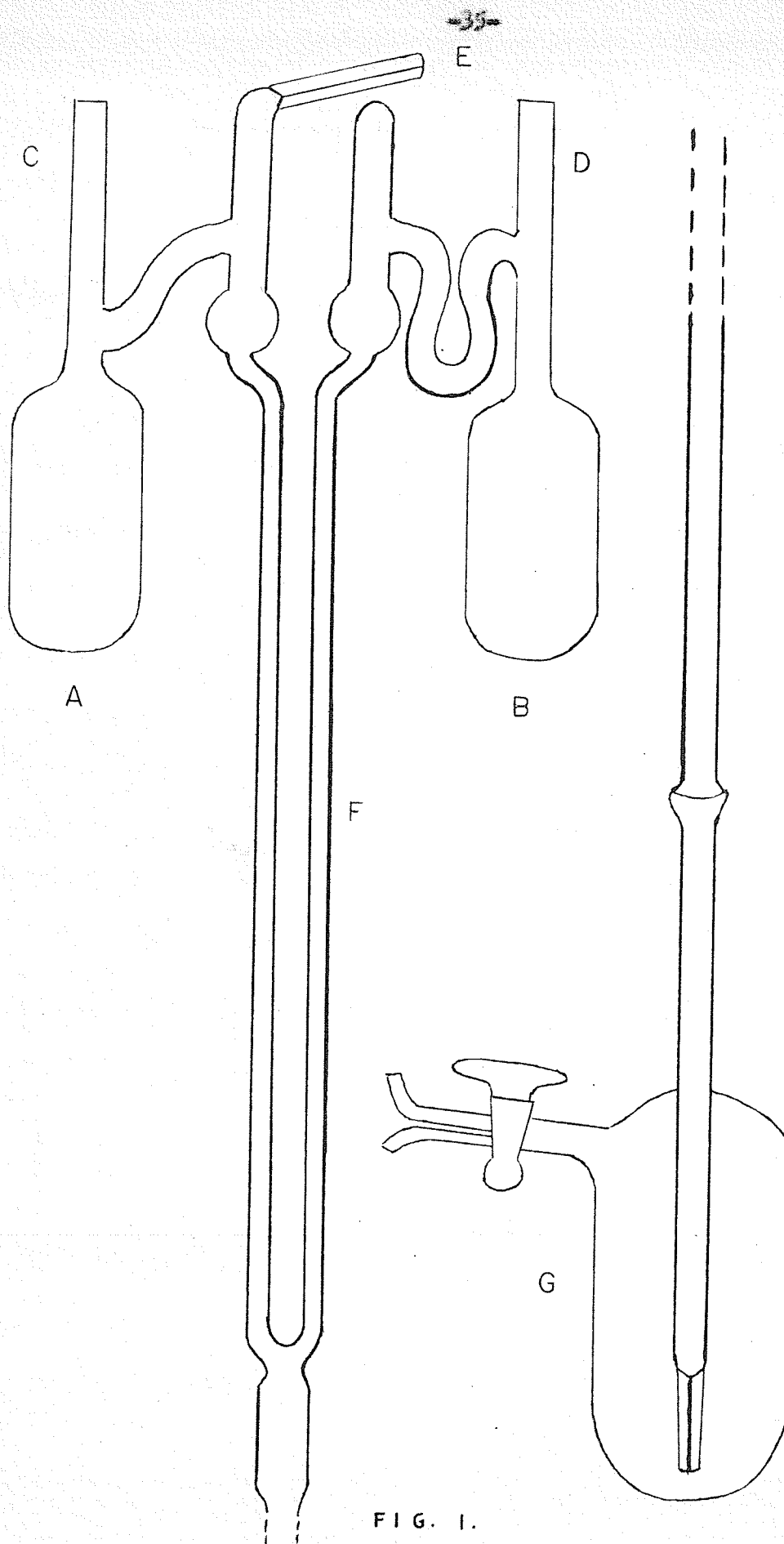


FIG. 1.

The Differential Manometer.

The differential manometer consisted essentially of two bulbs of approximately 50 ml. capacity labelled A and B in figure (1) each connected to an arm of the manometer tubes F of 20 cms. length. The lower ends of the manometer tubes were fused into the head of a long vertical tube of wide bore which passed through a bored neoprene rubber stopper firmly fixed in the bottom of the thermostat. The tube was 60 cms. long and was provided at its lower end with a few centimeters of 1 mm. capillary tubing. It terminated in a reservoir G which could be shut off from the atmosphere by a three-way vacuum stop cock. About 10 cms. above the reservoir the tube was provided with a ball and socket joint to facilitate the installation and removal of the apparatus. Joined to the upper tube of the vacuum stop-cock was a long piece of rubber tubing terminating in an auxillary reservoir bulb and held high above the reservoir G as shown in figure (3). Two large diameter tubes C and D fused to the upper end of the bulbs A and B were used in filling the bulbs with water and solution respectively. Joined to the aqueous side of the manometer was a piece of coarse capillary tubing E to which was connected rubber vacuum tubing leading to the air pump. The wide tube joining the manometer to the bulb B containing the solution was bent in the form of a U to minimize the possibility of the solution being thrown over into the manometer from bumping on thawing after evacuation.

The solution was introduced into the bulb B by means of a

thistle tube lowered into the wide bored tube D. About 30 ccs. of solution was used. The tube D was then sealed off with a torch. Similarly 30 ccs. of distilled water was added to the bulb A and the exit tube C sealed off. The apparatus was then lowered into the thermostat and the neoprene rubber stopper securely fitted into the bottom. The reservoir G was joined at the ball and socket joint and allowed to rest on a small table for additional support.

Mercury was added by means of the auxillary bulb until the tube, reservoir and rubber tubing were filled and the auxillary bulb about half-filled. The level of the mercury was adjusted with the greatest of ease by the manipulation of the stop-cock when the apparatus was exhausted. The capillary termination prevented violent rushing of the mercury which might have led to accident. The mercury level in the tube was then lowered below the ball and socket joint by lowering the auxillary bulb, the joint opened and about 1 cc. of silicone oil added. The silicone oil had a two-fold purpose. Firstly the silicone oil prevented the condensation of small amounts of water on the mercury meniscus which would lead to distortion. Secondly the silicone oil greatly minimized the possibility of the mercury vapor contaminating the silver nitrate solution.

After the ball and socket joint had been closed and clipped firmly in place the mercury was allowed to rise up the tube to a height above the U of the manometer. The rubber vacuum tubing was then joined to the capillary evacuation tube E and a stop-cock located between the

apparatus and the air pump closed. A freezing mixture of dry ice-acetone was prepared in an insulated metal container big enough to contain both bulbs at once. The container was placed in position so that both bulbs were well emersed. 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 pump was then opened and evacuation begun. The pumping down was continued for a half hour. During this time the apparatus was checked for leaks by utilizing a tesla coil. After pumping down the stop-cock was closed and the mercury again allowed to rise up above the U of the manometer, the freezing mixture removed and the contents of the bulbs allowed to thaw. On thawing the more dilute solutions no salt was found to come out of solution. However with solutions of 50% by weight and greater, crystalization of salt did occur. By gentle warming and topping the bulb for agitation the salt went back into solution. Before freezing down again the salt had redissolved completely.

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

After the final outgassing the capillary tubing leading to the air pump was sealed off with a torch. 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 completely it was agitated for a considerable length of time to insure homogeneity.

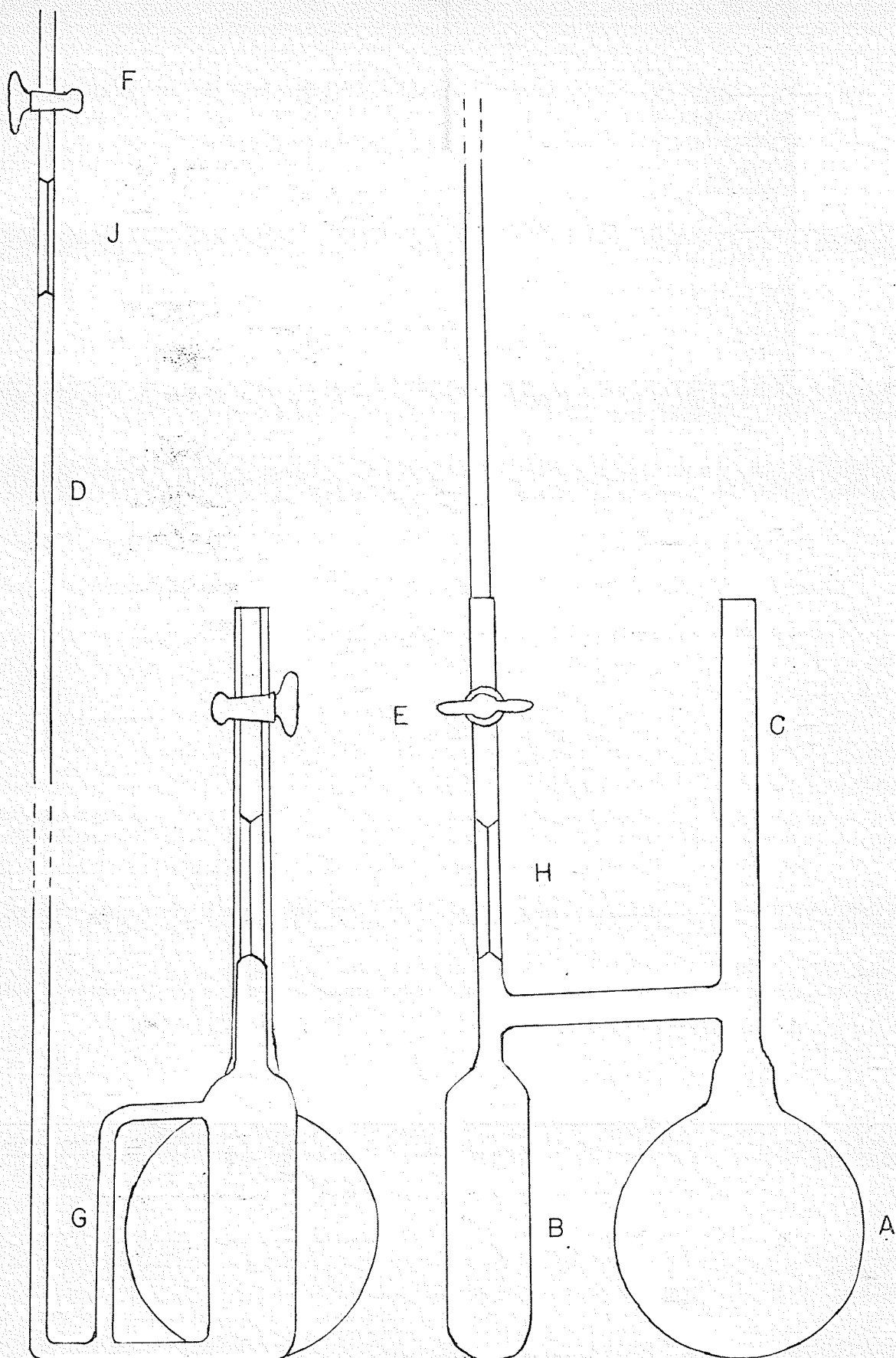


FIG. 2.

The Barometric Apparatus.

For solutions greater than 70 weight percent the differential apparatus had to be abandoned in favor of a direct barometric method. This became necessary on account of the salt being too concentrated to dissolve completely at room temperature. In order to dissolve the salt completely after thawing it was necessary to heat the solution considerably above room temperature. This caused considerable bumping to take place with the resulting danger of throwing some of the solution over into the manometer tubes. Also the heating of the solution bulb alone condensed considerable quantities of water over into the manometer. To overcome these difficulties one would have had to maintain the whole apparatus at the same elevated temperature and with the differential apparatus this was found impractical. Also since the manometer tubes were only 20 cms. long the measurement of vapor pressure differences greater than this was impossible. With the highly concentrated solutions at high temperatures the vapor pressure differences became greater than 20 cms. Because of these difficulties it was decided to use the more easily handled direct barometric apparatus for the measurements on the concentrated solutions.

The apparatus is shown in figure (2). It consisted of a barometric tube D of 6 mms. internal diameter and 90 cms. long connected at its lower end to a mercury reservoir B with an adjoining arm G also of 6 mms. diameter. Fused on to the upper end of the barometric tube was a short piece of coarse capillary tubing J which terminated in a vacuum

stop-cock F. Another piece of short capillary tubing H was joined immediately above the mercury reservoir and it also terminated in a vacuum stop-cock E. Just below the capillary tubing H a large diameter tube led to the solution bulb A by way of a wide bored outlet tube C.

Mercury was first added by opening the barometer stop-cock and pouring the mercury down the barometer tube until the reservoir was three quarters filled. Pressure tubing was then connected on to the stop-cocks E and F. The pressure tubing came together at a T joint before continuing to the vacuum pump. Both stop-cocks were opened and the apparatus put under vacuum. The mercury was heated and agitated vigorously to expel air from the body of the mercury and walls of the reservoir. Air was then allowed to seep gradually into both sides of the apparatus by opening stop-cocks E and F and disconnecting the pressure tubing behind a stop-cock located between the T joint and the pump. It was found that very little air found its way back into the body of the mercury and only slight amounts along the walls of the reservoir close to the mercury surface.

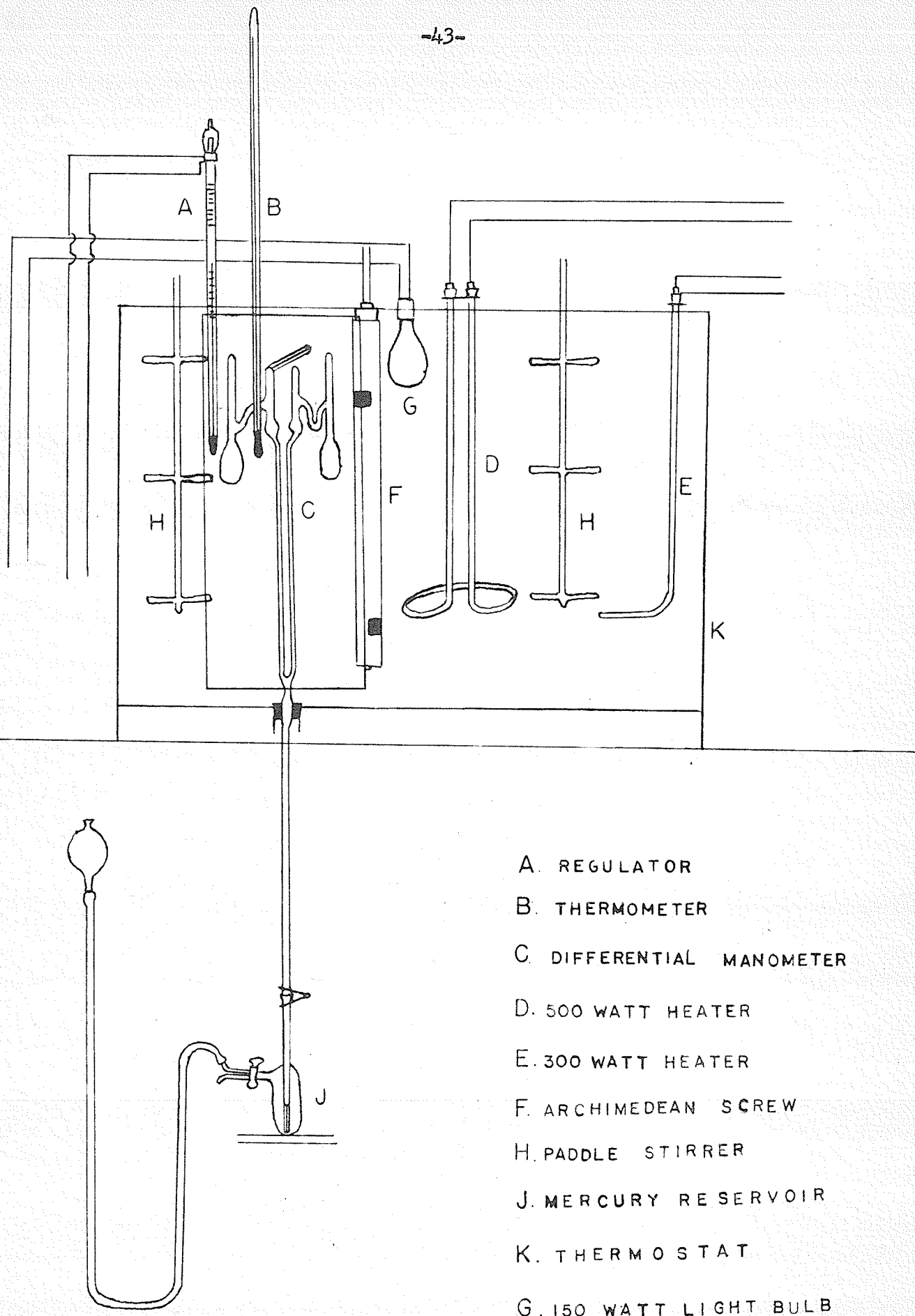
Since the salt would not completely dissolve at room temperature at concentrations above 70 weight percent the volumetric flask containing the salt and solution were first heated in a water bath well above its saturation temperature. The solution was then poured into the bulb A through a preheated thistle funnel which passed down the outlet tube C. The tube was then quickly sealed off to insure



minimum loss of water vapor and all stop cocks closed. The solution bulb was lowered into the freezing mixture of dry ice-acetone, the pressure tubing leading to the vacuum pump attached on above both stop-cocks and after ten minutes evacuation begun. After 30 minutes both stop-cocks were closed, the pressure tubing disconnected and the freezing mixture removed. Thawing was hastened by immersing the solution in a beaker of lukewarm water for short periods of time. Because of the possibility of air being locked up in the crystals or otherwise trapped by the crystals the whole apparatus was lowered into a large cylindrical glass tank filled to a level just above the stop-cock E with water preheated above the saturation temperature. The apparatus was agitated as vigorously as possible while the salt dissolved and continued until no air bubbles were seen to evolve from the solution. The apparatus was then removed from the water bath and allowed to cool to room temperature.

Since the solution was highly concentrated not much air was held in solution. Therefore the above procedure needed to be repeated only three times before finally sealing off the two capillaries below the stop-cocks.

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 centimeters of the barometer tube; the rest protruded above the oil surface. Therefore for vapor pressures above 40 cms. a stem correction



- A. REGULATOR
- B. THERMOMETER
- C. DIFFERENTIAL MANOMETER
- D. 500 WATT HEATER
- E. 300 WATT HEATER
- F. ARCHIMEDEAN SCREW
- H. PADDLE STIRRER
- J. MERCURY RESERVOIR
- K. THERMOSTAT
- G. 150 WATT LIGHT BULB

FIG. 3.

had to be applied to the mercury height. This was done by the use of an auxillary thermometer clamped to the barometer tube with its bulb at a point half-way between the surface of the oil bath and the mercury meniscus. This meant that there was a loss of accuracy in these measurements since the stem correction could be considered only approximate. However, the percentage error was not large at these higher vapor pressures.

Temperature Control.

The thermostat consisted of a rectangular copper tank of approximately 65 liter capacity into two sides of which were placed two flat glass windows. The windows were set in an iron frame gasket with Buna-N rubber and held firmly in place with set screws. The tank was well insulated by a surrounding wooden box lined with rock wool and powdered asbestos.

The thermostat was filled with a clear light oil (Marcol GX) affording clear vision of the manometer tubes. From time to time the oil had to be filtered in order to remove suspended foreign matter.

Heating was supplied by two heating coils and a 150 watt light bulb. One of the heating coils was 300 watts connected through a rheostat and supplied constant heat at all temperatures above 40°C. The other, a 500 watt heater, was used to hasten heating to the desired temperature and was not required when the bath was on control. The 150 watt light bulb was used as the 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 heating time lag of a lamp filament is very much shorter than an ordinary resistance heater so that a finer temperature control was achieved. Secondly 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. There was an upper and lower scale identical to one another. The mercury height i.e. temperature was indicated by the lower. The upper scale was used in setting the regulator at the 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 at the bottom was a wire which lead 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.

With efficient stirring it was found that very good control could be attained with this type of regulator. The regulator was checked against a Beckmann thermometer and control with .01-.02° was

consistant over the whole temperature range.

The temperature was measured with a mercury in glass thermometer graduated in tenths and calibrated against a Platinum resistance thermometer available in the laboratory.

The bath was stirred by means of two propeller type mechanical stirrers with three inch blades and one archemedes screw type stirrer. The pitch of the blades was adjusted so that stirring of the bath was maintained just below turbulence.

The Measurement of Vapor Pressures.

Two cathetometers were used to measure the differences in the mercury levels of the differential manometer. For small differences below 2.5 cms. a short range cathetometer was used which could be read to .01 mms. and estimated to .001 mms. For differences larger than 2.5 cms. in the differential manometer and for all readings with the absolute apparatus a 100 cm. range cathetometer was employed. This instrument could be read only to a tenth of a millimeter.

Both cathetometers were mounted opposite the window of the thermostat. Extra light was provided by a 60 watt light bulb mounted behind the rear window affording a very clear view of the mercury miniscus at all times.

After the temperature of the both had been set and was under control it was found that equilibrium conditions did not casually occur for about two hours at the lower temperatures. However, at the higher

temperatures equilibrium was established sometimes in as little as thirty minutes. When equilibrium was attained the manometer readings were taken. On some of the runs as many as twelve readings were taken and never less than six. The readings were averaged and corrected to 0°C.

EXPERIMENTAL RESULTS.

TABLE IV

The Vapour Pressures of Silver Nitrate Solutions, P_2 at Various
Temperatures Including the Corresponding Vapour Pressures
of Pure Water, P_3 .

Concentration		Temperature	P_2	P_3
Weight %	Molality	(°K)	(mms. of Hg.)	(mms. of Hg.)
9.98	0.654	303.22	31.64	31.94
		313.16	54.63	55.34
		323.16	91.37	92.56
		333.16	147.4	149.5
		343.16	230.4	233.8
		353.16	349.8	355.3
		363.16	517.5	525.8
		374.16	774.8	787.5
19.98	1.470	303.22	31.57	31.94
		313.16	54.36	55.34
		323.16	90.81	92.56
		333.16	146.0	149.5
		343.16	227.5	233.8
		353.16	344.9	355.3
		363.16	509.0	525.8
		374.16	760.7	787.5

TABLE IV. (Cont.)

Concentration		Temperature (°K)	P ₂	P ₃
Weight %	Molality		(mms. of Hg.)	(mms. of Hg.)
30.00	2.523	303.16	30.30	31.83
		313.16	52.63	55.34
		323.16	87.77	92.56
		333.16	141.3	149.5
		343.16	220.6	233.8
		353.16	334.8	355.3
		363.16	495.0	525.8
		375.16	767.5	815.9
40.00	3.924	303.16	29.50	31.83
		313.16	51.18	55.34
		323.16	85.40	92.56
		333.16	137.5	149.5
		343.16	214.5	233.8
		353.16	325.7	355.3
		363.16	481.4	525.8
		376.16	772.8	845.1

TABLE IV. (Cont.)

Concentration		Temperature	P ₂	P ₃
Weight %	Molality	(°K)	(mms. of Hg.)	(mms. of Hg.)
50.00	5.886	303.16	28.68	31.83
		313.16	49.78	55.34
		323.16	82.95	92.56
		333.16	133.6	149.5
		343.16	208.6	233.8
		353.16	316.3	355.3
		363.16	466.9	525.8
		376.16	749.1	845.1
59.29	8.573	304.21	29.33	33.77
		313.25	47.87	55.61
		323.30	79.70	93.15
		333.44	129.2	151.3
		343.53	202.7	237.6
		353.66	308.6	362.3
		363.72	457.5	537.2
		373.81	662.0	777.7
		378.76	787.1	925.1

TABLE IV. (Cont.)

Concentration		Temperature	P ₂	P ₃
Weight %	Molality	(°K)	(mms. of Hg.)	(mms. of Hg.)
69.99	13.73	303.16	26.15	31.83
		313.16	45.88	55.34
		323.16	75.79	92.56
		333.16	122.0	149.5
		343.16	189.6	233.8
		353.16	286.2	355.3
		363.16	421.5	525.8
		373.16	606.6	760.0
80.05	23.62	333.16	107.2	149.5
		338.16	134.2	187.6
		343.16	166.8	233.8
		348.16	206.2	289.2
		353.16	252.6	355.3
		358.16	307.9	433.6
		363.16	372.4	525.8
		368.16	447.9	634.0
		373.16	534.8	760.0

TABLE IV. (Cont.)

Concentration		Temperature	P ₂	P ₃
Weight %	Molality	(°K)	(mms. of Hg.)	(mms. of Hg.)
85.07	33.54	348.16	183.1	289.2
		353.16	223.8	355.3
		355.16	246.6	393.1
		358.16	271.8	433.6
		360.66	298.8	478.1
		363.16	328.6	525.8
		365.66	360.8	577.8
		373.16	471.6	760.0

TABLE V.

The Slopes $\frac{\Delta H_2}{\Delta H_3}$ of $\log P_2$ vs $\log P_3$ for Silver Nitrate Solutions and the Resulting Values for ΔH_2 and ΔH_1 at 50°C ($\Delta H_3 = 10,245$ cal/mole).

Concentration		Slope $\Delta H_2 / \Delta H_3$	ΔH_2 Cals/mole	ΔH_1 Cals/mole
Weight %	Molality			
0	0	1.000	10,245	0
9.98	0.654	0.9982	10,227	18
19.98	1.470	0.9929	10,172	73
30.00	2.523	0.9960	10,204	41
40.00	3.924	0.9958	10,202	43
50.00	5.886	0.9948	10,192	53
59.29	8.573	0.9948	10,192	53
69.99	13.73	0.9895	10,138	107
80.05	23.62	0.9893	10,135	110
85.07	33.54	0.9799	10,039	206

TABLE VI.

The Activity of Water p/p_0 in Silver Nitrate
Solutions at Various Concentrations and Temperatures.

Concentration		Temperature (°C)					
Mole fraction water.	30	40	50	60	70	80	90
.9883	.9906*	.9872	.9872	.9860	.9855	.9845	.9842
.9742	.9884*	.9823	.9811	.9766	.9731	.9707	.9680
.9565	.9519	.9510	.9482	.9452	.9435	.9423	.9414
.9340	.9268	.9248	.9226	.9197	.9175	.9167	.9156
.9041	.9010	.8995	.8962	.8936	.8922	.8902	.8880
.8017	.8216	.8291	.8188	.8161	.8109	.8055	.8016
.7015				.7171	.7134	.7109	.7083
.6234						.6299	.6250

* $t = 30.06^\circ$

TABLE VII.

The van't Hoff Factor, i and the Osmotic
Coefficient, g for Silver Nitrate Solutions
At 80°C .

Concentration		i	g
Weight %	Molality		
9.98	0.654	1.337	0.668
19.98	1.470	1.139	0.569
30.00	2.523	1.347	0.673
40.00	3.924	1.285	0.642
50.00	5.886	1.163	0.581
59.29	8.573	1.128 [*]	0.564 [*]
69.99	13.73	0.976	0.488
80.05	23.62	0.955	0.477
85.07	33.54	0.972	0.486

^{*} $t = 80.50^{\circ}$

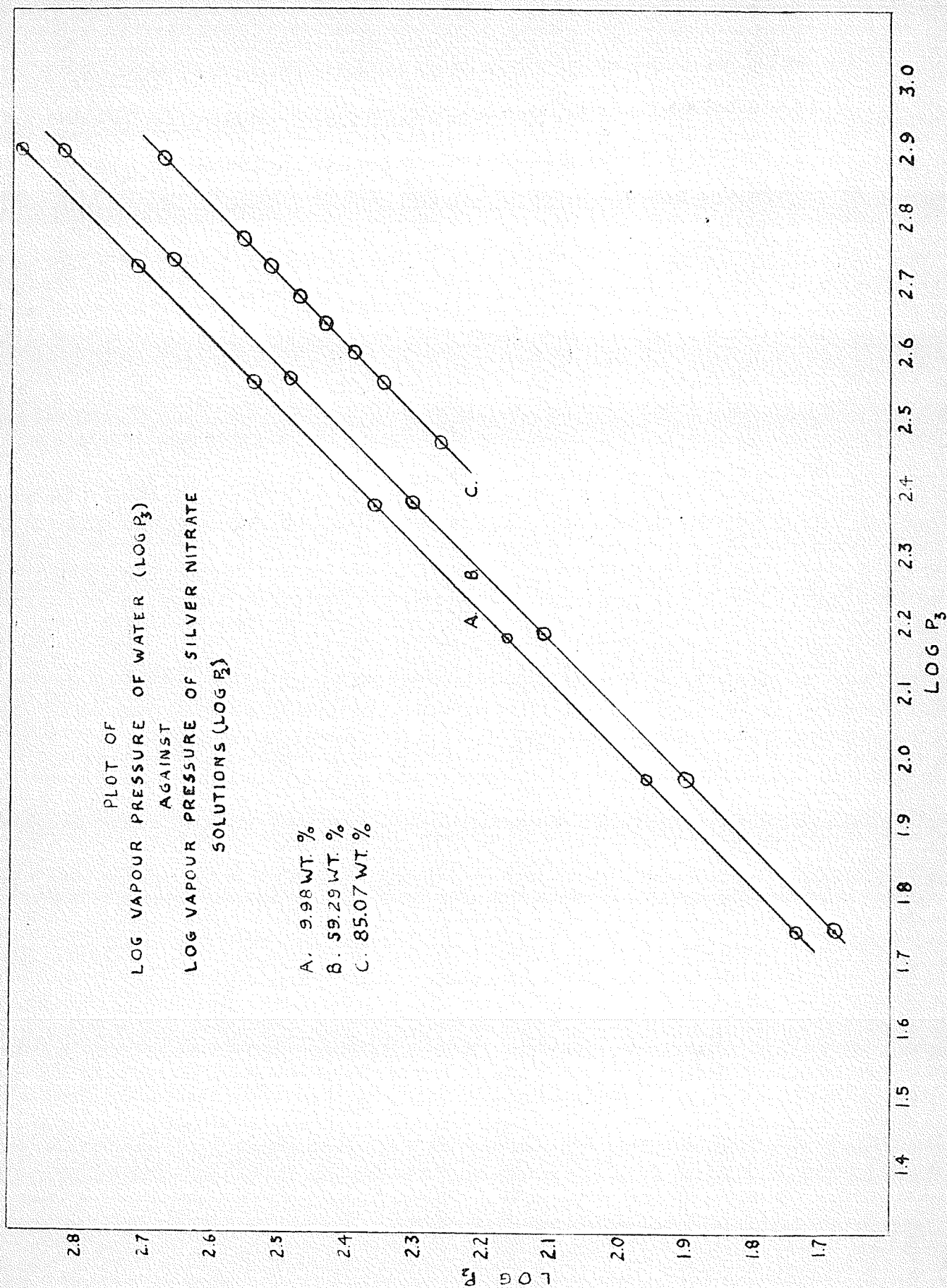


FIG. 4.

TABLE VII.

The Osmotic Pressure II of Solutions
of Silver Nitrate at Various Temperatures.

Concentration		II (atmospheres)		
Weight %	Molality	50°	70°	90°
9.98	0.654	18.7	22.2	25.2
19.98	1.470	27.7	41.8	51.9
30.00	2.523	77.2	88.8	96.4
40.00	3.924	117.1	131.9	141.0
50.00	5.886	159.4	174.4	189.9
59.29	8.573	227.0 [*]	243.4 ^{**}	257.1 ^{***}
69.99	13.73	290.9	320.6	353.4
80.05	23.62		516.8	551.3
85.07	33.54			751.5

^{*} t = 50.14°

^{**} t = 70.37°

^{***} t = 90.56°

DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS

No lengthy discussion of the purely experimental data on vapour pressures of silver nitrate solutions as tabulated in Table IV is necessary. The probable error in the measurements of the vapour pressures does not exceed 0.2% which renders the data good enough for most purposes, but their use in the determination of activity coefficients is doubtful since the calculation of these quantities demands very precise measurements of vapour pressure.

In Table V the latent heats of vaporization of water from pure water and from the various concentrations of silver nitrate solutions are given at 50°C. The value of 10,245 cal for pure water is an average of several accurately measured calorimetical determinations as given by Johnson and Molstad (27). Although the latent heats of vaporization as calculated by the Othmer method are also given to five significant figures, the method warrants the use of no more than three significant figures since the probable error is 1 to 1.5%. Therefore the ΔH_1 values up to 80 weight percent could be considered zero within experimental error. However, since there is a trend towards increasing ΔH_1 corresponding to increasing concentration it was thought that the values as tabulated might be of some significance. In any case it is evident that the latent heat of water evaporated from silver nitrate solutions changes little with increasing concentration; thus there is only a very small amount of heat

of solution to be considered in addition to the latent heat of evaporation of water itself. Similar conclusions can be drawn for other aqueous salt solutions such as sodium chloride. Also Hirschler (25) commented on Roehl's (37) work showing that the vapour pressures of certain aqueous saturated solutions, when plotted as $\log P$ vs $\frac{1}{T}$ give straight lines parallel to a similar plot for water. This is further evidence in the same direction.

As is seen from Table V the values of ΔH_1 are positive and increase with increasing concentration, that is heat is absorbed when a mole of water is added to a large amount of each of the solutions (the differential heat of dilution) and a slight increase in the amount of heat absorbed is evident with increasing concentration.

Interpreted differently there is apparently very little change in solvation energy with concentration. This fact alone does not infer that the silver and nitrate ion are naked in aqueous solution since many other salts such as sodium chloride whose ions are certainly hydrated show the same effect. One can conclude however that the solvation energy of the ions of silver nitrate remains sensibly constant over the concentration range investigated.

Although the results of this research do not indicate whether or not the silver and nitrate ions are hydrated in aqueous solution other investigators have concluded that both of these ions are naked. Van Ruyven (43) states that the electric forces of these

two ions are too feeble to bind a water molecule. His observations are based on the degree of ionisation calculated from the elevation of the boiling point and those calculated from conductivity measurements. Similarly Buchbock could not detect any evidence of hydration of the ions of silver nitrate.

It is interesting to compare the activity of water with the mole fraction of water as given in Table VI. On examination it is seen that there is surprisingly close agreement between the mole fraction and the activity over the whole concentration range indicating that silver nitrate solutions obey Raoult's law more closely than one would expect for an electrolyte. This effect might be explained on the basis of ion-pair formation which according to Robinson and Tait (36) increases rapidly with concentration in aqueous solutions of silver nitrate. These authors state that for silver nitrate solutions the best value for the distance of closest approach of the ions appears to be $2.5\overset{\circ}{\text{\AA}}$ which is well below the Bjerrum critical distance of $3.5\overset{\circ}{\text{\AA}}$ and therefore ion-pair formation is to be expected.

It has been stated (22) that from both theoretical and experimental observations the extent of formation of ion-pairs for a given ionic concentration is greater the smaller the size of the ions, the higher their valence, and the lower the dielectric constant of the solvent. The size of the ion in solution includes the molecules of solvent effectively attached. This suggests that

neither the silver nor the nitrate ions in silver nitrate solutions are greatly hydrated as otherwise the two ions could not approach close enough for effective ion-pair formation. However, no definite conclusions can be drawn regarding the hydration of these ions until a more effective method of determining the extent of ionic hydration is devised.

The calculated osmotic pressures of silver nitrate solutions at 50, 70 and 90°C. are presented in Table VII. The values obtained should be a close approximation to those that might be determined experimentally despite the use of the molar volume of water as a substitute for the partial molar volume. A detailed discussion of the results is not thought to be necessary. Suffice it to say that they serve to exemplify the very high osmotic pressures exerted in concentrated electrolytic solutions.

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