

SOLUBILITY OF SILVER CHLORIDE

AND RELATED STUDIES

A thesis presented for the degree of
Doctor of Philosophy

in the Faculty of Science of Leicester University

by

Salag Dhabanandana

The University,
Leicester.

July, 1967.

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STATEMENT

All of the experimental work, herein described, has been carried out by the author in laboratories of the Department of Chemistry, University of Leicester and of the Radiochemistry Section, School of Chemistry, Leicester Regional College of Technology between October 1964 and the present date.

The work has not been presented and is not being concurrently presented for any other degree.

Date 27th July, 1967.

Signed Salag Dhabanandana.

To My Father

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SUMMARY

The work described in this thesis is mainly concerned with measurements of the solubility of silver chloride in heavy water and in formamide, at various chloride concentrations and temperatures. A radiochemical technique has been developed, whereby silver chloride labelled with silver-110m is measured for its gamma-activity. The heat of precipitation of silver chloride in formamide has also been measured at 15° and 25°C. The solubility data have been analysed to yield solubility products and equilibrium constants for the formation of complexes. The heats of solution of silver chloride in heavy water and in formamide have been calculated from the temperature dependence of the solubility products. The value in heavy water is in close agreement with a published calorimetric figure. The value in formamide is in satisfactory agreement with the present measured heat of precipitation. All of the heats of solution are endothermic; but are less endothermic in formamide than in water. Other relevant thermodynamic quantities have also been calculated for comparison with the corresponding values in water. The results suggest that the amount of undissociated silver chloride is smaller in heavy water, but greater in formamide, than in water.

Preliminary emf measurements in hydrochloric acid solution

in formamide, using hydrogen, cadmium|cadmium chloride and silver|silver chloride electrodes are presented. The standard potential of the silver|silver chloride electrode at 25°C is in fair agreement with the available literature values.

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C O N T E N T S

Chapter		Page Number
I	Introduction to the Present Work	1
II	Previous Studies of Behaviour of Electrolytes in Heavy Water.	6
	2.1. Structural Model of Water	6
	2.2. E.M.F. Measurements	11
	2.3. Thermal Measurements	14
	2.4. Solubility Measurements	15
III	Electrolyte Studies in Formamide	18
	3.1. Structure and Bonding in Formamide	19
	3.2. Conductance Measurements	21
	3.3. Transference Numbers Measurements	24
	3.4. E.M.F. Measurements and Thermodynamic Properties	25
	3.5. Heats of Solution	27
	3.6. Solubility Measurements	30
IV	Experimental Technique for Determining Solubility	33
	4.1. Preliminary Considerations	35
	4.2. Selection of Method of Counting and Counting Technique	38
	4.3. Accuracy of Measurements	42

Chapter	Page Number
4.4. Preparation of Labelled Silver Chloride	47
4.5. Preparation of the Counting Source	47
4.6. Determination of Solubility	48
4.7. Sampling Technique	51
4.8. Method Employed in the Determination of the Concentration of Added Chloride Ions	52
4.9. Reproducibility of Technique	56
4.10. Treatment of the Data	59
4.11. Effect of Radioactivities on Solubilities	61
4.12. Effect of Adsorption on the Surface of Container	62
V Materials	64
5.1. Solvents	64
5.2. Standard Solutions	64
5.3. Radioactive Materials	65
5.4. Purification of Formamide	66
5.5. Summary of Previous Method Used in Purification of Formamide	67
5.6. Present Method Used in Purification of Formamide	72
5.7. Determination of Physical Constants	74

Chapter		Page Number
VI	Other Experimental Studies	78
	6.1. Calorimetric Measurement	78
	6.2. Preliminary E.M.F. Measurements	83
	6.3. Preparation of Electrodes	84
	6.4. Preparation of Hydrochloric Acid Solution	86
	6.5. Determination of Chloride Concentrations in Formamide	87
	6.6. Measurement of Potentials	88
VII	Results	89
	7.1. Solubility of Silver Chloride in Double- deionised water	89
	7.2. Solubility of Silver Chloride in Heavy water	90
	7.3. Solubility of Silver Chloride in Formamide	91
	7.4. Calorimetric Measurement of the Heat of Precipitation of Silver Chloride	93
	7.5. E.M.F. Measurements	94
VIII	Discussion	95
	8.1. Solubility of Silver Chloride in Heavy water	99

Chapter	Page Number
8.2. Solubility and Related Studies of Silver Chloride in Formamide	108
8.3. Preliminary E.M.F. Measurements	123
Appendix : Determination of Solubility of Silver Bromide in Water.	134
References	137

CHAPTER I

Introduction to the Present Work

Studies of the behaviour of aqueous solutions of both electrolytes and non-electrolytes have been, and still are, a subject of major importance. Recent years have produced a wealth of information concerning topics such as the structure of water, the effect of solutes on the structure of water, and the interactions between solute and solvent. Water as a solvent is unique for having a good solvent power, high melting and boiling points, low density, high dielectric constant and a maximum density at 4°C. In consequence, the major studies of electrolyte solutions have been directed towards the behaviour of aqueous rather than non-aqueous systems. Aqueous solutions of electrolytes have thus been extensively investigated by a wide variety of techniques, including spectroscopic, conductometric and thermodynamic measurements.

It is because of the unique properties of water that corresponding measurements in heavy water are of interest, so that direct comparison may be made. Heavy water has slightly more structure than light water since the deuterium bond is slightly stronger than a hydrogen bond. However, differences in various properties of solutions in water and heavy water are

usually small, and are probably due to structural effects since the dielectric constants are almost the same in each case. Studies of electrolyte solutions in heavy water are rather limited, but several recent examples are outlined in the following chapter. There appear, however, to be scarcely any studies of ionic equilibria^{1,2a,b,c} other than measurements of the dissociation constants of weak acids in heavy water. Hence, little is known of the extent of complex formation or of ion-pairing in heavy water as compared with water.

Although several studies of the solubilities of appreciably soluble electrolyte in heavy water have been made, scarcely any data on the solubilities of sparingly soluble electrolytes exist. Solubility studies of sparingly soluble salts can yield information concerning the formation of complexes in solution, and this is largely the purpose of the work described here. The present study consists, in part, of radiochemical measurements of the solubility of silver chloride in heavy water at various chloride concentrations and temperatures. Silver chloride was chosen since its solubility has been reliably studied in water^{3,4} and because it is known to form complexes of the type AgCl , AgCl_2^- etc., in water. The solubility data can then

be analysed to yield equilibrium constants for the formation of such complexes, together with the solubility product K_s , defined by

$$K_s = [\text{Ag}^+] [\text{Cl}^-] \gamma_{\text{AgCl}}$$

where $[]$ denotes molality concentration

γ denotes the mean ionic activity coefficient.

The solubility product is related to the standard free energy of solution $\Delta G^\ominus$ by

$$\Delta G^\ominus = -RT \ln K_s \quad (1)$$

and if the solubility product is measured over a range of temperatures, the standard heat of solution $\Delta H^\ominus$ can be determined from the relation

$$\frac{\partial \ln K_s}{\partial T} = \frac{\Delta H^\ominus}{RT^2} \quad (2)$$

Furthermore, the difference between the free energy of solution of silver chloride in the solvents is equal to the difference between the free energy of solvation in the two solvents since the lattice free energy is the same in each case. Similar considerations apply to differences in heats of solution. Hence, thermodynamic information concerning changes in solvation in going from one solvent to another, may be obtained.

Next to water, the most common class of solvents

used in electrolyte studies consists of water + organic solvent mixtures e.g. water + dioxan or water + ethanol. Here interest centres around the change in solvation due, at least in part, to the changes in the dielectric constant, since by altering composition, dielectric constant can be altered. Studies of electrolyte solutions in completely non-aqueous solvents, although becoming more abundant, are still rather limited. There is however a steady accumulation of data for a particular class of solvents, namely the amides of the lower fatty acids e.g. formamide and N-methyl formamide. These solvents are either liquids of high boiling point or solids of low melting point. They have very high dielectric constants and are good solvents for many electrolytes. The lowest member, formamide (HCONH_2) shows many similarities to water. It is strongly hydrogen bonded giving rise to its high boiling point and dielectric constant (at 25°C dielectric constant = 109 compared with 78.3 in the case of water). It will dissolve most compounds which are water soluble and can solvate ions more strongly than water as shown by measurements of heats and free energies of solution. Electrolytes which are fully dissociated in water appear to be fully dissociated in formamide, as indicated by conductance data. However, unlike water, it is unstable and decomposes on heating.

Some of the interesting studies of electrolyte solutions in formamide and related solvents are discussed in Chapter III. The remainder of the author's work described in this thesis consists of radiochemical measurements of the solubility of silver chloride in formamide at various chloride ion concentrations, and temperatures together with calorimetric, and preliminary emf measurements in formamide. Such measurements are not without difficulties. Owing to the thermal instability of the solvent, it is not possible to make solubility measurements at high temperatures. The results at 35°C show a greatly increased scatter over corresponding measurements in water or heavy water, despite the higher solubility in formamide.

Formamide was chosen for study since it is cheap and readily available, and because a considerable number of studies have already been made with this solvent. Silver chloride was again chosen, since there are very few data for sparingly soluble salts in formamide and since we wished to study the extent of complex formation in a solvent with a dielectric constant greater than that of water. The measurements are also of interest since it has been found^{5,6} (and we have confirmed) that the silver/silver chloride electrode functions satisfactorily in formamide.

C H A P T E R II

Previous Studies of Behaviour of Electrolytes in
Heavy Water

2.1. Structural Model of Water

Liquid water is a unique solvent possessing abnormal properties. For example its melting point, boiling point, heat of vapourisation and heat of fusion are all higher than would normally be expected from the hydride compounds of the other members of the oxygen family e.g., hydrogen sulphide.

The substitution of deuterium for hydrogen in the water molecule does not appreciably change the intermolecular distances (the bond distance D - O is 10^{-3} Å longer than that of H - O in liquid water ⁷) and has little effect on the nature of the bond forces. Hence proposed structures of light water are equally applicable to heavy water. However, the O - D bond is slightly stronger than the O - H bond leading to the more structural order in heavy water than in light water. Bernal and Fowler⁸ were the first to propose a theory, based on X-ray diffraction studies, that liquid water, over a short range and for a short time, retains the tetrahedrally co-ordinated structure of ice, together with a certain percentage of monomer with no hydrogen bonding. The most important feature is the

assumption of the *tridymite* form of quartz structure in liquid water, due to hydrogen bonds which break with a rise in temperature. Such a structure explains the abnormally high boiling point of water. However, later X-ray studies of liquid water provided evidence which contradicted Bernal and Fowler's model. In 1950, Pople⁹ suggested that when ice crystals melt to liquid water, the hydrogen bonds are not broken but bent (26° at 0°C and 30° at 100°C) although these bonds are rigid in ice. Therefore, the liquid state of this model consists of an irregular arrangement of water molecules with bent hydrogen bonds.

X-ray studies of hydrates supplied a new model for the tetrahedrally co-ordinated structure. Pauling¹⁰ suggested that in hydrates such as $\text{CH}_4 \cdot 6\text{H}_2\text{O}$, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, the water molecules are hydrogen bonded into a large cagelike structure, in which the Cl_2 or CH_4 molecule is held. Such compounds are called clathrates. Pauling then proposed that these hydrated compounds represented a type of hydrogen bonded structure in liquid water i.e., water being both guest and host in a tetrahedrally hydrogen bonded pentagonal dodecahedral lattice. In each dodecahedral cage there are 46 water molecules per unit in the hydrogen bonded cage structure with 8 additional water molecules forming no hydrogen bonds. This model predicts a density of 1.0 gm/cc . However, there has

been criticism, on the grounds that the model is too rigid to account for the observed fluidity of liquid water.

Frank and Wen¹¹ used Pople's model with some modifications to describe the non-hydrogen bonded water molecules. They assumed that the life time of the clathrate structures are as short as 10^{-10} seconds and described them as "flickering clusters". Frank and Wen's model is described as "dynamic" or "co-operative", i.e., they postulated that in most cases when one hydrogen bond breaks then typically the whole cluster will be destroyed. Equally the formation of one hydrogen bond can cause the formation of a whole cluster. Consequently, highly hydrogen bonded, short live clusters are embedded in the liquid among non-hydrogen bonded molecules which interact by means of dipole forces only. The clusters are presumably compact in shape since this gives maximum stability.

Recently Nemethy and Scheraga¹² have applied a modified form of Frank and Wen's flickering structure of water to heavy water. They computed the thermodynamic properties of liquid water from the partition function of a lattice that contained molecules with zero to four hydrogen bonds i.e., there are 5 different energy states, equally spaced, ranging from the lowest energy level (fully hydrogen bonded molecules in ice or in clusters in the liquid) to the highest level which is due to the non hydrogen bonded species. Since this model was

independent of volume, they were able to deal only with strictly thermal properties. When this theory was extended to apply to liquid heavy water¹³, the differences in masses and the resulting isotope effect on the vibrational frequencies of molecules were taken into account. Their conclusions indicate that more structural order exists in heavy water than in light water and this argument is supported by other work¹⁴⁻¹⁵.

Other workers,¹⁶⁻¹⁸ have been successful in applying the significant structure theory¹⁹ to water. Each group used different models of water and different approaches. They were able to explain and predict certain properties of liquid water and heavy water such as the entropy, heat capacity, molar volume, vapour pressure.

There are, in general, two main approaches to describe liquid water, "the uniformist" or "average approach" and the "mixture approach". The former assumes that liquid water is composed of water molecules which have more or less the same properties. The "mixture approach" assumes that there are at least two classes of water molecules, such that within a given class the molecules are behaving in a similar manner. There will be exchange reactions between these classes so that a time average must show all the molecules to have the same properties. Bernal and Fowler's and Pople's model fall into the former class whereas the others belong to the latter.

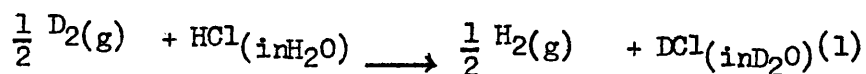
There are two points to be made so far as the "uniform" models are concerned. Firstly, the analysis treats the hydrogen bonds as electrostatic interactions and thus allows a large amount of O - H $\cdots$ O bending without a significant change in energy. If the co-valent contribution to the hydrogen bond is significant as recently suggested by Davis and Litovitz²⁰, a more restricted bending would be anticipated. Secondly, this approach results in a model which is difficult to treat in discussing the properties of water and solutions. On the other hand, the more recent Raman spectroscopic work indicates that mixture models are not completely satisfactory; hence the uniform model can not be ruled out entirely. Some physical properties of heavy water and water are shown in Table I.

Table I

Physical Properties	Heavy Water(D ₂ O)		Water (H ₂ O)	
	Value	Reference	Value	Reference
Molecular weight(on C ¹² scale)	20.028	21	18.015	21
Dielectric constant 25°C	77.937	) based on dielectric 22) constant of water=78.3	78.3	} 23
45°C	71.1925		71.51	
Temperature of maximum density	11.23°C		3.98°C	
Boiling point	101.42°C		100.00°C	
Melting point	3.81°C		0.00°C	
Triple point	3.82°C		0.01°C	
Density 30°C	1.10319)	24	0.99568)	25
50°C	1.0956)		0.9880)	

2.2. E.M.F. Measurements.

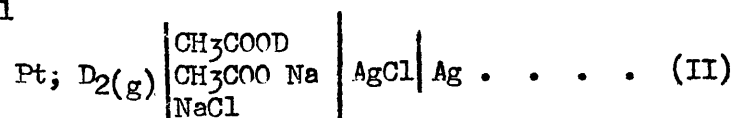
The standard emf of the cell $\text{Pt}; \text{D}_2(\text{g}) | \text{DCl in D}_2\text{O} | \text{AgCl} | \text{Ag} \cdot (\text{I})$ was measured, over a range of temperature by Noonan and LaMer²⁶ in 1939. The cell has been recently re-examined by Gary, Bates and Robinson²⁷ and also over a wider range of temperatures, by Lietzke and Stoughton²⁸. Both of these latter groups of workers were interested in obtaining the thermodynamic quantities for the reaction :-



by comparing the standard emf of the above cell with that of the corresponding cell with a hydrogen electrode in a solution of HCl in H₂O. Gary, Bates and Robinson²⁷ studied cell I at concentrations in the range 0.01 to 0.5 m and at temperatures from 5° to 45°C at 5°C intervals. The standard emf E° was evaluated at each temperature and at 25°C was found to be 0.21266 V or 8.92 mV higher than the value in H₂O on a molality scale. Using mole fraction scale the thermodynamic change $\Delta G^\circ, \Delta H^\circ, \Delta S^\circ, \Delta C_p^\circ$ for reaction (1) were calculated. Their results were found to be in excellent agreement with those of Noonan and LaMer²⁶. The activity coefficients of DCl in D₂O were calculated and compared with those in water. The differences of 0.002 - 0.003 in $\log \gamma^\pm$ are less dependent on dielectric constant than on the difference in densities

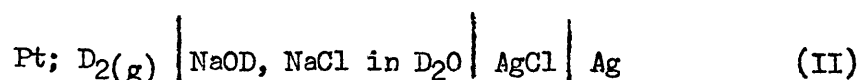
Lietzke and Stoughton²⁸ measured the emf of cell I at concentrations of DCl in D₂O from 0.01 to 1 m and at temperatures from 25 to 225°C. A direct comparison was made of the thermodynamic properties of HCl and DCl solutions using their own data for the thermodynamic properties of HCl in aqueous solution. The values of $E^\ominus$ for the deuterated system were compared with those of Gary, Bates and Robinson²⁷, the differences appeared to be larger than expected e.g., 3 mV difference was found at 25°C. From $E^\ominus$, they calculated activity coefficients for each concentration and temperature. The activity coefficient of DCl in D₂O was found to be lower than that of HCl in H₂O at all temperatures and concentrations. The difference between the activity coefficients is greater at 25°C and 200°C than at 90°C. This was explained by the fact that the dielectric constant of D₂O and H₂O become close together at about 100°C and then diverge again at higher temperatures.

Emf measurements have also been used to study the dissociation constants of weak deuterio acids in D₂O. For example deuterio acetic acid CH₃COOD has been studied²⁹ by using the cell



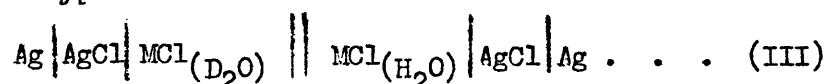
In general, deuterio acids in D₂O are found to be weaker than proto acids in H₂O.

The ionisation constant K_w of D_2O from 5° to $50^\circ C$ was derived from the emf of the cell³⁰



The values of pK_w in molality, molarity and mole fraction scales together with corresponding quantities for the self dissociation of H_2O and also ΔH° , ΔS° and ΔCp° for the self dissociation of D_2O were calculated. The ionisation constant pK_w of D_2O at $25^\circ C$ is 14.955 as compared with 13.997 for H_2O in molality scale.

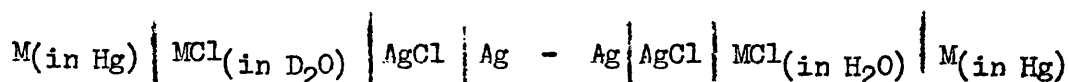
In 1962, Greyson³¹ studied the free energies of transfer of chlorides of lithium, sodium, potassium, caesium, ammonium and tetra methyl ammonium, from heavy water to water by using a cell of the type



Where M represents the cations mentioned above, and the double bar represents a cation exchange membrane. The assumption was made that all the transport processes across the membrane are negligible. The reproducibility was reported to be ± 0.3 mV. The free energies of transfer from D_2O to H_2O , for chloride of lithium, sodium and potassium were found to be 110, 140 and 180 calories/mole respectively. A decrease in entropy was also found for the transfer of electrolytes from D_2O to H_2O . In a

more recent paper,³² Greyson reported a re-investigation of the contribution of solvent transport across the membrane to the emf of the cell (III). He showed that although this contribution is not negligible, it has a negligible effect on the entropy of transfer since the transfer process is dominated by the enthalpy of transfer.

Emf measurements have been made on cell



where M is lithium, sodium, potassium and cadmium by Pentti Salomaa and Veli Aalto³³. Measurements have been made to various chloride concentrations of MCl. The free energy changes for the transfers at 25°C were calculated. They were of virtually the same magnitude i.e., around 210 - 220 calories/chloride ion (on a molarity scale) regardless of cation, which indicates that the contributions of the cations to the overall free energy changes must be small. Their results agree excellently with Noonan and LaMer²⁶ whereas Greyson's results³¹ are somewhat smaller.

2.3. Thermal Measurements.

Heats of solution ΔH° of electrolytes in D₂O have been measured calorimetrically by Lange and Martin³⁴ and more recently by Davies and Benson³⁵. The results in the case of

sodium chloride (the only electrolyte included in both studies) agree well. The isotope effect on the heat of solution i.e., $\Delta H^\circ(\text{D}_2\text{O}) - \Delta H^\circ(\text{H}_2\text{O})$ was calculated by both sets of workers and was found in general to be positive. The fluoride ion is the only singly charged ion for which a negative contribution to the isotope effect has been observed³⁵. By measuring the isotope effect for several electrolytes, Lange and Martin³⁴ were able to predict the isotope effect of a wide range of electrolytes, assuming the contributions of the cation and anion to be independent.

Wu and Friedman³⁶ measured heats of dilution of lithium chloride, sodium chloride and sodium iodide solutions in D_2O in the range of 1 to 3 m. In general their results agree with those of Birnthal and Lange^{37,38} with the exception of lithium chloride. These results as well as the solvent isotope effects on the entropies of solvation seem to be consistent with the model of aqueous solutions developed by Nemethy and Scheraga^{12,13}.

2.4. Solubility Measurements.

Although a number of solubility measurements of salts in D_2O have appeared in the literature³⁹⁻⁴⁴, most of these studies have been concerned with rather soluble salts such as sodium chloride, barium chloride, potassium permanganate, mercuric

cyanide, thallous nitrate, potassium nitrate, halides of potassium etc. All were measured in a medium of H_2O - D_2O mixture. By assuming there is a linear variation of solubility with D_2O content, the solubilities of these salts in 100% D_2O were obtained by extrapolation to pure D_2O . The work aimed simply at finding solubilities rather than studying complex formations. Solubility differences of salts in these two solvents are quite large. In general, salts are less soluble in D_2O than in H_2O , however the results are expressed, i.e., molality, molarity or aquamolality (the number of moles of solutes per 55.51 moles of solvent) scales.

Ramette and Dratz^{2a} determined the solubility product of silver bromate in D_2O by iodometric titration at 14.7°, 25° and 35°C. Solubilities of silver bromate at all temperatures are again lower in D_2O than in H_2O . The standard free energy, enthalpy and entropy of solution were calculated on molarity scale. They were all higher in D_2O than in H_2O . Their results indicate that the solvation enthalpy is more negative for H_2O than D_2O . They suggested that the lower solubility of silver bromate in D_2O is due to the enthalpy of solvation which outweighs an entropy of solvation which would favour higher solubility in D_2O .

Ramette and Broman^{2b} also measured the solubility product of cupric iodate in D_2O . They again calculated thermodynamic

changes for solution and concluded in this case the lower solubility was due to both an unfavourable entropy and enthalpy effect.

Solubilities of silver bromate in lithium perchlorate and lithium nitrate solutions in D_2O and H_2O were measured by Ramette and Spencer^{2c} in order to observe the association of silver and nitrate ions. According to their results, a one-tenth molar solution of silver nitrate is about 94% dissociated, and no significant difference in the extent of association in H_2O and D_2O was found.

CHAPTER III

Electrolyte Studies in Formamide and Related Solvents

Formamide and the other amides of the low aliphatic acids and their N-methyl derivatives form a class of liquids or low melting point solids with extremely high dielectric constants. Consequently, they are good solvents for many organic and inorganic salts. Formamide has the property of being both basic and acidic. This solvent solvates inorganic salts as does water. There is some evidence that formamide is held more strongly by crystalline salts than is water⁴⁵. Physical properties of this solvent are given below.

Table I. Physical Properties of Formamide

Property	Value	Reference
Freezing point °C	2.55	46
Boiling point °C	193 (1 atmos.)	47
Density gm/ml. 15°C	1.13756	48
25°C	1.1296	
35°C	1.12068	
Viscosity centipoise (25°C)	3.31	49
Dielectric constant 15°C	113.5	50
25°C	109.5	
35°C	105.6	
Specific conductance	(1-2) x 10 ⁻⁷	51
ohm ⁻¹ cm ⁻¹ at 25°C		

Formamide is highly associated in the liquid state as shown by studies of its physical and chemical behaviour as well as by its ultra-violet, infrared, and Raman spectra. Kahovec and Wassmuth⁵², and Rao⁵³ found from the Raman spectrum that formamide is highly polymerised at room temperature and breaks up into lower polymers at higher temperatures as well as in solutions in polar solvents such as water. Molecular association occurs through hydrogen bonding and hence its boiling point is very high for a low molecular weight compound. It has been suggested that the high viscosity and dielectric constant may be due to the fact that this compound forms a non-symmetrical linear type of polymer.

3.1. Structure and Bonding in Formamide.

Most investigators agree that the $\text{H}-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{N} \end{smallmatrix}$ part of formamide is planar but the position of the two hydrogen atoms bonded to the nitrogen atom is still unsettled. Some investigator such as Evans⁵⁴, on the basis of infrared spectra favoured the symmetrical arrangement of these two hydrogen atoms about the plane of the molecule. Kurland and Wilson⁵⁵, from X-ray diffraction studies of crystalline formamide concluded that the two hydrogen atoms are in the plane of the molecule. On the other hand Costain and Dowling⁵⁶'s results from microwave spectra of ten isotopic species of formamide indicate a non-planar structure of formamide, with the

$\text{H}_2\text{-N-C}$ group forming a shallow pyramid. Recently, Puranik et al ⁵⁷ evaluated force constants of formamide and found their results to be consistent with a non-planar structure. Spectral studies also revealed the tautomeric nature of amides i.e., keto $\rightleftharpoons$ enol, and certain aspects of its chemical behaviour may arise from the enol form. However, Kumler and Porter ⁵⁸ have stated that in formamide never more than 10% of the molecules are in the enol form at any instant. Nevertheless, more recent infrared ⁵⁹ and ⁶⁰ X-ray data seems to point to the existence of the amide group in a purely keto form. Pauling and Sherman ⁶¹ considered that the formamide molecule resonates, the possible resonance hybrids being $\text{HC}=\overset{\text{O}}{\text{NH}_2}$ (ground state) and $\text{HC}=\overset{\delta-}{\text{O}}=\overset{\delta+}{\text{N}}=\text{H}_2$ (excited state). They calculated the dipole moment of the excited form and found that it is three times that of the ground state form. Hence, Pauling ⁶² concluded that the resonance structure is responsible for the high dielectric constant of this solvent. This resonance structure was supported by other workers ^{63,64} but was contradicted by Bates and Hobbs ⁶⁵ who proposed a structure of the amide group based on dipole moment measurements on a series of aliphatic and aromatic amides in dilute benzene and dioxane solutions. Their structure seems to be consistent with the keto form and does not require significant contributions from the highly polar resonance hybrid of Pauling.

Other solvents, for example N-methyl formamide, N-methyl

acetamide and N-methyl propionamide have also been used for electrolyte studies, some of which are discussed later. N-methyl acetamide is a solid with melting point of 29.8°C and a dielectric constant of 178.9 at 30°C , and is again a good ionising solvent. Although the ultra violet spectrum suggests that the molecule exists in a state of resonance i.e., trans ~~trans~~^{cis}, the Raman and infrared spectra point to the almost exclusive existence of the trans configuration, and this is equally applicable to the other N-substituted^{at} amides. These amides are also highly associated as chain polymers.

3.2. Conductance Measurements

As Walden has pointed out, the nature of the solvent as well as the dielectric constant determines its dissociating power. Solutions of salts in formamide and other solvents having high dielectric constants such as N-methyl formamide and N-methyl acetamide are good electrolytic conductors. The earliest conductance data of salts in such solvents seem to be those of Davis, Putnam and Jones⁶⁶ and Davis and Johnson⁶⁷. They measured these values before the Debye - Huckel - Onsager theory appeared. Their results were corrected to the modern standard for conductance and were extrapolated to zero concentration by Notley⁵¹. Some of the re-calculated equivalent conductances at zero concentration (Λ_0) are tabulated on the next page.

Table II.

Salt	Λ_0 (cm ² ohm ⁻¹ equi. ⁻¹)	Salt	Λ_0 (cm ² ohm ⁻¹ equi. ⁻¹)
KCl	29.5	NaNO ₃	28.0
KI	29.1	KNO ₃	30.0
NaI	29.6	NH ₄ NO ₃	33.1
LiNO ₃	26.2	NH ₄ Br	32.2

Dawson, Newell and McCreary⁶⁸ reported the conductances of hydrochloric acid and potassium chloride in formamide of various concentrations and temperatures. The limiting conductance of hydrochloric acid was found to be 27.87 cm² ohm⁻¹ equi.⁻¹ whereas that of potassium chloride is 29.85 cm² ohm⁻¹ equi.⁻¹. Using an approximate method (trimethyl phenyl ammonium benzene sulphonate was used) Dawson and co-workers⁴⁹ obtained the limiting ionic conductances of the hydrogen ion and the potassium ion (10.6 and 11.5 cm² ohm⁻¹ equi.⁻¹ respectively.) These results indicate that the solvated proton is larger than the solvated potassium ion. The absence of abnormally high cation conductance in hydrochloric acid solution is a proof that the proton does not use the proton transfer mechanism as it does in water. Ion association was found to be completely absent up to 0.01M in this work. Other studies of some higher

valence type electrolytes and some 1-1 electrolytes which are incompletely dissociated in water⁷⁰, suggest (with the exception of thalious salts) complete dissociation in formamide. The slopes of the phoreogram are 10 - 40% smaller than those predicted theoretically. The limiting equivalent conductances for these salts were also evaluated.

The limiting transference numbers of cation and anion in potassium chloride solutions were measured at 25°C by Notley⁵¹. The limiting cation transference number was found to be 0.427, and this value was combined with the limiting conductance data from references(49) and (70), to yield the limiting equivalent conductances of various ions in formamide at 25°C. Notley's results again show that the hydrogen ion in formamide does not have the abnormally high mobility that it has in water and a number of other solvents.

Comprehensive studies of the conductance of more than 70 electrolytes in N-methyl acetamide have been made by Dawson and co-workers^(71,72,73). The Shedlovsky plot of the equivalent conductance at infinite dilution (Λ_∞) against concentration (C), again indicates that these electrolytes are completely dissociated in N-methyl acetamide. In most cases, excellent agreement was reported between observed results and those predicted by the Onsager equation.

Similar data for some alkali halides and two tetra alkyl

ammonium salts have been reported by French and Glover⁷⁴ for solutions in N-methyl formamide and N-methyl acetamide at 35°C and 45°C.

3.3. Transference Numbers Measurements.

Dawson and co-workers^{49,75} determined transference numbers of several electrolytes in formamide by the Hittorf method⁷⁵ and also estimated transference numbers from measurements of the equivalent conductance of trimethyl phenyl ammonium benzene sulphonate⁴⁹ (assuming that the limiting ionic conductance of very large cations and anions are approximately equal). The two methods showed satisfactory agreement, i.e., the limiting transference number of potassium ion in potassium chloride in formamide was 0.406⁷⁵ and 0.415⁴⁹ at 25°C. The transference numbers of H⁺ and K⁺ ions decrease on passing from water to formamide, thus suggesting that the cations are more strongly solvated in formamide than in water.

76

Using the Hittorf method, Gopal et al found that the transference numbers of the potassium ion K⁺ in potassium chloride in formamide show the opposite temperature and concentration dependence to that in water. The temperature variation of the transference number was explained by supposing that the secondary solvation shell must be involved in the transport process. Their limiting transference number of

the potassium ion in formamide is slightly higher than Dawson's.

Notley and ⁷⁷ Spiro measured cation and anion transference numbers of potassium chloride at 25°C at 5 concentrations ranging from 0.01 to 0.1 M using the moving boundary method. They analysed their results using the Debye - Huckel - Onsager theory and its extension. Their value of the limiting cationic transference number of potassium chloride was 0.427. This value is considerably higher than previously mentioned values, and is undoubtedly the most reliable.

3.4. E.M.F. Measurements and Thermodynamic Properties.

Pavlopoulos and ⁷⁸ Strehlow found that both the calomel and the silver|silver chloride electrode did not function reversibly in formamide since mercurous and silver ions oxidise the solvent. Instead, they found that the cadmium|cadmium chloride electrode functioned satisfactorily as an electrode of the second kind, since cadmium chloride has a low solubility in formamide. The hydrogen electrode was used to obtain the standard potential of the cadmium|cadmium chloride electrode, and the values obtained (on the molar scale) are -0.619 ± 0.004 volts and -0.617 ± 0.004 volts at 18°C and 25°C respectively. The $\text{Cd}|\text{CdCl}_2$ electrode was then used as a reference electrode in determining the standard potential of other electrodes. The order of electrode potentials was found to be the same as in water.

Mandel and Decroly⁵ and later Agarwal and Nayak⁶ measured the emf of the cell $\text{Pt; H}_2 \mid \text{HCl in formamide} \mid \text{AgCl} \mid \text{Ag}$ (at various HCl concentrations) from which the standard potential of the silver|silver chloride in formamide was obtained by using Hitchcock's method⁷⁹. Values from these two groups differed by 6 mV i.e., 0.204 ± 0.002 volts⁵ as compared with 0.1986 ± 0.0005 volts⁶. Both groups of workers found it necessary to extrapolate their emf values to zero time. The measurements of Agarwal and Nayak appear to be the more reliable and they used their results to calculate molal activity coefficients of hydrochloric acid in formamide in the concentration range of 0.002 to 0.12 m, the values varying from 0.9725 to 0.8917. Similar data were reported by Povarov et al⁸⁰ for the activity coefficients of sodium chloride and potassium chloride in formamide and N-methyl formamide at 25°C and at various concentrations, from emf measurements.

Mandel and Decroly⁸¹ measured the dissociation constants of formic and acetic acids in formamide by means of the cell $\text{Pt; H}_2 \mid \text{AH}(m_1), \text{ANa}(m_2) \text{NaCl}(m_3) \mid \text{AgCl} \mid \text{Ag}$.

Where AH represents the weak acid and ANa its sodium salt. They used the method of Harned and his co-workers⁸², and found that these acids are markedly weaker in formamide than in water. Dawson and Griffith⁸³ however, suggest that the extent of

dissociation of acetic, benzoic and propionic acids is greater in formamide than in water, This discrepancy is not yet resolved.

The emf of the cell $\text{Pt}; \text{H}_2 \left| \text{HCl}_{(m)} \right. \text{ in N-methyl acetamide} \left| \text{AgCl} \right| \text{Ag}$ was measured over the temperature range 35° to 70°C at 5°C intervals by Dawson, Zuber and Eckstrom⁸⁴. The standard potential of the silver|silver chloride electrode at each temperature was calculated as well as the values of ΔG° , ΔH° and ΔS° for the cell reaction. At each temperature the standard potential of the silver|silver chloride electrode in N-methyl acetamide is less than in water but greater than in formamide. The activity coefficients of HCl are closer to 1 in N-methyl acetamide than in water.

3.5. Heats of Solution

The heats of solution in formamide of all the alkali metal halides except lithium fluoride and sodium fluoride have been determined by Somsen and Coops⁸⁵. The measurements were carried out at $25 \pm 0.05^\circ\text{C}$ and at concentrations up to 0.01 molal, using an adiabatic calorimeter. The heats of solution were corrected to infinite dilution by adding the enthalpy of dilution as calculated from the Debye-Huckel theory.⁸⁶ The values of the heats of solution at infinite dilution thus obtained range from -76.39 kJ/mole for lithium iodide to $+3.429 \text{ kJ/mole}$ for potassium chloride. Integral heats of solution are

more exothermic than in water. They used their results to test a theory of ionic solvation due to van Eck⁸⁷. Since this theory is relevant to the present measurements of the heat of precipitation of silver chloride, it is outlined below :-

van Eck suggested that enthalpy of solvation of an ion (ΔH_s) consists of 3 terms i.e.,

$$\Delta H_s = \Delta H_c + \Delta H_{nc} + \Delta H_h$$

Where ΔH_c is the enthalpy contribution as a result of the charge on ion,

ΔH_{nc} is the enthalpy contribution which does not depend on the charge,

and ΔH_h is the enthalpy required to make a hole in the solvent in order to accommodate the ion.

van Eck has shown that the values of $-\Delta H_c$ of inert gas type cations can be put equal to the sum of ionisation potential (I) and electron affinity (E) of the corresponding metal ions.

If the assumption is made that this theory is valid for formamide and water, the enthalpy of solvation of a salt is built up additively from the individual values of the ions in the following way :-

$$\begin{aligned} \text{in water : } \Delta H_s^w(Mx) &= \Delta H_s^w(M^+) + \Delta H_s^w(X^-) \\ &= -(I_m + E_m) + \Delta H_{nc}^w + \Delta H_h^w + \Delta H_s^w(X^-) \end{aligned}$$

$$\begin{aligned}\text{in formamide: } \Delta H_S^F(\text{Mx}) &= \Delta H_S^F(\text{M}^+) + \Delta H_S^F(\text{X}^-) \\ &= -(I_m + E_m) + \Delta H_{\text{nc}}^F + \Delta H_h^F + \Delta H_S^F(\text{X}^-)\end{aligned}$$

$$\text{Then since } -\Delta H_S(\text{Mx}) = \Delta H_{\text{crystal}}(\text{Mx}) - \Delta H_{\text{solution}}^{\Theta}(\text{Mx}),$$

combination of these equations gives,

$$\begin{aligned}\Delta H_{\text{solution}}^{\Theta}(\text{H}_2\text{O}) - \Delta H_{\text{solution}}^{\Theta}(\text{HCONH}_2) &= \Delta H_{\text{nc}}^W + \Delta H_h^W - \Delta H_{\text{nc}}^F + \Delta H_h^F + \\ &\quad \Delta H_S^W(\text{X}^-) - \Delta H_S^F(\text{X}^-)\end{aligned}$$

For salts having the same anion, the right hand side of this equation has a constant value assuming that ΔH_{nc} and ΔH_h are constant for the different ions. In consequence, the last equation predicts a nearly constant and cation independent difference in the heat of solution in water and in formamide for salts with a common anion. Table IV shows the difference in heat of solution of alkali metal halides in formamide and in water in k cal/mole. The data seem to confirm this prediction except in the case of the lithium halides. Somsen and Coops have explained this by suggesting that ΔH_c for lithium ion is different in water and formamide.

Table IV

Anion Cation	F	Cl	Br	I
Li	-	+0.54	+1.66	+3.13
Na	-	+3.03	+4.26	+5.62
K	-1.07	+3.29	+4.56	+5.92
Rb	-1.06	+3.30	+4.48	+5.97
Cs	-1.00	+3.15	+4.39	+5.7

Similar measurements were carried out for some alkali metal halide in anhydrous N-methyl formamide, by Weeda and Somsen⁸⁸.

The heats of solution of these salts at infinite dilution range from -88.34 ± 0.208 kJ/mole for lithium iodide to $+2.96 \pm 0.042$ kJ/mole for caesium iodide.

3.6 Solubility Measurements.

Solubility data for electrolytes in this class of solvent are rare. The data reported are mostly for soluble salts, and some of the data are not reliable. Colton and Brooker⁸⁹ used crude formamide as a solvent in studying the solubilities at 25°C of calcium, magnesium, potassium and sodium salts. Gopal and Hussain⁹⁰ investigated the solubilities of many electrolytes in pure formamide from 25° to 50°C at 5°C intervals. The analysis of the saturated solution was carried out by either

evaporation of weighed samples ~~as~~ in the case of halides and sulphates, by precipitation. All determinations were made in triplicate and their results appear to be reliable. There are however, marked discrepancies between the data of Colton and Brocker and of Gopal and Hussain. The latter workers found that the solubilities of different electrolytes are in general greater in water than in formamide, except the halides and nitrate of lead. The temperature coefficient of solubility in most cases is smaller in formamide than in water. This coefficient is negative for sodium chloride in contrast to that in water, indicating the evolution of heat on solution. In general, the solubility of the halides follow the same pattern of behaviour as in water i.e., iodide > bromide > chloride.

Povarov and co-workers⁹¹, using a radiochemical technique determined the solubility of silver chloride labelled with silver-110m in pure formamide, pure N-methyl formamide and in solutions of sodium chloride and caesium chloride. No temperature control was exercised, the measurements being made at room temperature ($18 \pm 2^\circ\text{C}$). They found a solubility product for silver chloride in formamide of 5.3×10^{-9} and in N-methyl formamide of 4.1×10^{-11} . Their value in formamide is substantially higher than the value reported in this thesis.

Solubilities of both inorganic and organic compounds such as the chloride, bromide, and iodide of ammonium and potassium,

and dioxane, cyclohexane, toluene etc., in N-methyl acetamide were measured by Dawson and co-workers⁹² at 40°C. Similar measurements, but confined to the chloride and bromide of sodium, potassium and ammonium, in N-methyl formamide were carried out by Strack and co-workers⁹³ over the temperature range 0° to 35°C. The latter group of workers compared their results with those in N-methyl acetamide, water, ammonia and formamide from which they concluded that solubilities are quite specific in nature and must depend upon specific interaction between solvent and solute, rather than on bulk dielectric constant effects.

CHAPTER IV

Experimental Technique for Determining Solubility

Radiochemical methods have been used widely in the study of two phase equilibria, particularly solid liquid equilibria. Solubility studies of sparingly soluble salts need sensitive methods which are capable of detecting even the small quantity of solute that passes into solution. Radiotracers seem to be almost ideally suited for such work since large numbers of almost routine analyses are usually required which, with their aid may be achieved rapidly and with reasonable sensitivity and precision. Jonte and Martin³, Lieser⁹⁴ and Kraus⁹⁵ are among workers who employed radiochemical techniques in determining solubilities of sparingly soluble salts in aqueous solution. Jonte and Martin³ measured the solubility of silver chloride labelled with silver-110m at fairly high specific activity, i.e., 0.088 mCi/mg. In order to prepare standard labelled solution, they electroplated radioactive silver onto a platinum disc and subsequently dissolved the weighed deposits in a minimum quantity of diluted nitric acid. Perchloric acid was then added and after a few repetitions of evaporation, the residue was dissolved in distilled water. The equilibrium mixtures were prepared by mixing the standard solution of silver nitrate with a standard solution of sodium chloride; assays of the

saturated solutions were carried out by evaporation and counting, using an end window G.M. counter, for the activity of silver-110m. The amounts of dissolved silver chloride were calculated by comparing the count rates obtained with that of an evaporated aliquot from one of the standard silver nitrate solutions. This method and also those of Lieser⁹⁴, and Kraus⁹⁵, will be termed here the "comparison method".

94

Lieser⁹⁴ has performed an extensive investigation of the solubilities and complex formations of silver halides in appropriate halide solutions in water at 18°C. Silver-110m was used as the tracer in silver chloride and silver bromide studies but silver-111 in silver iodide experiments, because silver iodide is the least soluble salt among the three and therefore the more energetic particles from silver-111 were needed to raise the efficiency of counting. The counting of samples was achieved by using a liquid G.M. counter. The specific activities of silver isotopes varied from 2 to 12 mCi/g. A reference curve was constructed relating known quantities of silver halides, dissolved in sodium thiosulphate solution, with count rate. Hence, by comparison with the reference curve, The quantities of dissolved silver halides in the equilibrium solutions were obtained.

A final example is the work of Kraus⁹⁵ who suggested the use of a "packed bed" method for the measurement of solubility. A

packed bed of crystals of silver chloride (containing a known amount of tracer with sufficiently high activity to yield an effluent of convenient count rate) was prepared in a column at controlled temperature; the solvent or solution of interest was passed through this bed and the effluent counted by means of a scintillation counter housed at the end of the column. Extremely rapid equilibrium occurs if the distribution coefficient D (amount per kilogramme solid/amount per litre solution) is high i.e., the materials are extremely insoluble. In order to obtain the solubility, the count rate of the effluent was compared with that of a standard solution.

Silver-110m is also used as tracer, in the present work, for the study of the solubility of silver chloride in water, heavy water and formamide, but the preparation of reference counting sources, and those from equilibrium solutions, is different from those in the work summarised above. Details are given in the following sections.

4.1. Preliminary Considerations.

The nature and energy of radiations, the half life, the method and the cost of production of radionuclide are all important factors in choosing a suitable isotope for a tracer study. Table I summarises various data relating to the radioactive decay of the various silver isotopes.

Table I. Physical Data of Silver Isotopes.

Isotope	Half-life	Type of Decay and Particle energies MeV	energies (γ) MeV	Internal conversion (i.e.)	Price list in RCC cat. 1965-66 (min. cost)
Silver-105	40 d.	E.C 100%	0.064 - 9.8%	11.2%	£30 for 200 Ci
			0.280 - 32.4%	0.6%	
			0.319 - 4 %		
			0.331 - 4 %		
			0.344 - 35.6%	0.4%	
			0.393 - 2 %		
			0.443 - 9.3%	0.1%	
			0.618 - 1 %		
			0.644 - 8.4%		
			others of less than 1% intensity		
Silver-108	2.4 m.	1.02 - 2%	0.63 - 2 %		
		1.65 - 94%			
		E.C. 4%			
Silver-110m	253 d.	I.T. 2%	0.116 - 0 %	2 %	£ 7 for 1 mCi
			0.085 - 65%	0.45 - 1 %	
			0.530 - 33%	0.62 - 1 %	
			0.66 - 93 %		
			0.68 - 13 %		

Cont. Table 1 Physical Data of Silver Isotopes

Isotope	Half-life	Type of Decay and Particle energies MeV	energies (γ) MeV	Internal conversion (i.e.)	Price list in RCC cat. 1965-66 (min.cost)
			0.69 -10 % 0.71 -17 % 0.74 - 2 % 0.76 -23 % 0.82 - 7 % 0.89 -72 % 0.94 -34 % 1.38 -24 % 1.48 - 5 % 1.51 -12 % 1.56 - 2 %		
Silver-110	24 s.	2.21- 5 %	0.66 - 5 %		
		2.87- 95 %			
Silver-111	7.5 d.	0.69- 6%	0.247- 1 %		£40 for 5 mCi
		0.79- 1%	0.340- 6 %		
		1.04-93%			

Although silver-111 emits fairly energetic β particles which
will facilitate the use of the simplest form of radiation detector

i.e., a G.M. counter at a reasonably high efficiency, it also has a short half-life and is, in addition, relatively expensive. On the other hand silver-110m has a comparatively long half-life i.e., 253 days and can be purchased at a much lower price. Although the decay scheme is rather complicated, it is still possible to measure the level of its activity with adequate efficiency by means of a simple scintillation counting technique. With these factors in mind, silver-110m was chosen as a radioactive tracer in the work reported here.

Chlorine-36 whose half-life is 3×10^5 years and is a β emitter ($E_{\max} = 0.714$ MeV) was used in a few experiments where attempts were made to determine radiochemically, the concentration of the added chloride ions. This method is described in section 4.8.

4.2. Selection of Method of Counting and Counting Technique

This involves consideration of the form of the counting source and the type of radiation detector. Solid counting sources were used in the present work, for two reasons. Firstly, the silver chloride reference counting source was the actual sample from which the saturated solution was prepared, so that the inaccuracy was smaller than with the "comparison method" used by previous workers. Secondly, a higher counting efficiency can be obtained with solid sources than with solutions. Hence, the specific activity of the labelled silver can be kept quite

low in order to avoid the possible effect of this parameter on the solubilities (see section 4.11)

Since silver-110m is both a β and γ emitter, the count rate of a source may be measured by means of a β particle detector (e.g. a G.M. counter) or a γ detector (e.g. a scintillation counter). A scintillation counting technique was employed here for the following reasons.

1. The observed count rate for a silver chloride counting source with a scintillation counter ($1\frac{1}{2}$ " diameter x 1" NaI (Tl) crystal) was approximately double that for the same source with an end window G.M. counter (Mullard MX123). However, against this increased efficiency of the scintillation counter, the background count rate for the G.M. counter was considerably lower.
2. Higher counting rates are possible with a scintillation counter than with a G.M. counter as the resolving time of the former is of the order of only a few microseconds. This is valuable in the counting of reference sources where count rate as high as 60,000 to 80,000 counts per minute were encountered.
3. There is no problem of self absorption with γ -counting, whereas a solid source of a few milligrammes prepared for β -counting with an end window G.M. tube, has to be of a uniform thickness to ensure uniform absorption of radiation by the

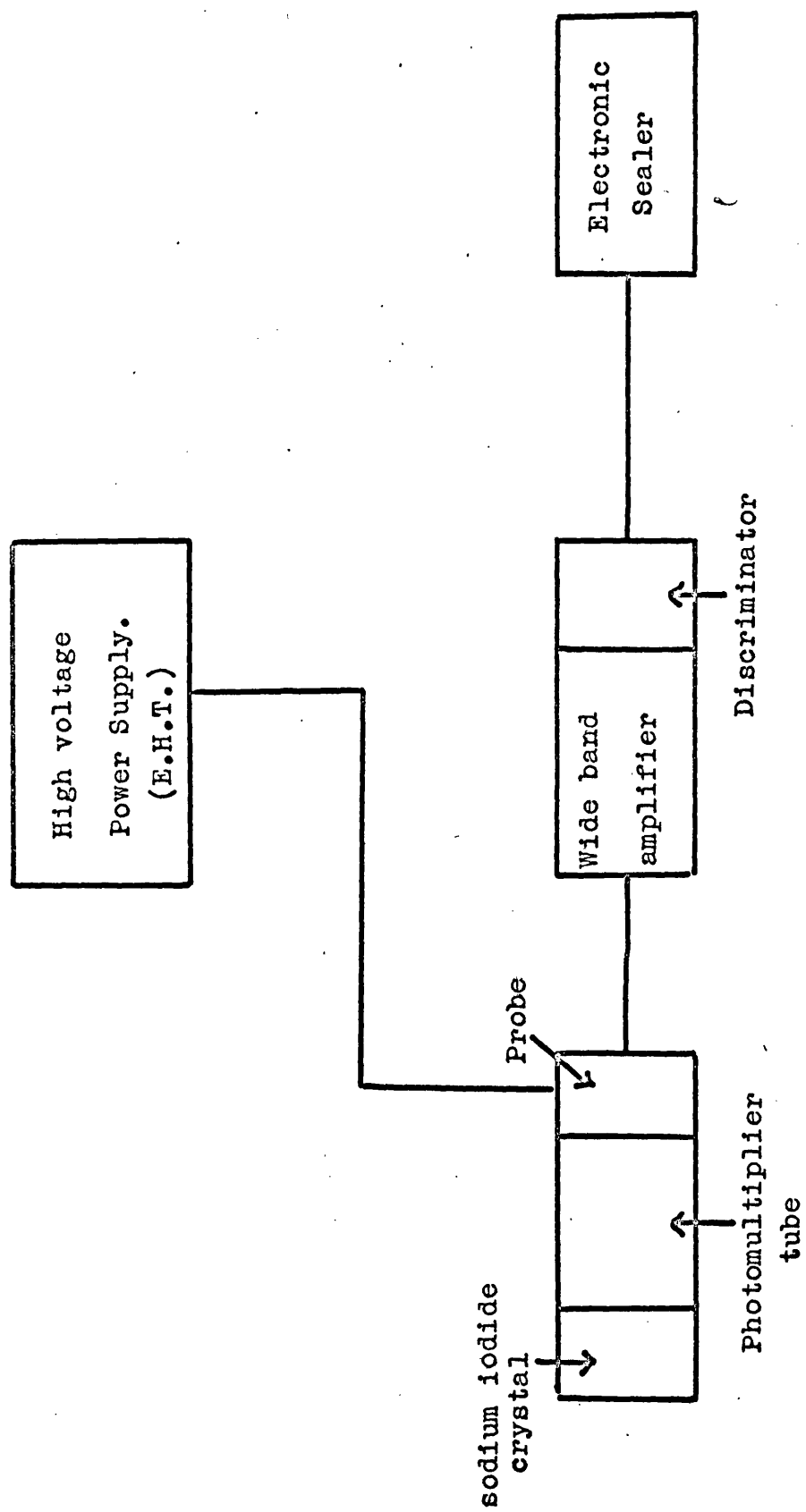


Fig. 4.1.a The scintillation counting system used in this research.

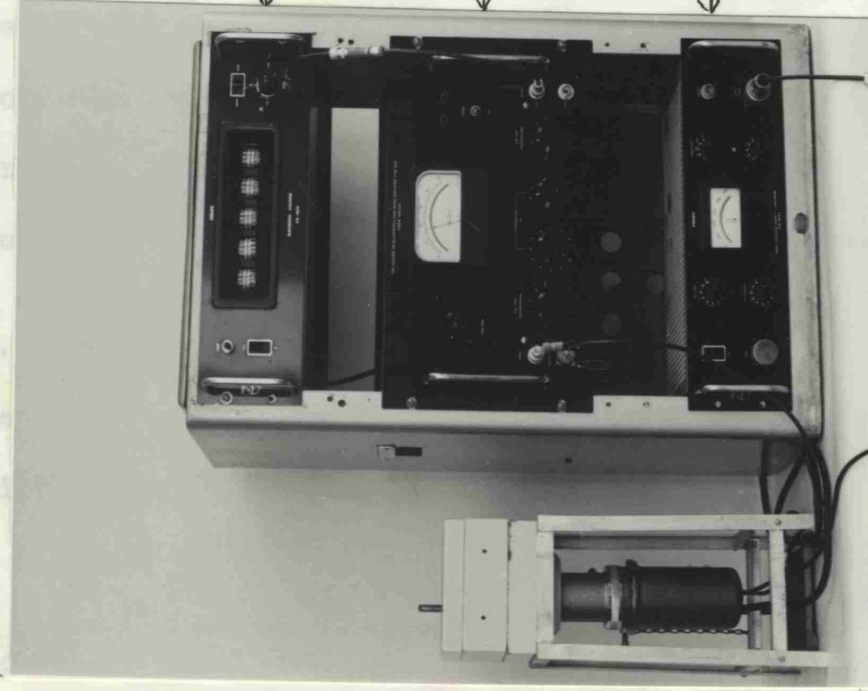
A NaI crystal



A photomultiplier tube

A probe unit

A scintillation counter head without a light tight cap on.



An electronic scaler

A wideband amplifier

A high voltage unit

A scintillation counter head with a lead shield.

sample itself, and a correction for this self absorption is necessary in comparing one sample with another. Self absorption can vary with the physical form of the sample (e.g. particle size and distribution) and it is very difficult to reproduce this precisely from one sample of silver chloride to another. This is perhaps the chief consideration in the selection of the scintillation method for these experiments.

4. The overall stability of the scintillation counter is rather better than that of the G.M. counter, over the long period of time involved in this project.

Thus, throughout this work, unless otherwise mentioned, a scintillation counting system was used. It consisted of an electronic scaler (Philips type P.W.4032), a high voltage unit (Philips type P.W.4022), a wideband amplifier (Isotope Development Limited type 652), a scintillation counter head (Isotope Development Limited type 653/A), a sodium iodide (Tl) crystal $1\frac{1}{2}$ " x 1" (Ekco). A block diagram is shown in Fig.4.1.

The performance of the counter was checked regularly by several methods.

1. Plotting a characteristic curve. This is a graph of the count rate due to the source, including background, as a function of applied E.H.T voltages at various discriminator bias voltages (usually 5, 15 and 20 volts). In Fig.4.2, the typical

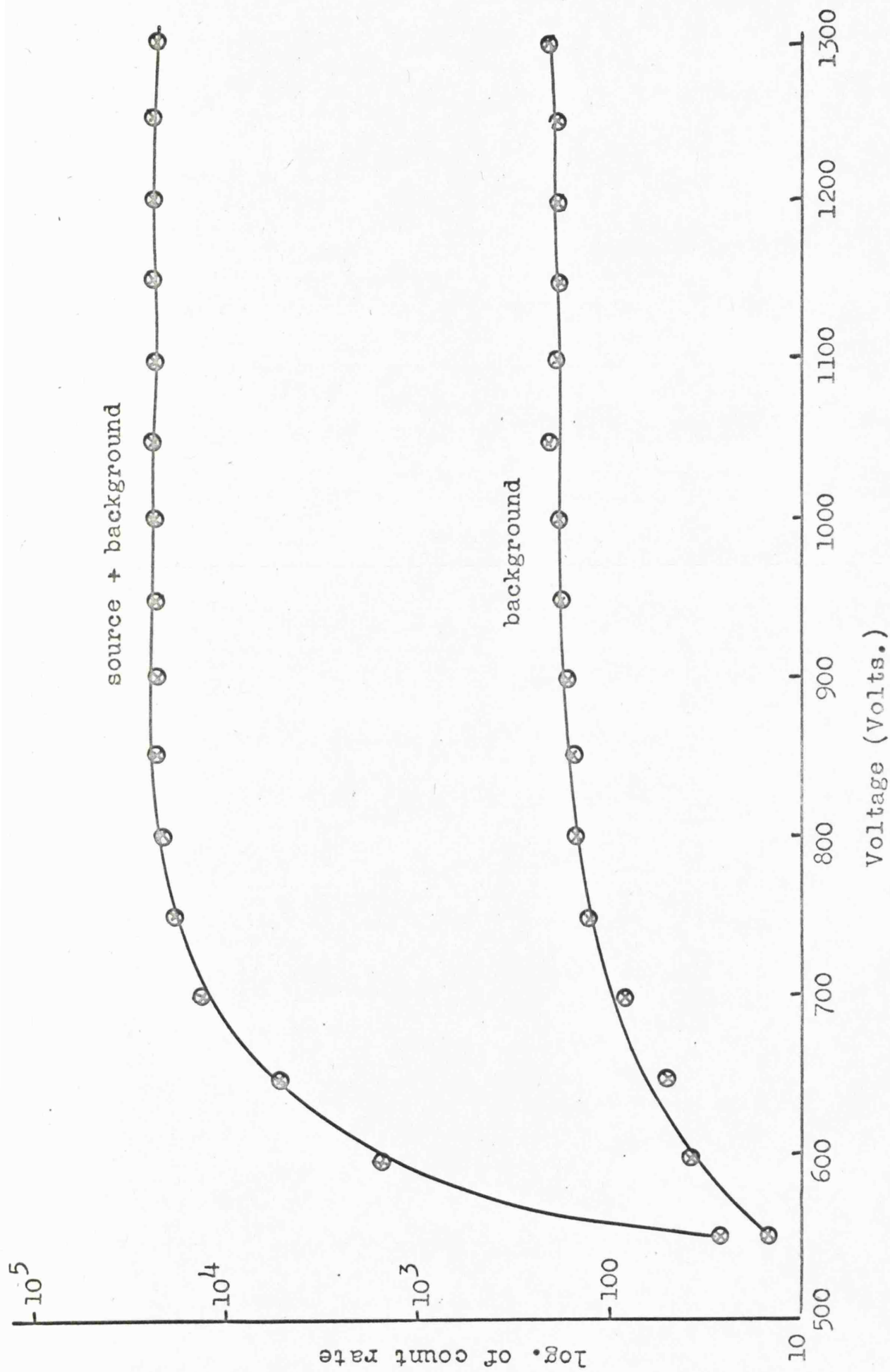


Fig. 4.2. The characteristic curve of a γ -scintillation counter.

characteristic curve of this particular scintillation counting system, using silver-110m as a source, is shown together with that for background radiation under the same conditions. The operating E.H.T voltage was selected as that corresponding to a high net count rate due to the source and a reasonably low background along the part of the curve where a relatively slow change in count rate with E.H.T voltage occurred. The curve at 20 volts discriminator bias was preferred to those at 5 and 15 volts.

2. Testing for non-random errors by either t-test or Chi squared test (see section 4.3. 1)
3. Measuring the decay of a standard silver-110m source, and comparing the half-life obtained with the accepted value.

The counting time for background radiation was usually one hour and for the sample, long enough to obtain about 10,000 counts in order to maintain an approximately constant random error (see section 4.3. 1). In some experiments when very low count rates were involved, the source plus background and background alone were alternately counted for a certain period (20 minutes or half an hour) until about 10 readings of each were obtained; the t-test was then used to estimate the significance of the difference (i.e., the count rate due to the source alone).

The count rates were corrected for background and decay of silver-110m during the course of each experiment. Background was usually approximately 198 ± 2 counts per minute.

4.3. Accuracy of Measurements.

4.3. 1 Statistical Accuracy in the Measurement of Radioactivity.

Since the decay of a radionuclide is a random process, a Poisson distribution can be applied in the measurement of radioactivity. However if the average number of recorded counts is large, it is possible to approximate the Poisson distribution to the Gaussian or Normal distribution. If "m" is the average count of many determinations, the chance of any particular observation, being within given limits may be estimated from the so-called "standard deviation" (σ). This is the square root of the arithmetic mean of the squares of all the deviations from the mean value. When a normal distribution is assumed, σ is also equal to the square root of the mean count. If a very large number of determinations of a set of random events is made, it may be shown that 32.7% of these will deviate from the mean by an amount greater than σ , and 4.5% by an amount greater than 2σ . There is then 68.3% chance that a single measurement will differ from the mean count by less than σ and a 95.5% chance that it will be within 2σ of the mean. It is necessary to record a total of 10,000 counts in order to

reduce the relative standard deviation to 1%, and there is still about one chance in three that any particular observation will differ from the hypothetical mean by more than this 1%.

Test for non-random errors. It is of interest to know if the observed variations are reasonably consistent with expectation. The t-test and Chi squared test are simple to use and have a wide application.

t-test. If a sample is counted, many times, and if a set of several successive readings differs from the mean by more than 1.96σ (σ is standard deviation), a non-random deviation may be assumed to be influencing the results. In order to test by this method, two sets of readings of the same sample under the same condition are taken. Normally each set contains five readings, and each reading is of about 10,000 counts. The mean of the first five is denoted by $\bar{X}$ and of the second by $\bar{Y}$. If the total time involved in counting is T, then

$$t = \frac{(\bar{X} - \bar{Y}) T}{2 \sqrt{\sum x + \sum y}}$$

and if t is greater than 1.96, it may be suspected that a non-random error is present. This may be confirmed by several repetitions of the test; if t consistently exceeds 1.96, then a non-random error is almost certainly present.

Chi squared test. This is a measure of the correspondence

between the distribution assumed, and that observed. Chi-square χ^2 , involved the true variance (the average of the squares of the deviations from the true mean). For a large number of observations, this true variance approaches the normal variance (which can be defined similarly to true variance, but the deviations is taken from the arithmetic mean, and can be shown to be equal to the mean count). For the case of a normal distribution this assumes the formula :-

$$\chi^2 = \frac{(X_1 - \bar{X})^2}{\bar{X}}$$

Where X_1 = readings taken

$\bar{X}$ = arithmetic mean.

χ^2 itself has a frequency of distribution. Assuming the observations to be truly represented by a normal distribution, P is the probability of a similar set of observations giving a value of χ^2 as great as, or greater than, that obtained from the set used to compute χ^2 ; P is associated with the area under the distribution curve. In most standard text books of Statistics, values of P have been calculated and tabulated for various values of χ^2 and either the number of degrees of freedom or the number of measured values. In practice, if P lies between 5 and 95%, the difference between the theoretical and observed distribution (and consequently the difference between the standard deviations) may be regarded as reasonable. If P is unreasonably

small, i.e., less than 5%, it is evidence that some fault in the counting assembly is causing the distribution of the counts obtained to be other than that expected from the law of radioactive decay. If P is greater than 95%, a systematic variation in counting rate throughout the experiment is suggested. Again, the test should be repeated several times to confirm that non-random errors are present.

4.3.2. Accuracy in volume and weight measurements.

The consistency of the efficiency of measuring and transferring a quantity of solution by means of a 1 ml. graduated pipette, was checked. Five 1 ml. quantities of standard solution of silver nitrate were pipetted into 5 pre-weighed weighing bottles and each was weighed to obtain the weight of 1 ml. of silver nitrate solution. The weighings were carried out with a Metler semimicrobalance type B.6 with ± 0.02 mg accuracy.

Results are shown on the next page.

Table II

No.	weight of weighing bottle (gm.)	weight of weighing bottle + silver nitrate (gm)	net weight of 1 ml. of silver nitrate (gm)
1	4.52712	4.53359	1.00647
2	4.57315	4.57985	1.00670
3	4.46683	4.47326	1.00643
4	4.29310	5.20955	1.00645
5	4.22481	5.23124	1.00643

These results indicate the reproducibility of the weighing and of the volume measurement, which are important in the experiments reported here.

4.3.3. Thermostat Baths

Two types of regulator were used. At low temperature work, the temperature of the bath was controlled by a contact thermometer whereas at higher temperatures, a mercury toluene type was employed. The temperature of the bath using contact thermometer was controlled to within $\pm 0.01^{\circ}\text{C}$, while that of the mercury-toluene regulator bath could be maintained to within $\pm 0.02^{\circ}\text{C}$. In all cases the temperatures were measured with thermometers calibrated against N.P.L. certified mercury in glass thermometers.

4.4. Preparation of Labelled Silver Chloride

0.1 to 0.5 ml. of radioactive silver (in the form of silver nitrate solution and containing a negligible amount of inactive silver nitrate, details are given in Chapter 5) was added to a centrifuge tube containing 1 ml. of a standard solution of 0.1 M silver nitrate. The tube was wrapped in black paper to avoid excessive exposure to light. After standing for a few minutes to ensure complete equilibrium between radioactive silver and the inactive silver in the standard solution, an equivalent amount of sodium chloride i.e., 0.25 ml of 0.4 M solution, was added and a precipitate of silver chloride was formed. Heating was found unnecessary since the volume of the "precipitating mixture" was usually kept small i.e., less than or about 1.5 mls. and a well formed precipitate was always obtained. The precipitate was then subjected to centrifuging and the supernate decanted; this was followed by several washings of precipitate with double de-ionised water (see Chapter 5) or heavy water or formamide depending on which solvent was being studied. Each time the supernate was removed by decantation.

4.5. Preparation of the Counting Source

At the beginning of this research, attempts were made to prepare the counting source by transferring the precipitate of

silver chloride directly into a small aluminium planchette and allowing it to dry under an infrared lamp, but this method yielded a poor source since the surface was cracked, and decomposition of silver chloride took place. Filtering of the precipitate through a pre-dried and weighed small filter paper (Whatman No.42) mounted on a de-mountable buchner funnel of 1 cm. diameter proved to be a much more satisfactory procedure for making a good silver chloride counting source. The precipitate was left in the funnel under the applied suction from a vacuum pump for half an hour. The precipitate and filter paper were carefully removed from the funnel and kept in a desiccator overnight before the chemical yield was determined. It was found that drying the source in the oven at 150°C did not alter the value obtained for the yield of silver chloride. The theoretical yield of silver chloride was 16.6 mg. and in most cases about 16.0 mg. yield was obtained. The filter paper which in turn supported the precipitate was mounted on an aluminium planchette, uncovered, and was counted for the activity level of silver-110m in silver chloride. For the reference source, the normal count rate was between 60,000 to 80,000 counts per minute above background.

4.6. Determination of Solubility

This section describes the basic technique which was developed and used for all the solubility determinations.

A weighed sample of silver chloride reference sample was counted in order to obtain the correlation factor between the count rate and the weight of the sample. This factor is termed "the specific count rate" and is expressed in counts per minute per gramme. This reference source was then transferred to the appropriate solvent, contained in a volumetric flask or a glass ampoule, and the latter then sealed off. Samples were left in a thermostat bath which maintained the desired temperature and were shaken frequently. Since this was carried out manually, the time taken to reach equilibrium, which was established experimentally, was usually between 7 and 10 days. The equilibrium solution was then withdrawn into a preweighed weighing bottle containing the same quantity of the same standard solution of unlabelled silver nitrate as was used in the preparation of the reference sample. The apparatus was designed in such a way that the sampling of the equilibrium solution was carried out by filtration through a sintered glass disc while the whole apparatus was immersed in the thermostat bath. Details are discussed under 4.7. The weight of the equilibrium solution was then determined, after which an appropriate solution of sodium chloride was added, and the precipitate formed was filtered through a pre-weighed filter paper (in separate experiments it was ascertained that the weight of a filter paper was unchanged by carrying out "dummy" filtrations without precipitate). The chemical yield of the precipitate

as well as its count rate, were determined. By comparing the specific count rate of the final source with that of the reference sample the amount of silver chloride in the equilibrium solution was calculated.

Example Solubility of silver chloride in heavy water at 45°C.

Weight of reference silver chloride source (source I) = 15.9 mg
 Corrected counting rate of reference source = 82456 counts/min
 Weight of equilibrium solution taken = 24.1813 gm
 Weight of precipitate of silver chloride prepared from the equilibrium solution (source II) = 16.55 mg
 Corrected counting rate of source II = 459.6 counts/min
 Taken into account decay of silver-110m (correction factor = 10:9.7 for 10 days) and also for incomplete precipitation; the final counting rate of source II = $\frac{459.6 \times 10 \times 16.6}{9.7 \times 16.55}$ = 475.2 counts/min

Therefore, the dissolved silver chloride in 24.1813 gm of equilibrium solution = $\frac{15.9 \times 475.2}{24.1813 \times 82456}$ mg.

$$\begin{aligned} \text{i.e.,} \quad &= \frac{15.9 \times 475.2 \times 10^3 \times 10^3}{24.1813 \times 82456} \text{ gm of silverchloride/} \\ &\text{kg of heavy water} \\ &= \frac{15.9 \times 475.2 \times 10^6 \times 10^{-6}}{24.1813 \times 82456 \times 143.5} \text{ mole of silverchloride/} \\ &\text{kg of heavy water} \end{aligned}$$

$$= 26.4 \times 10^{-6} \text{ mole of silverchloride/kg of heavy water}$$

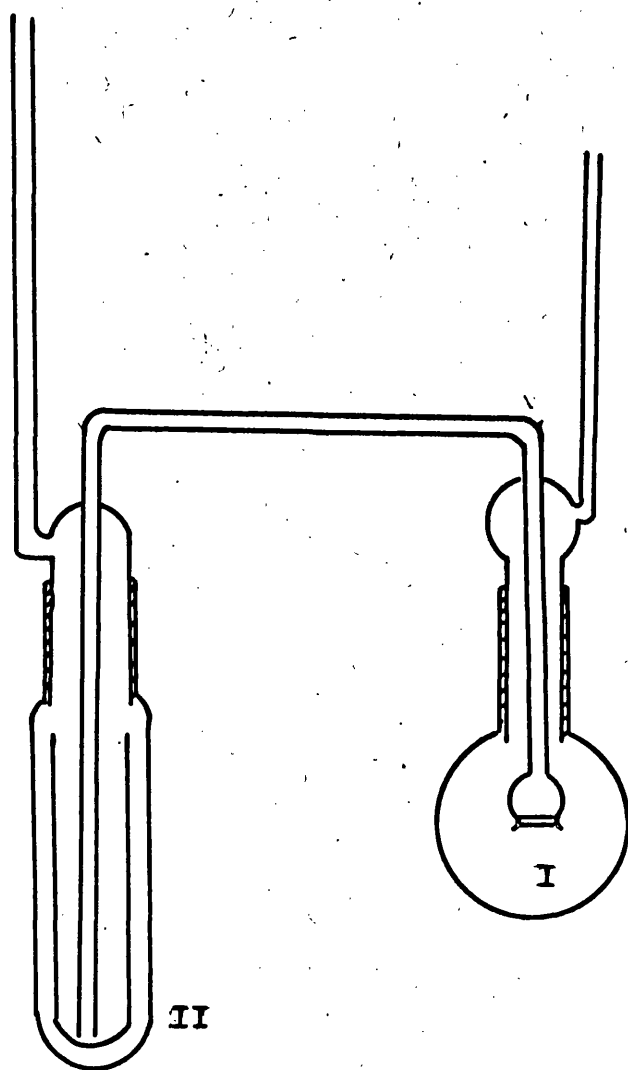


Fig. 4.3. Sampling Apparatus.

4.7 Sampling Technique

The apparatus designed for these experiments is illustrated in Fig. 4.3. It consists of two compartments, one labelled "compartment I" is for the equilibrium solution. Compartment II is a flask containing a weighing bottle which in turn contains a pre-weighed quantity of a standard solution of silver nitrate. A glass tube, which is the part of the stopper of compartment I, is connected to a vacuum line. These two compartments are connected via a glass U tube one end with a sintered glass disc of porosity grade 4 dipping underneath the surface level of the saturated solution. Compartment I, II and the glass U tube can be taken apart, but when they are assembled and completely immersed in the thermostat bath, the joints are air tight, waterproof and leakproof.

The sampling apparatus was left in the same thermostat bath, as the sample for one hour before the sampling of the equilibrium solution took place (an equilibrium solution was produced according to section 4.6). The glass ampoule or the volumetric flask containing the equilibrium solution was opened in the bath, but with care to avoid ingress of water, the contents were quickly transferred into compartment I, and the whole apparatus was left for 5 to 10 minutes in the bath before filtering, to allow the equilibrium solution to regain its previous temperature. The time involved in transferring was

normally less than 2 minutes and the change in temperature was very small. A suction was then applied and the solution was filtered through the sintered glass disc into a weighing bottle; the time involved in this process was between 5 and 10 minutes depending on the viscosity of the solvent. By employing this technique, various problems which otherwise may have arisen were eliminated, i.e., the sintered glass disc prevented solid silver chloride from entering into compartment II; therefore there was no question as to whether small amounts of solid silver chloride were mistakenly included with the equilibrium solution and since the temperature during the sampling process was that of the thermostat bath, there was no possibility of re-precipitation due to temperature depression or increased-dissolution of silver chloride due to temperature elevation. The sampling process was carried out at room temperature when this was very near to the temperature of the equilibrium solution, and results were completely reproducible.

4.8. Method Employed in the Determination of the Concentration of Added Chloride Ions.

4.8.1 Direct Weighing. Jonte and Martin³ calculated the chloride concentration by subtracting the amount precipitated as silver chloride from that added as sodium chloride in the standard solution, but a particular efficiency of precipitation had to be assumed. The method used in this work was simply to

prepare a solution of known sodium chloride concentration, either by direct weighing or by dilution of a standard solution. Since the concentration of sodium chloride was, in most cases very small, a semimicrobalance was used, and for the more dilute solutions careful dilution by weighing was carried out. However, the weighing technique was discarded in favour of the dilution since a carefully prepared solution could be used for many experiments. In the high concentration region, direct weighing was used and each weighed quantity of sodium chloride was dissolved in usually 25 ml. of the solvent in question. In the case of the solvent being heavy water, the volume of the samples was kept as low as possible, consistent with accuracy, in order to conserve heavy water. The manipulation described above, was carried out in a glove box in an atmosphere of dry air or inert gas such as nitrogen, except in the case when water was used as a solvent.

4.8.2 Double Labelling

Since the determination of chloride ion concentrations in the very dilute region is rather difficult to achieve with high degree of accuracy by simple analytical techniques, a "double labelling" technique i.e., one in which the chlorine was also labelled, was therefore employed in the determination of chloride ion concentrations in the first few experiments where water was used as a solvent. Briefly, doubly labelled silver

chloride was prepared by mixing a solution of silver nitrate labelled with silver-110m and a sodium chloride solution labelled with chlorine-36. The count rate of silver-110m in the sample could be measured without interference from that of chlorine-36 by using a γ scintillation counter, provided that the activity of chlorine-36 was not sufficiently high to induce bremsstrahlung radiation. (This is similar in properties to X-rays and is detectable by a γ scintillation counter.) The count rate due to chlorine-36 in the silver chloride source was then determined by using an end window G.M. counter. Unfortunately, however, the G.M. counter also counts γ and β radiations emitted by silver-110m, but since the relative efficiency of counting for silver-110m by a γ scintillation counter (insensitive to chlorine-36, a pure β emitter) and a G.M. tube was known, the G.M. count rate due to silver-110m and, hence, the net count rate due to chlorine-36 could be computed. The double labelled sample was then transferred into an appropriate container, the same labelled sodium chloride solution as was used as a precipitating agent earlier, was added to give an excess of sodium chloride. The solvent under investigation was then added in sufficient amount to give the desired concentration of chloride ion. After the whole system had reached equilibrium, two aliquots of the equilibrium solution were withdrawn, one added to a standard solution of silver nitrate (inactive), and the other to an inactive standard

sodium chloride solution. The precipitates of silver chloride in both solutions were obtained by adding the appropriate precipitating agent. The precipitate from the first aliquot containing all of the silver-110m was counted by a ✓ scintillation counter while the second, containing all of the chlorine-36 was counted by both scintillation and G.M. counter. The solubility of silver chloride was estimated in the first aliquot, based on the count rate of silver-110m. In the second aliquot, the solubility of silver chloride was calculated from the count rate for chlorine-36 after correction for interference from silver-110m. The value found in the latter case was, of course, higher than that found from the first aliquot, since the count rate of chlorine-36 included that present in the solution in excess. It followed that the difference in solubilities between the two samples represented the amount of silver chloride which was formed with the excess chlorine-36; thus the amount of added chloride was estimated. This technique was abandoned because it could be used only in a very dilute solution, otherwise the chlorine-36 interfered with the counting of silver-110m. Also, two aliquots of an equilibrium solution were needed in each determination. In addition, it was found that the experimentally determined concentrations of chloride ions were in accord with the "calculated" results from dilution and hence there was no reason to continue experimental determinations.

4.9. Reproducibility of Techniques

The techniques described above were thoroughly tested for reproducibility by measuring the solubility of silver chloride in water at 5°, 25°, and 45°C. After some improvements in sampling and analysing techniques had been made, the results obtained were slightly higher than those reported previously such as those of Owen and Brinkley⁹⁶ who used emf measurements. The difference probably arises from the fact that with the radiochemical technique, total silver in the saturated solution is measured, rather than only silver ions, as in the emf work. After this factor had been taken into account the present solubility data is in good agreement with the most precise previous estimations of solubility of silver chloride in water at various temperatures⁹⁶. Results are tabulated in table III.

Table III Solubilities of Silver Chloride in Water at 5°, 25°
45°C

Temperature °C	Solubilities $\mu\text{gm/kg}$	Solubilities (S) $\times 10^5$ (moles/kg)		Solubilities from ref(96) mole/kg $\times 10^5$
			Average	
5	789.7	0.550		0.506
25	1901.0	1.322		
	1906.0	1.324		
	1928.0	1.343	1.348	1.340
	1921.5	1.338		
	1955.0	1.365		
45	4377.0	3.0501	3.075	3.030
	4384.0	3.055		
	4417.2	3.120		

The next step was to study the behaviour of silver chloride as an electrolyte, i.e., the chemical equilibria in the presence of chloride ions. All of this work was carried out in double de-ionised water. Although there is considerable literature concerning silver chloride complexes, e.g. those presented by Forbes⁹⁷ Forbes and Cole⁹⁸, Leden⁹⁹, Mironov¹⁰⁰, Fomin¹⁰¹, Lieser⁹⁴ and Jonte and Martin³, the last mentioned author's work was chosen to be repeated, and special attention was paid to a very low concentration of chloride ions. It was thought sufficient to

limit the work, at this stage, to 25°C. As this work was confined to a region of low chloride ion concentrations, high complexes were not expected to be present. There was no other salt added to the system apart from sodium chloride; therefore ionic strengths were low, and taken as the total chloride concentrations in the equilibrium solution. From ionic strengths, mean ionic activity coefficients were calculated, using the Debye-Huckel Limiting Law i.e.,

$$\log \gamma_{\pm} = \frac{-A \sqrt{I}}{1 + \sqrt{I}}$$

where A = Debye-Huckel constant = $\frac{0.5107}{\text{mole}^{-1/2} \text{kg}^{1/2}}$ for water at 25°C

$\gamma_{\pm}$ = mean ionic activity coefficient

I = ionic strength

Results are shown in Table IV.

Table IV Solubility of silver chloride in water in moles/kg at 25°C.

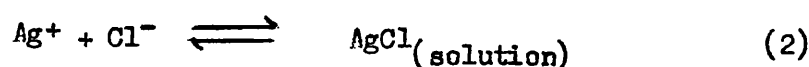
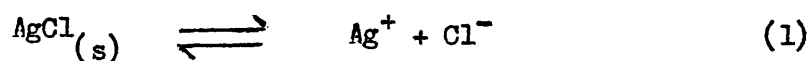
$S \times 10^6$	$10^3 [Cl^-]$	$\gamma_{\pm}$	$\frac{1}{[Cl^-] \gamma_{\pm}}$
0.608	1.680	0.9558	652.7
0.770	1.077	0.9855	1069.0
0.210	1.021	0.9682	1066.0
0.701	0.3916	0.9780	2670.0
1.365	0.1750	0.9852	5888.0
2.120	0.0970	0.9890	10545.0
5.240	0.0360*	0.9932	28160.0
5.300	0.0349*	0.9934	29040.0
11.31	0.1618	0.9954	62380.0
13.48 average in pure water	0.01348	0.9960	74700.0

N.B. * indicate the results from double labelling method.

Treatment of the data was similar to that given in reference (102) and is summarised below.

4.10. Treatment of the Data

At low chloride concentrations, the assumption is made that higher complexes of the form $AgCl_2^-$ are not formed and that only two chemical equilibria may be considered :-



Equilibrium constant for equation (1) is the solubility product K_s and is given by

$$K_s = [\text{Ag}^+] [\text{Cl}^-] \gamma_{\pm}^2$$

where $[\text{Ag}^+]$ is the molality of the silver ions

$[\text{Cl}^-]$ is the molality of the chloride ions

$\gamma_{\pm}$ is the mean ionic activity coefficient of
silver ion and chloride ion

The association constant K_1 , from equation (2) is given by

$$\begin{aligned} K_1 &= \frac{[\text{AgCl}] \gamma_o}{[\text{Ag}^+][\text{Cl}^-] \gamma_{\pm}^2} \\ &= \frac{[\text{AgCl}] \gamma_o}{K_s} \end{aligned} \quad (3)$$

Where $[\text{AgCl}]$ is the molality of undissociated silver chloride and γ_o is the activity coefficient of undissociated silver chloride and have a value close to unity at the low ionic strengths employed. Hence equation (3) becomes

$$K_1 = \frac{[\text{AgCl}]}{K_s} \quad (4)$$

The total silver concentration S as measured by the solubility measurements is given, on substitution, by

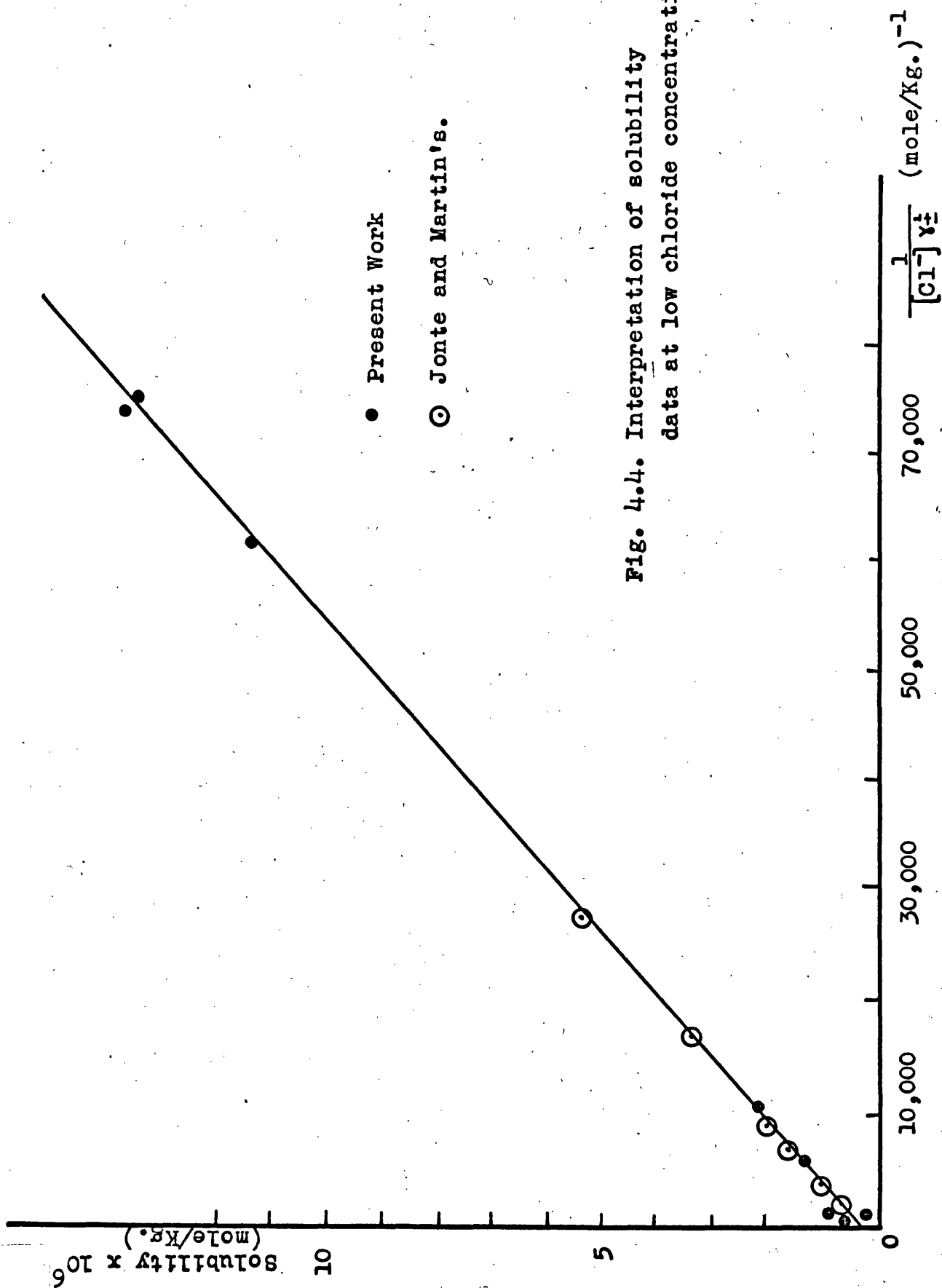


Fig. 4.4. Interpretation of solubility data at low chloride concentrations.

$$\begin{aligned}
 S &= [\text{Ag}^+] + [\text{AgCl}] \\
 &= \frac{K_s}{[\text{Cl}^-] \gamma_{\pm}^2} + K_1 K_s \quad (5)
 \end{aligned}$$

Hence a plot of total solubility S against $\frac{1}{[\text{Cl}^-] \gamma_{\pm}^2}$ should

yield a straight line of slope K_s and intercept $K_1 K_s$ and this is shown in Fig.4.4. $K_1 K_s$ and K_s are 0.35×10^{-6} mole/kg and 1.77×10^{-10} mole²/kg² respectively, in good agreement with Jonte and Martin's but the present investigation was extended to a much lower concentrations of added chloride ions.

4.11. Effect of Radioactivities on Solubilities

103

Spitsyn et al.¹⁰³ were the first group to begin an extensive investigation of the influence of radiation in heterogeneous chemical processes, and reported the changes in behaviour when radioactive materials are used at the tracer levels. A subsequent report of Ramette and Anderson¹⁰⁴ failed to confirm any noticeable effect of specific activity of sulphur-35 on the solubilities of barium sulphate and lead sulphate labelled with sulphur-35. However, in the same article the authors have mentioned the unpublished work of Hoffer¹⁰⁵ who found that the solubilities of silver iodate samples labelled with silver-110 in the specific activity range 0.04 - 6.0 mCi/g. were higher than the accepted value, that the time for the system to reach

equilibrium was also longer than the time required by the non-radioactive salt, and that the size of the precipitate of labelled silver iodate was too small for ordinary filtration. Bovington, in a recent publication¹⁰⁶ has concluded that, in his investigation of the effect of radiation on solubilities, the solubility of lead sulphate in water is in good agreement with Ramette's but that of barium sulphate is 10% higher than the normal value. Electron microscopy revealed damage on the crystal lattice of these salts and this was thought to be due to self irradiation. It is of interest to note that these workers use a considerably higher specific activity than was used in the present work; their lowest level was 0.04 mCi/g, whereas only 0.003 mCi/g was the normal level of the activity involved in the work presented in this thesis. There was no evidence of any effect of specific activity on the observed solubilities, the particles size of silver chloride was found to be normal, and the filtration was carried out without difficulty.

4.12. Effect of Adsorption on the Surface of Container.

107

Recently West et al have established the adsorption characteristics of silver on various common storage containers by using a radiochemical technique; silver-110m and silver-111 were used as tracers. They found that the maximum adsorption for all materials studied (i.e., borosilicate glass, flint, polyethylene and silicone coated containers) was approached in

between 10 and 30 days. Results from the present study show no effect of adsorption on the surface of the container. This may be due to the fact that at the time of analysis for the solubilities in the equilibrium solution, the adsorption had already reached the state of equilibrium. A series of experiments on the solubility of silver chloride in water at 25°C has been carried out using ordinary pyrex, polyethylene, P.T.F.E. coated flasks; results did not show any difference beyond normal experimental error, and they were close to what was considered as the best literature value. The results, tabulated in Table III, were obtained, in order, using polyethylene, P.T.F.E. coated flasks and for the last three results pyrex flasks were used.

CHAPTER V

Materials

This chapter is concerned with the sources and purification of all the materials used in this work, together with criteria of purity. In particular, the preparation of pure formamide is dealt with in detail.

5.1. Solvents

Double deionised water was prepared by deionsation of tap water, by successive passage through two "Elgastat" units. The second unit always contained an almost fresh cartridge of resin. The so called "double deionised water" gave a specific conductance of $9.3 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$.

"Norsk Hydro" heavy water (99.7% minimum) supplied by I.C.I. was used without further purification. The water (H_2O) content was shown by N.M.R to be less than 0.3%.

The purification of formamide is described in section 5.4.

5.2. Standard Solutions

The standard solutions of silver nitrate and sodium chloride were made from A.R. grade reagents. Silver nitrate was used without further purification. Sodium chloride was

purified by re-crystallisation few times from water+ ethanol solution. The final crop of crystals was dried in the oven at 140°C for 48 hours and was kept, prior to use, in a desiccator. Standard solutions were made up in double deionised water, except for the work involving heavy water, in which case the standard solutions were made up in heavy water.

5.3. Radioactive Materials.

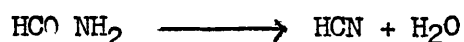
Silver-110m was obtained from the Radiochemical Centre, Amersham, in the form of silver nitrate in nitric acid solution. The total amount of silver present was very low, i.e., 0.001 mg of $\text{Ag}^+/\mu\text{Ci}$. The stock solution was made up by injecting the silver-110m tracer solution from the multidose glass vial, using a hypodermic syringe, into a flask containing double deionised water, and this was used in the measurements of the solubilities of silver chloride throughout this research. This stock solution was of relatively high activity and only a very small volume of it was needed in each measurement, hence an increase of the volume of the "precipitating mixture", which can cause the formation of a colloid, was avoided. Furthermore, the amount of the inactive silver nitrate or so called "silver nitrate carrier" which was associated with the radioactive tracer, could be kept to such a low value that it could be regarded as negligible. Silver-110m has a half-life of 253 days; thus the activity will decrease appreciably in the course of one

month and this must be taken into account when making a stock solution which maybe used throughout such a period. In all cases the activity in the stock solution at the time of preparation was between 0.2 - 0.5 μ Ci/ml. and usually only 0.1 to 0.5 ml. were taken for labelling the silver nitrate carrier solution.

Chlorine-36 was obtained from the Radiochemical Centre in the form of 2.2M hydrochloric acid. The standard solution of sodium chloride was labelled with chlorine-36 by the method already described for silver-110m. This labelled solution was used only when the double labelling technique was employed.

5.4. Purification of Formamide

Formamide is a rather viscous hygroscopic liquid which undergoes hydrolysis readily, yielding decomposition products such as ammonia, formic acid and ammonium formate¹⁰⁸ It dissolves many drying agents such as magnesium perchlorate, anhydrous sodium sulphate, calcium chloride and reacts with others such as phosphorus pentoxide and calcium oxide. Silica gel is also ineffective as a drying agent. Formamide decomposes on heating as follows :-



109

~~or as Ram Chand Paul Malhotra et al have suggested that the~~

~~autoionisation of formamide is~~



The decomposition of formamide is also believed to be catalysed by acids and alkalis, and may also be brought about by the action of light. Because of its reactivity and instability the purification is difficult, and pure formamide should not be allowed to stand for an extended period of time before being used.

5.5. Summary of Previous Methods Used in Purification of Formamide.

It is obvious that the purification of formamide should involve drying and separating this compound from its decomposition products and other impurities. The whole process has to be carried out at a low temperature to avoid thermal decomposition and care has to be taken to avoid exposing it to moist air. Physical properties of pure formamide are given in Table I of Chapter III.

Previous workers started from the addition to formamide of drying agents such as sodium sulphate or calcium oxide, followed by fractional distillation under reduced pressure. Several workers also utilised fractional crystallisation either before or after distillation. The whole process was always performed in an atmosphere freed from carbon dioxide and water. The

quantity of pure formamide produced by the above conventional method was usually small. Most early workers used the freezing point as a criterion of purity. More recent workers measured conductance as well and a limited number measured the water content. An outline of the procedure used by some of the earlier workers is given below.

Formamide has been a subject of interest since the beginning of the century. In 1914 English and Turner¹¹⁰, 1915 Davis and Putnam¹¹¹ and 1918 Bran¹¹² purified formamide by fractional distillation under reduced pressure, the melting point of the final product being between 2.2 to 2.25°C. Merry and Turner¹¹³ introduced fractional freezing and found that the melting point of crude formamide was raised from 0.6°C to 0.68°C after 6 successive freezings. English and Turner¹¹⁰, by 20 successive freezings were able to raise the melting point to 1°C. Smith⁴⁶ modified these methods and claimed that eventually formamide with a freezing point of 2.55°C and with specific conductance at 20°C of $1.9 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ was obtained. Smith continued purification by distillation until a fraction freezing at 2.25°C was obtained. This moderately pure formamide was then frozen several times, the freezing point being raised by about 0.2° - 0.3°C after each freezing. The conductance continued to decrease after the freezing point had reached its maximum.

In 1936, Verhoek¹⁰⁸ neutralised crude formamide with sodium

hydroxide before purification by distillation and fractional crystallisation. A final product with specific conductance $(1-2) \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$ was obtained. Verhoek also followed the decomposition of pure formamide and found that its specific conductance increased by a factor of 8 to 10 in 10 days or 2 weeks. There was also a gain in the weight of formamide, when it was exposed to the atmosphere, of 0.2% in 1 hour, 1% in $5\frac{1}{2}$ hours and 10% in 140 hours, presumably due to the uptake of moisture.

By fractional distillation at very low pressure (0.1 mm) and consequent low temperature (51-58°C), Dawson and Co-workers⁶⁸ obtained formamide of conductance $(1-3) \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$ without the aid of fraction freezing. Dawson and Co-workers⁴⁹ also used fractional distillation at 1 mm. pressure followed by fractional freezing. No freezing points were quoted, but other physical constants are given in Table I.

¹¹⁴
Albright and Gosting using fractional distillation and freezing, obtained formamide of freezing point 2.4°C and specific conductance of $(6.5 \times 10^{-6}) \text{ ohm}^{-1}\text{cm}^{-1}$; the change in specific conductance was found to be less than $10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}\text{hr}^{-1}$. They followed the decomposition of formamide over a period of one year and concluded that the decomposition to ionisable products contributed less than 0.05 equivalent litre⁻¹ or less than 0.3% by weight on the assumption that the decomposition

product was ammonium formate. They also calculated that the freezing point of 2.4°C corresponded to less than 0.1% by weight if the impurity is water.

Other workers^(5,69,78,85,91,115) purified formamide by the aforementioned methods, with differences in drying agents and temperatures and pressures of distillation. Mandel and Decroly⁵ claimed a freezing point of 2.9°C which seems very high in comparison with the normally accepted value of about 2.55°C . Johari and Tewari⁶⁹ like Dawson⁶⁸ fractionally distilled at a very low pressure (0.1mm) and temperature ($54^{\circ} - 56^{\circ}$). Pavlopoulous and Strehlow⁷⁸ appear to be the first workers to quote the water content of the final product.

Notley and Spire¹¹⁶ have developed a new method of purification which is less troublesome and is capable of producing pure formamide in litre quantities. The method is based on deionisation of formamide by means of ion exchange resins. They removed water by passing formamide slowly through a column packed with 1 kilogramme of 3 A molecular sieve in the form of $\frac{1}{16}$ pellets. The column was electrically heated to about 60°C to speed up the rate of water removal. The dried sample was then treated with a mixed bed of ion-exchange resins, (Amberlite IR-120 cation exchange resin in the sodium form and Amberlite IRA 400 anion exchange resin in the chloride form)

loaded respectively with H^+ and $HCONH^-$ to remove ionic impurities.

This procedure regularly produced formamide of specific conductance as good as, or better than, $2 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$.

This value increased by about 2×10^{-7} each day the deionised formamide stood unused. However, the freezing point is $2.3 - 2.35^\circ\text{C}$ which is substantially lower than the generally accepted value of about 2.55°C , and indicates the presence of non-ionic impurities.

Table I. Physical Constants of Purified Formamide at 25°C
(unless otherwise stated)

Workers	Freezing point $^\circ\text{C}$	Specific conductance $\text{ohm}^{-1} \text{ cm}^{-1}$	Dielectric constant	Visc. poise	Density gm/cm	Water content molarity
Smith ⁴⁶	2.55	1.9×10^{-6} at 20°C	-	-	-	-
Verhoek ¹⁰⁸	-	$(1-2) \times 10^{-6}$	-	-	-	-
Dawson et al ⁶⁸	-	$(1-3) \times 10^{-5}$ at 20°C	-	-	-	-
Dawson et al ⁴⁹	-	$(0.9-1.5) \times 10^{-5}$	109.6	0.0331	1.1296	-
Albright and Gosting ¹¹⁴	2.4	6.5×10^{-6}	-	-	-	-
Gopal and Srivastava ¹¹⁵	-	10^{-5}	-	-	-	-
Mandel and Decroly ⁵	2.9	-	109.5	-	-	-
Povarov et al ⁹¹	-	4×10^{-5}	-	-	-	-
Johari and Tewari ⁶⁹	-	$(2-4) \times 10^{-6}$	-	-	-	-
Pavlopoulos and Strehlow ⁷⁸	2.55	7×10^{-6}	-	-	-	0.016

Table 1 cont..

Workers	Freezing point °C	Specific conductance $\text{ohm}^{-1}\text{cm}^{-1}$	Dielectric constant	Visc. poise	Density gm/cm	Water content molarity
Somsen and Coops ⁸⁵	2.56-2.58	-	-	-	-	0.011
Notley and Spiro ¹¹⁶	2.3-2.35	$(1-2) \times 10^{-7}$	-	-	-	0.008-0.01
Present work	2.45-2.55	in the order of 10^{-6} e.g. 5×10^{-6}	-	-	-	0.002-0.004

5.6. Present Method Used in Purification of Formamide.

The present work necessitates the purification of large quantities of pure formamide, which would be difficult by fractional freezing techniques. The method of Notley and Spiro¹¹⁶ is attractive, but has not been used since the present method was developed before their work became known to us and also because we were not satisfied with a freezing point of $2.3 - 2.4^{\circ}\text{C}$.

The formamide used here was purified entirely by fractionally distilling twice and as low a temperature and pressure as was obtainable. By this means, formamide with a freezing point of $2.45 - 2.55^{\circ}\text{C}$ and specific conductance of about $(5 - 8) \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$, water content of between $(0.002 - 0.004)$ molar was obtained without the aid of any drying agents. The pure formamide once obtained was stored in the dark and in a cold room

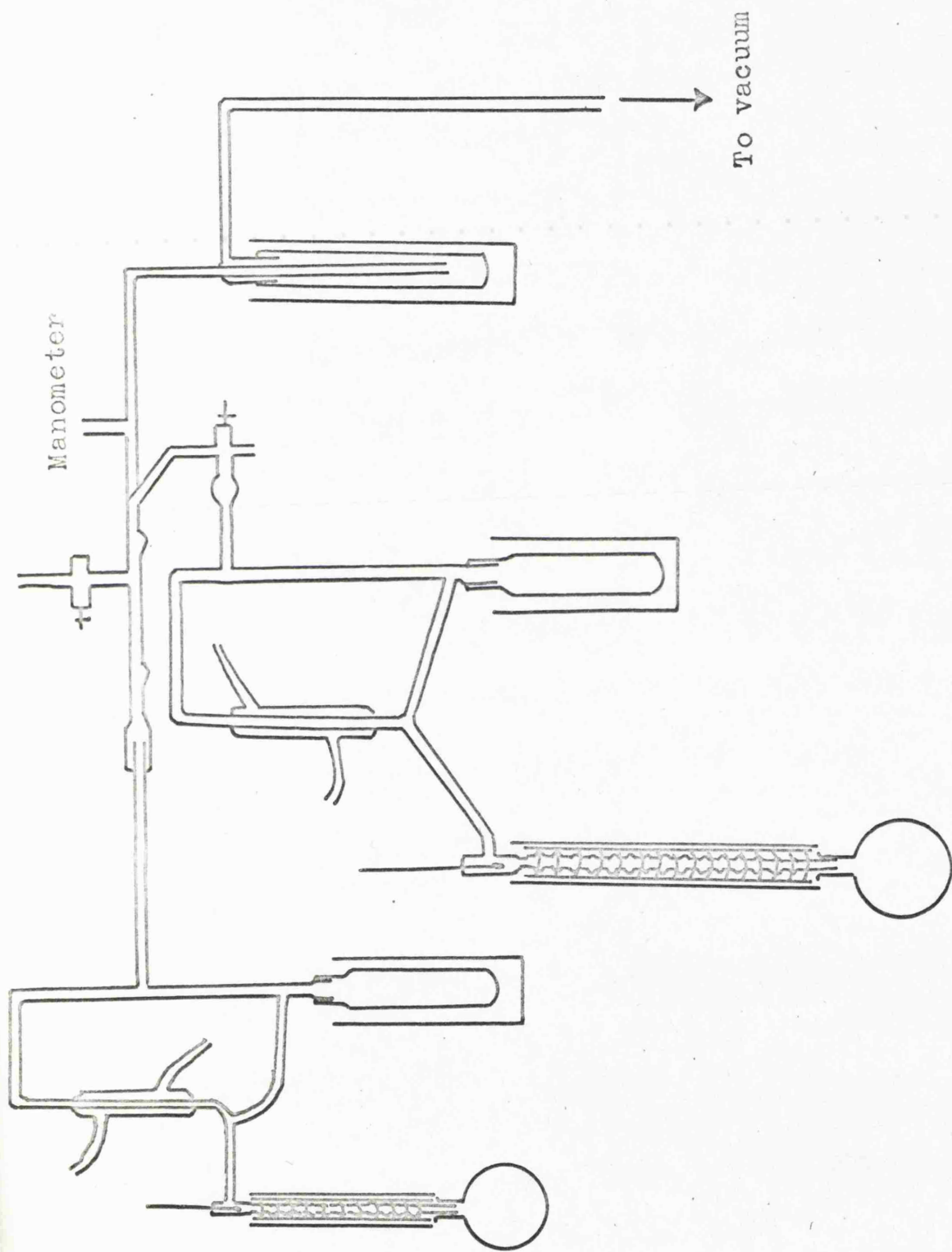


Fig. 5.1. Distillation plant.

at -10°C .

The actual distillation procedure can be summarised as follows. Technical grade formamide (obtained from Messrs. B.D.H., Fison, and Hopkin and Williams) was distilled under a reduced pressure between 0.3 - 0.1 mm. of mercury and at a temperature of about 60°C through a modified column of the type described by Ray¹¹⁷. These columns are 1 centimetre in diameter and 1 metre long and are each equipped with a small reflux head and an electrically heated jacket. The distillate was collected in a receiver cooled with "Drikold" in acetone. The two columns were assembled as shown in Fig.5.1, both being joined to the same vacuum line. One column was kept exclusively for the first distillation and four 100-200 ml. fractions were collected from a starting sample of 500 ml. crude formamide. The second, third and fourth fractions were retained and were combined and re-distilled through a second column. Again only the last three fractions were used throughout this work. The second fraction was combined with the second, third and fourth fractions from the first distillation, to be re-distilled. Usually about 200-250 ml. of pure formamide were obtained within 16-20 hours. Attempts were made to distill formamide a third time, but the water content was found to increase. Shaking crude formamide with charcoal before distillation¹¹⁸ has also been tried but no marked

improvement was found. Karl Fischer water determinations were carried out on each fraction together with freezing point and conductance measurements. The third and the fourth fractions from the second distillation were consistent in giving a freezing point between $2.45 - 2.55^{\circ}\text{C}$, a water content between $0.002 - 0.004$ molar and a specific conductance of the order of $10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$. Typical results are given below.

Table II

Properties	Crude formamide	1st distillation				2nd distillation			
		1st frac.	2nd frac.	3rd frac.	4th frac.	1st frac.	2nd frac.	3rd frac.	4th frac.
Freezing point $^{\circ}\text{C}$	1.9-2	2.35	2.35	2.4	2.45	2.45	2.45	2.50	2.55
Water content (molarity)	0.02	0.01	0.01	0.007	0.004	0.004	0.0035	0.003	0.002
Specific conductance ($\text{ohm}^{-1}\text{cm}^{-1}$)	6.69×10^{-4}	5×10^{-4}	2.07×10^{-4}	8.95×10^{-5}	8×10^{-5}	6.9×10^{-5}	4.6×10^{-5}	1.29×10^{-5}	5×10^{-6}

5.7. Determination of Physical Constants.

5.7.1. Karl Fischer Titration.

A Townsen and Mercer Karl Fischer titration apparatus type M 35 was used to measure the water content of formamide samples. This apparatus uses the "dead stop" method for determining the end point of the titration. In this method, a constant potential

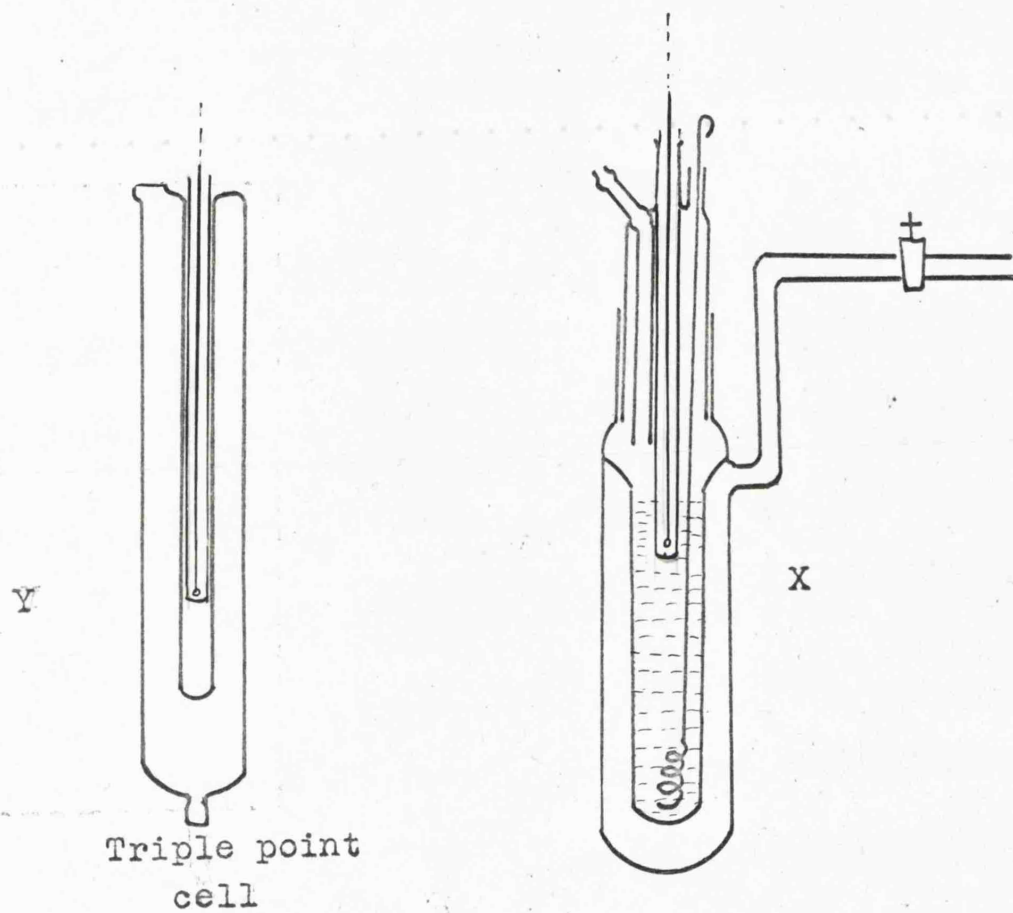


Fig. 5.2. Freezing Point Apparatus.

difference of 10 - 25 mV is applied to a pair of platinum electrodes immersed in the solution. The end point of the titration is indicated by the sudden change in current. The solution was stirred by bubbling through dry air. A back titration, in which an excess of reagent was added to the sample and back titrated with water in methanol solution, was used, since this is more satisfactory than the direct titration¹¹⁹. During the back titration, current flows through the galvanometer when the solution contains excess Fischer reagent and drops to zero when the equivalence point is reached owing to the electrodes becoming polarised.

The Karl Fischer reagent was standardised with a standard solution of water in methanol obtained from Messrs. B.D.H., containing 5 mg. of water/ml. or alternatively with a standard water in methanol solution prepared by drying methanol using the method of Vogel¹²⁰ and adding a known weight of water. The total water content of this solution was then determined by back titration against Karl Fischer reagent¹²¹. The standard water in methanol solution was stable over a period of several months, if protected from evaporation.

5.7.2. Freezing Point Determinations

The freezing points were determined using the apparatus shown in Fig.5.2. Temperatures were measured with a copper -

constantan thermocouple, one junction of which was immersed in oil in the glass tube. The tube was surrounded by the formamide sample in the vessel X. The other junction, also immersed in oil in a second glass tube, was in the centre well of the triple point cell which has ice, liquid water and water vapour in equilibrium. The triple point cell was prepared in this laboratory according to the method described in reference (122) The freezing point vessel X, was cooled with Drikold in acetone. The emf was measured using a Tinsley vernier potentiometer type 4363E coupled with a Tinsley type MR 4 galvanometer. The emf of the freezing point assembly decreased rapidly from about 600 ~~mV~~ and with pure formamide the value became steady at 95 -96 ~~mV~~, corresponding to a freezing point of 2.55°C from the thermocouple calibration curve. The triple point temperature (0.01°C) has to be subtracted from the apparent value in order to get the real freezing point of the sample.

The thermocouple was kindly provided by Dr. J.M. Pollock of the Regional College of Technology, Leicester. It has been calibrated at the N.P.L. by Dr. Pollock, using an N.P.L. certified platinum resistance thermometer and a Mueller Bridge. The emf of the thermocouple over the temperature range 0° - 120° C is given by

$$E = at + bt^2 + ct^3$$

Using a computer, the equation for this particular

thermocouple was found to be

$$E = 38.1696t + 4.54788 \times 10^{-2} t^2 - 3.32901 \times 10^{-5} t^3$$

Where t is temperature in $^{\circ}\text{C}$

Measurements were also carried out using a pure ice bath instead of a triple point cell but the time involved in obtaining a constant temperature was found to be longer than when using the triple point cell. The triple point cell was found to maintain a constant temperature for several hours, more than long enough for each freezing point determination.

5.7.3. Conductance Measurements.

Each specific conductance measurement was carried out at 25°C using a conductivity cell with a cell constant of 1.1 at 25°C and volume of about 10 ml. together with a Universal Bridge type B 221 manufactured by Messrs. Wayne Kerr.

CHAPTER VI

Other Experimental Studies6.1. Calorimetric Measurements

Although silver chloride is more soluble in formamide than in water, its solubility is still much too low for its heat of solution to be measured directly. The heat of solution of this salt in formamide was therefore obtained indirectly by measuring the heat of precipitation of silver chloride formed by mixing silver nitrate and potassium chloride solutions, at 15 and 25°C.

6.1.1. Preparation of Silver Nitrate Solution in Formamide.

It was obviously necessary, during the course of this work to prepare silver nitrate solution. However, it was found experimentally that a solution of silver nitrate in formamide turns black within a few minutes after preparation, producing a silver mirror. The rate of reaction increases with increasing silver ion concentration, but is almost completely inhibited in the presence of a few drops of an aqueous solution of nitric acid or perchloric acid. In this work, fairly dilute silver nitrate solutions were used and were stabilised by a small amount

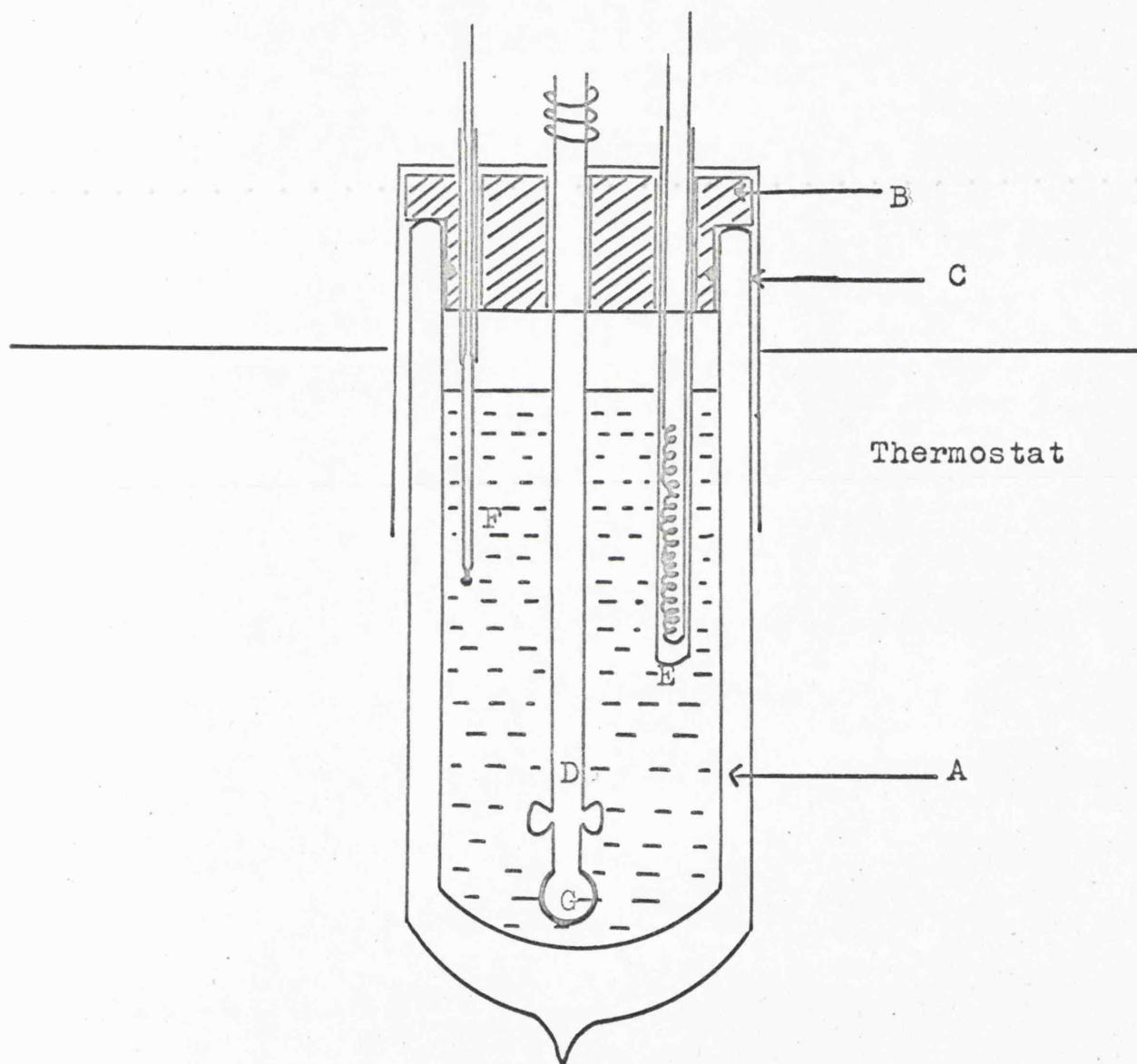


Fig. 6.1. Sketch of calorimeter.

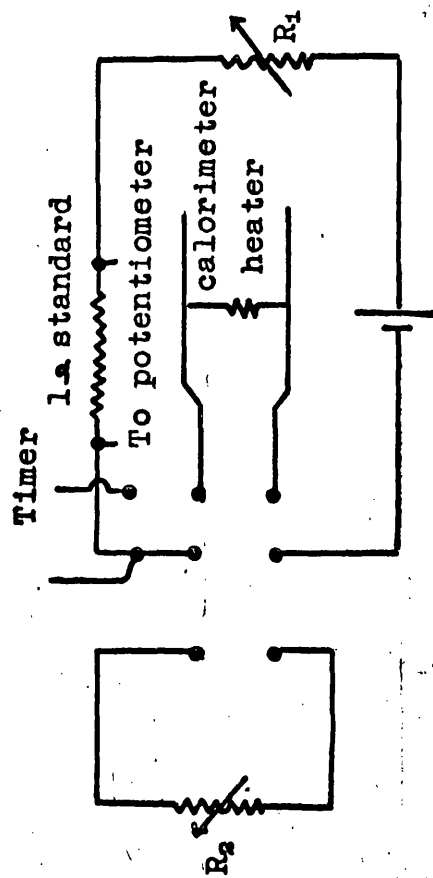
of concentrated aqueous nitric acid (10 drops of concentrated nitric acid in 120 ml. of formamide). It is difficult to assess the effect on the heat of precipitation, of the added impurities i.e., water, H^+ and NO_3^- ions, but as they are present in so small a quantity, the error is probably less than the experimental error in each measurement. Excess silver nitrate solution was used in every run, and the results based on the known amount of potassium chloride.

6.1.2. Apparatus

The calorimeter is shown in Fig.6.1 and consists of a cylindrical Dewar flask of about 150 ml. capacity. Into this fits a Teflon stopper B, attached to an isothermal brass shield C. The stopper carries a glass stirring rod D, a heater E, and a thermistor F. A thin walled glass bulb G of about 5 ml. capacity, containing the potassium chloride solution, is fused onto the glass stirring rod. The heating coil is wound from a 38 s.w.g. "Eureka" resistance wire and temperature changes are measured by a single thermistor type F of resistance 200 ohms at $20^\circ C$ (supplied by Messrs. Standard Telephones and Cables Ltd.). The heating and thermistor circuits are shown in Fig.6.2. and have been described thoroughly elsewhere^{123,124}.

The heating current is controlled by a decade box, R_1 , and is measured by measuring the potential across a standard 1 ohm

Heater circuit



Thermistor circuit

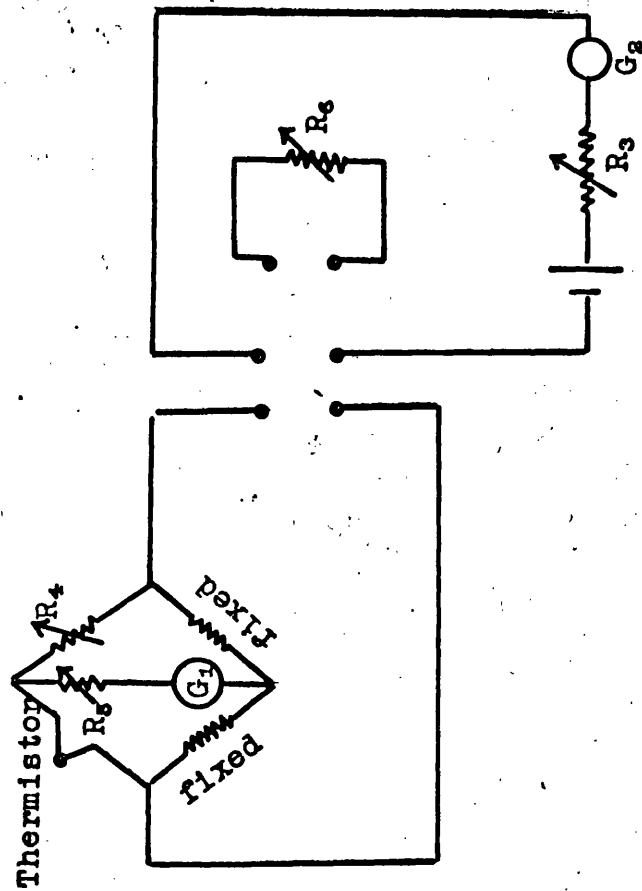


Fig. 6.2. Heater and Thermistor circuit.

resistance (Tinsley type 1659). The switch connecting the calorimeter automatically actuates an electronically operated stop watch (Messrs. Camera Cuss & Co.).

The thermistor forms one arm of a Wheatstone bridge, two others arms being fixed resistances. The bridge is balanced by means of a decade box R_4 and R_5 in series with the galvanometer G_1 controls the sensitivity of the bridge. The galvanometer G_1 is a Tinsley type 4500 LS having a maximum sensitivity of 1200 mm/ μ A, with a scale at 1 metre.

6.1.3. Experimental Procedure

2 to 3 mls. of potassium chloride solution in formamide at a relatively high concentration i.e., 0.4 m were introduced into the glass bulb G by means of a hypodermic syringe. The solution was then frozen in acetone - Drikold mixture before sealing off the bulb. Since formamide easily decomposes on heating, care was taken in sealing off the glass bulb and also in fusing it onto the glass stirring rod. The weight of the solution in the bulb was obtained from the difference in the weight of the bulb before and after filling. 120 mls. of 0.04m stabilised silver nitrate solution in formamide were placed in the Dewar flask and the assembled calorimeter was left in the thermostat bath for about 24 hours before commencing a measurement. When the two solutions were to be mixed, the bulb

was broken against the bottom of the flask by pushing down the glass stirring rod during the rotation. The change in the temperature of the calorimeter caused by the formation of the silver chloride precipitate was measured by the deflexion of the galvanometer G_p . Readings were taken at $\frac{1}{2}$ minute intervals before mixing and were continued for about 20 minutes after mixing.

A heating calibration was then carried out, whereby a known amount of heat (comparable to the amount of heat liberated by the precipitation) was introduced electrically. An example of the calculation is given in 6.1.4. and the results are tabulated in Chapter VII.

The reproducibility of the measurement was tested by measuring the heat of precipitation of silver chloride in water at 25°C. These results are also given in Chapter VII and the mean value, 15.67 ± 0.187 kcal/mole is in good agreement with the literature values, 15.74 kcal/mole¹²⁵. Attempts to measure the heat of dilution of 0.4m potassium chloride in formamide were also made, but it was too small to be measured accurately with the present calorimeter. The value lies below 0.1 kcal/mole and no corrections for dilution were made, and the measured heats of precipitation with sign changed, are therefore regarded as being standard heats of solution of silver chloride in formamide. The overall accuracy of the measurements is probably

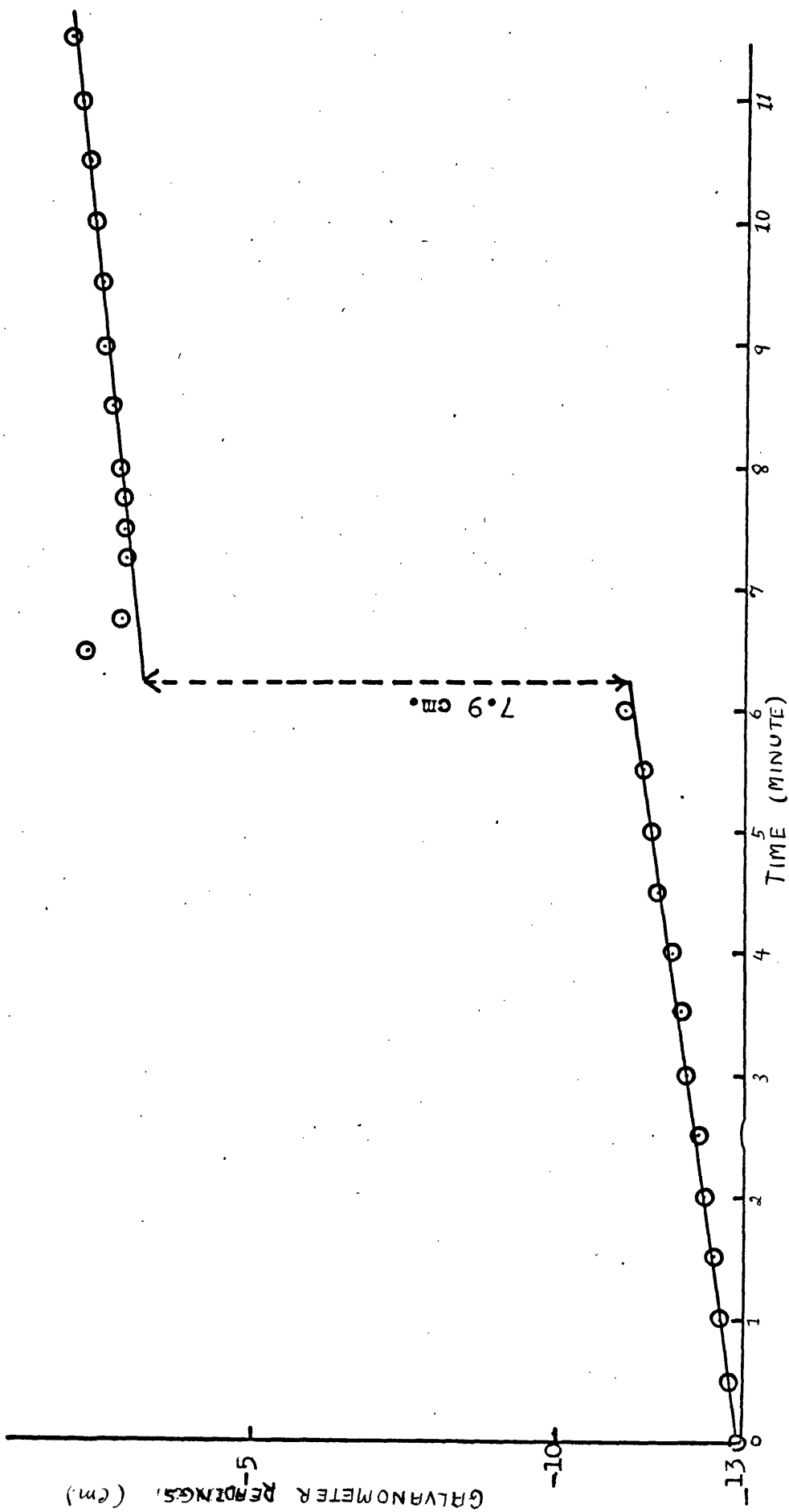


Fig. 6.3a. Mixing

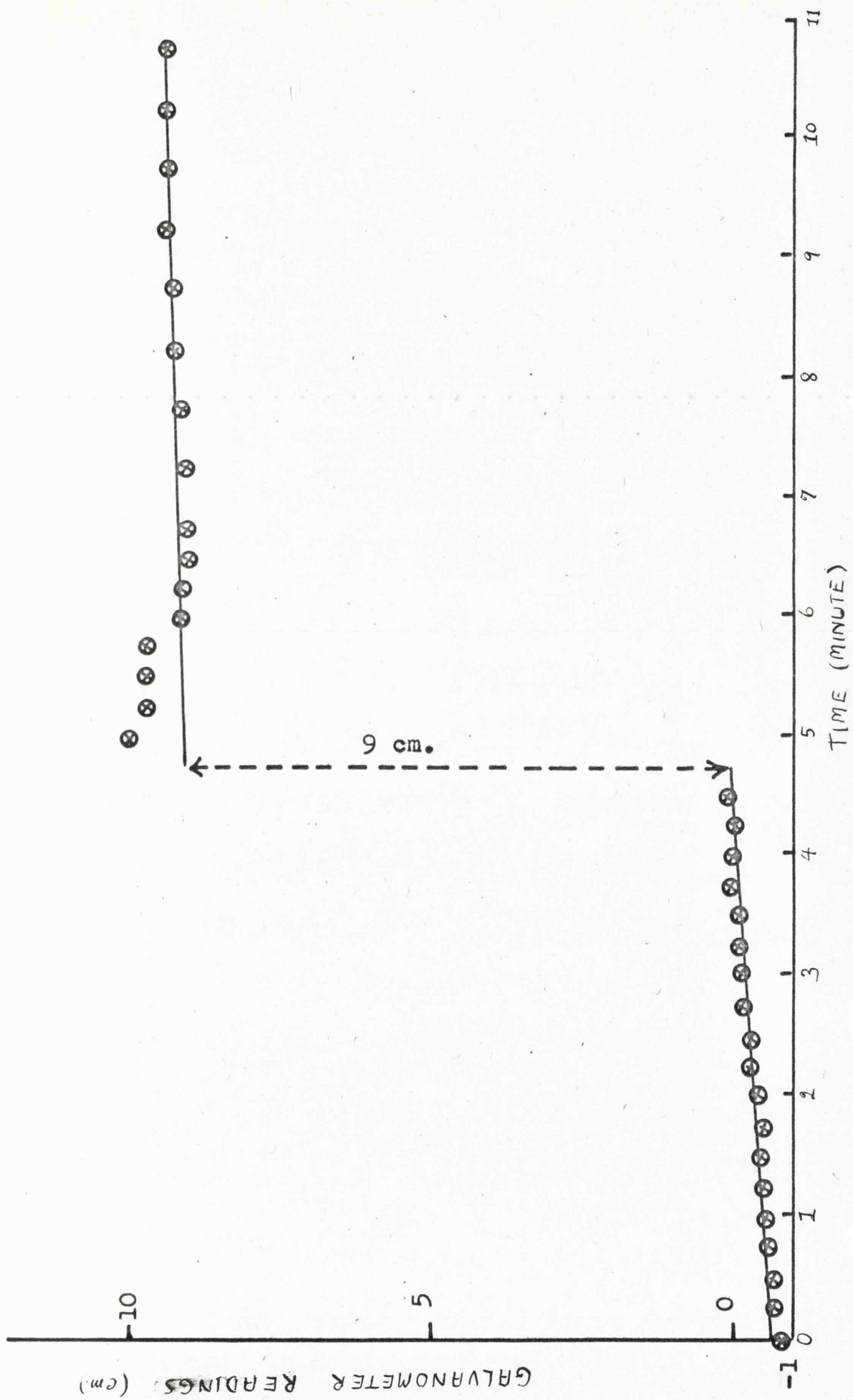


Fig. 6.3b. Calibration

within 0.3 kcal/mole.

6.1.4. A Typical Run

The graphs of galvanometer readings against time are shown for both the mixing and calibration in Fig.6.3. The following data were recorded :-

Temperature of measurement = 25°C

Concentration of potassium chloride solution in

formamide = 0.337 m

Weight of potassium chloride solution taken = 1.4728 gm.

Heater resistance "r" = 30.638 ohms.

Heating current "i" = 0.1746 amps

Heating time "t" = 28.38 sec.

Galvanometer deflexion for mixing = 7.9 cm.

Galvanometer deflexion for calibration = 9.0 cm.

Since, heat dissipated = $\frac{i^2 r t}{4.184}$ calories

Then, heat introduced electrically = $\frac{(0.1746)^2 \times 30.638 \times 28.38}{4.184}$ calories,

and heat liberated during precipitation

$$= \frac{(0.1746)^2 \times 30.638 \times 28.38 \times 7.9}{4.184 \times 9.0} \text{ cals.}$$

it follows that the heat of precipitation of this reaction

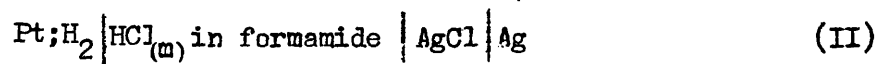
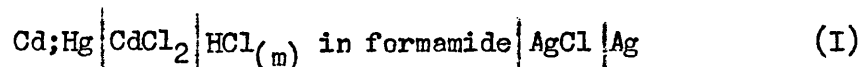
$$= \frac{(0.1746)^2 \times 30.638 \times 28.38 \times 7.9}{4.184 \times 9.0 \times 1.4728 \times 0.337} \text{ kcals/mole}$$

$$= 11.20 \text{ kcals/mole.}$$

6.2. Preliminary E.M.F. Measurements.

The emf of the cell $\text{Pt}; \text{H}_2 | \text{HCl}_{(\text{m})}$ in formamide $| \text{AgCl} | \text{Ag}$ has been measured by Mandel and Decroly⁵ and later by Agarwal and Nayak⁶. Their values of the standard potential E° for silver|silver chloride electrode differ by 6 mV at 25°C. Earlier the reproducibility of the silver|silver chloride electrode in hydrochloric acid in formamide solution was reported by Pavlopoulos and Strehlow⁷⁸ to be unsatisfactory whereas the emf of the cell $\text{Cd} | \text{CdCl}_2(\text{solid}) | \text{HCl}$ in anhydrous formamide $| \text{H}_2; \text{Pt}$ was reproducible to at least ± 1 mV. The behaviour of the cadmium|cadmium chloride, cadmium amalgam|cadmium chloride and silver|silver chloride electrodes have been thoroughly¹²⁶ investigated by Muju'. His findings indicate that these electrodes function reproducibly in potassium chloride in formamide solution at various temperatures. It was therefore thought worthwhile to examine the reproducibility of these electrodes in hydrochloric acid solution in anhydrous formamide and to re-measure the standard electrode potentials of the silver|silver chloride and cadmium|cadmium chloride electrodes in the above mentioned solution. The following experiments were carried out jointly with Muju.

Measurements were made simultaneously on the 3 cells,



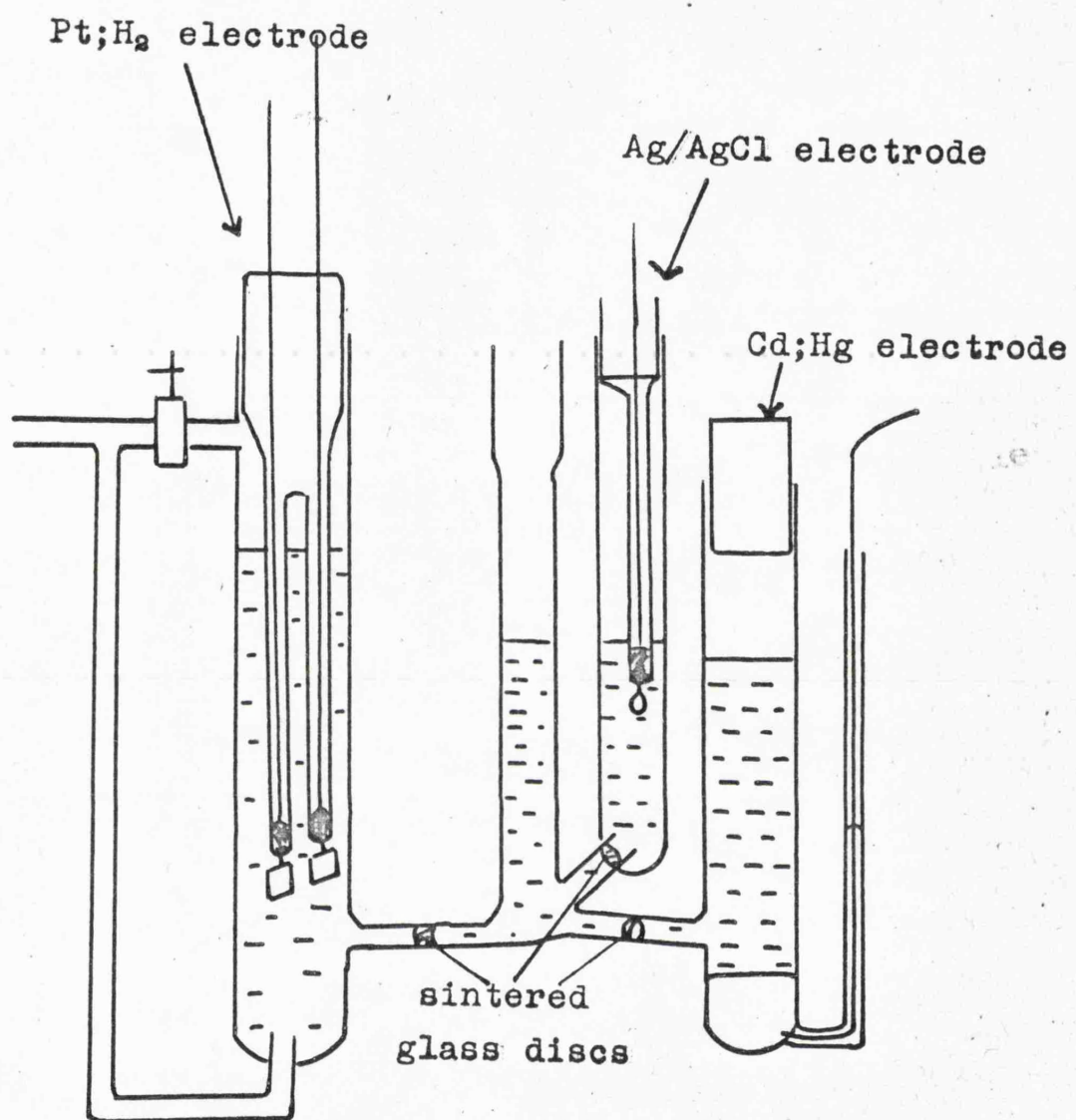


Fig.6.4. Triple cell.

and $\text{Cd;Hg} \mid \text{CdCl}_2 \mid \text{HCl}_{(m)} \text{ in formamide} \mid \text{H}_2; \text{Pt}$ (III)

Using a pyrex glass cell vessel with 3 electrode compartments, as shown in Fig.6.4. The middle compartment is for filling the cell with solution. The sintered glass disc were placed along each side arm. About 110 mls. of solution were needed to fill this triple cell.

6.3. Preparation of Electrodes.

6.3.1. The hydrogen electrodes These were prepared according to Hills and Ives^{127a}. The cylinder hydrogen gas was freed from oxygen by passing through a Deoxo catalytic purifier (Engelhard Industries Ltd.) before bubbling through a presaturator and the cell solution.

6.3.2. The cadmium amalgam|cadmium chloride electrodes.

10% cadmium in mercury amalgam was used and prepared by the method recommended by La Mer¹²⁸. A bar of very pure cadmium (99.999% Koch-Light GN(Z) Zone refined) was suspended in a saturated solution of A.R. Cadmium sulphate and was made the anode. A pre-weighed quantity of mercury formed the cathode at the bottom of the beaker. The quantity of cadmium that formed an amalgam with mercury could be adjusted by the amperage and duration of the current during electrolysis. The amalgam formed was then washed several times with de-ionised water and

finally was dried by blotting the water using filter paper. The amalgam was kept in formamide, in a flask with a ground glass stopper and was dried in a similar manner as described above before transferring into a cell compartment; its surface was then covered with a very thin layer of pure anhydrous cadmium chloride.

6.3.3. The silver|silver chloride electrodes. These were of the thermal electrolytic type and were prepared by the method recommended by Janz ^{127b}. Briefly, a clean thin platinum wire spiral, sealed into glass tubing, was coated with a paste of pure silver oxide. The silver oxide was then reduced to silver thermally. The coating and reduction of the silver oxide were repeated after which the electrode was chloridised. The chloridising was carried out, making the silver electrode the anode and a platinum electrode the cathode, 1 M hydrochloric acid being used as the chloridising solution. The current and the time of electrolysis were calculated for the conversion of 20% of the silver to silver chloride. The electrodes prepared by this method were transferred immediately after chloridising ^{127c} to a bias cell containing dilute deoxygenated aqueous hydrochloric acid and were allowed to age for a week and the bias potential measured. Only those which showed a potential difference of 0.1 mV or less, were used.

Electrodes of all types mentioned above were left in pure

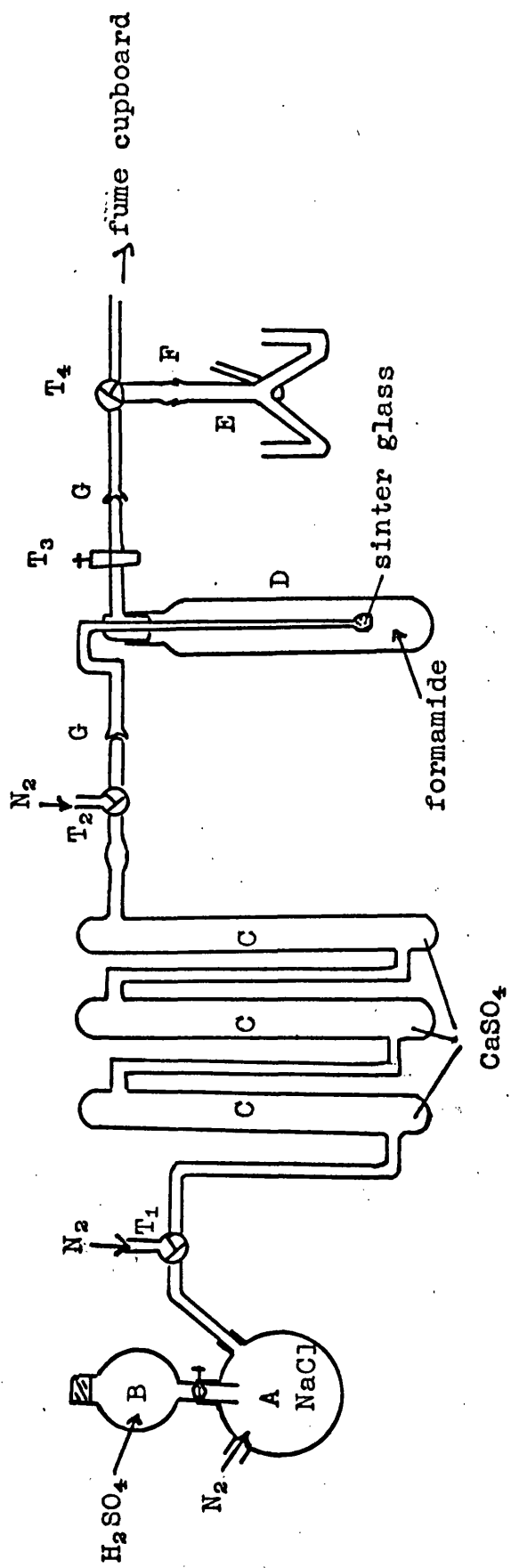


Fig. 6.5. HCl generator.

formamide overnight prior to use.

6.4. Preparation of Hydrochloric Acid Solution

Since the presence of traces of moisture can affect emf measurements in non-aqueous solvents, the preparation of hydrochloric acid solution was carried out in the complete absence of moisture, using the arrangement shown in Fig.6.5. The various components are of pyrex glass and the taps and quickfit joints were coated using a P.T.F.E. spray.

Before assembling the apparatus, dry sodium chloride was placed in flask A, concentrated sulphuric acid in the separating funnel B and pure formamide (prepared as described in Chapter V) was placed in the vessel D. The cell E with its electrodes in position was connected to the system via the solution filling compartment socket at the exit F. A steady stream of dry nitrogen gas was first passed through the apparatus and was kept flowing throughout the preparation of the solution. By adjusting the three way stopcocks T_1 and T_2 and the rate of flow of dry nitrogen gas, the hydrogen chloride gas produced on adding the sulphuric acid to the sodium chloride was passed through the three tubes labelled "C" (packed with calcium sulphate and asbestos), into the formamide in the vessel D. When the formamide contained a sufficient amount of hydrochloric acid, the gas generator was then disconnected from

the rest of the system by means of the stopcock T_2 . The prepared solution was transferred to the cell vessel by inverting the vessel D and applying a slight pressure of nitrogen gas via T_2 . The vessel D could rotate about the ball and socket joints G. The solution was allowed to flow gently into the cell vessel E so as not to disturb the electrodes.

The stock solution prepared by this procedure was in some cases used to prepare a more dilute solution. The dilution and the filling of the cell were then carried out in a glove box in an atmosphere of dry nitrogen.

6.5. Determination of Chloride Concentrations in Formamide.

In the present work, a potentiometric titration was used to determine the concentration of hydrochloric acid in formamide, although other workers^{6,129} employed Fajan's method, or converted⁷⁸ formamide to other compounds before potentiometric titration was carried out.

The formamide solution of hydrochloric acid was titrated against an aqueous standard solution of silver nitrate in the presence of a silver electrode, using a silver|silver chloride electrode as a reference. The silver|silver chloride electrode was immersed in a saturated aqueous solution of potassium chloride and was the negative electrode. A potassium nitrate salt bridge was used. The results were uniformly good and the

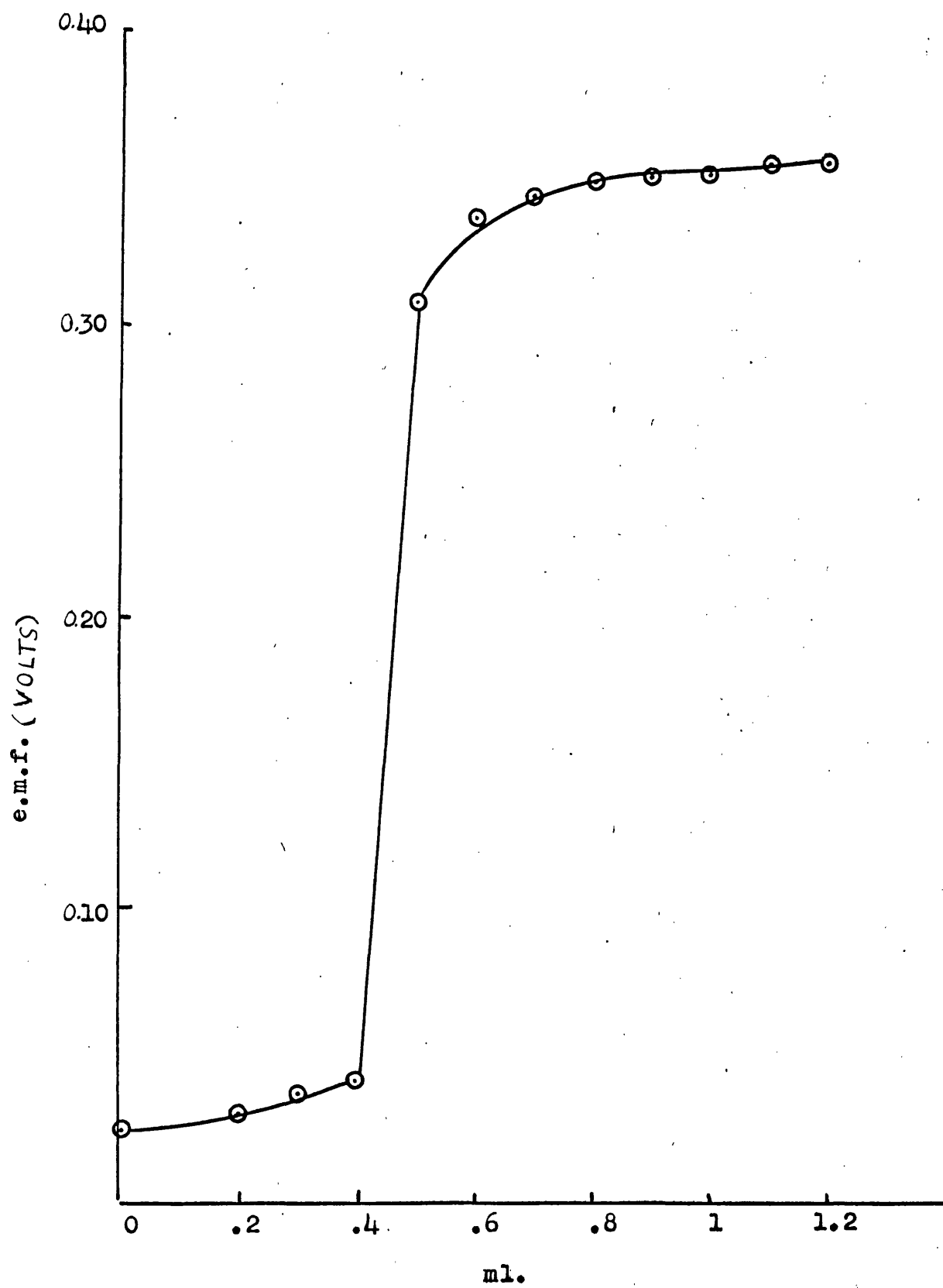


Fig. 6.6. Titration curve

abrupt vertical change in the emf curve at the equivalence point of the titration was obtained in every concentration used. The accuracy of the measurement was estimated to be within $\pm 0.05\text{ mV}$. A typical emf curve is shown in Fig. 6.6.

6.6. Measurement of Potentials

The emf measurements were made with a Tinsley type 4363E vernier potentiometer in conjunction with a Tinsley type MR4 galvanometer and a Tinsley type 1368 Weston standard cell. The measurements were made at 25°C . Although polarization of the electrodes in some non aqueous solvents has been reported no such effect was observed in this study. The galvanometer was found to be as good, as a null point indicator, as the Electronic Instruments Ltd. type 33B-2 Vibron electrometer. The first emf reading was taken 30 - 45 minutes after starting the hydrogen flow. The emf of the cells II and III were found by extrapolating to zero time, a procedure which was also used by Mandel and Decroly⁵ and Agarwal and Nayak⁶. Results are given in Chapter VII.

CHAPTER VII

Results7.1. Solubility of Silver Chloride in Double-deionised WaterTable I Solubility of silver chloride, in moles/kg. in pure water

5°C	25°C	45°C
0.550 x 10 ⁻⁵	1.343 x 10 ⁻⁵	3.050 x 10 ⁻⁵
	1.338 x 10 ⁻⁵	3.055 x 10 ⁻⁵
	1.365 x 10 ⁻⁵	3.120 x 10 ⁻⁵
Mean 0.550 x 10 ⁻⁵	1.348 x 10 ⁻⁵	3.075 x 10 ⁻⁵
2 σ	0.023 x 10 ⁻⁵	0.064 x 10 ⁻⁵

N.B. σ is standard deviation from the mean and is the root mean square deviation.

Table II Solubility of silver chloride in water in the presence of added sodium chloride at 25°C.

[NaCl] x 10 ⁵ (moles/kg.)	S x 10 ⁵ (moles/kg.)
167.94	0.061
107.62	0.077
102.08	0.021
39.08	0.070
17.36	0.136

Table II cont...

$[\text{NaCl}] \times 10^5 (\text{moles/kg.})$	$S \times 10^5 (\text{moles/kg.})$
15.05	1.131
9.486	0.212
3.076	0.524
2.960	0.530

7.2. Solubility of Silver Chloride in Heavy WaterTable III Solubility of silver chloride, in moles/kg. in pure heavy water.

	25.1°C	45°C
	1.161×10^{-5}	2.62×10^{-5}
	1.176×10^{-5}	2.64×10^{-5}
Mean	1.168×10^{-5}	2.63×10^{-5}
25'	0.015×10^{-5}	0.02×10^{-5}

Table IV Solubility of silver chloride in heavy water in the presence of added sodium chloride

25.1°C		45°C	
[NaCl] x 10 ⁵ (moles/kg)	S x 10 ⁵ (moles/kg)	[NaCl] x 10 ⁵ (moles/kg)	S x 10 ⁵ moles/kg
2340.0	0.470	2847.8	0.265
48.02	0.040	454.1	0.065
48.01	0.066	333.1	0.041
19.29	0.084	170.9	0.036
9.722	0.165	48.95	0.141
6.243	0.233	34.79	0.215
4.937	0.281	16.73	0.353
4.073	0.331	3.57	1.41
		1.31	2.08

7.3. Solubility of Silver Chloride in Formamide.

Table V Solubility of silver chloride, in moles/kg in pure formamide.

15°C	25°C	35°C
6.50 x 10 ⁻⁵	10.4 x 10 ⁻⁵	22.81 x 10 ⁻⁵
6.43 x 10 ⁻⁵	10.8 x 10 ⁻⁵	22.23 x 10 ⁻⁵
		22.28 x 10 ⁻⁵
		22.12 x 10 ⁻⁵
Mean 6.46 x 10 ⁻⁵	10.6 x 10 ⁻⁵	22.36 x 10 ⁻⁵
2 σ 0.071 x 10 ⁻⁵	0.04 x 10 ⁻⁵	0.53 x 10 ⁻⁵

Table VI Solubility of silver chloride in formamide in the presence of added sodium chloride.

15°C		25°C		35°C	
[NaCl] x10 ⁻⁵ (moles/kg)	S x10 ⁵ (moles/kg)	[NaCl] x10 ⁵ (moles/kg)	S x10 ⁵ (moles/kg)	[NaCl] x10 ⁵ (moles/kg)	S x10 ⁵ (moles/kg)
3469.0	6.50	4814.0	13.04	940.2	12.36
2708.0	4.36	4516.0	10.33	741.6	13.12
822.7	2.56	3638.0	10.22	137.4	14.50
618.8	1.99	3365.0	9.15	119.1	15.30
472.2	1.76	1212.0	4.26	61.05	15.40
326.7	1.64	1153.0	4.49	54.94	14.34
254.0	1.77	735.0	3.38	32.64	14.90
104.5	1.79	670.8	3.34	30.53	16.88
30.12	2.40	359.1	3.55	21.37	18.62
14.13	3.35	165.8	3.62	3469.0	15.3
7.218	3.83	156.8	3.62	1781.4	14.1
		72.95	4.18		
		31.55	4.75		
		9.076	7.50		
		3.026	9.05		

7.4. Calorimetric Measurement of the Heat of Precipitation of Silver Chloride.

Table VII Calorimetric measurement data in water at 25°C

Concentration of KCl solution (moles/kg)	Weight of KCl solution (gm.)	Heat of precipitation ΔH° (kcal/mole)
0.4019	2.1115	- 15.66
0.4019	2.6759	- 15.53
0.4019	1.6362	- 15.79
0.2000	2.7599	- 15.70
		Mean - 15.67
		2 σ 0.187

Table VIII Calorimetric measurement data in formamide at 25°C.

Concentration of KCl solution (moles/kg)	Weight of KCl solution (gm.)	Heat of precipitation ΔH° (kcal/mole)
0.337	2.7669	- 10.85
0.337	2.6650	- 11.16
0.337	1.4728	- 11.21
0.390	3.3388	- 11.12
		Mean - 11.08
		2 σ 0.2766

Table IX Calorimetric measurement data in formamide at 15°C

Concentration of KCl solution (moles/kg)	Weight of KCl solution (gm.)	Heat of precipitation ΔH° (kcal/mole)
0.387	0.9452	- 11.18
0.351	1.9280	- 11.06
		Mean - 11.12
		2 σ 0.12

N.B. In every measurement, the concentration of silver nitrate solution was one-tenth of that of potassium chloride solution used.

7.5. E.M.F. Measurements.

Table X The cell Pt; H₂ | HCl(m) in formamide | AgCl | Ag.

Concentration of HCl in formamide (moles/kg)	Time (hours)	emf (volts)	emf at zero time (E) (volts)
0.008165	1.5	0.4489	0.4462
	2.5	0.4505	
	3.0	0.4515	
	3.5	0.4527	
0.01633	1.0	0.4205	0.4092
	2.6	0.4355	
	3.33	0.4406	
	4.0	0.4459	

Cont..

Table X cont..

Concentration of HCl in formamide (moles/kg)	Time (hours)	emf (volts)	emf at zero time (E) (volts)
0.04651	2.33	0.3576	0.3566
	2.57	0.3578	
	3.33	0.3582	
	3.66	0.3583	
0.0669	2.30	0.3386	0.3384
	3.0	0.3385	
	3.5	0.3384	
	4.0	0.3384	
	4.5	0.3384	
	5.0	0.3384	
	5.5	0.3384	

Table XI The cell $\text{cd; Hg}|\text{CdCl}_2|\text{HCl}_{(m)} \text{ in formamide}|\text{H}_2;\text{Pt}$

Concentration of HCl in formamide (moles/kg)	Time (hours)	emf (volts)	emf at zero time (E) (volts)
0.008165	1.5	0.3175	0.3200
	2.5	0.3160	
	3.0	0.3155	
	3.5	0.3145	
0.01633	1.0	0.3405	0.3515
	2.6	0.3255	
	3.33	0.3204	
0.04651	2.33	0.4022	0.4021
	2.60	0.4021	
	3.35	0.4021	
	3.66	0.4019	
0.0669	2.35	0.4218	0.4216
	3.05	0.4218	
	3.55	0.4216	
	4.0	0.4215	
	4.5	0.4214	
	5.0	0.4213	
	5.5	0.4214	

Table XII The cell $\text{Cd; Hg} \mid \text{Cd Cl}_2 \mid \text{HCl}_{(m)} \text{ in formamide} \mid \text{AgCl} \mid \text{Ag}$

Concentration of HCl in formamide (moles/kg)	Time (hours)	emf (volts)	emf average (E) (volts)
0.008165	1.55	0.7690	0.7693
	2.55	0.7692	
	3.05	0.7695	
	3.55	0.7695	
0.01633	1.05	0.7605	0.7606
	2.65	0.7605	
	3.33	0.7608	
0.04651	2.35	0.7598	0.7600
	2.60	0.7600	
	3.35	0.7601	
	3.66	0.7600	
	4.0	0.7600	
	4.5	0.7600	
	5.0	0.7600	

Cont....

Table XII cont...

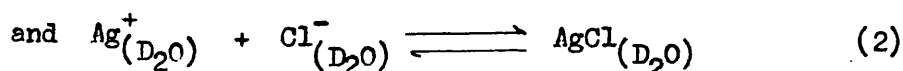
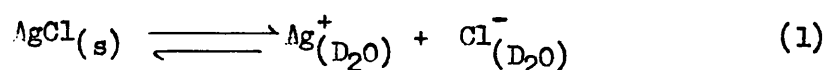
Concentration of HCl in formamide (moles/kg)	Time (hours)	emf (volts)	emf average (E) (volts)
0.0699	2.35	0.7601)	0.7599
	3.05	0.7602)	
	3.55	0.7599)	
	4.05	0.7599)	
	4.6	0.7596)	
	5.5	0.7599)	
	6.0	0.7598)	

N.B. The hydrogen electrode consisted of a pair of platinum foil squares and the bias potential between them was measured before every reading and was found to be between 0.0001 and 0.0002 V.

CHAPTER VIII

Discussion8.1. Solubility of Silver Chloride in Heavy Water.

It can be seen from Chapter IV that at low chloride concentrations the solubility of silver chloride in heavy water can be described by two chemical equilibria :-



The corresponding equilibrium constants are defined by

$$K_s = [\text{Ag}^+] [\text{Cl}^-] \gamma_{\pm}^2 \quad (3)$$

$$\text{and } K_1 = \frac{[\text{AgCl}]}{K_s} \gamma_o \quad (4)$$

Where K_s denotes the solubility product, K_1 denotes the association constant, $[]$ denotes molality, $\gamma_{\pm}$ denotes the mean ionic activity coefficient of the silver and chloride ions, and γ_o denotes the activity coefficient of undissociated silver chloride.

If γ_o is taken as unity, the total silver concentration

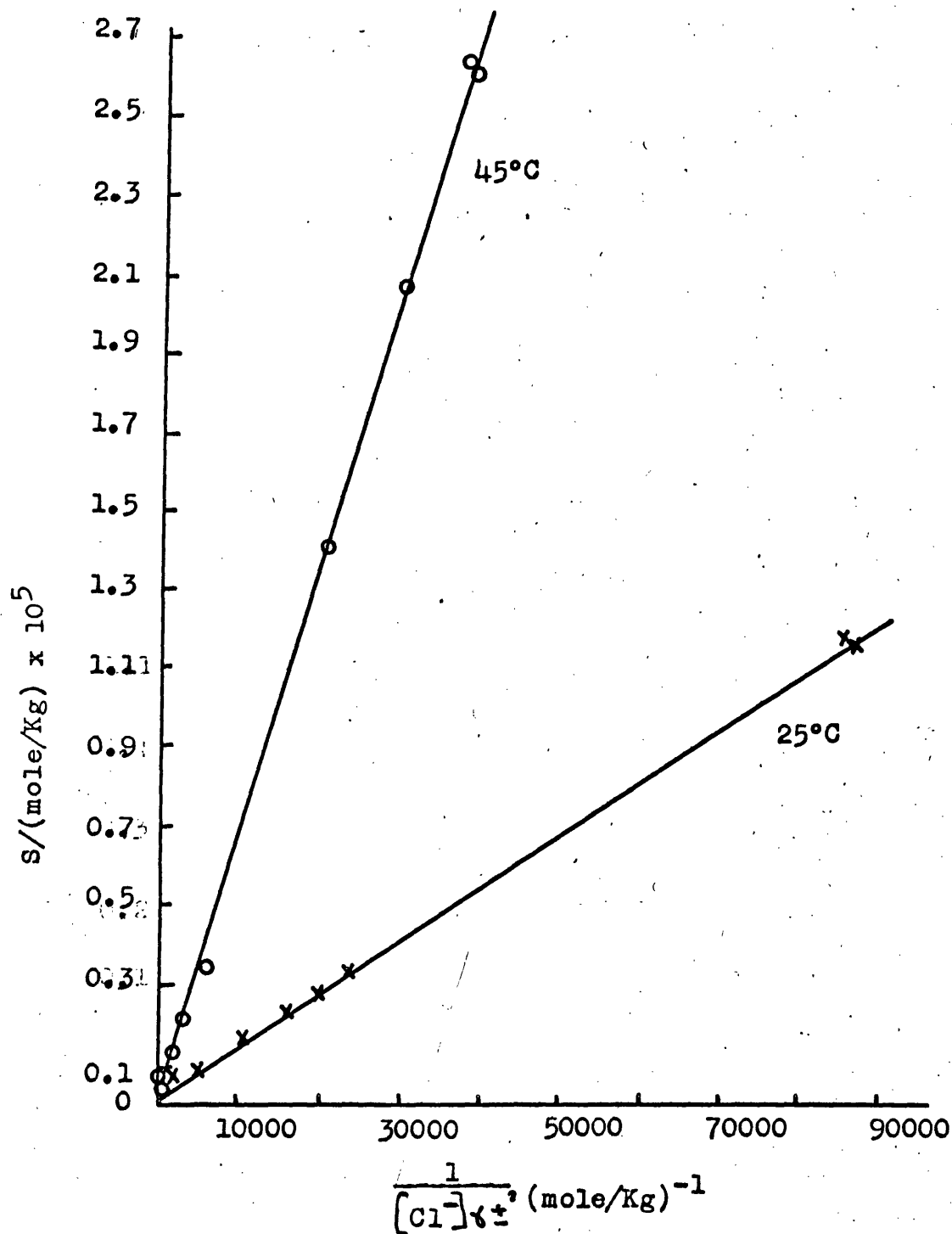


Fig. 8.1. Interpretation of solubility data of silver chloride in D_2O at low chloride molalities at 25.1°C and 45°C.

S is given by

$$\begin{aligned} S &= [\text{Ag}^+] + [\text{AgCl}] \\ &= \frac{K_s}{[\text{Cl}^-] \gamma_{\pm}^2} + K_1 K_s \end{aligned} \quad (5)$$

A plot of S against $\frac{1}{[\text{Cl}^-] \gamma_{\pm}^2}$ should give a straight line of slope K_s and intercept $K_1 K_s$. The intercept $K_1 K_s$ therefore represents the amount of undissociated silver chloride in solution, and the actual chloride ion concentration, $[\text{Cl}^-]$ was corrected for this i.e., $[\text{Cl}^-] = S - K_1 K_s + [\text{NaCl}]$ (6)

The solubility of silver chloride in heavy water at 25.1°C and 45.0°C is shown plotted in this way in Fig.8.1.. All of the appropriate data are recorded in tables I and II.

Table I Solubility of silver chloride in heavy water in moles/kg. at 25.1°C.

$S \times 10^5$ (mole/kg)	$[\text{Cl}^-] \times 10^5$ (mole/kg)	$\gamma_{\pm}$	$\frac{1}{[\text{Cl}^-] \gamma_{\pm}^2}$ (mole/kg) ⁻¹	$-\log [\text{Cl}^-]$
0.47	2340.3	0.8475	59.50	1.63
0.040	47.91	0.9738	2201.0	3.32
0.066	47.93	0.9738	2199.0	3.32
0.084	19.23	0.9828	5382.0	3.71
0.165	9.737	0.9880	10520.0	4.01
0.233	6.326	0.9904	16120.0	4.20 Cont..

Table 1 cont..

$S \times 10^5$ (mole/kg)	$[Cl^-] \times 10^5$ (mole/kg)	$\gamma_{\pm}$	$\frac{1}{[Cl^-] \gamma_{\pm}^2}$ (mole/kg) ⁻¹	$-\log [Cl^-]$
0.281	5.068	0.9912	20080.0	4.29
0.331	4.254	0.9920	23880.0	4.37
1.161 pure	1.161	0.9959	85710.0	4.93
1.176 pure	1.176	0.9959	86830.0	4.93

Table II Solubility of silver chloride in heavy water in moles/kg.
at 45.0°C.

$S \times 10^5$ (moles/kg)	$[Cl^-] \times 10^5$ (mole/kg)	$\gamma_{\pm}$	$\frac{1}{[Cl^-] \gamma_{\pm}^2}$ (mole/kg) ⁻¹	$-\log [Cl^-]$
0.265	2848.0	0.8297	51	1.55
0.065	454.1	0.9226	260	2.34
0.041	353.1	0.9312	346	2.48
0.036	170.9	0.9500	649	2.23
0.141	49.04	0.9726	2155	3.31
0.215	34.96	0.9777	3176	3.45
0.353	17.03	0.9832	6074	3.77
1.41	4.93	0.9910	20550	4.31
2.08	3.34	0.9926	30420	4.47
2.62	2.62	0.9936	38660	4.58
2.64	2.64	0.9936	38300	4.58

Activity coefficients were calculated from the expression,

$$-\log \gamma_{\pm} = \frac{A \sqrt{I}}{1 + \sqrt{I}}, \text{ where } I \text{ is the ionic strength} = \frac{1}{2} \sum M_i Z_i^2.$$

The ionic strength is thus equal to the actual chloride concentration as shown in equation (6). A is the appropriate Debye-Huckel constant for heavy water and was calculated from the expression :-

$$A (\text{mole}^{-\frac{1}{2}} \text{ kg}^{\frac{1}{2}}) = \frac{1.823 \times 10^6 \rho^{\frac{1}{2}}}{(DT)^{3/2}} \quad (7)$$

Where ρ denotes density, D denotes dielectric constant, and T denotes absolute temperature.

At 25.1°C A is 0.5413 $\text{mole}^{-\frac{1}{2}} \text{ kg}^{\frac{1}{2}}$ and at 45.0°C is 0.5622 $\text{mole}^{-\frac{1}{2}} \text{ kg}^{\frac{1}{2}}$.

It is seen from Fig.8.1 that a good straight line is obtained (except for some points at high chloride concentrations where AgCl_2^- complexes are formed). Solubility products K_s and values of K_1 obtained from the slopes and intercepts respectively are given in table III compared with those in water. The statistical errors were obtained from the simple least squares plot and they are expressed as 2σ (σ is the root mean square deviation).

Table III

	25.1°C		45.0°C	
	Water	Heavy Water	Water(3)	Heavy Water
$K_s(\text{mole/kg})^2$	$(1.77 \pm 0.035) \times 10^{-10}$	$(1.33 \pm 0.026) \times 10^{-10}$	(9.234×10^{-10})	$(6.82 \pm 0.05) \times 10^{-10}$
$K_s(\text{mole fraction scale})$	5.73×10^{-14}	5.33×10^{-14}	(3.06×10^{-13})	2.74×10^{-13}
$K_1(\text{mole/kg})^{-1}$	$(1.97 \pm 0.05) \times 10^3$	$(1.1 \pm 0.5) \times 10^3$	(1.4×10^3)	$(3 \pm 3) \times 10^2$

The solubility products are given in mole fraction units as well as in molalities, because although the molar volume of the two solvents are similar¹³, there is about 10% difference in the molecular weights of water and heavy water. A comparison of solubilities in water and heavy water should therefore be based on a given number of moles of solvent. Thus mole fraction units or aquamolality are generally used. The latter unit is defined as the number of moles of solute per 55.51 moles of solvent. Solution of the same aquamolality in the two solvents are at very nearly the same volume concentration¹³⁰. The solubility in heavy water at 25°C is 2.34×10^{-7} whereas that in water at the same temperature is 2.45×10^{-7} both expressed in mole fraction units. It is evident that because the values of these solubilities depend on the concentration unit used, the relationship involving the free energy of solution i.e.,

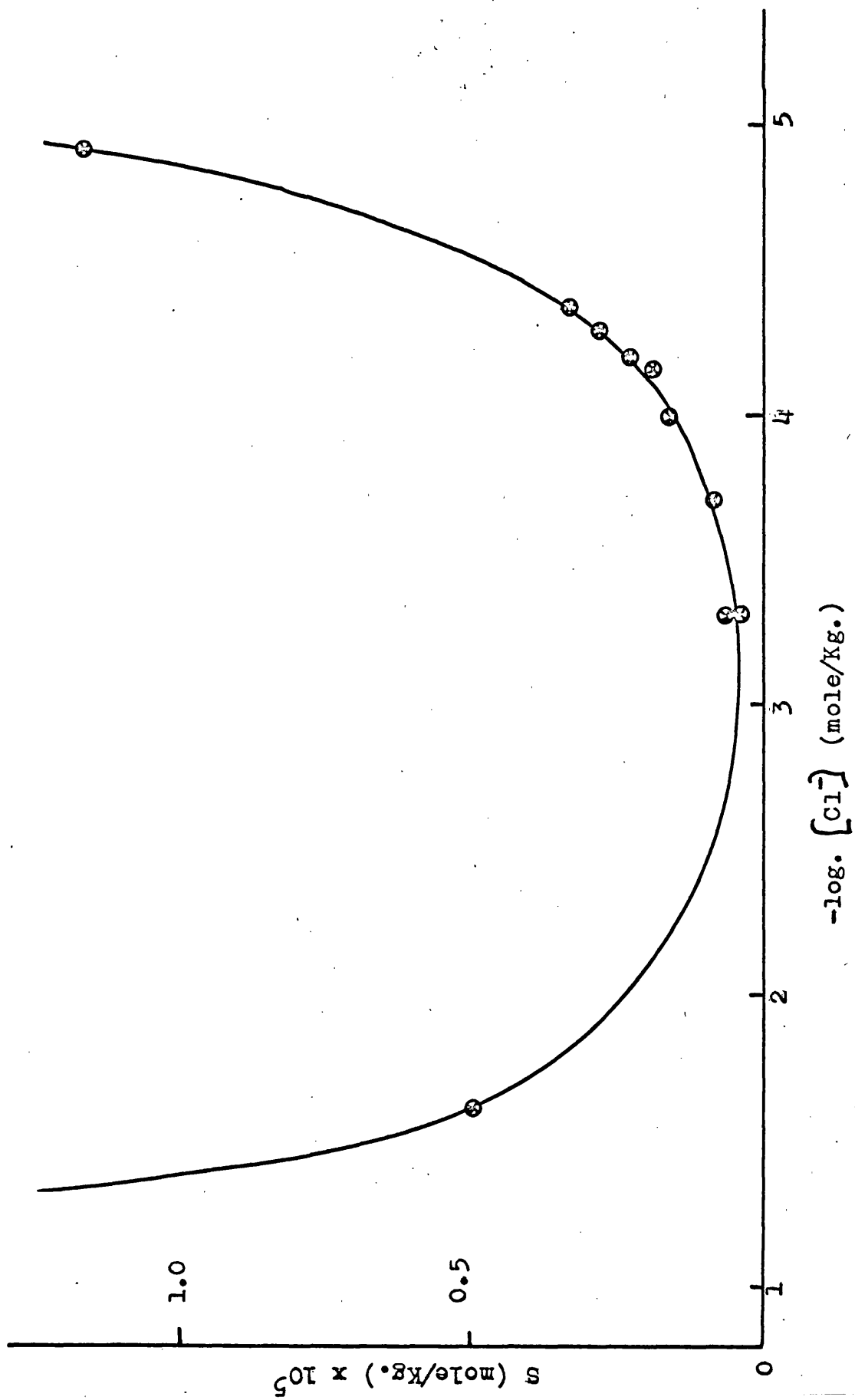


Fig. 8.2. Solubility of silver chloride in sodium chloride solutions in D_2O at $25.1^\circ C$.

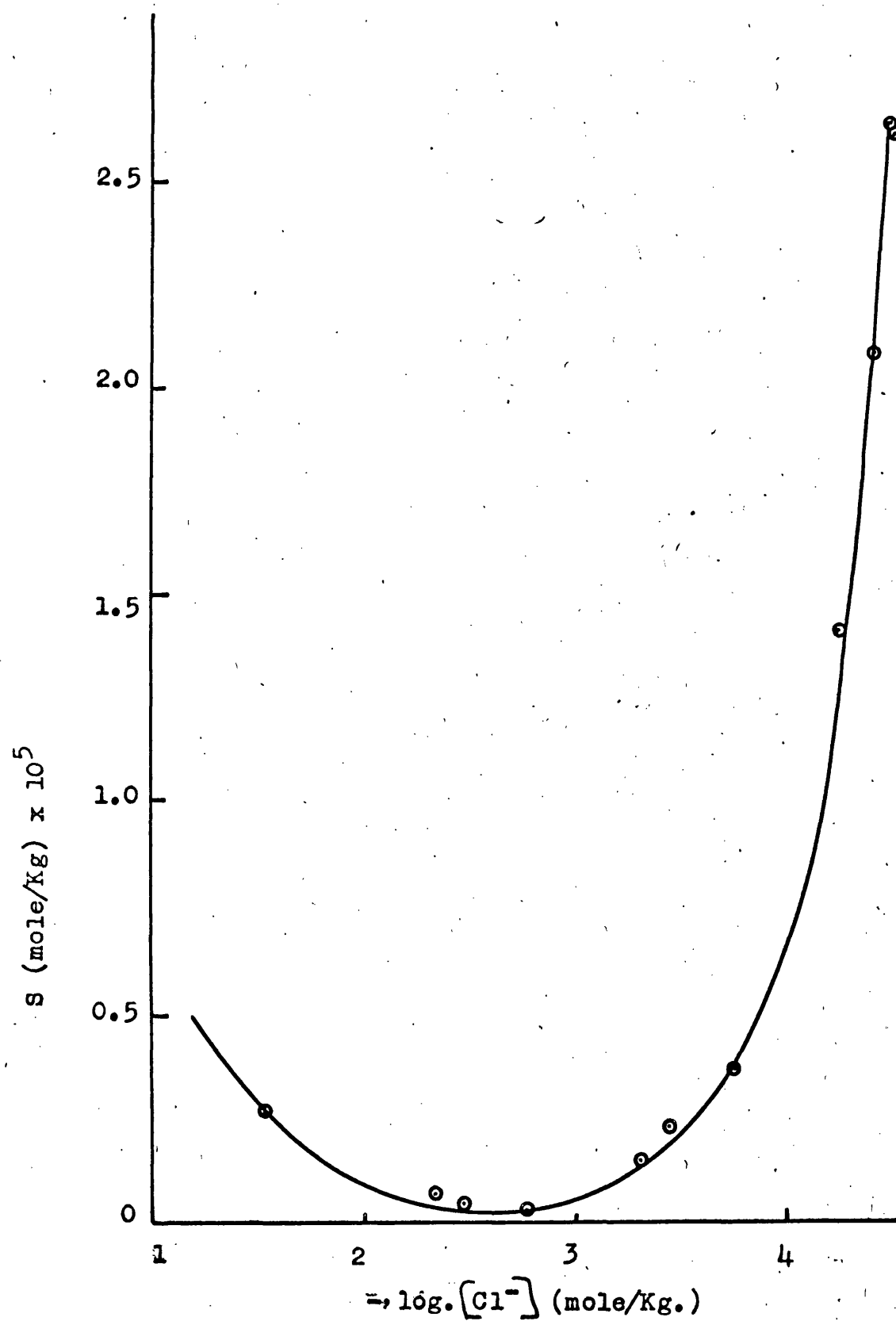


Fig. 8.3. Solubility of silver chloride in sodium chloride solutions in D_2O at $45^\circ C$.

$\Delta G_{\text{solution}}^{\circ} = -RT \ln K_s$ will also vary with the particular unit used in computing them.

The intercepts in Fig.8.1 cannot be determined with high accuracy and large uncertainties have been assigned to the values of K_1 . Since there is excellent agreement between the present data in water and that of Jonte and Martin³ (illustrated in Fig.4.4), the value of K_1 in heavy water at 25.1°C is compared with that in water obtained from this research. The value at 45.0°C in heavy water is compared with that in water derived by extrapolating the solubility data at 15°, 25° and 35°C of Jonte and Martin, since there is no such data at 45°C available in water. It can be seen from table III that at 25.1°C, K_1 in heavy water is about half the value in water and at 45.0°C rather less than half. Silver chloride is thus a stronger electrolyte in heavy water than in water.

The solubilities of silver chloride at 25.1° and 45.0°C as a function of $-\log [\text{Cl}^-]$ are shown graphically in Figs.8.2 and 8.3 respectively. The solubility first decreases with increasing concentration of chloride ions because of the common ion effect, until the minimum solubility as a function of chloride concentration is reached. At this point the effect of complex formation has increased sufficiently to just balance the common ion effect, after which the complex formation tendency becomes

greater and the solubility continues to increase with increasing chloride ion in the solution. Detailed measurements were not made at higher chloride concentrations, owing to the limited time available and, especially, the expense of heavy water.

8.1.1. Temperature dependence.

If the assumption is made that the heat of solution ΔH° of silver chloride in heavy water is constant over the temperature range under investigation (this assumption is of course not strictly true since ΔH° in water varies from 16.026 kcal/mole at 15°C to 15.313 kcal/mole at 35°C)⁹⁶, then ΔH° can be calculated from the relationship,

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (8)$$

The heat of solution calculated from the above formula is 15.5 kcal/mole at 35°C, although the uncertainty is probably at least 0.1 kcal with such a large temperature interval. The heat of transfer ΔH_t of silver chloride from water to heavy water is evaluated from the difference between the heat of solution in water of 15.31 kcal/mole obtained by Owen and Brinkley⁹⁶ from emf measurements at 35°C and the above value in heavy water. It is reasonably consistent, in view of the uncertainties involved, with the value of 0.49 kcal/mole for the heat of transfer at 25°C as calculated by Lange and Martin³⁴ and thus confirms the reliability of the solubility data. The latter workers carried out

extensive measurements of the differences in the integral heats of solution of many electrolytes in heavy water and water. They showed that the differences in isotope effects of two similarly charged ions e.g. Cl^- and Br^- ions are independent of the common oppositely charged ion.

The heat of solution $\Delta H^\ominus$, the heat of transfer $\Delta H_t^\ominus$ and the free energy of transfer $\Delta G_t^\ominus$ for the process:

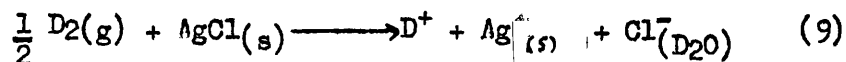
$\text{AgCl}(\text{inH}_2\text{O}) \longrightarrow \text{AgCl}(\text{inD}_2\text{O})$ are tabulated in table IV. The free energy of transfer, $\Delta G_t^\ominus$, of silver chloride at 25.1°C is somewhat smaller than the values for alkali metal halides (110, 140 and 180 calories/mole for lithium chloride, sodium chloride and potassium chloride respectively³¹, and about 210 - 220 calories/chloride ion for the chlorides of lithium, sodium, potassium and cadmium³³). This indicates that silver chloride does not cause significant disturbance in the surrounding water structure. According to Frank and Evans¹³¹, cations smaller or more highly charged than the potassium ion such as lithium, sodium and magnesium ions are net structure formers, while the potassium ion (ionic radius $1.33 \text{ \AA}^\ominus$) is slightly structure breaking. However, the silver ion, whose ionic radius is $1.26 \text{ \AA}^\ominus$, can be regarded as giving a very small contribution to either effect, whereas the chloride ion is slightly structure - breaking (the entropy of solution of potassium and chloride ions in water is -25.3 and $26.6 \text{ cal deg}^{-1} \text{ mole}^{-1}$ respectively)¹³²; as a result silver chloride

will adapt itself properly into the surrounding water structures and cause only slight differences in the structure of water and heavy water. A small value of the free energy of transfer is therefore observed in this case.

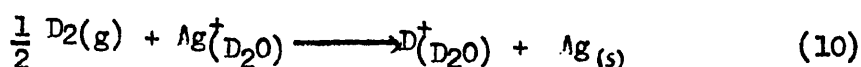
Table IV $\Delta G_t^\ominus$, $\Delta H_t^\ominus$ for the process $\text{AgCl}(\overline{\text{H}_2\text{O}}) \rightarrow \text{AgCl}(\text{D}_2\text{O})$
and $\Delta H^\ominus$

	25.1°C	35.0°C	45.0°C
Free energy of transfer $\Delta G_t^\ominus/\text{cal}$ (mole fraction scale)	47		37
Heat of transfer, $\Delta H_t^\ominus/\text{kcal}$		0.2	
Heat of solution $\Delta H^\ominus$ (kcal/mole)		15.5	

The cell $\text{Pt}; \text{D}_2(\text{g}) | \text{DCl in D}_2\text{O} | \text{AgCl} | \text{Ag}$ has been studied by Gary, Bates and Robinson²⁷ and also by Lietzke and Stoughton²⁸ the results of whom differ slightly. The thermodynamic data of Gary, Bates and Robinson for the cell reaction



are combined with equation (1) to yield the following equation



Hence the values of $\Delta G^\ominus$ and $\Delta H^\ominus$ for reaction (10) can be evaluated from the sum of the corresponding quantities for

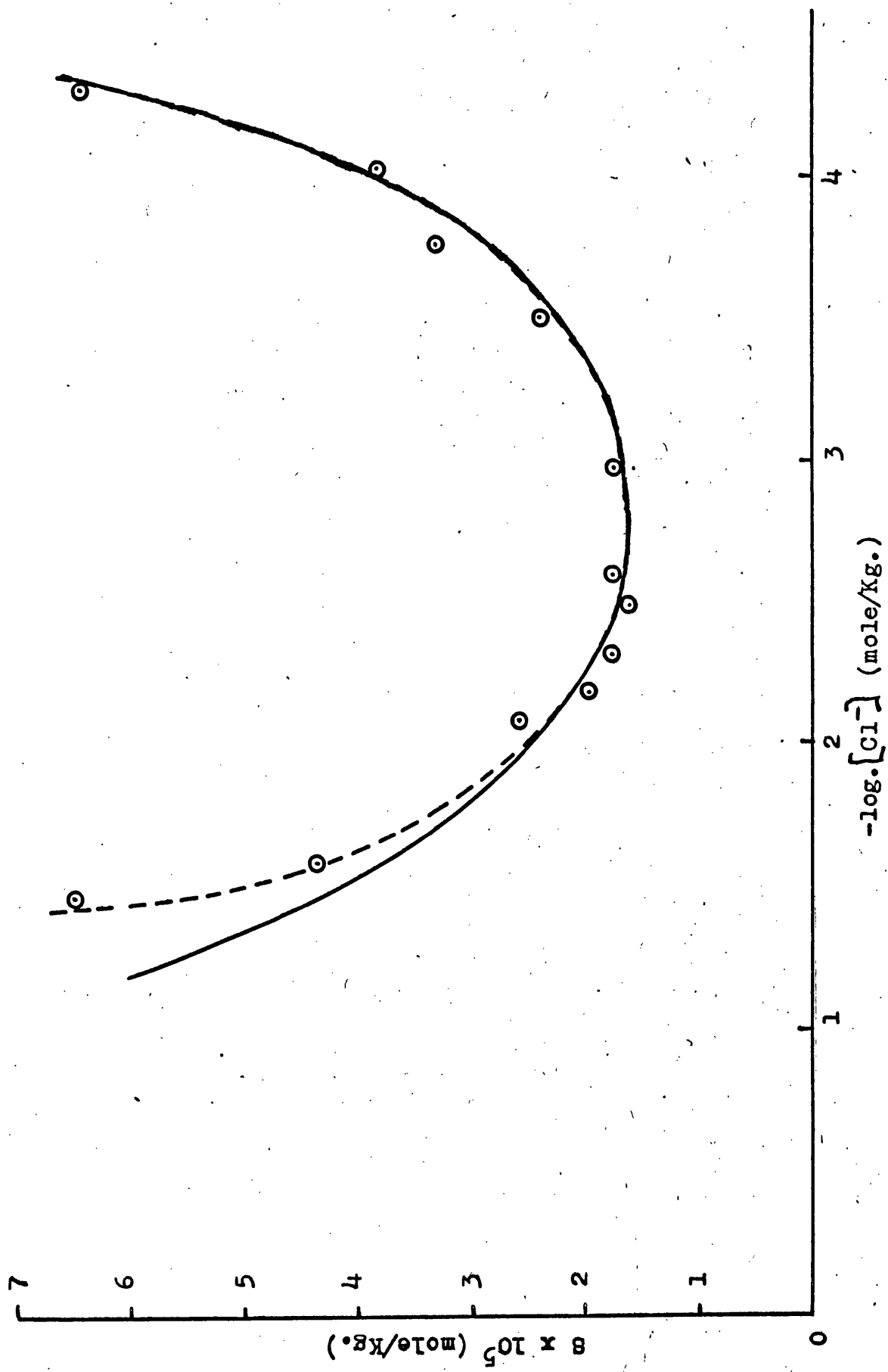


Fig. 8.4. Solubility of silver chloride in sodium chloride solutions in formamide at 15°C

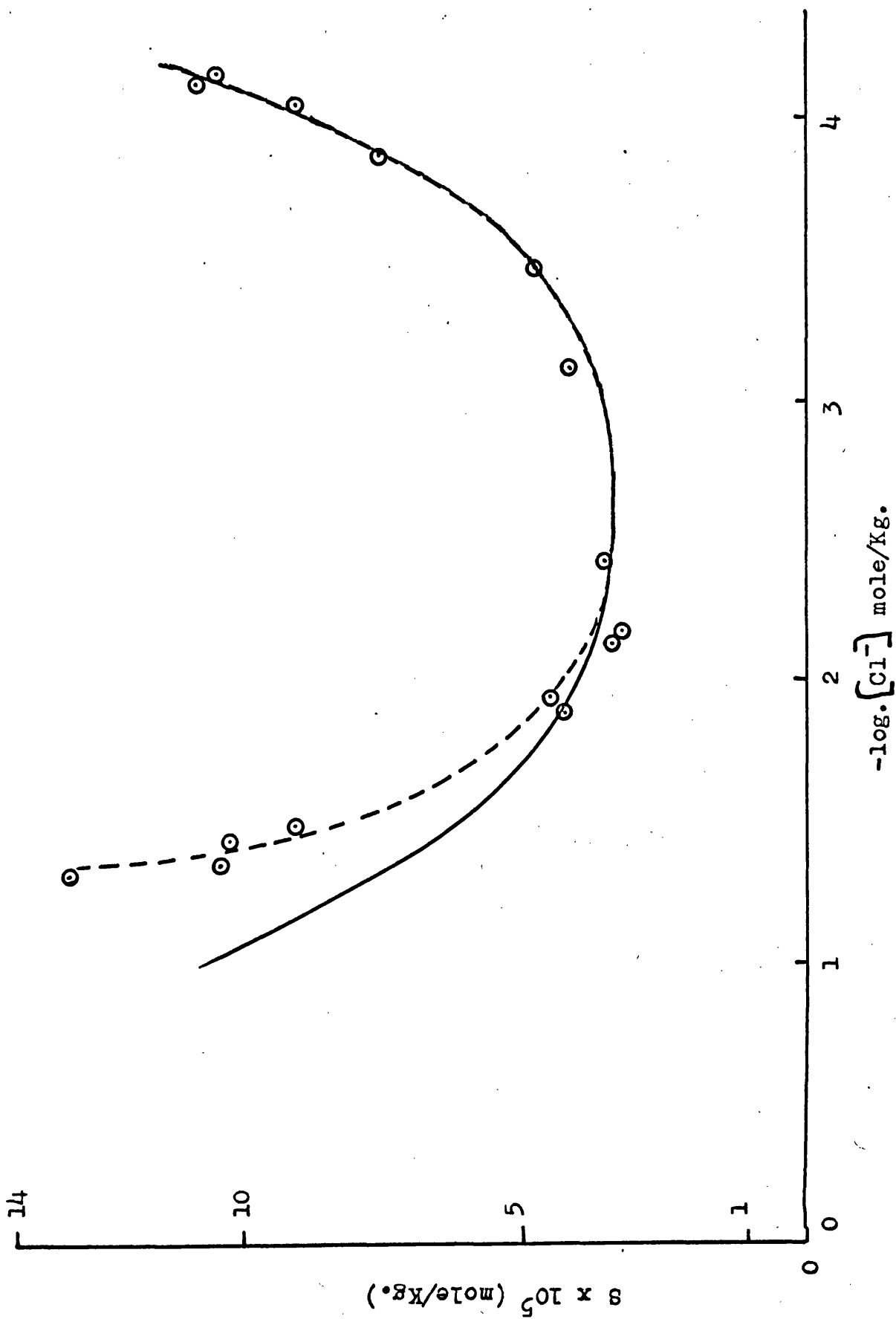


Fig. 8.5. Solubility of silver chloride in sodium chloride solutions in formamide at 25°C.

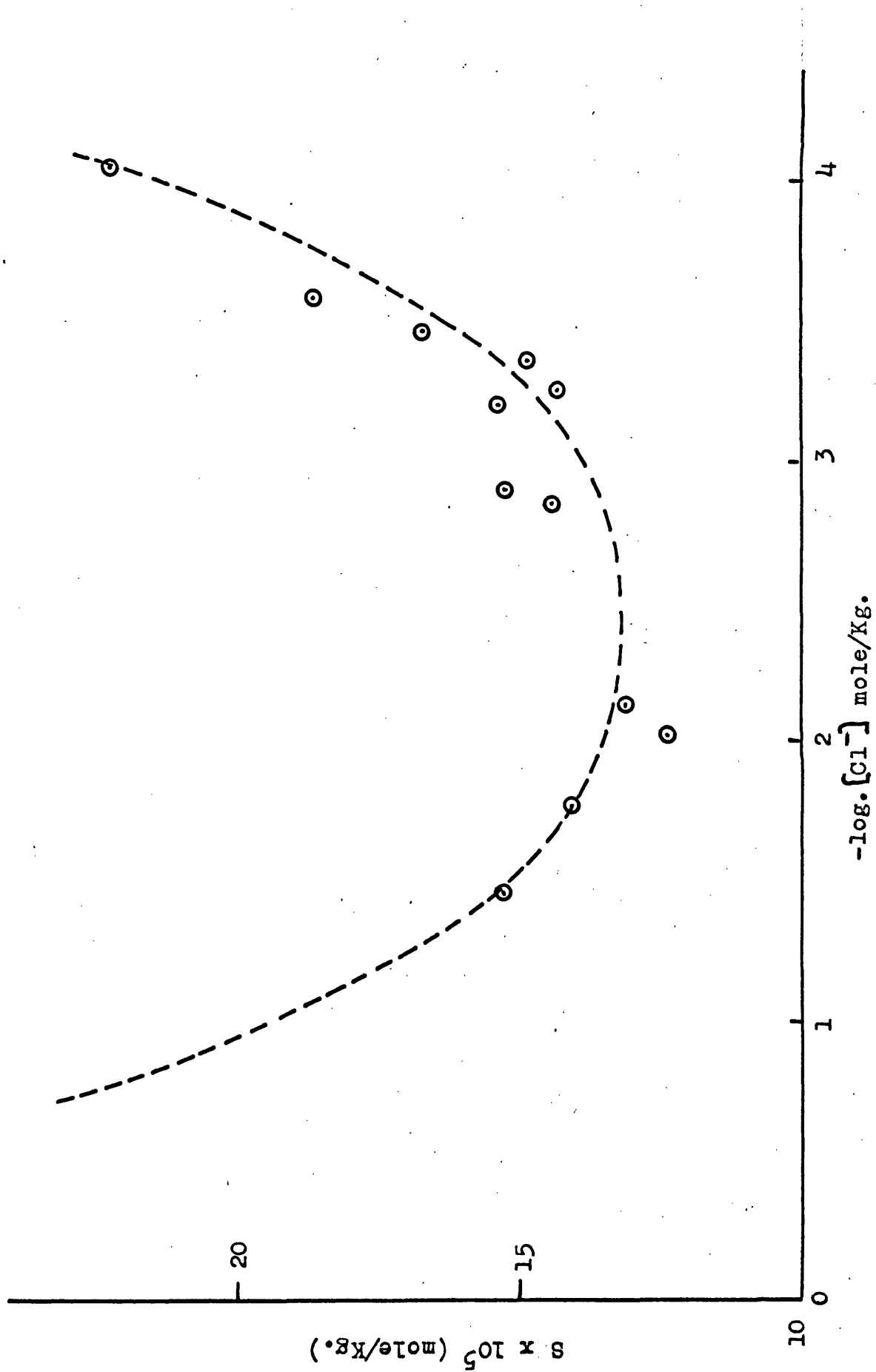


Fig. 8.6. Solubility of silver chloride in sodium chloride solutions in formamide at 35°C.

equation (1) and (9). The values of $\Delta G^\ominus$ are -18.38 and -17.90 kcal at 25.1° and 45.°C respectively, while $\Delta H^\ominus$, calculated from the temperature dependence of $\Delta G^\ominus$ is -25.6 kcal. The values of $\Delta G^\ominus$ are of course related to the standard potential, $E_{Ag}^\ominus$ of the silver electrode on the deuterium scale by $\Delta G^\ominus = -E_{Ag}^\ominus F$. It may be noted that in this case the values are independent of the choice of concentration scale.

8.2. Solubility and Related Studies of Silver Chloride in Formamide.

Although the solubilities of silver chloride in formamide are much higher than in water, the general form of the solubility curve in Figs 8.4, 8.5 and 8.6 shows the same decrease in solubility followed by an increase, as the chloride concentration increases. Hence it appears that complex formation occurs in formamide, and the assumption can then be made that at low chloride concentrations, the same equilibria as in aqueous solution (equations 1 and 2) apply. Since the amount of undissociated silver chloride in formamide is so high, it was necessary to use a successive approximation treatment in order to calculate the actual chloride ion concentration $[Cl^-]$. An approximate value of the amount of undissociated silver chloride in solution was obtained initially, using the total chloride in solution in the plot of S against $\frac{1}{[Cl^-]^2}$. The approximate value

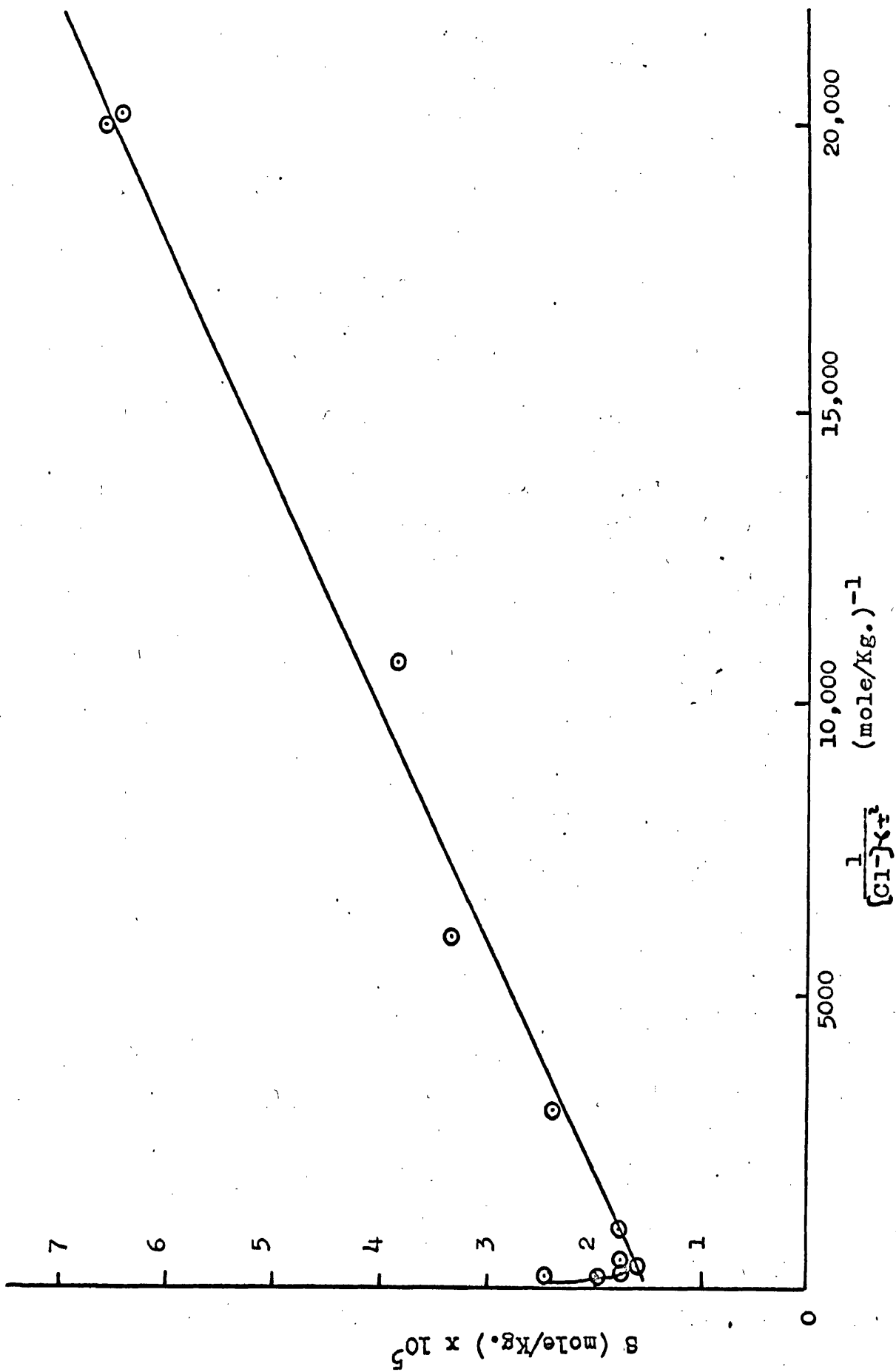


Fig.8.7. Interpretation of solubility data of silver chloride in formamide at low chloride molalities at 15°C.

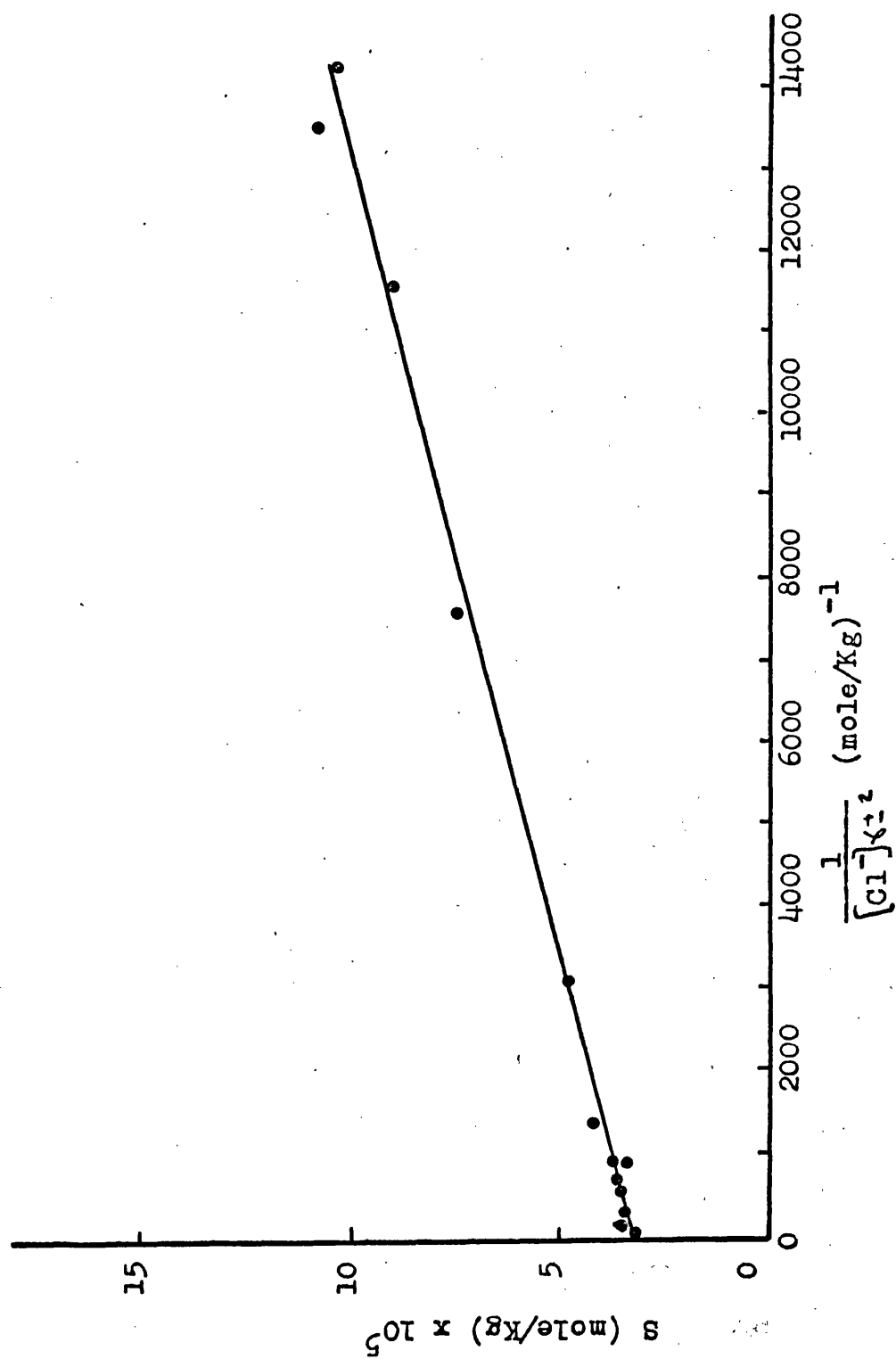


Fig. 8.8. Interpretation of solubility data of silver chloride in formamide at low chloride molalities at 25°C.

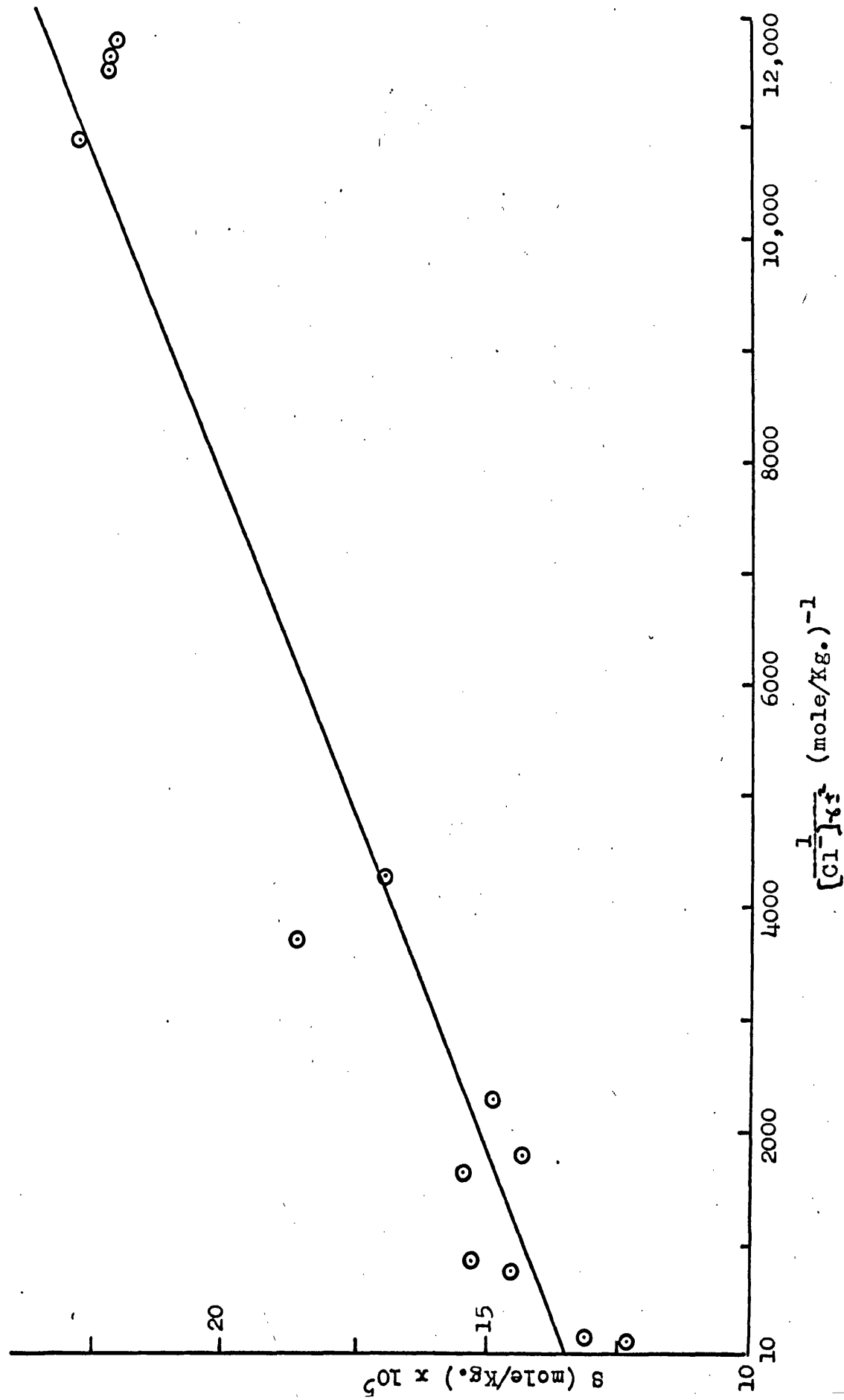


Fig. 8.9. Interpretation of solubility data of silver chloride in formamide at low chloride molalities at 35°C.

was then used to calculate the actual chloride ion concentration $[Cl^-]$ more accurately, using equation (6). This procedure was repeated until a constant value of the intercept of the graph was obtained. Three cycles of this treatment were needed at 15° and 25°C whereas four cycles were carried out at 35°C. The least squares method was applied in fitting the straight line through the points. Tables V, VI and VII show the corrected values of the relevant quantities of S against $\frac{1}{[Cl^-]^2}$. Figs. 8.7, 8.8, and 8.9, show the appropriate plots, from which it can be seen that the experimental scatter is markedly higher, particularly at 35°C, than in water or heavy water. This may be due to partial thermal decomposition of formamide at 35°C, since such behaviour was not observed to the same extent at the lower temperatures. This possibility is discussed in section 8.2.2.

The values of the intercept (K_1K_s) and the slope (K_s), and the association constant K_1 are given in Table VIII in comparison with those in water. The results are quoted together with the statistical errors obtained from the simple least squares plots.

Table V Corrected solubility data of silver chloride in
formamide at 15°C.

$S \times 10^5$ (mole/kg)	$[Cl^-] \times 10^5$ (mole/kg)	$\gamma_{\pm}$	$\frac{1}{[Cl^-] \gamma_{\pm}^2}$ (mole/kg) ⁻¹
6.505	4.955	0.9947	20010
6.43	4.88	0.9947	20200
3.83	9.45	0.9929	10740
3.35	16.88	0.9907	6039
2.40	30.92	0.9872	3318
1.79	104.7	0.9766	1002
1.77	254.2	0.9661	421
1.64	326.7	0.9616	331
1.76	472.4	0.9526	233
1.99	619.2	0.9464	180

Table VI Corrected solubility data of silver chloride in
formamide at 25°C.

$S \times 10^5$ (mole/kg)	$[Cl^-] \times 10^5$ (mole/kg)	$\gamma_{\pm}$	$\frac{1}{[Cl^-] \gamma_{\pm}^2}$ (mole/kg) ⁻¹
10.8	7.5	0.9936	13510
10.4	7.1	0.9939	14260
9.05	8.78	0.9929	11550
7.50	13.28	0.9915	7660
4.75	33.0	0.9868	3113 Cont..

Table VI cont.

$S \times 10^5$ (mole/kg)	$[Cl^-] \times 10^5$ (mole/kg)	$\gamma_{\pm}$	$\frac{1}{[Cl^-] \gamma_{\pm}^2} (\text{mole/kg})^{-1}$
4.18	78.83	0.9802	1407
3.68	115.0	0.9757	913
3.62	157.0	0.9727	673
3.62	166.0	0.9709	639
3.55	359.0	0.9594	302
3.34	671.0	0.9462	166
3.38	735.0	0.9421	153

Table VII Corrected solubility data of silver chloride in
formamide at 35°C

$S \times 10^5$ (mole/kg)	$[Cl^-] \times 10^5$ (mole/kg)	$\gamma_{\pm}$	$\frac{1}{[Cl^-] \gamma_{\pm}^2} (\text{mole/kg})^{-1}$
22.12	8.62	0.9931	11760
22.28	8.78	0.9931	11550
22.23	8.73	0.9931	11610
22.81	9.31	0.9929	10900
18.62	29.49	0.9880	3866
16.88	33.91	0.9865	3032
14.90	44.04	0.9846	2341
14.34	55.78	0.9828	1856 cont..

Table VII cont.

$S \times 10^5$ (mole/kg)	$[Cl^-] \times 10^5$ (mole/kg)	$\gamma_{\pm}$	$\frac{1}{[Cl^-] \gamma_{\pm}^2} (\text{mole/kg})^{-1}$
15.40	62.95	0.9814	1648
15.30	120.9	0.9750	870
14.50	138.4	0.9732	763
13.12	741.2	0.9416	152
12.36	939.1	0.9354	122

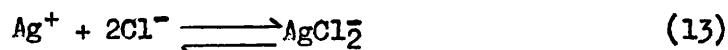
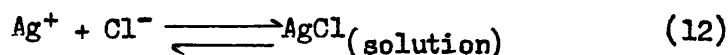
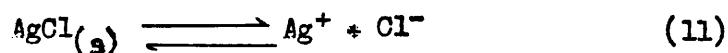
Values of K_s in $(\text{mole/kg})^2$, K_s in mole fraction scale,
 Table VIII K_1 in $(\text{mole/kg})^{-1}$ and $K_1 K_s$ in (mole/kg) .

	15°C		25°C		35°C	
	Formamide	Water	Formamide	Water	Formamide	Water
K_s	$(2.5 \pm 0.22) \times 10^{-9}$	7.02×10^{-11}	$(5.2 \pm 0.3) \times 10^{-9}$	1.77×10^{-10}	$(8.5 \pm 2) \times 10^{-9}$	4.15×10^{-10}
K_s (mole fraction scale)	5.062×10^{-12}	2.28×10^{-14}	10.53×10^{-12}	5.73×10^{-14}	1.72×10^{-11}	13.48×10^{-14}
K_1	$(6.2 \pm 0.7) \times 10^3$	2.287×10^3	$(6.4 \pm 0.8) \times 10^3$	1.97×10^3	$(1.5 \pm 0.5) \times 10^4$	1.688×10^3
$K_1 K_s$	$1.55 \pm 0.18) \times 10^{-5}$	1.6×10^{-7}	$(3.3 \pm 0.3) \times 10^{-5}$	3.0×10^{-7}	$(13.5 \pm 0.7) \times 10^{-5}$	7.0×10^7

K_1 is much greater in formamide than in water at all three temperatures. However, the very large amount of undissociated silver chloride in formamide is due to the much enhanced solubility of silver chloride in formamide, as well as to the larger values of K_1 .

The solubility product of silver chloride at each temperature is considerably higher than in water. Various workers have measured the solubilities of soluble salts in formamide^{89,90,91} and most electrolytes, except the halides and nitrate of lead, are less soluble in formamide than in water. Povarov and co-workers⁹¹ appear to be the only group of workers to measure the solubility of silver chloride in formamide and their results are higher than those obtained from this study. Little use can be made of their data since their measurements were made at room temperature ($18 \pm 2^\circ\text{C}$) and the few measurements they made in the presence of sodium chloride were all at rather high chloride ion concentrations. The treatment of their data is also not made clear.

If the high complex AgCl_2^- is formed at higher chloride concentrations, the chemical equilibria in the system can be represented by



The corresponding equilibrium constants of equation (11), (12) and (13) are

$$K_s = [\text{Ag}^+] [\text{Cl}^-] \gamma_{\pm}^2 \quad (14)$$

$$K_1 = \frac{[\text{AgCl}]}{K_s} \quad (15)$$

and

$$K_2 = \frac{[\text{AgCl}_2^-]}{[\text{Ag}^+] [\text{Cl}^-]^2 \gamma_{\pm}^2} \quad (16)$$

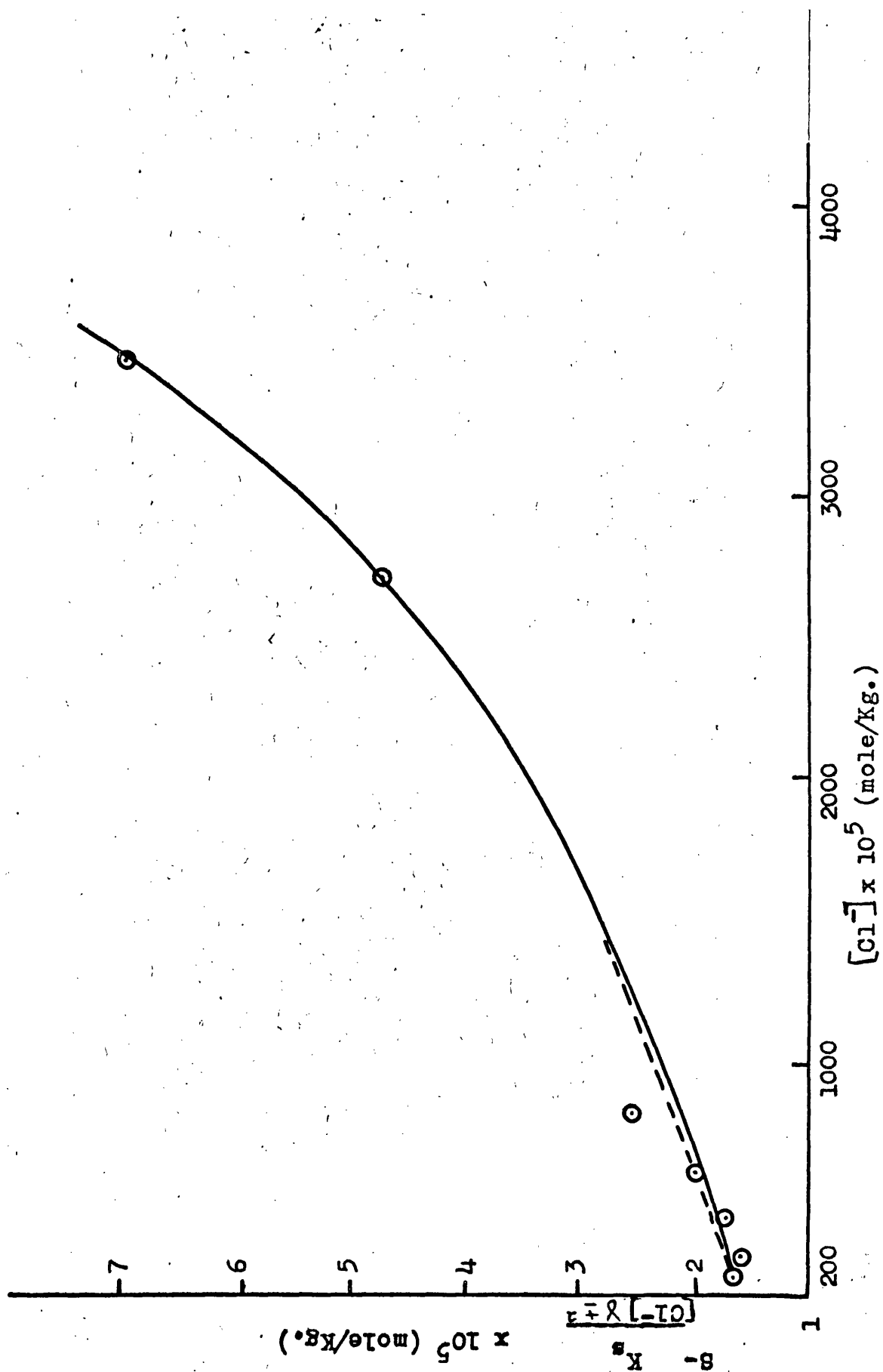


Fig. 8.10. Interpretation of solubility data of silver chloride in formamide at higher chloride molalities at 15°C.

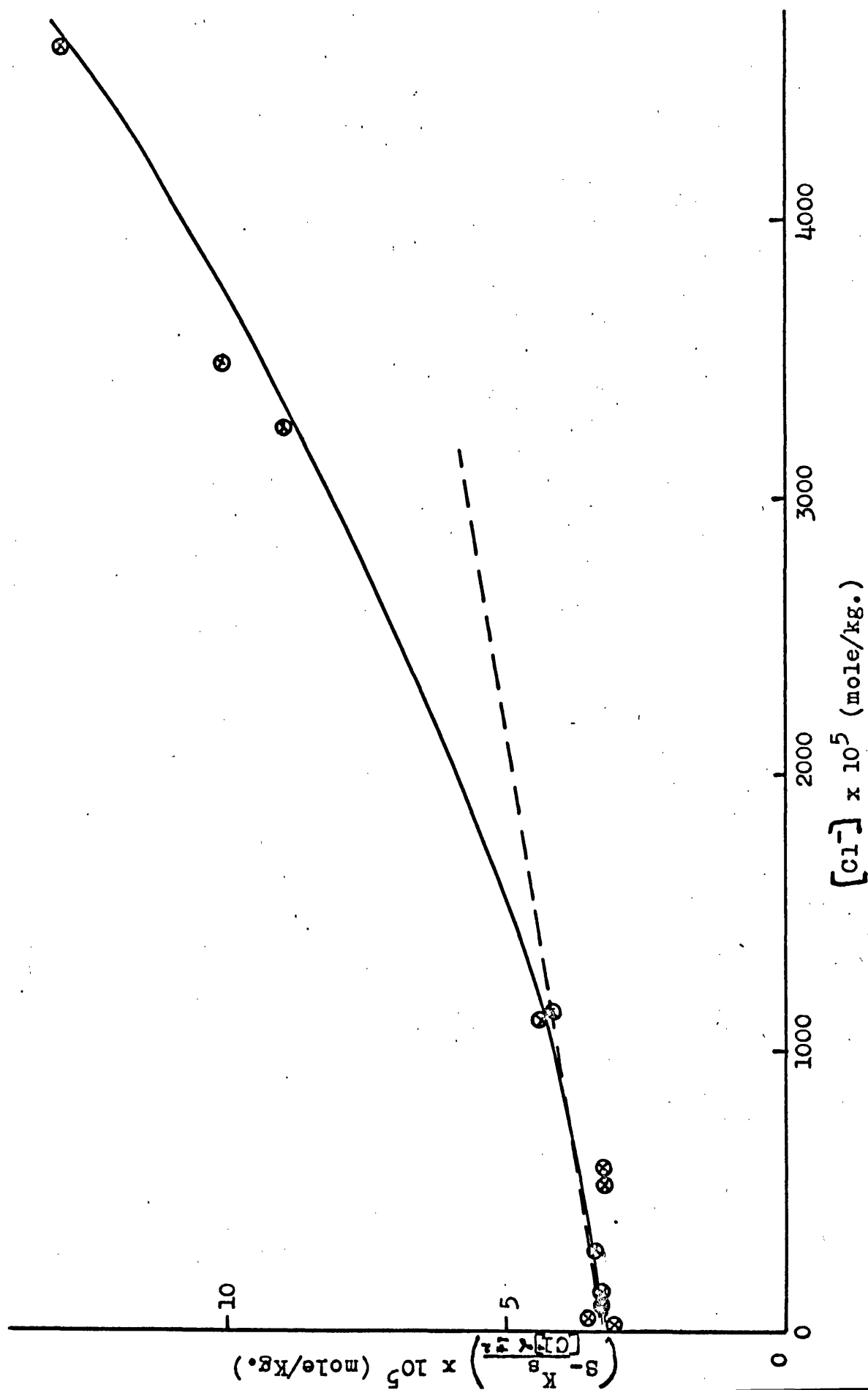


Fig. 8.11. Interpretation of solubility data of silver chloride in formamide at high chloride molalities at 25°C.

Assuming that the activity coefficients of singly charged ions are the same, and that the activity coefficient of silver chloride in solution is unity.

The total silver concentration, S , measured as solubility is represented by

$$S = [Ag^+] + [AgCl] + [AgCl_2^-]$$

$$\text{or } S = \frac{K_s}{[Cl^-] \gamma_{\pm}^2} + K_1 K_s + K_2 K_s [Cl^-] \quad (17)$$

$$\text{therefore } S - \frac{K_s}{[Cl^-] \gamma_{\pm}^2} = K_1 K_s + K_2 K_s [Cl^-] \quad (18)$$

Provided complexes higher than $AgCl_2^-$ are not present, the plot of $S - \frac{K_s}{[Cl^-] \gamma_{\pm}^2}$ against $[Cl^-]$ should give a straight line

with $K_1 K_s$ as the intercept and $K_2 K_s$ as the slope. From the plots of the data at 15° and 25°C in Fig 8.10, 8.11, the points fall on a slight curve. This suggests that the solubility depends (at least in part) upon the concentration of chloride raised to a power higher than unity. In other words complexes higher than $AgCl_2^-$ are present. The data plotted in Fig 8.10, and 8.11, expressed in moles/kg are given in table IX.

Table IX

15°C				25°C			
$S \times 10^5$	$\frac{K_s}{[Cl^-] \gamma_{\pm}^2} \times 10^5$	$\frac{(S-K_s)}{([Cl^-] \gamma_{\pm}^2)} \times 10^5$	$[Cl^-] \times 10^5$	$S \times 10^5$	$\frac{K_s}{[Cl^-] \gamma_{\pm}^2} \times 10^5$	$\frac{(S-K_s)}{([Cl^-] \gamma_{\pm}^2)} \times 10^5$	$[Cl^-] \times 10^5$
6.50	0.0091	6.49	3474.0	13.04	0.0140	13.026	4824
4.36	0.0114	4.35	2711.0	10.22	0.0373	10.18	3645
2.56	0.0344	2.53	823.7	9.15	0.0192	9.131	3371
1.99	0.0451	1.94	619.0	4.26	0.0490	4.211	1213
1.76	0.0583	1.70	472.4	4.49	0.0513	4.438	1154
1.64	0.0827	1.56	326.7	3.55	0.0618	3.488	359
1.77	0.1054	1.66	254.2	3.62	0.3281	3.292	166
				3.62	0.3456	3.27	157
				4.18	0.7222	3.46	74
				4.75	1.59	3.16	33

Straight lines were drawn based on the few points in the low chloride ion concentration region at both 15°C and 25°C and estimated values of K_2 were obtained from the slopes ($K_2 K_s$). No estimate was made at 35°C owing to the large uncertainties in the solubility data. The estimate K_2 at 15°C is $3.3 \times 10^5 (\text{mole/kg})^{-2}$ and at 25°C is $1.7 \times 10^5 (\text{mole/kg})^{-2}$. However the uncertainties are large and it is not believed that any significance can be attached to the temperature dependence of K_2 (see section 8.2.2.).

Hence the solubility data at not too high chloride

concentrations can be represented at 15° and 25°C by the equations

$$S \text{ (mole/kg)} = \frac{2.5 \times 10^{-9}}{[Cl^-] \gamma_{\pm}^2} + 1.55 \times 10^{-5} + 8.3 [Cl^-] \times 10^{-4} \quad (19)$$

at 15°C and,

$$S \text{ (mole/kg)} = \frac{5.2 \times 10^{-9}}{[Cl^-] \gamma_{\pm}^2} + 3.3 \times 10^{-5} + 8.5 [Cl^-] \times 10^{-4} \quad (20)$$

at 25°C. The continuous curves drawn in Figs 8.4 and 8.5 are calculated from equations (19) and (20). As expected the curves diverge from the experimental values (dotted line) at the high chloride concentrations, although the fit at 15°C is rather better than at 25°C. It does not seem sensible to extend the analysis to 35°C and the dotted curve drawn through the points in Fig. 8.6. has no mathematical significance.

8.2.1. Correlation with calorimetric data

When the solubility product is measured over a range of temperatures, the standard heat of solution ΔH° can be computed using equation (8) or its alternative form,

$$\log K_s = -\frac{\Delta H^\circ}{2.303RT} + C \quad (21)$$

Hence, if $\log K_s$ is plotted against $\frac{1}{T}$, a straight line with slope $-\frac{\Delta H^\circ}{2.303R}$ should be obtained from which the standard heat

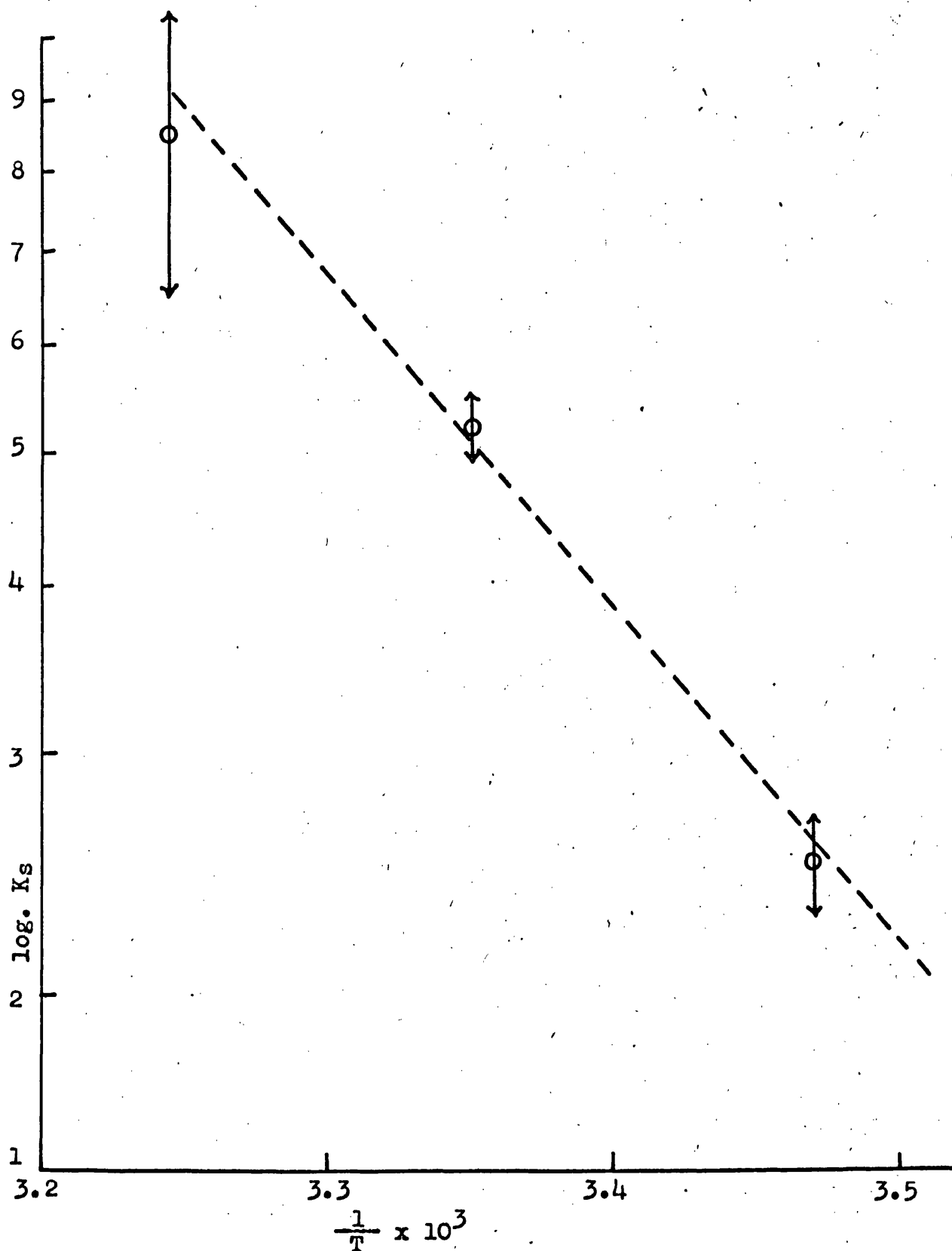


Fig. 8.12. Temperature dependence of solubility Product (K_s)

of solution ΔH° can be derived. In practice, this relationship can give a slight deviation from linearity since the heat of solution over a temperature range may be not quite constant.

The plot of $\log K_s$ against $\frac{1}{T}$ is shown in Fig. 8.12, from which it is seen that a slight curve is obtained. It is worth noting that a plot of $\log K_s$ against $\frac{1}{T}$ for silver chloride in water is also slightly curved in the same sense. However, it is possible to draw a straight line which falls well within the standard deviations quoted in table VIII.

The standard heat of solution of silver chloride in formamide, measured calorimetrically is 11.1 kcal/mole at both 15° and 25°C. The straight line in Fig. 8.12 has been deliberately drawn to correspond with this value, and is in satisfactory agreement with the experimental points. This serves to confirm the overall reliability of the solubility data, despite the rather large uncertainties in the values of K_s and K_1 . The magnitude of the heat of solution is also near to that predicted by the van Eck theory of ionic solvation⁸⁷ as discussed in Chapter III. A consequence of his theory is that for salts with the same anion the differences between the standard heats of solution in two solvents should be constant and independent of the cation. Somsen and Coops⁸⁵ have shown experimentally that the difference in the heat of solution of the alkali metal halides (except for lithium) in water and formamide is consistently around the value of + 3.3 kcal/mole. On the basis of this theory and on the heat of solution of silver chloride in

water at 25°C (+ 15.74 kcal/mole)¹²⁵, the predicted heat of solution of silver chloride in formamide is $(15.74 - 3.3) = 12.4$ kcal/mole. Allowance, of course has to be made for the difference in ionic configuration of silver ion and alkali metal ions. This theory is therefore useful as a guide to the magnitude of the standard heat of solution of silver chloride in formamide if not to its precise value. In table X, the heat of solution obtained from the calorimetric measurements and the predicted value of the heat of solution by the van Eck theory are listed.

Table X

Temperature °C	Heat of solution from calorimetric measurements (kcal/mole)	Predicted heat of solution (kcal/mole)
15	11.12 ± 0.12	12.4
25	11.08 ± 0.28	

The heat of the reaction $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl}(\text{solution})$ can be determined from the temperature dependence of the values of K_1 , if these values are sufficiently reliable. However, a plot of $\log K_1$ against $\frac{1}{T}$ is nowhere near linear. The errors in K_1 are large, particularly at 35°C since K_1 depends on both the slope

and the intercept. The values of K_1 suggest that undissociated silver chloride may be formed endothermically from its ions. This contrasts with water where undissociated silver chloride is formed exothermically³ but nevertheless seems reasonable since the silver ion and chloride ion are more strongly solvated in formamide than in water.

8.2.2. Uncertainties in experimental data in formamide

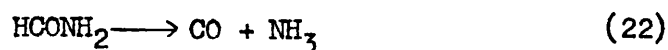
It is evident from the results that despite the higher solubility in formamide the uncertainty in all the measurements is considerably greater than in water or heavy water. The scatter in the results is greater than would be expected from a consideration of errors due to counting and the volumetric and gravimetric techniques involved. This is particularly true at 35°C, and it is believed that the increased scatter is partially due to thermal decomposition of formamide. In view of this it is necessary to consider how reliable the solubility measurements in formamide are.

There are three possibilities which need to be considered :-

1. It has been pointed out earlier that a solution of silver nitrate in formamide rapidly darkens, unless stabilised, with the reduction of silver ion to silver. It is therefore reasonable to suppose that the silver ions in the saturated silver chloride solution may be similarly reduced. However,

with the very dilute solutions used, the reduction, if it occurs, must be very slow. No trace of darkening was found with samples left in the thermostat bath 5-7 days, although if left for much longer periods some samples, at 35°C only, became slightly tinged and gave very high results, which were disregarded. Hence, provided the samples are not left too long in the thermostat the results appear to be satisfactory.

2. Formamide will decompose on heating in two ways, of which one is



The presence of traces of ammonia would probably cause the formation of complexes of the type $\text{Ag}(\text{NH}_3)_2^+$, which would result in the solubilities being too high.

3. The alternative way in which formamide may decompose is



Since silver cyanide is less soluble than silver chloride in water, the possibility exists that cyanide ions could be controlling the solubility of silver chloride in formamide. In order to test this, 2 measurements of the solubility of silver cyanide in formamide were made at 25°C; the results obtained are 1.28×10^{-5} mole/kg and 1.32×10^{-5} mole/kg. Hence silver cyanide is more soluble than silver chloride in formamide and it seems unlikely that the presence of cyanide ions could control the

solubility.

In order to test the reproducibility at 35°C, 4 measurements of the solubility of silver chloride in pure formamide were made. The samples were left in the thermostat bath for varying length of time, between 5 and 10 days and the results all lie in the range 22.1×10^{-5} mole/kg to 22.8×10^{-5} mole/kg (see table VII). However, a fifth sample, treated identically to the others and kept in the thermostat bath for 10 days became tinged brown, and gave a solubility of roughly twice the above figures.

It does seem possible that a systematic error could make the results at 35°C uniformly high, and might cause the intercept to be too large, without altering the slope of the plot on Fig. 8.9 much. In general the reproducibility obtained, together with the satisfactory temperature dependence of the solubility products, suggest that the uncertainties although rather large, are not too serious.

8.2.3. Concluding remarks

There is considerable evidence (e.g. from transference number, conductance measurements and heats of solution) that ion - solvent interactions in water and formamide are different. Formamide seems to be held more firmly by the ions than water; and this greater extent of solvation may be responsible for a higher solubility of silver chloride in formamide than in water.

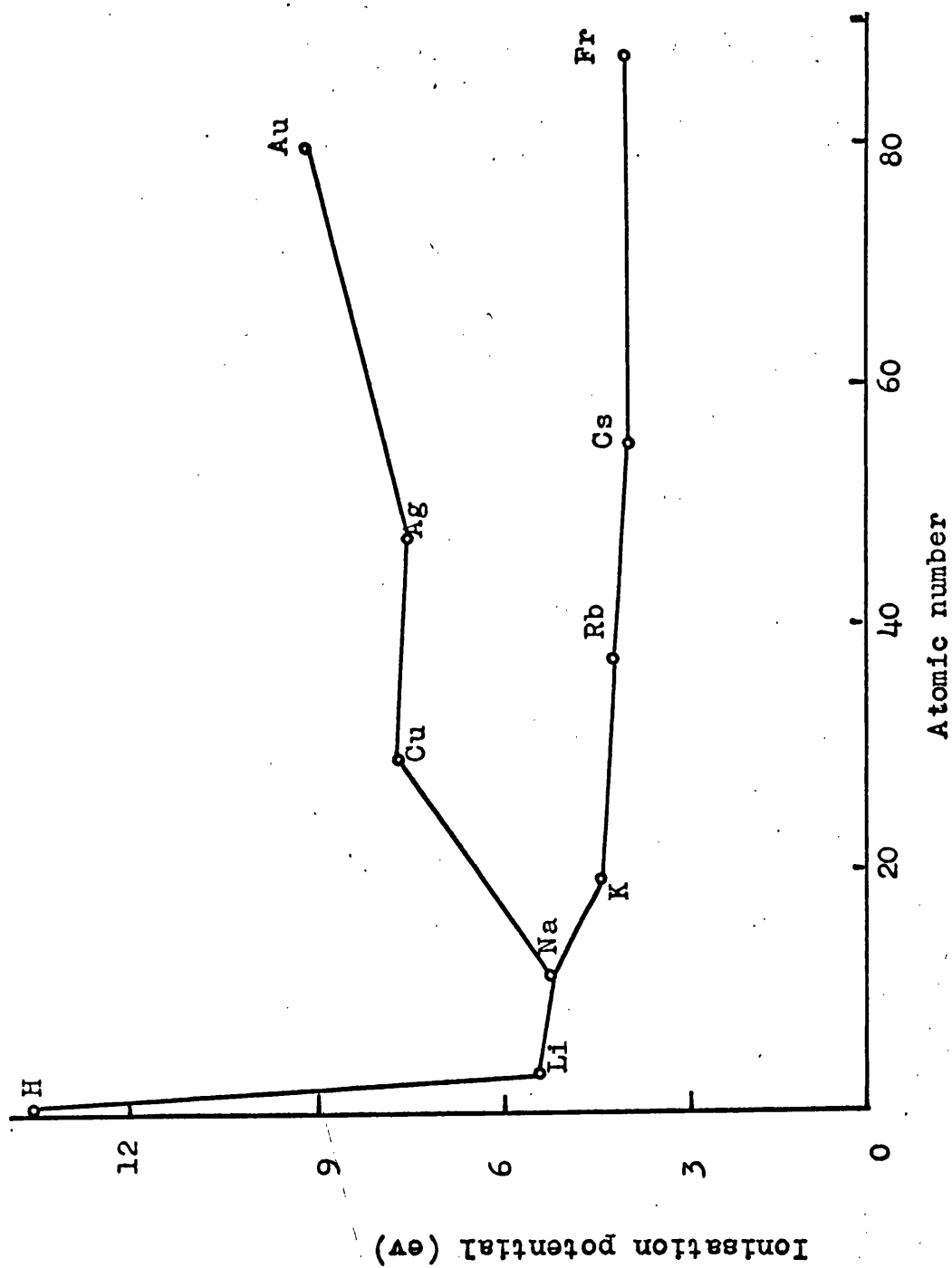


Fig. 8.13. Ionisation potentials against atomic numbers (d^0 and d^{10} elements)

In addition, silver normally has coordination number of 2 but no linear complex of silver involving oxygen as ligand has been observed. This may explain the high solubility of silver chloride in formamide where coordination with the solvent may be through the nitrogen atom. Almost complete lack of experimental data on the behaviour of silver chloride in formamide except for a few measurements of the standard electrode potential of the silver/silver chloride electrode in formamide has restricted the discussion of the results obtained here. Solubilities of alkali metal halides in formamide are well established but it may be misleading to compare those with that of silver chloride since the alkali metal ions have d^0 whereas the silver ion has d^{10} electronic configuration. The d^{10} configuration has a considerable influence on the chemistry of these elements, as shown for example by the ionisation potentials. Fig.8.13 shows the ionisation potentials plotted against atomic numbers of the d^0 and d^{10} elements¹³³; from which the marked difference between those two groups of elements can be seen. Silver halide crystals show more evidence of polarization, as indicated for example by the data in table XI relating to lattice energies.

Table XI Crystal energies of solids (in kcal/mole)¹³⁴

Salt	Calculated crystal energies	Experimental crystal energies
KF	193	192
KCl	168	167
KBr	161	161
KI	152	151
AgF	220	228
AgCl	199	216
AgBr	195	214
AgI	186	211

This effect is paralleled by the sharp increase in the stability of the corresponding complexes, AgX, in aqueous solution¹³⁵. There are no comparable effects with the alkali metal halides.

Results from the present work lead to the conclusion that solubilities are quite specific in nature and must depend on quite specific interactions between solvent and solute.

8.3. Preliminary E.M.F. Measurements.

The most fundamental method of determining standard electrode potential employs cells without liquid junctions, formed from a hydrogen electrode and an anion reversible

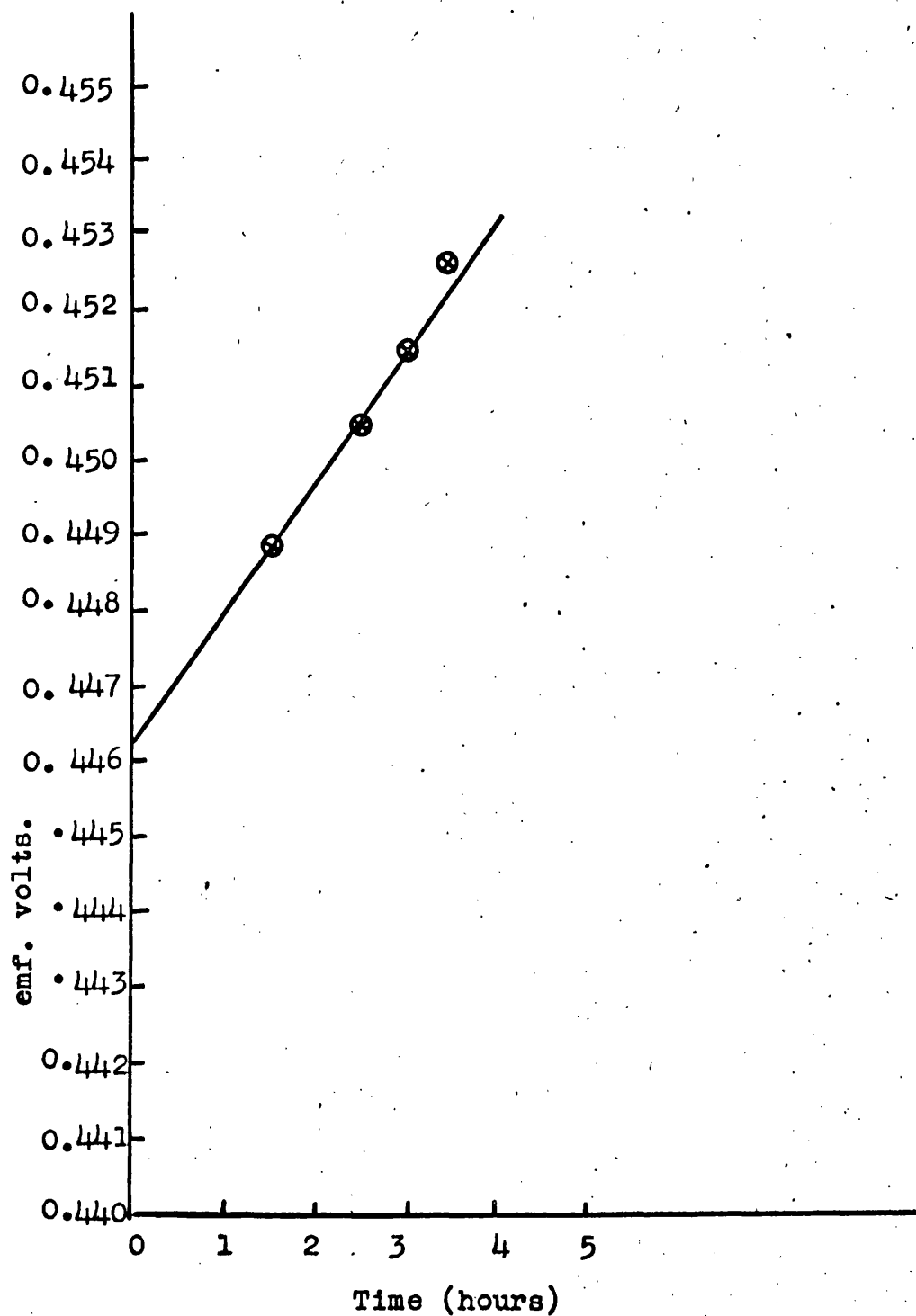


Fig.8.14. Observed emf against time (cell I)

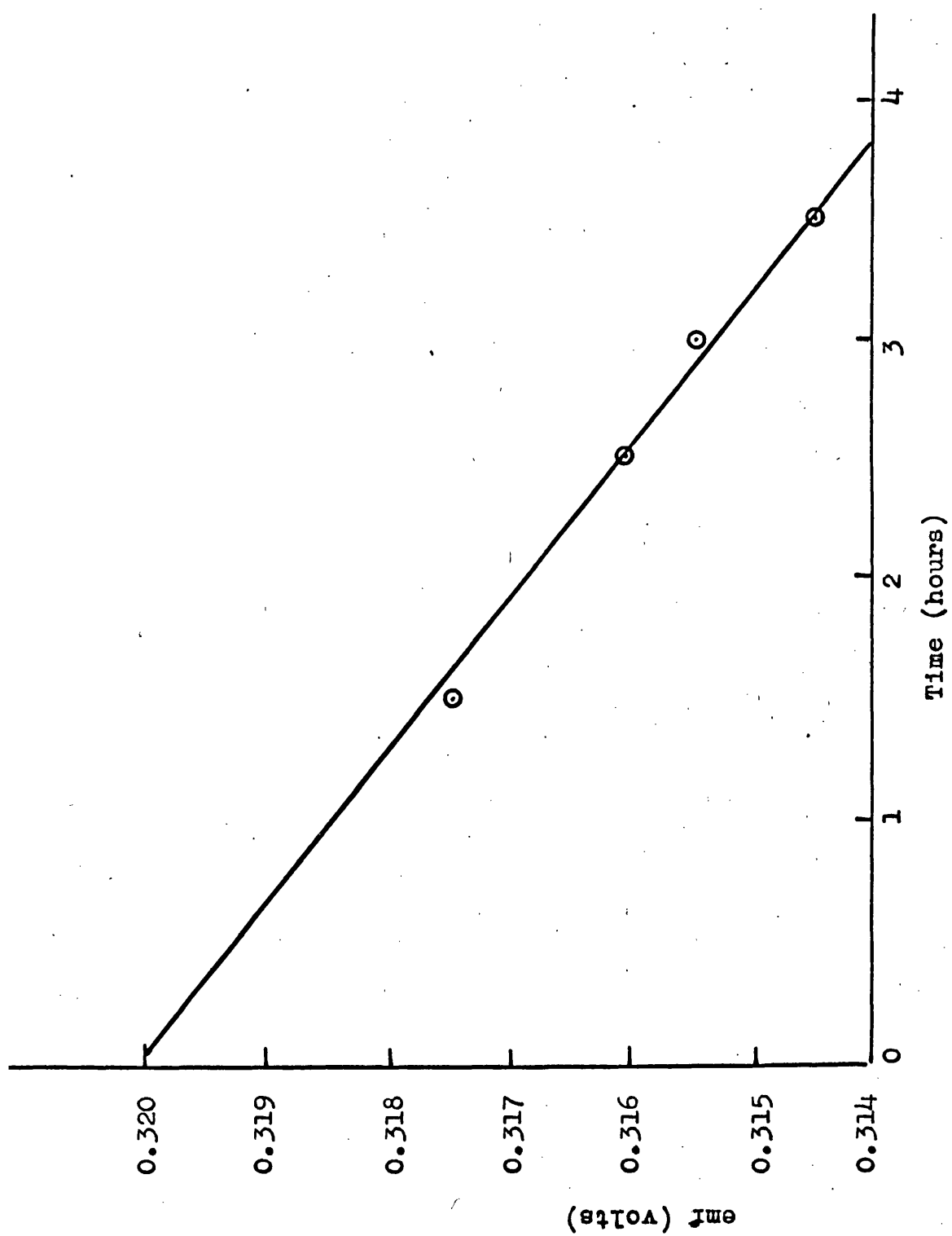
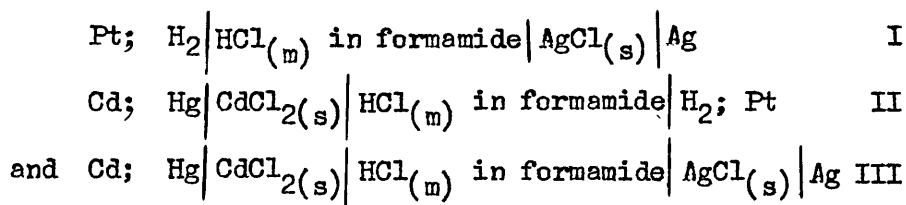


Fig.8.15. Observed emf against time (cell II)

electrode. If the standard emf of this type of cell is found it can be identified with the standard potential of the electrode under investigation.

In this study the emf of the following cells were measured at 25°C using the triple cell (described in Chapter VI).



The emf's of cell I and II were extrapolated to zero time as illustrated in Figs 8.14 and 8.15 respectively.

8.3.1. Cell I. Pt; H₂ | HCl_(m) in formamide | AgCl_(s) | Ag

The emf of Cell I is given by

$$E = E^\ominus - \frac{2RT}{F} \ln m_{\text{HCl}} \gamma_{\text{HCl}} \quad (24)$$

since the correction for the partial pressure of hydrogen to 1 atmosphere was found to be negligible in comparison with the experimental error.

The mean ionic activity coefficient $\gamma_{\pm}$ may be expressed by

$$\log \gamma_{\pm} = -A\sqrt{m} + Bm \quad (25)$$

Hence, on combining equations (24) and (25) the following equation is obtained,

$$E + \left(\frac{2RT}{F} \times 2.303 \right) \left(\log m_{\text{HCl}} - A\sqrt{m} \right) = E' = E^\ominus + \frac{2RT}{F} \times 2.303 Bm \quad (26)$$

Where E is the emf of the cell at zero time and m is the concentration of hydrochloric acid in formamide, expressed in mole/kg. For formamide, taking the dielectric constant as 109.5 and the density as 1.1296 g/ml. at 25°C, the value of A is $0.3286 \text{ mole}^{-\frac{1}{2}} \text{ kg}^{\frac{1}{2}}$.

If E' is plotted against m , a straight line should be obtained with the standard electrode potential ($E^\ominus$) as the intercept and $-\left(\frac{2RT}{F} \times 2.303\right) B$ as the slope.

The summary of the emf data for cell I is given in Table XII.

Table XII

	m (moles/kg)	E (volts)	E' (volts)
Present Work	0.008165	0.4462	0.1957
	0.01633	0.4092	0.1929
	0.04651	0.3566	0.1906
	0.0669	0.3384	0.1893
Agarwal and Nayak's ⁶ results	0.00927	0.4425	0.1983
	0.029	0.3840	0.1955
	0.045	0.3613	0.1937
	0.055	0.3525	0.1943
	0.0673	0.3410	0.1923
	0.0821	0.3322	0.1926 cont..

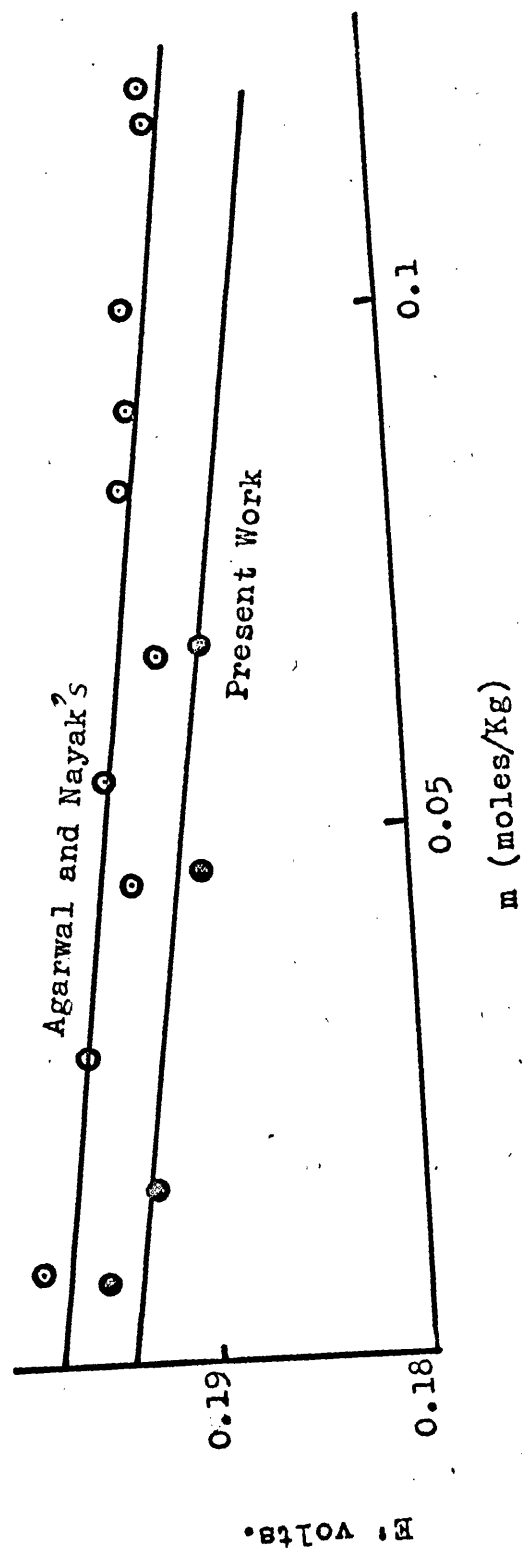


Fig. 8.16. Plot of E' as a function of molality. (cell I)

Table XII cont.

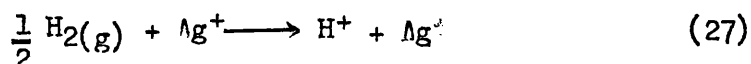
	m (moles/kg)	E (volts)	E' (volts)
	0.09149	0.3270	0.1924
	0.1038	0.3210	0.1921
	0.1185	0.3135	0.1905
	0.1205	0.3132	0.1910

In Fig. 8.16 values E' are plotted against the corresponding value of m . The standard electrode potential (E°) of the silver silver chloride electrode in formamide at 25°C was found on extrapolation to zero molality, to be 0.1940 $\pm$ 0.0002 volts. This value is lower than the values 0.204 volts found by Mandel and Decroly⁵ and 0.1986 volts found by Agarwal and Nayak⁶. Mandel and Decroly obtained their E° value (on the molality scale) using a value of $\frac{(2RT \times 2.303)\Delta}{F}$ in equation (26) given (incorrectly) on the molarity scale, i.e., 3.65×10^{-2} instead of 3.888×10^{-2} . They do not give sufficient data to re-analyse their results.

Agarwal and Nayak, on the other hand, give the emf's of cell I at each concentration but not the value of the constant Δ used in their calculation for E' . For comparison Agarwal and Nayak's data has been re-calculated using the same value of Δ as was used in this study and the results are given in Table XII.

The E' values are plotted against m and are shown in Fig.8.16. Their new $E^\ominus$ value, found by the least squares method is 0.1975 volts instead of 0.1986 volts quoted by Agarwal and Nayak⁶. This re-calculated value is in fair agreement with the rather tentative value obtained in the present work and suggests that Mandel and Decroly's value is too high. Mandel and Decroly are the only workers to extend their measurements to a range of temperatures⁸¹ and in view of the discrepancies between the various $E^\ominus$ values at 25°C, it is clear that a more detailed study is required at 25°C and also at other temperatures.

By combining the solubility product of silver chloride in formamide at 25°C with the standard emf $E^\ominus$ of cell I, the standard free energy change $\Delta G^\ominus$ of the reaction



in formamide can be obtained, using the same procedure as described in section 8.1. in the case of heavy water. The standard emf of cell I was taken as 0.1957 volts, this being the mean of the present $E^\ominus$ value and that of Agarwal and Nayak. The standard free energy change $\Delta G^\ominus$ is - 15.86 kcals. The standard electrode potential of silver electrode in formamide is given by $\Delta G^\ominus = -E_{\text{Ag}}^\ominus F$ and is found to be 0.6878 volts at 25°C.

8.3.2. Cell II Cd; Hg | $\text{CdCl}_2(\text{s})$ | $\text{HCl}(\text{m})$ in formamide | H_2 ; Pt

The emf of Cell II is given by

$$E = E^\ominus + \frac{RT}{F} \ln m_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\pm}^2 \quad (28)$$

However, the solubility of cadmium chloride in formamide is considerably higher than silver chloride as shown by the data of Pavlopoulos and Strehlow⁷⁸ and by Muju¹²⁶. Pavlopoulos and Strehlow calculated the solubility product K_s from the standard electrode potentials of the cadmium and of the cadmium|cadmium chloride electrodes in formamide at 25°C. They obtained the value $5 \times 10^{-8} (\text{mole/l})^3$ which is equivalent to $3.4 \times 10^{-8} (\text{mole/kg})^3$. These values indicate that the chloride ion concentration in the cell solution, contributed by the dissolved cadmium chloride cannot be ignored. Pavlopoulos and Strehlow corrected for the chloride ions contributed by the cadmium chloride, assuming complete dissociation. This assumption is not necessarily valid, but their treatment was adopted here and is summarised below.

In the solution, let $m_{\text{H}^+} = m_{\text{HCl}} = x$ and

$m_{\text{CdCl}_2} = m_{\text{Cd}^{2+}} = y$, then $m_{\text{Cl}^-} = x + 2y$.

The solubility product K_s of cadmium chloride is given by $\{m_{\text{Cd}^{2+}}\} \{m_{\text{Cl}^-}\}^2$ (the activity coefficients are assumed to be near or equal to unity).

$$\text{Hence, } K_s = y (x + 2y)^2 \quad (29)$$

When $y \ll x$ equation (29) reduces to

$$2y = x \left\{ -\frac{1}{4} + \sqrt{\frac{1}{16} + \frac{K_s}{x^3}} \right\}$$

$$\text{It follows that } y = \frac{x}{2} \left\{ -\frac{1}{4} + \sqrt{\frac{1}{16} + \frac{K_s}{x^3}} \right\} \quad (30)$$

In order to include the chloride ion concentration from the dissolved cadmium chloride in the cell solution equation (28) must be re-written as

$$E = E^\ominus + \frac{RT}{F} \ln x (x + 2y) \gamma_{\pm}^2 \quad (31)$$

$\gamma_{\pm}$ can be evaluated using equation (25) except that m becomes replaced by ionic strength I , where I is given by $I = \frac{1}{2} (4y + x + x + 2y) = x + 3y$. The resulting equation is

$$\begin{aligned} E - \left(\frac{RT}{F} \times 2.303 \right) \left\{ \log x (x+2y) - 2A \sqrt{x+3y} \right\} &= E' \\ &= E^\ominus + \left(\frac{2RT}{F} \times 2.303 \right) (x+3y)B \end{aligned} \quad (32)$$

The K_s value of $3.4 \times 10^{-8} (\text{mole/kg})^3$ as reported by Pavlopoulos and Strehlow was used in equation (30) for determining the value of y . The accuracy of this K_s value is open to doubt and the solubility product of cadmium chloride is at present being re-measured by Muju¹²⁶ whose result is not yet available. The emf data of cell II are recorded in table XIII.

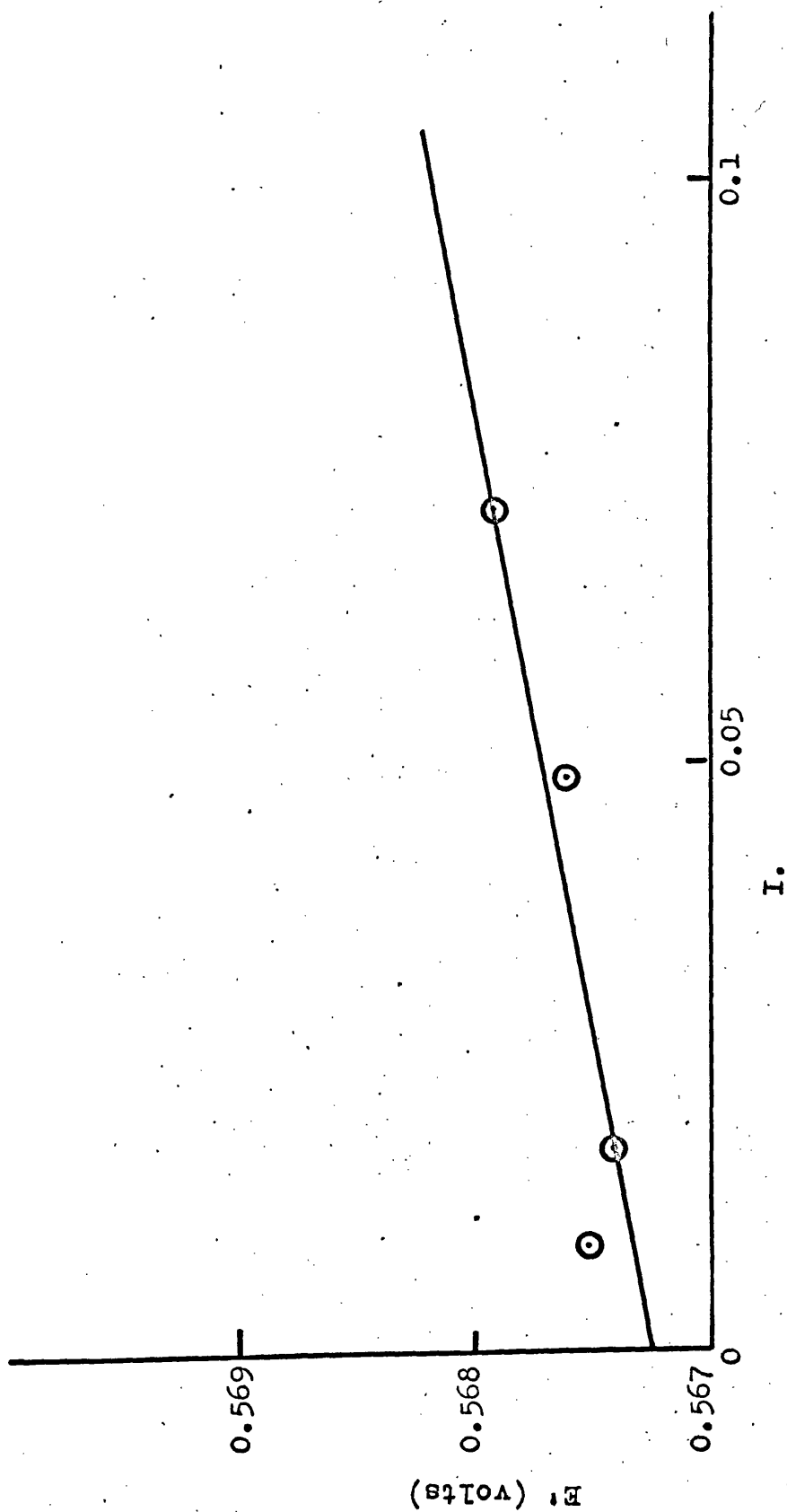


Fig. 8.17. Plot of E' as the function of ionic strength. (Cell II)

Table XIII

I	E (volts)	E' (volts)
0.00946	0.3196	0.5675
0.0171	0.3521	0.5674
0.07204	0.4216	0.5679
0.0479	0.4021	0.5675

Fig. 8.17 shows the plot of E' against the ionic strength. The intercept of the straight line yields the standard electrode potential $E^\ominus$ of the cadmium amalgam|cadmium chloride electrode; it is found to be equal to - 0.5672 volts.

Parks and LaMer¹²⁸ have measured the emf of the cell
 $\text{Cd; Hg(2 phase amalgam)} | \text{CdSO}_4(0.5M) | \text{Cd}_{(\text{metal})}$ at 10 degree
 intervals from 0-30°C. The emf of the cell corresponds to the
 spontaneous process $\text{Cd}_{(\text{s})} \longrightarrow \text{Cd:Hg(2 phase amalgam)}$. In other
 words the measured emf is the correction factor in converting
 from the pure cadmium electrode to the cadmium amalgam, or vice
 versa. The value at 25°C was obtained graphically from Parks
 and LaMer's data and was found to be 0.0505 volts.

As the standard electrode potential of the cadmium
 amalgam|cadmium chloride electrode in formamide at 25°C is

- 0.5672 volts, then the standard electrode potential of the cadmium|cadmium chloride electrode is therefore -0.6177 volts. The only available literature value of the standard electrode potential of the cadmium|cadmium chloride electrode is that of Pavlopoulos and Strehlow⁷⁸ who reported the value - 0.617 $\pm$ 0.004 volts on the molar scale. This is equivalent to -0.611 volts on molality scale.

8.3.3. Cell III $\text{Cd; Hg|CdCl}_2(\text{s})|\text{HCl}(\text{m})$ in formamide| $\text{AgCl}(\text{s})|\text{Ag}$.

For the purpose of comparison, the emf of cell III, (using a cadmium amalgam electrode) was also corrected to that of the cell using a pure cadmium|cadmium chloride electrode i.e., $\text{Cd|CdCl}_2(\text{s})|\text{HCl}(\text{m})$ in formamide| $\text{AgCl}(\text{s})|\text{Ag}$, by the addition of 0.0505 volts¹²⁸ to the emf of cell III. The results are given in Chapter VII and are also tabulated below.

Table XIV

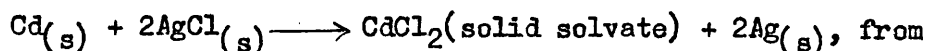
I	emf of cell III (volts)	emf of cell III corrected for Cd CdCl_2 electrode (volts)
0.009105	0.7693	0.8198
0.01702	0.7606	0.8111
0.07204	0.7600	0.8105
0.0479	0.7599	0.8104

The emf's of the cell except for the value at the lowest

chloride ion concentration, is between 0.8104 and 0.8111 volts and is consistent, within the experimental error with the value of 0.810 ± 0.001 volts for emf of the cell,

$\text{Cd}|\text{CdCl}_2(\text{s})|\text{KCl}(\text{m})$ in formamide $|\text{AgCl}(\text{s})|\text{Ag}$ as studied by Muju.¹²⁶

The cell reaction can be written as follows :-



which it can be seen that the emf of this cell is independent of the concentration of hydrochloric acid or of potassium chloride in formamide. Hence, the emf of this type of cell should be equal to the numerical sum of the standard electrode potentials of the cadmium|cadmium chloride and the silver|silver chloride electrodes. The combination of the two standard electrode potentials i.e., $E^\ominus_{\text{Ag}|\text{AgCl}}$ and $E^\ominus_{\text{Cd}|\text{CdCl}_2}$ yields 0.8117 volts as the emf of the cell $\text{Cd}|\text{CdCl}_2(\text{s})|\text{HCl}(\text{m})$ in formamide $|\text{AgCl}(\text{s})|\text{Ag}$. If allowance is made for the uncertainty owing to the small number of measurements involved in this work, this emf value compares satisfactorily with the value between 0.8104 and 0.8111 volts obtained from the direct measurement.

One of the advantages of using the triple cell is that the emf of the three cells can be measured simultaneously under identical experimental conditions. Owing to the limited time available, only preliminary work could be presented in this thesis, but it is hoped that more extensive studies will be carried

out in the future.

The validity of extrapolating to zero time as used by previous workers and in the present work, is questionable, since it assumes that equilibrium is reached rapidly and the subsequent drift in emf readings is due to decomposition of formamide in the presence of hydrochloric acid. In some cases practically steady values for the emf, which remained constant for about 24 hours were obtained in less than $\frac{3}{4}$ of an hour after the assembled cells had been left in the thermostat bath. In other experiments, drifts of the emf with time were observed, but the extent of this behaviour is less than that observed by Agarwal and Nayak. It is possible that the equilibrated emf may be established more reliably by approaching the equilibrium from a high temperature and by following the emf of the cell for a longer period of time.

A P P E N D I X

Determination of Solubility of Silver Bromide in Water

The solubility of silver bromide in water at various temperatures has been measured using a similar technique to that described for silver chloride (see page 48). These measurements were made in order to test the technique on a material of lower solubility than silver chloride and with the possibility of studying the solubility of silver bromide in solvents other than water.

1 ml. of 4 m. silver nitrate solution was labelled with silver-110m and silver bromide was precipitated by the addition of 0.5 ml. of 4 m sodium bromide solution. About 17.3 mg. of silver bromide precipitate were usually obtained from these quantities, i.e., the chemical yield was approximately 85%. The remainder of the experimental procedure was essentially as described in Chapter IV.

The difficulty of dealing with the much less soluble bromide may be overcome by either using a higher specific activity of the labelled silver, or the use of a much larger volume of equilibrium solution for the preparation of the final counting source. The latter procedure is complicated by the fact that silver bromide, precipitated from relatively large solution volumes, *coagulates* badly and gives a poor counting source. However, since it is

radio-silver rather than silver bromide that is being assayed, there is no reason why the final counting source should be in the form of the bromide. Accordingly, counting sources were prepared from the equilibrium solutions as silver chloride, exactly as described in Chapter IV.

The use of higher specific activity radio-silver in the determinations did, of course, provide counting sources (prepared from equilibrium solutions) with count rates significantly above background, but suffered from the disadvantages of needing a reference source with rather a high count rate (possibly resulting in "lost counts", owing to the limited resolving time of the counting apparatus), and of possibly introducing "radioactivity effects"¹⁰⁶ on the solubility of the material.

Yet, another approach to the problem is to label the bromide ion with bromine-82, rather than the silver; however, the half-life of this nuclide (34 hours) is inconveniently short, and such labelling was therefore not used. The results are tabulated together with values reported in the literature from emf measurements⁹⁶ in table I.

Table I

Temperature °C	Solubility in water in moles/kg (this study).	Solubility in water in moles/kg (96)
25	0.732 x 10 ⁻⁶ 0.710 x 10 ⁻⁶	0.704 x 10 ⁻⁶
35	1.281 x 10 ⁻⁶	1.213 x 10 ⁻⁶
45	2.20 x 10 ⁻⁶ 2.25 x 10 ⁻⁶	1.997 x 10 ⁻⁶

There is good agreement between these two sets of data, but again the results obtained by the tracer technique are higher than those from emf measurement. This is of course to be expected since in the tracer technique the total dissolved silver bromide in the solution is measured, whereas the solubility from emf work is given in terms of ionic concentrations. It is also worth mentioning that silver bromide will probably be more associated than silver chloride in water, owing to the higher polarisability of the bromide ion than the chloride ion. Hence the differences between the solubilities of silver bromide obtained from the tracer technique and from the emf measurements are greater than those observed in the case of silver chloride. Since these studies appear promising, it is hoped that they may be continued.

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