

"Some Additivity Relationships in Magnetic  
Susceptibility Measurements"

A Thesis submitted to  
*The* University of London  
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by  
Sogra Fatima Ahmed Husain

Bedford College.  
University of London.

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(7) Summary.

- (1) The magnetic mass susceptibility of a number of salts of ammonium and potassium have been measured, and also, a certain <sup>number of</sup> salts of magnesium, zinc and cadmium. Systematic relationships suggested by earlier workers for the potassium and ammonium halides, sulphates, nitrates etc, were confirmed both in the solid states and in solution.
- (2) The present values of molar susceptibility of the halides of ammonium and potassium were measured in both the solid state and in solution. The susceptibilities of salts in solution were about 1% higher than for the solid state, except in the case of certain divalent salts and the nitrates as a group.
- (3) Measurements on double salts of magnesium and zinc with ammonium and potassium were made. Additivity relationships in these salts in the dissolved state were found to be valid. Slight deviations were found in the crystalline state. In comparing the molar susceptibility of the double salt with its molar volume it was <sup>found</sup> ~~of~~ that, in the case of double salts containing the ammonium ion, the experimental molar volume and molar susceptibility are both larger than the calculated, and so differ from the calculated in the same direction. The relationship with the molar volumes was more complex in the case of potassium double salts. There

is a fair correlation between the magnitude of the deviation for the two properties. The deviation from additivity was found to be larger in the case of certain divalent elements.

- (4) A series of measurements on divalent salts in solution was made at different concentrations. Some simple salts and acids were measured. In some cases the susceptibility of the salts and acids were constant in solution and showed no variations, while others showed slight change; a fall in susceptibility of the salt with increasing concentration being observed.
- (5) The susceptibility of solutions of salts of certain divalent elements showed a marked variation with the concentration. These changes were explained in terms of the concept of hydration number. This may include, in addition to simple hydration of the cation, more complex ion formation or the formation of ion pairs.
- (6) Measurements on solutions of zinc halides with equivalent properties of univalent electrolytes showed systematic relationships.

## Preface

The work described in this Thesis was carried out in the laboratories of the Chemistry Department, Bedford College, under the supervision of Dr. V.C.G. Trew.

The writer wishes to express her sincere appreciation of the help and encouragement she has received from Dr. Trew during the course of this work, and also to thank Professor E.E. Turner for providing facilities for research.

She is also indebted to the Central Government of Pakistan for the grant of study-leave during the tenure of which the work has been done.

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(1) INTRODUCTION

(1)  
 On the basis of the electronic theory, Langevin put forward an electronic theory of magnetism, employing the concepts of electrons moving in closed orbits around a massive nucleus. Diamagnetism is a universal property common to all types of matter since it represents the underlying magnetic effect induced by an applied magnetic field upon the movement of the electrons within the atom. According to the classical (1) theoretical treatment of atomic magnetism developed by Langevin a magnetic moment is produced as the result of the orbit of each electron within an atom, but if there is an even number of electrons with paired spins, the resultant moment is zero, and the system exhibits only diamagnetism. Larmor showed in 1905, that if a system of electrons is rotating about an atomic nucleus, on applying a magnetic field to the system the velocities, and hence angular momenta of the electrons are altered. A precession effect is induced by the magnetic field (Larmor precession). Langevin developed the theory of diamagnetism showing that the precession effect due to the field tended to induce currents which give rise to a field opposite in direction to the inducing field, and the substance thus exhibits diamagnetism. The magnitude of this diamagnetic effect for a free spherically symmetrical atom or ion is given by the Langevin equation.

$$\chi_A = \frac{e^2 N}{6m c^2} \sum_n \bar{r}^2$$

where  $e$  the electronic charge =  $(4.8022 \pm 0.0001) \times 10^{10}$  abs e.s.u.,  
 $c$  the velocity of light =  $(2.99790 \pm 0.00001) \times 10^{10}$  cm. sec.<sup>-1</sup>  
 $N$  the Avogadro number =  $(6.0228 \pm 0.0001) \times 10^{23}$  moles and  $\sum_n \bar{r}^2$   
 is the mean square radius summed over all the  $n$  orbits within  
 the atom or ion.

Substituting the values for the various constants this becomes:-

$$\chi_A = 2.83 \times 10^{10} \sum_n \bar{r}^2$$

or if  $r$  is expressed in units of normal radius of the hydrogen atom  $r_0 = 0.528 \times 10^{-8}$  cm, the expression for the ionic or atomic diamagnetic susceptibility becomes

$$\chi_A = -0.789 \times 10^6 \sum_n \bar{r}^2 \text{ e.m.u/g atom.}$$

The molecular diamagnetic susceptibility of a polar salt is theoretically assumed to be the sum of the individual values for the separate ions without any interaction between the ions.

The above classical expression for the diamagnetic susceptibility of a free atom or ion, in "empty space" represents an ideal condition, not in general holding under experimental conditions and hence experimental values will tend to be different from the theoretical ones.

In the field of organic chemistry following the earlier work of Curie, Pascal<sup>(2)</sup> has pointed out the existence of an additive law and has recognised the constitutive influence of



certain types of bonds. It is now recognised that amongst inorganic compounds also there are many factors such as valency, crystal structure and complex formation which may influence the magnetic susceptibility. Susceptibility measurements may be used, therefore, in the investigation of chemical problems.

The additivity law has been most widely studied mainly in the field of organic compounds.

In the year 1918, Alpheus W. Smith, and Alva W. Smith (3) studied the magnetic behaviour of some binary mixtures of organic liquids e.g. acetone-water, acetone-ethylalcohol, acetic acid-water, acetic acid-benzene. They showed that the specific susceptibility of a mixture was an additive function of the susceptibilities of the two components, and varied linearly with the percentage concentration of one of the components. Between 1924 and 1926, (4) Trifonou studied several systems, but in only a very few cases, e.g. benzene-m-xylene and allyl mustard oil-dimethyl aniline mixtures, was strict additivity displayed. In the year 1931, systematic (58) investigations were made on mixtures by a number of workers, including Ranganadham, Buchner, Rao, Garssen, Kido, Venkatacharia, Seely, Trew and Spencer.

(5) Buchner investigated the completely miscible pairs ethylalcohol - carbon disulphide, and acetone - chloroform, and the incompletely miscible pairs phenol-water, and methyl alcohol - carbon disulphide. Each mixture showed only small deviation from additivity.

(6)

Ranganadham investigated the mixtures benzene - carbon tetra chloride, acetone - chloroform, acetone - water, ethylalcohol-water. While each showed small deviations from additivity, it occurred to the least extent in the non polar mixtures. Molecular deformation, dipole-dipole interaction, and compound formation were suggested to explain the deviations. As a result of the above combined effort it has now been established that the additivity law in general holds good in mixtures of organic liquids and thus the susceptibility concentration curves are nearly straight lines. Deviations occurring due to the above effects, are only of the order of some few per cent of the total susceptibility.

The literature on magnetic susceptibility of inorganic salts and solutions is extensive, but comparatively few workers have studied, except for paramagnetic substances, the additive relationships between simple and complex salts or of salts in aqueous solutions of varying concentration. Most workers have assumed an additive relationship to hold.

The diamagnetic susceptibility of salts calculated from measurements in solution and in the crystalline state are so close to each other that their difference and exact relationship have often been overlooked. In 1932, Kido carried out a series of systematic measurements of the magnetic susceptibility of salts of a number of cations with various anions and noted a linear relationship between molecular magnetic mass susceptibility and the number of electrons in the cation for series of salts with the

(7)

same anion, but made no allowance for small differences due to change in co-ordination number of the ions.

(8, 9, 10.)

Brindley and Hoare, presented a set of data for the alkali halides which appear to be very reliable. From their data they were able to show the validity of an additive rule, for ions forming a polar salt, in general, in the dissolved as well as in the crystalline state and thereby they calculated the susceptibilities of individual ions in both states. In addition they derived values for ions in different co-ordination states. More recently the work on ammonium compounds by Bedwell, Spencer and Trew<sup>(11)</sup> showed results similar to those of Brindley<sup>(loc-cit)</sup> for the ammonium salts.<sup>(12)</sup> <sup>(13)</sup> Klemm and Trew pointed out independently that the molecular magnetic susceptibility of salts of the same cation was not a linear function of the number of electrons in the cation, but had a characteristic 'zig-zag' plot. Since this, Prasad and co-workers<sup>(14-15)</sup> in the years 1949-52 have obtained very different results for the experimental susceptibilities of ammonium salts, alkali salts and also the alkaline earths, and again suggested a linear relationship between the molecular susceptibility and the number of electrons in the cation. Therefore it is worth investigating the relationship of the susceptibility to the electronic structure of the ions.

There is also a considerable divergence in the recorded values of the specific susceptibility for many compounds in the magnetic literature. For example the values for the specific susceptibility of magnesium sulphate hepta-hydrate =  $-.546 \times 10^6$  and for zinc sulphate hepta-hydrate =  $-.496 \times 10^6$  had been obtained by

(16)  
 Prasad, Dharmatti and Kanekar. However, in a later communication  
 (17)  
 Prasad, Dharmatti and Amin have reported these susceptibilities  
 to be  $-.550 \times 10^6$  and  $-.480 \times 10^6$  respectively. These discrepancies  
 and others therefore led the present worker to remeasure the  
 susceptibilities of a large number of simple salts, before  
 investigating more complex relationships. Having clarified the  
 position with the simple salts, the present work was mainly undertaken  
 to investigate further the additivity law in double salts and simple  
 and complex salts in their aqueous solutions.

The problem of whether the susceptibility of a salt in  
 solution remains constant with change of concentration has been  
 studied mainly on paramagnetic substances. Thus it was found by  
 Cabrera, Moles and Guzman, (18) by Weiss and Bruins (19) and by Brant (20)  
 that the magnetic susceptibility per gram molecule of simple salts  
 of nickel in aqueous solution is constant and independent of the  
 concentration. (21) Weiss and Frankhamps have shown that the same  
 applies to the simple ferrous salts, while Cabrera and his co-workers (22)  
 have found that the salts of chromium give constant values. Under  
 certain experimental conditions, simple cobaltous salts have been  
 found to have a constant molecular magnetic susceptibility by  
 Brant. (20) On the other hand variation of the susceptibility with  
 the concentration has been found in some cases. Cobaltous salts  
 have been studied by Cabrera and his co-workers, (22) also Piccard and  
 Cherbuleiz (23) and Cabrera and Moles (24) have found the susceptibility of  
 cupric salts varies with the concentration. The latter authors  
 have also found that the susceptibility of ferric salts depends

upon the concentration of hydrogen ion in the solution. The aim of this part of the present work was to see whether any variation in diamagnetic susceptibility with the concentration could be detected and to study the effect of complex ion formation, if any, upon the magnetic susceptibility of diamagnetic salts in aqueous solution. The compounds which have been studied are zinc chloride, zinc bromide, zinc iodide, silver nitrate, and cadmium iodide and certain mixtures of these salts with alkali salts with which they form complex ions. In order to study the effect of concentration on the susceptibility and possible complex ion formation it was necessary first to measure the susceptibility of all the acids and salts utilized in these measurements. The molecular susceptibility of the salts ammonium chloride, potassium chloride, potassium iodide, and of the acids hydro-chloric, hydro-bromic, hydriodic, and acetic were measured. Values for the above were checked where ever available and found to be agreeing fairly with those of other workers.

The present work can be grouped under the following headings:-

- I. The susceptibilities of simple salts of Groups I & II of the periodic table.
- II. The relationships between the susceptibility of complex salts and their simple components.
- III. The effect of concentration of solutions on the susceptibility of dissolved ions.

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## (2) EXPERIMENTAL.

### PREPARATION & ANALYSIS OF THE SUBSTANCES.

1. The salts studied in the investigation were obtained as pure as possible and whenever available. Analar reagents or Kahlbaum's "extra pure" compounds were used. The measurements on Analar substances were made without further purification. In other cases the pure salt employed was recrystallized from distilled water and 95% ethyl alcohol. Other salts chiefly double salts, were prepared and were used only after ascertaining their purity. A good commercial specimen was used as a starting material and was tested for para and ferro-magnetic impurities. All acids used were tested and shown to be free from iron by the thioglycollic acid test. For every measurement, freshly prepared and dry specimens were used. Deliquescent compounds were stored in an evacuated desiccator.

2. Qualitative tests were carried out for iron, cobalt and nickel, as these ferromagnetic impurities could cause considerable error in the diamagnetic susceptibility.

(a) IRON. A purple colouration is given on the addition of an ammoniacal solution of thioglycollic acid to the test solution.

(It is sensitive to 1 part in 5,000,000).

(b) NICKEL. A Red Colouration of nickel dimethyl glyoxime is given when dimethyl glyoxime is added to the ammoniacal test solution.

(The sensitivity of the reaction is about 1 part in 500,000, parts of solution).

(c) COBALT. An orange colouration is given on the addition of the reagent  $\alpha$  - nitro -  $\beta$  - naphthol together with dilute caustic soda and a little ammonium chloride to the test solution.

(Sensitive to 1 part in 1,000,000).

(Preparation:- dissolve 0.2 gms of  $\alpha$  - nitro -  $\beta$  - naphthol in 100 ml of cold glacial acetic acid and dilute with 100 ml of hot water and filter.

3. The purified substances were then analysed quantitatively. The results are given in detail on the following pages.

#### 1. Magnesium Chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ )

##### Preparation

Magnesium carbonate was neutralized with hydrochloric acid, and the solution evaporated until it was about to crystallize and then it was allowed to cool. The crystals were filtered and allowed to dry <sup>rapidly</sup> between filter paper in air. As they were deliquescent, they were stored in a desiccator over calcium chloride.

##### Analysis

	I	II
1. wt. of $MgCl_2 \cdot 6H_2O$	= .6236 g	.6332 g
11. .. .. $Mg_3P_2O_7$	= .3420 g	.3450 g
Magnesium found	= 11.87%	11.89%
Magnesium Calculated	11.96%	

1. DETAILS OF THE PREPARATION AND ANALYSIS  
OF SALTS.

Magnesium Compounds.

The method of analysis used was to determine the magnesium content of the salt with ammonium phosphate. (Quantitative Analysis by Cumming & Kay (p. 332)). The magnesium ammonium phosphate was in some cases ~~this was~~ ignited to the pyro-phosphate in a Gooch crucible ( $2 \text{ Mg NH}_4\text{PO}_4 = 2 \text{ NH}_3 + \text{H}_2\text{O} + \text{Mg}_2\text{P}_2\text{O}_7$ ), or in others, <sup>cases</sup> was filtered into a sintered crucible, dried at  $45^\circ\text{C} - 50^\circ\text{C}$ , and weighed as the hexa-hydrate of magnesium ammonium phosphate.

1. Magnesium Chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ )

Preparation

Magnesium carbonate was neutralized with hydrochloric acid, and the solution evaporated until it was about to crystallize and then it was allowed to cool. The crystals were filtered and allowed to dry <sup>rapidly</sup> between filter paper in air. As they were deliquescent, they were stored in a desiccator over calcium chloride.

Analysis.

	I	II
i wt. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	= .6236 g	.6332 g
ii .. .. $\text{Mg}_2\text{P}_2\text{O}_7$	= .3420 g	.3450 ,,
Magnesium found	= 11.97%	11.89%
Magnesium Calculated	11.96%	



2. Magnesium bromide hexahydrate. ( $\text{Mg Br}_2 \cdot 6\text{H}_2\text{O}$ ).Preparation.

Magnesium carbonate and hydrobromic acid were mixed in approximately molecular proportions. The dark red coloured liquid was evaporated on a sand bath and then set aside for crystallization. Crystals were washed with 95% ethyl alcohol until they were almost white. Being deliquescent they were stored in a bottle and kept in a desiccator.

Analysis.

The bromide content of this compound was determined as silver bromide by precipitating with 0.1N silver nitrate solution in the presence of nitric acid. It was carefully protected from light. The precipitate was collected in a dry weighed sintered crucible and was dried in an air oven at the temperature  $150\text{C}^\circ$ . (The method used in this estimation is described by Vogel <sup>(25)</sup> Vol. 1. p. 476).

Results:-

	I	II
wt. of $\text{Mg Br}_2 \cdot 6\text{H}_2\text{O}$ taken =	.2026 g.	.2030 g
.. .. . AgBr =	.2589 g.	.2599 g
Bromide ion found =	54.38%	54.48%
.. .. calculated =	54.68%	

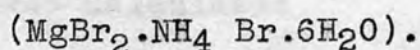
3. Magnesiumiodide octahydrate, ( $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ ).Preparation.

It was prepared by the combined action of magnesium and iodine in water. (26) Magnesium foil and iodine were mixed in molecular proportions, then distilled water was poured in. A violent action took place. The solution which was brownish was filtered off, and evaporated on a water bath until very concentrated. Then it was placed in a desiccator containing sulphuric acid. Crystals were washed with benzene and were at once transferred to a specimen bottle and kept in an evacuated desiccator. It was very deliquescent.

Analysis.

	I	II
wt. of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$	= .6585 g.	.5665 g
.. .. $\text{Mg} \cdot \text{NH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	= .3826 g.	.3292 g
Magnesium found	= 5.758%	5.759%
.. .. calculated	= 5.759%	5.759%

## 4. Magnesium ammonium bromide hexahydrate.



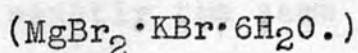
The required molecular quantities of Analar magnesium bromide and ammonium bromide were dissolved in water and the mixed solutions were evaporated on a water bath and when the solution was fairly concentrated it was kept aside for (27) crystallisation. The white needle like crystals were recrystallised from water and alcohol respectively. Then the

specimen was preserved in a stoppered bottle and placed in a desiccator.

Analysis.

	I	II
wt. of $\text{Mg Br}_2 \cdot \text{NH}_4 \text{Br} \cdot 6\text{H}_2\text{O}$	= .7599 g.	.7396 g.
.. .. $\text{Mg}_2\text{P}_2\text{O}_7$	= .2161 g.	.2100 g ;
Mg found	= 6.210%	6.200%
.. calculated	= 6.23%	

5. Magnesium Potassium Bromide hexahydrate.

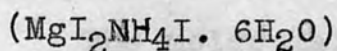


It was prepared by mixing the <sup>equi-</sup>molecular solutions of its components, and then evaporated and crystallised out from hot (27) 95% alcohol. Bromide was estimated in exactly the same manner as was employed in the case of magnesium bromide.

Analysis

	I	II
wt. of $\text{Mg Br}_2 \cdot \text{K Br} \cdot 6\text{H}_2\text{O}.$	= .4555 g.	.4546 g.
wt. of Ag Br	= .6232 g.	.6220 g .
Bromide ion found	= 58.19%	58.20%
Bromide Calculated	= 58.29%	

6. Magnesium ammonium iodide hexahydrate.



Preparation. This was prepared by mixing the <sup>equi-</sup>molecular solutions of magnesium iodide hexahydrate and ammonium ~~phosphorus pentoxide~~ iodide. This solution was evaporated in a desiccator containing phosphorus pentoxide. Thus a slow evaporation took place and

fine crystals of magnesium ammonium iodide hexa-hydrate were obtained. (27) These crystals were transferred to a sintered crucible attached to a pump having a calcium chloride tube fitted to the mouth of the crucible with the help of a cork. The crystals were washed with benzene and thence transferred to a stoppered bottle. Being very deliquescent they were stored in an evacuated desiccator.

#### Analysis.

The compound was estimated as silver iodide. The method is exactly the same as employed for the estimation of magnesium iodide. (Quantitative analysis by Cumming & Kay p. 332).

	I	II
wt. of $Mg I_2 \cdot NH_4 I \cdot 6H_2O$	= .7410 g.	.5100 g.
.. .. $Mg NH_4 PO_4 \cdot 6H_2O$	= .3422 g.	.2346 g.
Magnesium found	= 4.574%	4.556%
Magnesium calculated	= 4.577%	

#### 7. Magnesium ammonium chloride hexahydrate.

( $Mg Cl_2 \cdot NH_4 Cl \cdot 6H_2O$ ).

#### Preparation:

The molecular quantities of the components were mixed in the form of solutions and then evaporated until fairly concentrated. The crystals were recrystallised twice from hot water and 95% ethyl alcohol respectively (J.W. Mellor; vol. IV; p. 306).

	I	II
wt. of $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$	= .4658 g .	.4986 g .
.. .. $\text{Mg}_2 \text{P}_2 \text{O}_7$	= .2020 g .	.2162 g .
Magnesium found	= 9.467%	9.466%
.. .. calculated	= 9.469%	

### 8. Ammonium iodide $\text{NH}_4\text{I}$ .

A specimen of Harrington's ammonium iodide (pure chemical) was recrystallised from hot 95% alcohol. To avoid decomposition it was dried in a desiccator kept in subdued light and then analysed gravimetrically as silver iodide. (Vogel Part I Page 476).

Analysis. About 0.2 g. of ammonium iodide containing approximately 0.1g of iodine was weighed out, and dissolved in 150 <sup>milli</sup>litres of water and 0.5 millilitres of concentrated nitric acid was added.

A solution of .1N silver nitrate was added slowly with constant stirring. Completion of the precipitation was tested by adding a little more silver nitrate which caused no further precipitation. The suspension was heated to boiling, allowed to settle, and while cooling, was kept in a dark place. After two hours the precipitate was transferred to a weighed dried sintered crucible and washed with 0.1% nitric acid, until free from silver nitrate. The precipitate was dried in an air oven at 150°C to a constant weight.

Results:-

	I	II
wt. of $\text{NH}_4 \text{I}$	= .1828 g.	.1819 g .
.. .. Ag I	= . 2961 g.	.2946 g .
Iodide found	= 87.55%	87.54%
Iodide calculated	= 87.58%	

#### 9. Ammonium bromide. ( $\text{NH}_4 \text{Br}$ )

Ammonium bromide was prepared by neutralizing ammonium carbonate by hydro-bromic acid. The same method was employed as described previously in the case of magnesium bromide hexahydrate.

#### Analysis.

The bromide was estimated as silver bromide in a manner exactly similar to that employed in the estimation of ammonium iodide. It was protected well from light during estimation.

	I	II
wt. of $\text{NH}_4 \text{Br}$	= .1421 g .	.1496 g .
.. .. AgBr	= .2725 g	.2868 g
Bromide Found	= 81.59%	81.57%
Bromide calculated	= 81.57%	

#### 10. Magnesium potassium Chloride hexa-hydrate. ( $\text{Mg Cl}_2 \cdot \text{KCl} \cdot 6 \text{H}_2\text{O}$ )

The required molecular quantities of the pure magnesium

chloride hexa-hydrate and potassium chloride were dissolved in water and the mixed solutions were evaporated on a water bath. White needle-like crystals were recrystallized first from hot water and then from 95% alcohol. The salt was stored in a stoppered bottle in a desiccator.

Analysis.

The specimen was analysed as silver chloride as previously.

	I	II
wt. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .	= .2016 g.	.2006 g.
.. .. $\text{AgCl}$	= .3118 g.	.3110 g.
Chloride found	= 38.25%	38.34%
.. .. calculated	= 38.27%	

11. Magnesium ammonium <sup>sulphate</sup> hexa-hydrate ( $\text{Mg SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ )

This compound was prepared as usual by evaporating the mixed molecular solutions of its component salts. The crystals were washed and recrystallised from hot water.

Analysis.

	I	II
<u>By the pyro-phosphate method.</u>		
wt of $\text{Mg SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$	= .3982 g.	.5120 g.
.. .. $\text{Mg}_2\text{P}_2\text{O}_7$	= .1220 g.	.1582 g.
Magnesium found	= 6.690%	6.746%
.. .. calculated	= 6.744%	

## 12. Magnesium Potassium Sulphate. hexa-hydrate .

( $\text{Mg SO}_4 \cdot \text{K}_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ ). Pure Chemical) was

Preparation.

This salt was prepared in the same manner as the ammonium compound. The dry crystals were analysed gravimetrically as magnesium pyro-phosphate.

Analysis.

	I	II
wt of $\text{Mg SO}_4 \text{K}_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$	= .5738 g.	.5556 g.
.. .. $\text{Mg}_2 \text{P}_2 \text{O}_7$	= .1585 g.	.1535 g.
Magnesium found	= 6.029%	6.033%
.. .. calculated	= 6.038%	

13. Magnesium Sulphate hepta-hydrate ( $\text{Mg SO}_4 \cdot 7\text{H}_2\text{O}$ )

The pure material was recrystallized from distilled water and analysed in exactly the same manner as described for the estimation of magnesium chloride hexa-hydrate.

Analysis.

	I	II
wt . of $\text{Mg SO}_4 \cdot 7\text{H}_2\text{O}$ .	= .6548 g.	.6566 g.
.. .. $\text{Mg}_2 \text{P}_2 \text{O}_7$	= .2943 g.	.2971 g.
Magnesium found	= 9.815%	9.881%
.. .. calculated	= 9.87%	



Cadmium iodide ( $\text{CdI}_2$ ).

14. A specimen of May & Baker's <sup>salt</sup> (Pure Chemical) was recrystallised from water and then analysed as the ammonium phosphate mono-hydrate.

Analysis. To the solution approximately containing 0.23g of cadmium in 100 millilitres of water was added an excess amount of diammonium hydrogen phosphate, (Analar reagent) with constant stirring. The precipitate was allowed to stand overnight. After having washed the crystalline precipitate with water and 60% ethyl alcohol respectively it was dried at  $100^\circ\text{C}$  in an air oven to a constant weight.

	I	II
wt. of $\text{CdI}_2$ .	= .6026 g.	.6088 g.
.. .. $\text{Cd NH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$	= .4002 g.	.4046 g.
Cadmium found	= 30.66%	30.68%
.. .. calculated	= 30.69%	

-----

Analysis of Silver Nitrate.

15. Finely powdered silver nitrate (Analar reagent) was heated at  $150^\circ\text{C}$  for one to two hrs. and then allowed to cool in a desiccator. Exactly 8.4960 g. of dry silver nitrate was weighed and made to 500 ml, of solution in a volumetric flask.

Silver nitrate taken = 8.496 0 g

Preparation of Sodium Chloride (Standard).

Finely powdered sodium chloride was heated at  $150^\circ\text{C}$  for 2-3 hours and allowed to cool in a desiccator. Very carefully 2.923 g. of

it was weighed and dissolved to make 500. ml of solution in a standard flask.

Silver nitrate solution was titrated against sodium chloride solution, using freshly prepared potassium chromate solution as an indicator. The required quantity of silver nitrate was noted. A blank titration was also performed to make a correction for the indicator.

### Analysis.

- i. 25 ml of sodium chloride solution was used for each titration.
- ii. mean volume of silver nitrate used = 25.05 ml.

### Blank titration.

1 ml of indicator was added to 25. ml of water.

∴ The amount of silver nitrate required = .03 ml.

∴ The final volume of silver nitrate

$$= (25.05 - .03)$$

$$= 25.02 \text{ ml.}$$

$$\therefore 25.02 \times N_1 = 25 \times 0.1N_2$$

$$N_1 = \frac{25 \times 0.1N_2}{25.02}$$

$$= .0999 \text{ N}$$

wt. of original hydrobromic acid taken

= .3480 g.

.3156 g.

wt. of original silver bromide

= .4228 g.

.2819 g.

Percentage of Hydrobromic acid in the solution

= 52.22%

Grams per litre = 16.9744 g

,, ,, 500 ml = 8.4872 g

∴ Percentage of silver nitrate found

$$= \frac{8.4872 \times 100}{8.4960}$$

$$= 99.89\%$$

#### 16. ANALYSIS OF SOLUTIONS OF HYDRO-BROMIC & HYDROCHLORIC ACID.

(M.&B's Chemical).

The bromide ion content in hydrobromic acid and chloride ion content in hydrochloric acid were determined as silver bromide and silver chloride by precipitation with 0.1N silver nitrate solution, in the presence of nitric acid. The precipitate was carefully protected from light. It was then collected in a dry weighed crucible and was dried in an air oven at the temperature of 150° C to a constant weight (vogel (I) p 476).

#### Analysis.

##### Hydrobromic acid.

wt. of original hydrobromic acid taken	I = .3480 g.	II .2156 g.
wt. of original Silver bromide	= .4228 g.	.2618 g.
Percentage of Hydrobromic acid in the solution	= 52.22%	52.20%

Hydrochloric acid.

	I	II
wt. of the original hydrochloric acid taken	= .3108 g.	.2495 g.
wt. of the silver chloride	= .4322 g.	.3152 g.
hydro-chloric acid found	= .35.37%	35.35%

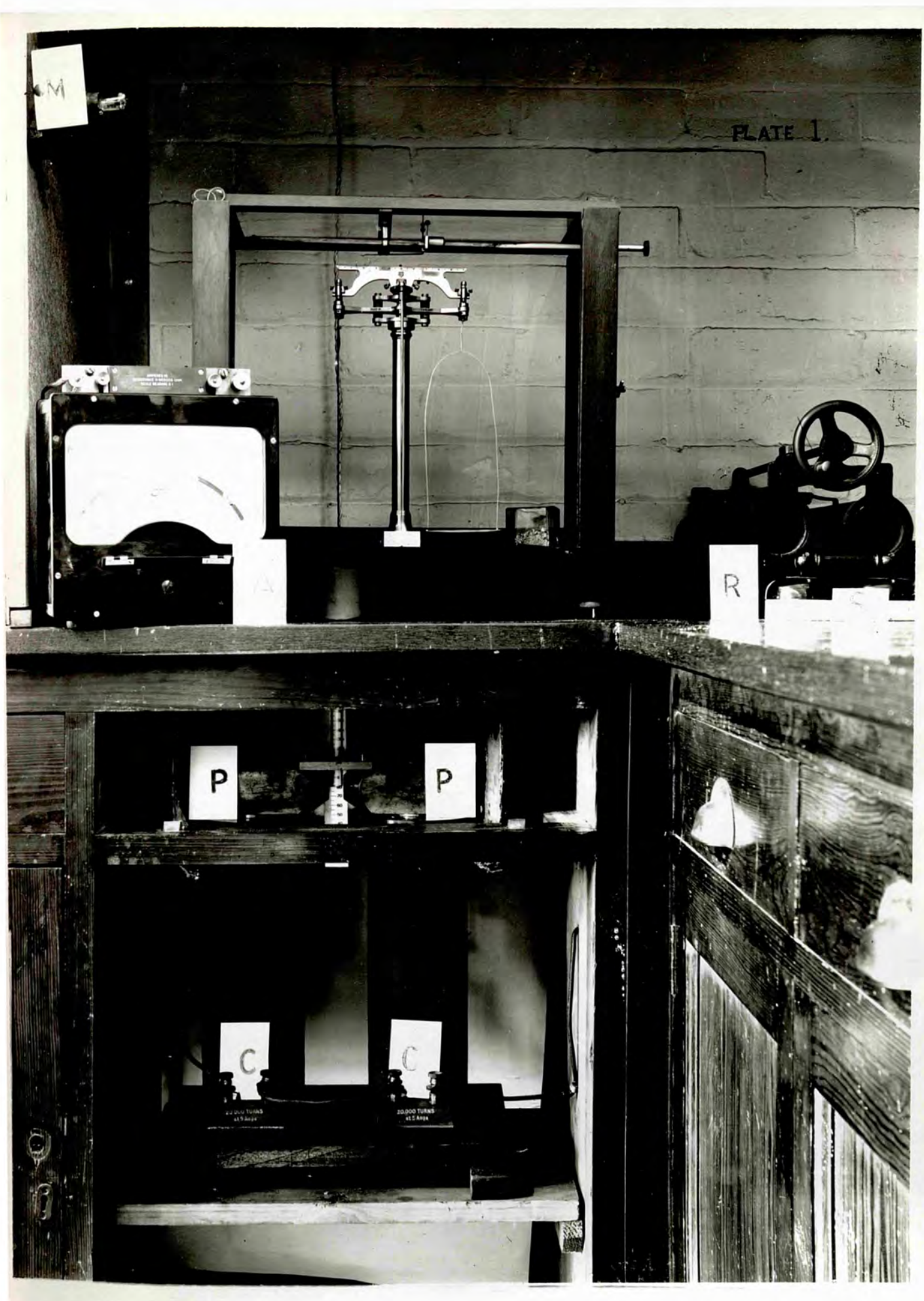
## II. MEASUREMENT OF MAGNETIC MASS SUSCEPTIBILITY.

The susceptibilities of the compounds were measured in the solid state and in solution by the Gouy method, using a type of Gouy balance originally designed by Sugden<sup>(28)</sup> and modified by Trew and Watkins<sup>(29)</sup>. The essential feature of the method is the determination of the force due to a differential magnetic field upon a cylinder of material suspended from one arm of an accurate analytical balance in such a way that the lower end of the cylinder is situated between the pole-pieces, i.e. in the maximum field while the other end extends far enough to be practically in zero field.

The method is based on the principle that in a non-homogenous magnetic field, all substances experience a force which induces a tendency for dia-magnetics to move away from the region of greatest field intensity, and for para-magnetics and ferro-magnetics to move into the region of maximum field intensity. The difference in weight of the specimen when the current inducing the field is off and on is a measure of the magnetic force acting on the specimen, the force being directly proportional to the magnetic susceptibility. The measurements employed are relative measurements comparing the force on the specimen with that on standard substances whose susceptibility is known.

The apparatus is shown in plate I and diagram on the following page.





M

PLATE I.

A

R

P

P

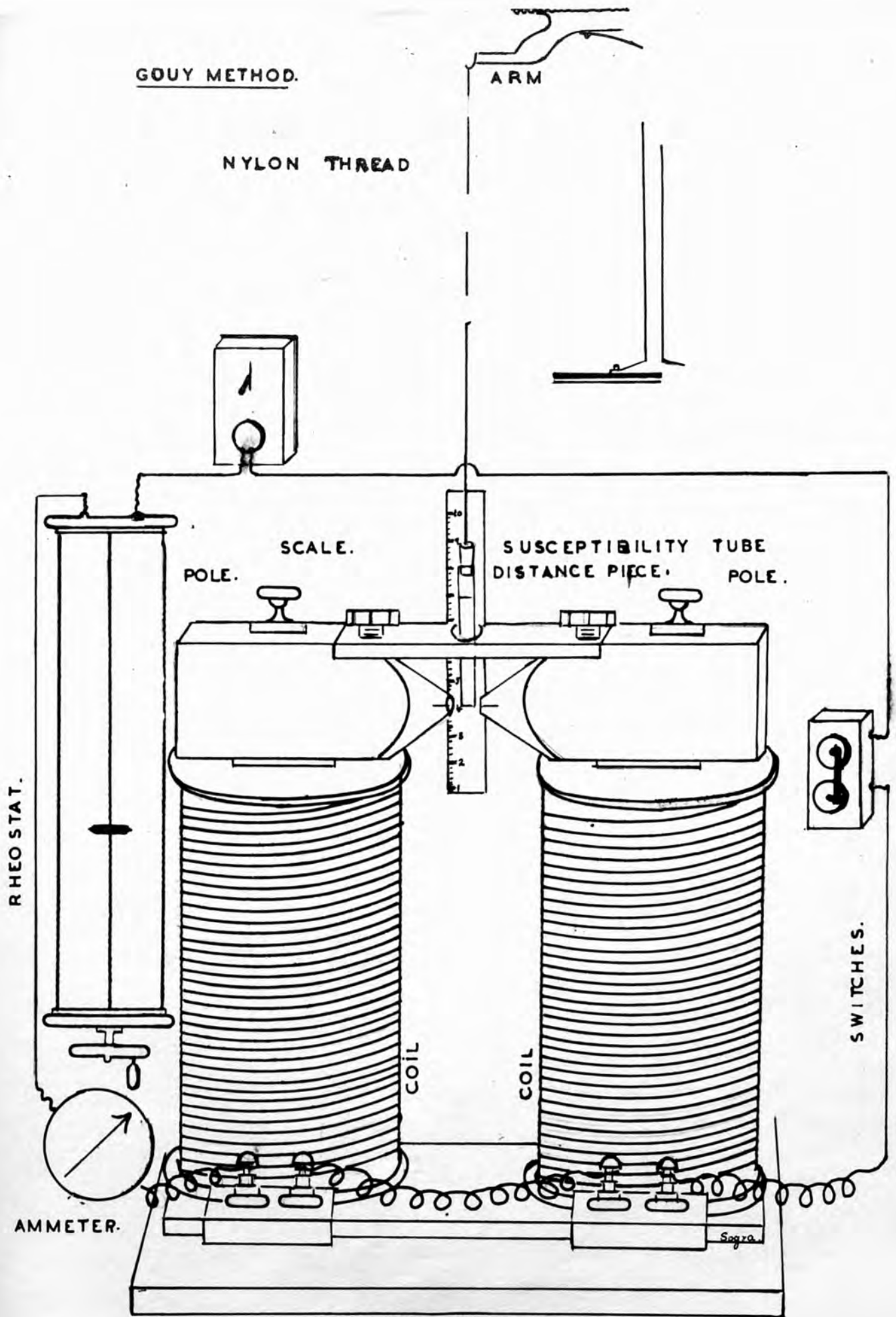
C

C

20,000 TURNS  
41.5 Amps

20,000 TURNS  
41.5 Amps

GOUY METHOD.



**ELECTRO MAGNET.**

Diagram II.



The above expression (1) can be written:-

$$\chi = \frac{2F L}{W(H_1^2 - H_2^2)} + \frac{K_2 \times LA}{W}$$

$K_2$  = Volume susceptibility of air =  $.0294 \times 10^{-6}$

$$\therefore \chi = \frac{2F L}{W(H_1^2 - H_2^2)} + \frac{.0294 \times 10^{-6} \times LA}{W}$$

In this equation  $LA = V$  = volume of the material

$$\therefore \chi = \frac{2F L}{W(H_1^2 - H_2^2)} + \frac{.0294 \times 10^{-6} \times V}{W}$$

Since diamagnetic susceptibilities are of the order  $10^{-6}$ , multiplying by  $10^6$ ,

$$\therefore 10^6 \chi = \frac{2FL \times 10^6}{W(H_1^2 - H_2^2)} + \frac{.0294 \times V}{W}$$

When  $L$  is sufficiently large then  $H_2$  becomes zero; and this was assumed to be the condition in the experiment. Also, for a given length of specimen and aperture between the pole pieces, the length of the specimen  $L$  and the fields  $H_1$  and  $H_2$  were constant.

$$\text{Hence } 10^6 \chi = \frac{\Delta F}{W} + \frac{.0294 \times V}{W}$$

Where  $a = \frac{2L \times 10^6}{H_1^2}$  and is a constant for the apparatus.

For convenience,  $F$  was measured in mg.  $L$  in cm.  $V$  in cc, and  $W$  in gms; and  $a$  was expressed in C.G.S. units.

$$a = \frac{2L}{H_1^2} \times \frac{981 \times 10^6}{1000}$$

This expression was used to calculate the field strength.

The coils of the magnet in *diag (1)* contained 20,000 turns, and with a pole gap of 1.5 cm and a current of 3 Amperes at 200 volts gave a field of 4,588 gauss. The method of calculation of the field strength is given on P. ( 40 ).

The current was controlled by a variable rheostat connected in series with the coils. The poles were kept at a fixed distance by the brass distance piece for all comparative measurements as the field varies with pole-separation.

The weighing was performed by means of a sensitive Bunge short-beam balance, mounted above the electro-magnet as shown in the plate. The left-hand pan was replaced by a hook which carried a nylon thread by which the specimen tube was hung. The tube was suspended centrally by passing the nylon thread directly through the middle of the rubber stopper. This enabled the specimen to be readily suspended in the same position in the field from one reading to the next. Nylon thread was chosen for its cheapness and its strength. It does not tend to kink in the same way as platinum or phosphor-bronze wire. A further advantage of its use is that it is very easy to adjust

to any required length. The susceptibility of the specimen was measured in a glass tube having a mark not less than 7.0 cm. from the bottom. The tube being 0.6 cm. in radius, gave an area of cross-section of material between the pole pieces of  $1.13 \text{ cm}^2$ . The glass of the tube has a low magnetic susceptibility. All precautions were taken to obtain a pure standard for reference, such as pure benzene. May & Baker's "molecular weight" benzene was used as starting material, and was recrystallised by freezing and redistilled, the middle fraction only in each case (one third) being employed. The purity was tested by determination of the refractive index (using the sodium D line at  $20^\circ\text{C}$ ) with a Pulfrich refractometer. The samples used were found to have a refractive index  $N_D^{20} = 1.5011$ , in good agreement with the figure given by Timmermans <sup>(30)</sup> for pure benzene.

Unsaturated hydrocarbons in the samples of benzene used as standards were shown to be absent on shaking with concentrated sulphuric acid. No appreciable yellow colour was obtained. Thiophene was shown to be absent by the isatin test. Benzene was used throughout as the standard substance as it is relatively easy to obtain a pure specimen and its magnetic susceptibility has been well established i.e.

$-10^6 \chi = .7023$  C.G.S. units. A suitable experimental technique for the determination of mass susceptibility of the liquids by the "Gouy" method previously described has been devised by Frenck <sup>(31)</sup> and Trew. A number of special points for ensuring greater

precision have been adopted.

In the "Gouy" method of determining magnetic mass susceptibility when the top of the specimen is in zero field and the bottom is in field  $H_1$  the susceptibility is given by:-

$$10^6 \chi = \frac{aF}{W} + \frac{.0294 \times V}{W}$$

Where  $F$  is the resultant force on the liquid under investigation, and the other terms are as before:-

$$10^6 \chi = \frac{aF}{W} + \frac{.0294}{d} \quad \text{where } d =$$

density of specimen =  $\frac{W}{V}$

Hence for liquid A;

$$10^6 \chi_A = \frac{a F_A}{W_A} + \frac{.0294}{d_A}$$

$$\text{or } 10^6 \chi_A = \frac{a F_A}{V d_A} + \frac{.0294}{d_A}$$

where  $V$  = volume of specimen to the mark.

similarly for a standard liquid B;

$$10^6 \chi_B = \frac{a F_B}{V d_B} + \frac{.0294}{d_B}$$

$$\therefore \frac{10^6 \chi_A - .0294/d_A}{10^6 \chi_B - .0294/d_B} = \frac{F_A d_B}{F_B d_A}$$

Substituting the measured values of  $F_A$  and  $F_B$  the densities  $d_A$

and  $d_B$  of the specimens at the temperature of the experiment and the known value of  $\chi_B$  gives  $\chi_A$  whence

$$10^6 \chi_A = \left[ (10^6 \chi_B - \frac{.0294}{d_B}) \times \left( \frac{F_A d_B}{F_B d_A} \right) \right] + \frac{(.0294)}{d_A}$$

The above mentioned method eliminates several errors,  $F_A$  and  $F_B$  can be measured to within 0.1 - 0.2%. An accurate thermometer between the poles of the magnet was used to record temperatures at which experiments were carried out.

In addition to the above modified 'Gouy' technique and method for liquids a better technique for measurements on solids, developed by Trew (in process of publication) (32) was employed. An improved method of packing the material in the susceptibility tube was used and removal of air from the interstices of the solid was ensured. The method as described below is suitable for those solids which were insoluble and did not react with benzene. (Any suitable inert solvent can be used in principle). The method eliminates several sources of error inherent in the previous method of packing. The resultant diamagnetic susceptibilities so obtained on solids are slightly higher than the values previously published due to the elimination of several errors. The possible sources of error are considerable and have recently been discussed by French & Harrison, and by Eggleston Evans & Richard. (33) French & Harrison pointed out that measurements on solids might be inaccurate owing to the air in the interstices (34)

of the packed solid, and to the neglect of a meniscus correction when comparing a volume of a packed solid with that of a liquid. A method of measurement of the susceptibility of solids was adopted in this work which eliminates both of these sources of error. The method developed by Trew consists of packing the solid whose susceptibility is to be measured uniformly, under the liquid <sup>which</sup> is employed as standard. The susceptibilities in this work are calculated from the relations which follow from the equation:-

$$10^6 \chi = \frac{a F}{W} + \frac{.0294x V}{W}$$

Where all terms are as before.

Hence for a standard material, which was benzene.

$$10^6 \chi_B = \frac{a F_B}{W_B} + \frac{.0294xV}{W_B} \text{ -----(1).}$$

similarly for the mixture i.e. the salt + benzene:-

$$10^6 \chi_T = \frac{a F_T}{W_T} + \frac{.0294xV}{W_T} \text{ -----(2).}$$

To eliminate  $a$  divide expression (2) by (1).

$$\frac{(10^6 \chi_T - \frac{.0294xV}{W_T})}{(10^6 \chi_B - \frac{.0294xV}{W_T})} = \frac{F_T \times W_B}{F_B \times W_T}$$

$$\text{or } (10^6 \chi_T - \frac{.0294xV}{W_T}) = (10^6 \chi_B - \frac{.0294xV}{W_B}) \times \frac{F_T \times W_B}{F_B \times W_T}$$

Substituting the measured values of  $F_T$  and  $F_B$ , of  $W_T$  and  $W_B$ , and the known value of  $X_B$ , gives  $X_T$ , the susceptibility of the packed mixture ( $\times 10^6$ ).

Assuming strict additivity, it follows that

$$10^6 X_T = x \times 10^6 X_{\text{salt}} + y \times 10^6 X_{\text{benzene}}$$

where  $x$  and  $y$  are the weight fractions of salt and benzene in the tube up to the mark.

hence  $x \times 10^6 X_{\text{salt}} = 10^6 X_T - y \times 10^6 X_{\text{Benzene}}$

$$10^6 X_{\text{salt}} = \frac{10^6 X_T - y \times 10^6 X_{\text{Benzene}}}{x}$$

iii. DETAIL OF MAGNETIC SUSCEPTIBILITY MEASUREMENT.

To carry out a measurement on a solid, some pure benzene was placed in the susceptibility tube to fill it about half full, and about .02 gms of powdered solid material whose susceptibility was required was added at a time and the tube was tapped at intervals to remove <sup>air</sup> bubbles and ensure uniform sedimentation. After having filled the material to the mark in this way the excess of benzene was removed from the top carefully with a fine capillary dropper, before taking a measurement, great care being taken to ensure filling exactly to the mark.

The weight of the material packed was noted. This could be easily found by weighing the container of the material before and after packing. The tube was then weighed with and without the presence of the magnetic field in the usual manner and thus the total thrust on the solid and benzene was noted. The tube was centrifuged. The contents of the tube were drawn in slightly in most cases and the above procedure repeated. The tube was always centrifuged to a constant weight. The results in <sup>the</sup> Tables (Appendix) show that remarkably consistent values were obtained in this way. Care was taken to place the specimen always in the same position in the field and in such a way that one end of it lay exactly at the centre of the pole pieces and the other end in a region where the field was negligible. Weighings were made to 0.01 mg, the last place being determined by the oscillation method, using standard weights and allowing



only small amplitudes of swing to ensure that the tube did not swing out of the uniform field. The magnet and apparatus below the bench were boarded in to prevent draughts. Care was taken not to allow the coils to become too hot as convection currents caused by heating disturb the oscillations. This was avoided by exciting the magnet for a short period only, and enclosing the coil below the magnet yoke with a plastic polythene cover which acted as a partial thermal insulator. The balance was shielded from the magnet by a sheet of wire gauze placed under the pan to cut off any stray small residual field which might influence the stainless steel milligram weights.

$$10^6 \chi_T = .01904 \quad \left[ \begin{array}{l} .60193 \\ -1.45304 \end{array} \right]$$

$$10^6 \chi_T = -.50322$$

$$10^6 \chi_T = -.59080 \quad -.01904$$

$$= -.57026$$

W<sub>1</sub> salt packed = 8.3656 g, W<sub>2</sub> = 2.2878 g; W<sub>T</sub> = 11.3639 g.

$$x = \frac{8.3656}{11.3639} \quad ; \quad y = \frac{2.2878}{11.3639}$$

where x and y are the weight fractions of salt and benzene in the tube up to the mark and  $10^6 \chi$  benzene = -.7383

$$\text{hence } y \cdot 10^6 \chi_B = .09373 \quad x (-.7383)$$

$$= -.12477$$

assuming additivity:-

$$10^6 \chi_T = x \cdot 10^6 \chi_S + y \cdot 10^6 \chi_B$$

Examples of Calculations.

Calculations for potassium chloride (solid). Packed in Benzene.

Temperature 20.40°

$v = 7.703$  c.c.,  $W_B = 6.72647$  g.  $F_B = 6.56$  mg.  $W_T = 11.35395$  g.  
 $F_{Tube} = 0.27$  mg.  
 F is an upward thrust throughout, as all materials investigated were diamagnetic.

$$F_T = 8.88 \text{ mg thrust upwards}$$

$$\text{i.e. wt with field off} = 17.58465 \text{ g.}$$

$$\text{,, ,, field on} = 17.57550 \text{ g.} \therefore \text{Total Thrust} = 9.15 - 0.27 = 8.88 \text{ mg}$$

$$\text{I. } \left[ 10^6 X_T - \frac{.0294 \times 7703}{11.35395} \right] = \left[ \frac{8.88 \times 6.72647}{11.35395 \times 6.56} \right] \left[ .7023 - \frac{.0294 \times 7.703}{6.72647} \right]$$

$$\left[ 10^6 X_T - .01994 \right] = \left[ .80195 \times (-.73596) \right]$$

$$\begin{aligned} &= -.59020 \\ 10^6 X_T &= -.59020 + .01994 \\ &= -.57026 \end{aligned}$$

$$W_s \text{ salt packed} = 8.3666 \text{ g, } W_{B_1} = 2.9873 \text{ g; } W_T = 11.35393 \text{ g.}$$

$$x = \frac{8.3666}{11.35395} ; y = \frac{2.9873}{11.35395}$$

Where x and y are the weight fractions of salt and benzene in the tube up to the mark and  $10^6 X_{\text{Benzene}} = -.7023$

$$\text{hence } y \cdot 10^6 X_B = \frac{.29873}{11.35395} \times (-.7023)$$

$$= -.18477$$

Assuming Additivity:-

$$10^6 X_T = x \cdot 10^6 X_S + y \cdot 10^6 X_B$$

$$10^6 \chi_S = -.57026 + .18477$$

$$= -.38549$$

$$10^6 \chi_S = -.38549 \times \frac{11.35395}{8.3666}$$

$$= -.5231$$

After having taken this reading the tube was centrifuged (the contents of the tube were drawn down slightly in most cases) and the above procedure was repeated.

$$\text{II} \quad V = 7.703 \text{ cc}; W_B = 6.72647 \text{ g}; F_B = 6.56 \text{ mg}, W_T = 11.49155.$$

$$F_T = 8.94 \text{ mg.}$$

$$\left[ 10^6 \chi_T - \frac{.0294 \times 7.703}{11.49155} \right] = \left[ \frac{8.94 \times 6.72647}{11.49155 \times 6.56} \right] \times (-.73596.)$$

$$\left[ 10^6 \chi_T - .01970 \right] = \left[ (-.79770) \times .73596 \right]$$

$$= -.58707$$

$$10^6 \chi_T = -.58707 + .01970$$

$$10^6 \chi_T = -.56737$$

$$W_S = 8.5678 \text{ g}; W_B = 2.9237 \text{ g}, W_T = 11.49155 \text{ g.}$$

$$x = \frac{8.5678}{11.49155}, \quad y = \frac{2.9237}{11.49155}, \quad y 10^6 \chi_B = \left[ \frac{2.9237}{11.49155} \times (-.7025) \right]$$

$$= -.17862$$

$$10^6 \chi_T = x 10^6 \chi_S + y 10^6 \chi_B$$

$$x \times 10^6 \chi_S = -.56737 + .17862$$

$$= -.38875$$

$$\therefore 10^6 \chi_s = -.5214$$

III.  $V = 7.703 \text{ c c}, W_B = 6.72647 \text{ g}, F_B = 6.56 \text{ mg}.$

$$W_T = 11.5538 \text{ g}.$$

$$F_T = 8.98 \text{ mg}.$$

$$\left[ \frac{10^6 \chi_T - .0294 \times 7.703}{11.55380} \right] = \left[ \frac{8.98 \times 6.72647}{11.5538 \times 6.56} \right] \times [(-.73596)]$$

$$\left[ 10^6 \chi_T - .01960 \right] = [(-.79695) \times .73596]$$

$$= -.58652$$

$$10^6 \chi_T = -.58652 + .01960$$

$$= -.56692$$

$$W_s = 8.6399 \text{ g}; W_B = 2.9110 \text{ g}; W_T = 11.55380 \text{ g}.$$

$$x = \frac{8.6399}{11.55380}; y = \frac{2.9110}{11.55380}; y \cdot 10^6 \chi_B = \frac{-2.9110 \times .7023}{11.55380}$$

$$= -.17694$$

$$10^6 \chi_T = x \cdot 10^6 \chi_s + y \cdot 10^6 \chi_B$$

$$x \cdot 10^6 \chi_s = -.56692 + .17694$$

$$= -.38998$$

$$10^6 \chi_s = -.5215$$

$$\therefore \text{mean } 10^6 \chi_s = .5216$$

$$-10^6 \chi_M = 38.89$$

(Error = 0.2%)

DETAILS OF CALIBRATIONS OF APPARATUS.

I. The magnetic field was calibrated by the use of substances of accepted susceptibility. Benzene ( $\chi = 7.023 \times 10^{-6}$  C.G.S. units, which has a zero temperature co-efficient, and water ( $\chi = 7.200 \times 10^{-6}$ ) C.G.S. units, which has a very low temperature co-efficient, were used in the calibration. A solution of copper sulphate of 31%<sup>(g/100g)</sup> composition was also used.

Determination of variation of field with the current.

The manner in which the magnetic field varied with the current in the coil was investigated by determining the magnetic force exerted on a 7.5 cm long tube filled with the 31% copper sulphate solution at 16.5°C<sup>o</sup> (room temperature), using different exciting currents, with the pole-pieces at a fixed pole separation of 1.5 cm. A graph of the pull on the copper sulphate solution against exciting current was plotted on figure (1)a. A similar experiment with water was also carried out<sup>Figure (1) b.</sup> Both these graphs show that the saturation current was at about 5 ampères. Hence it was essential when working at a lower current, to ensure that the current was accurately fixed throughout the measurement. This was adjusted with the help of a very sensitive rheostat shown in the diagram (II), in series with the coils, the readings of the Crompton moving coil ammeter A being kept at 3.00 ampères during the experiments.

-11.3

THRUST ON CUSO<sub>4</sub> SOLUTION.

-10.3

-9.3

AMPÈRES

2.5 3.0 3.5 4.0 4.5 5.0

FIG I a.

THRUST ON WATER.

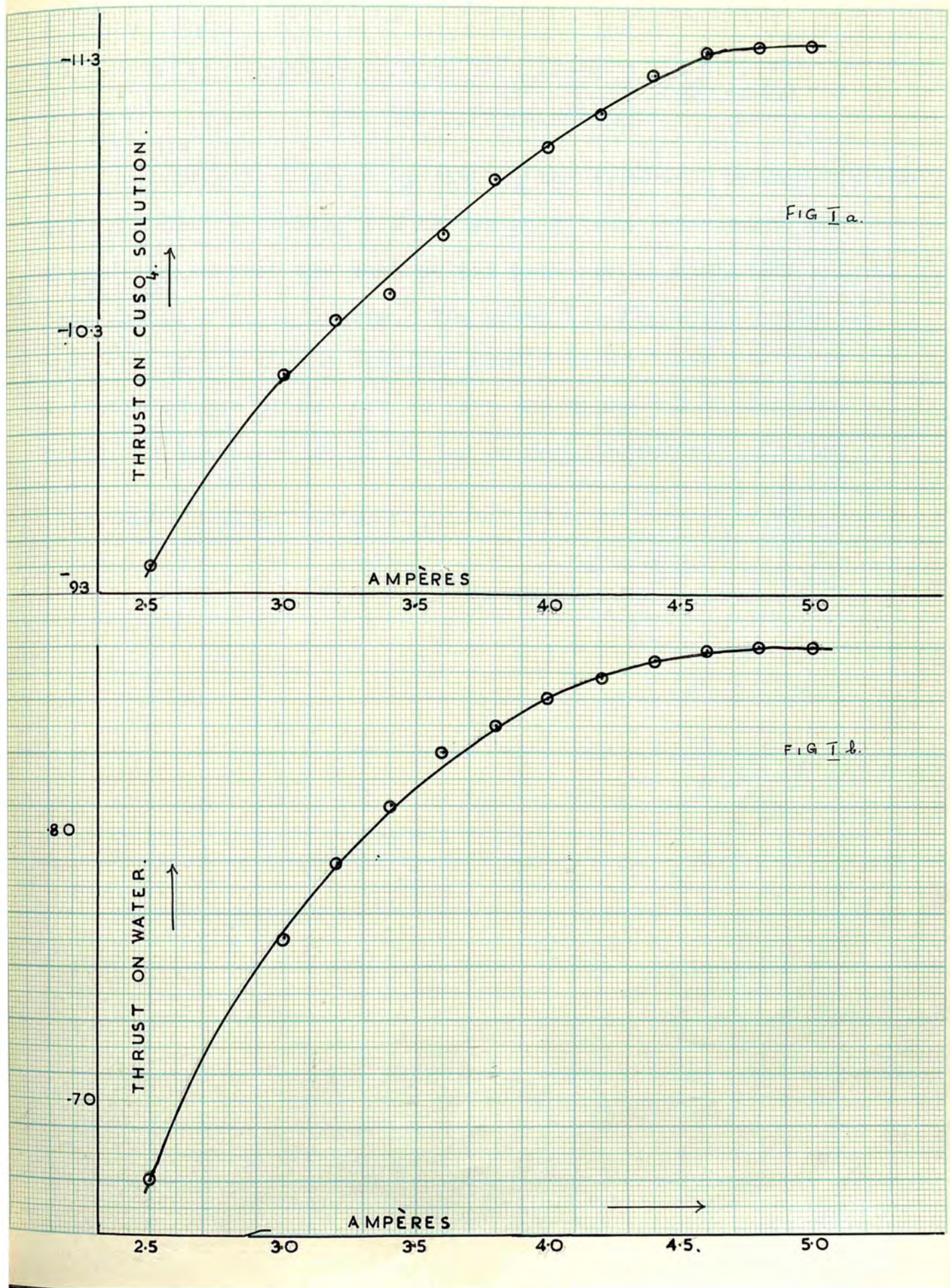
80

70

AMPÈRES

2.5 3.0 3.5 4.0 4.5 5.0

FIG I b.



II.

THE VARIATION OF MAGNETIC FORCE ON THE SPECIMEN  
WITH THE HEIGHT OF THE BASE OF THE TUBE ABOVE  
THE POLE - PIECE CENTRE.

This was determined by filling the tube with benzene to the mark and then measuring the thrust at 3 amps, shortening the suspension so that the base of the tube was at different heights from the pole-piece centre. The graph (in figure II) indicates that the length of the specimen should be at least 4.0 cm or a little longer to be sure to have the upper end in the zero field. A constant length of 7.0 cm was, therefore, adopted.

THRUST ON BENZENE

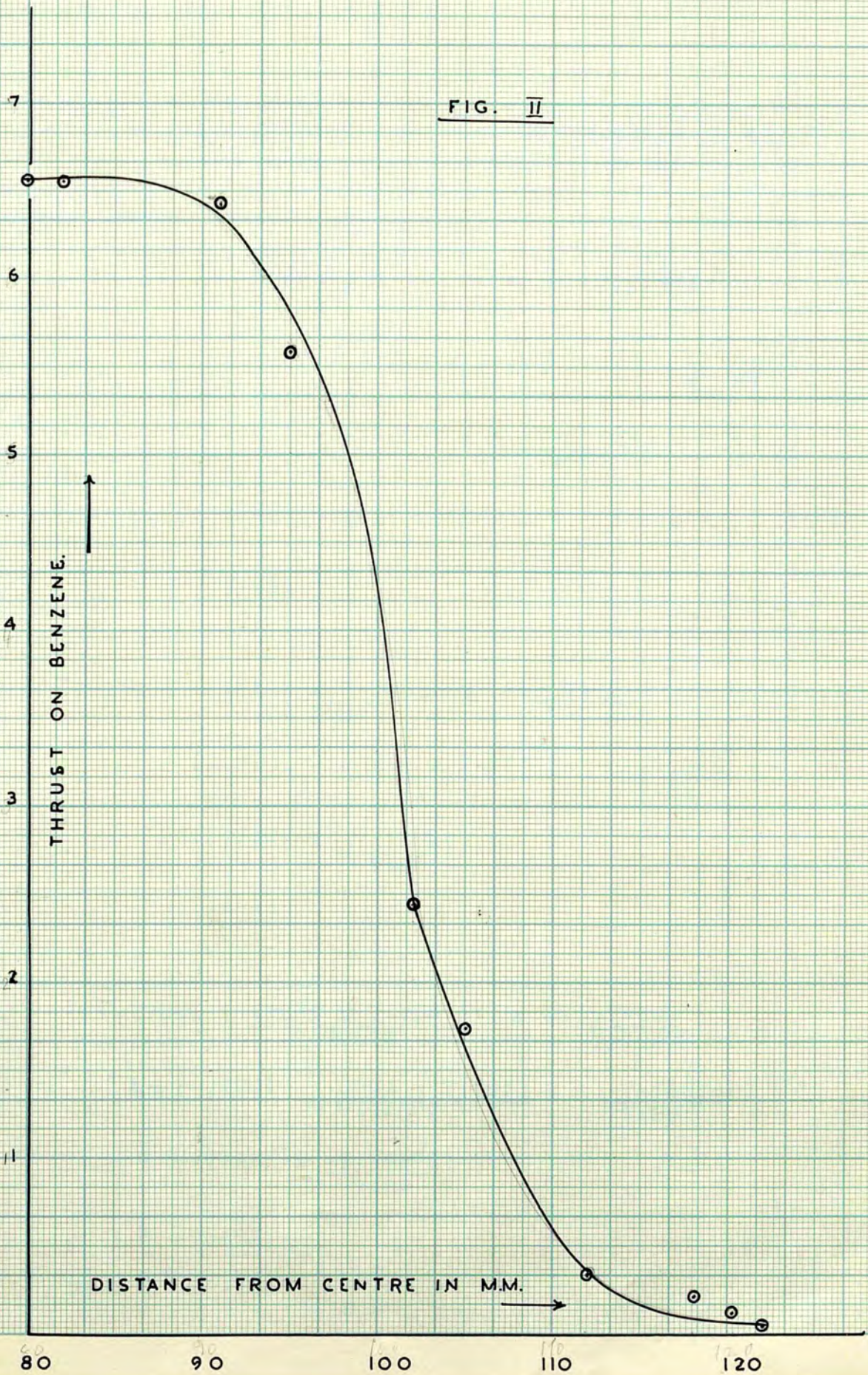
DISTANCE FROM CENTRE IN MM

80

90

100

FIG. II





Calculation of Balance Constant  $a$ .

$$X \text{ water} = \frac{a F}{\text{wt. of water to the mark}} + \frac{.0294 \times \text{Volume of tube}}{\text{wt. of water to the mark}}$$

$$\text{I.} \quad (-.7201 - \frac{.0294 \times 7.703}{7.67789}) = (a \cdot \frac{-7.633}{7.67789})$$

$$\begin{aligned} \therefore a &= (-.7201 - \frac{.0294 \times 7.703}{7.67789}) \times (-\frac{7.67789}{7.633}) \\ &= (-.7201 - .02949) \times (-\frac{7.67789}{7.633}) \\ &= -.7495 \times (-\frac{7.67789}{7.633}) \\ &= .75399 \end{aligned}$$

$$\text{II.} \quad (-.7201 - \frac{.0294 \times 7.703}{7.71028}) = a(\frac{-7.65}{7.71028})$$

$$\therefore a = (-.7201 - \frac{.0294 \times 7.703}{7.71028}) \times (-\frac{7.71028}{7.65})$$

$$= (-.74947 \times \frac{-7.71028}{7.65})$$

$$= .75537$$

$$\text{III.} \quad (-.7201 - \frac{.0294 \times 7.703}{7.74572}) = a(\frac{-7.69}{7.74572})$$

$$\therefore a = (-.7201 - \frac{.0294 \times 7.703}{7.74572}) \times (\frac{-7.74572}{7.69})$$

$$= (-.74933 \times \frac{-7.74572}{7.69})$$

$$= .75475.$$

$$\therefore \text{mean } a = .7547$$

Calculation of field strength:-

$$d = .7547 \text{ and } L = 8.100\text{cm.}$$

Therefore from the equation

$$d = \frac{2 L}{H_1^2} \times 10^6$$

$$H_1 = \sqrt{\frac{2 \times 8.1 \times 10^3 \times 984}{.7547}}$$

$$= \sqrt{\frac{1589220}{.7547}}$$

$$= \sqrt{21057638}$$

$$= 4,588 \text{ gauss.}$$

SUMMARY OF CALIBRATION

The calibration curves bring out the following points; for consistent results all these should be considered.

- (1) The pole-piece separation must be constant.
- (2) The exciting current must be kept constant.
- (3) The length of the specimen column must exceed 4.0 cm in length.
- (4) The tube must always be in the same position i.e. in the centre of the field and be adjusted vertically. This was ensured by the scale shown in the diagram of the apparatus.

### Density measurements

The density of the various solids and solutions investigated was measured to enable the effective molecular volumes of the salt to be calculated, as it was thought that some comparison might be found between changes in density or molecular volume and susceptibility.

The density of a solid is a scalar property, and the most exact methods <sup>of measurement</sup> are (1) The hydrostatic balance method, <sup>and</sup> (2) methods involving the use of a specific gravity bottle or pyknometer of some type. <sup>(44)</sup> The specific gravity bottle method was used to measure the density of the solids. A known weight  $W$  of solid was put into a c.c. bottle, covered with the purified benzene, whose density was previously measured relative to distilled water and found to agree with the accepted value. Air bubbles were extracted by shaking and tapping the bottle. The specific gravity bottle was placed in a thermostat at  $20^{\circ}\text{C}$  for about half an hour and was then filled to the mark and its weight  $W_2$  was found. The solid was removed and the bottle was filled with benzene alone and the procedure repeated and  $W_1$  was noted. Density of the solid was thus calculated from the formula

$$\text{Density of the solid} = \frac{W \times d}{(W + W_1 - W_2)}$$

Where  $W$  is the weight of the substance,  $W_1$  the weight of the bottle and benzene,  $W_2$  the weight of the bottle, benzene and solid, and  $d$  the density of benzene

### Determination of the Densities of solutions.

The densities were determined, relative to the density of water at 20°C, using a two millilitre graduated pycnometer. It had a ground glass stopper to prevent evaporation. It was also provided with a platinum wire for easy attachment to the balance.

The balance used for this purpose was an accurate Sartorius analytical balance sensitive to 0.1 mg. The density of the

$$\text{solution} = \frac{\text{wt. of solution to the mark}}{\text{wt. of water to the mark}} \times .99823.$$

$$\text{where } d_{4}^{20} \text{ H}_2\text{O} = .99823$$

The buoyancy correction was not applied as it amounted to only about one unit in the fourth place for most solutions.

The various densities measured, and the effective molecular volumes calculated from these (i.e.  $Mwt/d_{4}^{20}$ ) are recorded in <sup>the</sup> Table on p 42 a. <sup>molecular volumes are also included in later Tables.</sup> The relationship between the susceptibilities and densities and other properties are discussed in the sections dealing with results.

KI.	3.0337	136.02	34.72
K <sub>2</sub> SO <sub>4</sub> .	2.5438	174.26	62.76
MgCl <sub>2</sub> ·6H <sub>2</sub> O.	1.5931	203.85	128.03
MgSO <sub>4</sub> ·6H <sub>2</sub> O.	2.0639	203.26	141.60
MgCl <sub>2</sub> ·6H <sub>2</sub> O.	2.0716	422.02	203.84
ZnSO <sub>4</sub> ·7H <sub>2</sub> O.	1.6702	227.64	146.89
ZnCl <sub>2</sub> .	3.2134	133.27	46.74
MgSO <sub>4</sub> ·7H <sub>2</sub> O.	1.6302	225.34	135.97

Densities & Effective Molecular Volume of Salts.

42 a.

Double salts.	Densities at 20° C.	Molecular weight.	Calc. Molar Volume.
$MgCl_2NH_4Cl.6H_2O.$	1.5057.	256.82	170.56
$MgBr_2NH_4Br.6H_2O.$	1.9886	390.05	196.14
$MgI_2NH_4I.6H_2O.$	2.3442	531.24	226.62
$MgCl_2KCl.6H_2O.$	1.6155	277.88	172.00
$MgBr_2KBr.6H_2O.$	2.1349	411.27	192.64
$MgI_2KI.6H_2O.$	2.5291	552.18	218.33
$MgSO_4(NH_4)_2SO_4.6H_2O.$	1.7003	360.63	212.09
$MgSO_4K_2SO_4.6H_2O.$	2.1422	402.75	188.00
$ZnSO_4(NH_4)_2SO_4.6H_2O.$	1.8992	401.67	211.49
$ZnSO_4K_2SO_4.6H_2O.$	2.2449	443.70	197.64
Single salts.			
$NH_4Cl$	1.5328	53.50	34.90
$NH_4Br.$	2.4128	97.96	40.60
$NH_4I.$	2.4995	144.96	57.99
$(NH_4)_2SO_4$	1.7768	132.14	74.37
$KCl$	1.9909	74.56	37.45
$KBr$	2.6839	119.02	44.34
$KI.$	3.0337	166.02	54.72
$K_2SO_4.$	2.6496	174.26	65.76
$MgCl_2.6H_2O.$	1.5881	203.33	128.03
$MgBr_2.6H_2O.$	2.0639	292.25	141.60
$MgI_2.8H_2O.$	2.0716	422.28	203.84
$ZnSO_4.7H_2O.$	1.9702	287.44	145.89
$ZnCl_2.$	2.9154	136.29	46.74
$MgSO_4.7H_2O.$	1.6360	246.50	150.67

(3) Results.The diamagnetic susceptibility of a Series of salts in the crystalline state and in solution

Table I summarises the results obtained for the diamagnetic susceptibility of the simple salts investigated in the solid state and in aqueous solution. Measurements were carried out at room temperature. Detailed Tables of individual measurements will be found in the appendix at the end of the Thesis. The values for the molar susceptibility of salts in solution given in Table I were calculated, as by previous workers, assuming additivity, from the relationship.

$$\chi_{\text{Measured}} = W_1 \chi_{\text{solvent}} + W_2 \chi_{\text{solute}}$$

Where  $W_1$  and  $W_2$  are the weight fractions of solvent, (i.e. grams solvent or solute per gram of solution). The molar susceptibility then follows by multiplying by the molecular weight. The fourth column of Table I shows the molar susceptibility values recorded by other investigators where these are available. In the last column the molecular volumes of the salts calculated from the densities are recorded. The values for the diamagnetic susceptibilities of salts in the crystalline states were generally in good agreement with those of other workers, <sup>but</sup> tend to be slightly higher in certain cases than the previous values reported, probably because of the

Table I

Experimental Molar Susceptibilities of potassium, ammonium  
magnesium and zinc simple salts.

Salts	State	$-10^6 \chi_M$	$-10^6 \chi_M$ . Literature	Molecular Volume $V = \frac{M}{d}$
$NH_4Cl$	solid	36.73	(43) (63) (62) (11) 34.2 ; 35.7 ; 36.2 ; 36.7 32.37 (14)	34.9
" "	solution	38.47	38.5 (11)	
$NH_4Br$	solid	46.96	(42) (63) (62) (11) 47.4; 46.7; 46.2; 47.0; 42.59 (14)	40.60
" "	solution	49.18	49.8 (11)	
$NH_4I$	solid	64.07	(43) (63) (62) (11) 66.0; 69.5; 64.1; 64.4; 59.84 (14)	57.99
" "	solution	66.39	66.4 (11)	
KCl	solid	38.89	(64) (43) (63) (8) 39.1; 35.8; 36.15; 38.8 (65) 39.4; 38.47 (14)	37.40
" "	solution	40.94	(66) (65) 34.74; 39.4;	
KBr	solid	49.84	(64) (43) (63) (8) 49.15; 48.2; 48.1; 49.2; (14) (65) 42.59; 50.3;	43.40 b
" "	solution	52.09	40.82 (66)	

Salts	State	-10 <sup>6</sup> .X <sub>M</sub>	-10 <sup>6</sup> .X <sub>M</sub> . Literature	Molecular Volume $V = \frac{M}{d}$
KI	solid	65.84	(64) (43) (63) (8) 63.8; 62.7; 63.9; 65.7	54.70
" "	solution	68.40	-	
MgCl <sub>2</sub> ·6H <sub>2</sub> O	solid	50.80	(67) (64) 50.44; 47.45	128.03
" "	solution	52.71	-	
MgBr <sub>2</sub> ·6H <sub>2</sub> O	solid	72.89	(67) 71.84	141.60
" "	solution	74.38	-	
MgI <sub>2</sub> ·8H <sub>2</sub> O	solid	109.69	(67) (75) 109.42; 111.4	203.84
" "	solution	111.68	-	
MgSO <sub>4</sub> ·7H <sub>2</sub> O	solid	44.23	(2) (14)b (17) (43) 46.57; 44.85; 43.86; 41.00; 43.34; (61) 45.07; (68)	150.67 b
" "	solution	48.69	(68) 43.18;	
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	solid	42.91	-	
" "	solution	47.60	-	



Salts	State	$-10^6 \cdot \chi_M$	$-10^6 \cdot \chi_M$ . Literature	Molecular Volume $V = \frac{M}{d}$
$MgCO_3 \cdot 3H_2O$	solid	32.46		
$ZnCl_2$	solid	55.72	(43) 58.2	46.74
" "	solution	60.49		
$ZnBr_2$	solid	78.96		
" "	solution	88.40		
$ZnI_2$	solid	108.72		
" "	solution	112.65		
$ZnSO_4 \cdot 7H_2O$	solid	45.67	(14)b (69) (43) (17) 47.25; 41.50; 44.6; 52.08;	145.89
" "	solution	52.91		
$Zn(NO_3)_2 \cdot 4H_2O$	solid	51.39		
" "	solution	62.37		

improved method of measurement. Of the factors tending to cause errors in the susceptibility, for which allowance must be made, the most important are as previously indicated (a) a meniscus correction, for the correct volume of the tube and (b) a correction for the presence of air enclosed in the packed solid. The effect of these factors has been considered to some extent by previous workers. Nettleton and Sugden considered the former in detail but do not mention a correction for air. Very recently these two points have been emphasised by French and Harrison who have also reported a slightly higher susceptibility for solids after having made correction for the above. In the previous methods of packing, the solid substance contains a variable volume of air in the interstices of the solid particles. The paramagnetism of the oxygen of this air will tend to cause a lowering in the diamagnetism, and hence a lower value for the diamagnetic susceptibility is obtained.

In the present method of measurement the solid is surrounded by the standard liquid while the susceptibility is being measured and hence the effect of air between the solid particles, for which French and Harrison derived a correction, is entirely eliminated. In addition, the liquid meniscus is the same when the force on the solid is measured as when that on the standard is obtained, so deleting this further source of error. Centrifuging the material to a constant weight <sup>of specimen</sup> in the tube also serves to ensure a uniform packing of the material throughout the whole 7 cm. length. In measurements on liquids the effect of dissolved

(34)

oxygen has been reported by Eggleston and Evans to influence measurements of diamagnetic susceptibility and they recommend that for greater accuracy these measurements should be made in the absence of air. In the present measurements the standard liquid is likely to contain a similar amount of air while the force on the specimen is being measured to that which it has when being employed as standard and hence any error due to dissolved air will be reduced to a minimum. In measurements on solutions these were all subjected to similar exposure to air and hence it is unlikely that errors due to dissolved air will be appreciable. Checks on the thrust on the benzene standard were made at intervals and its susceptibility relative to water was determined and in no case could any appreciable variation which might be due to a difference in the dissolved air content be detected. A few observations, were made on the susceptibility of purified benzene to check its susceptibility with respect to water. The results are given below.

Magnetic Susceptibility of Benzene

- $10^6 \chi$	- $10^6 \chi$	- $10^6 \chi$	
0.70232	0.70217	0.70238	Mean 0.70229

Recent values found for benzene at 20C.

Authors	$-10^6\chi$
(37)	
Cabrera & Fahlenbrach	0.6803
(38)	
Trew & Spencer	0.7098
(39)	
Seely	0.6977
(40)	
Angus & Hill	0.7023
(31)	
French & Trew	0.702
Cutforth & Selwood	0.7065

The present value for benzene agrees fairly well with the values of other investigators. The mean figure  $-0.7023 \times 10^6$  was used for the calculations. The values in Table I column 4 also show that for a number of the salts the values found by Prasad and co-workers are in many cases much lower than the present values neither do they agree with those of other workers where available. The recorded values in Table I show that the susceptibility of ions in moderately dilute solution is always higher than in the crystalline state, except in the case of the double salt  $MgSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$  which seems to be anomalous. It is already well established that the susceptibility of ions in crystals is less than the sum of the free ions calculated.

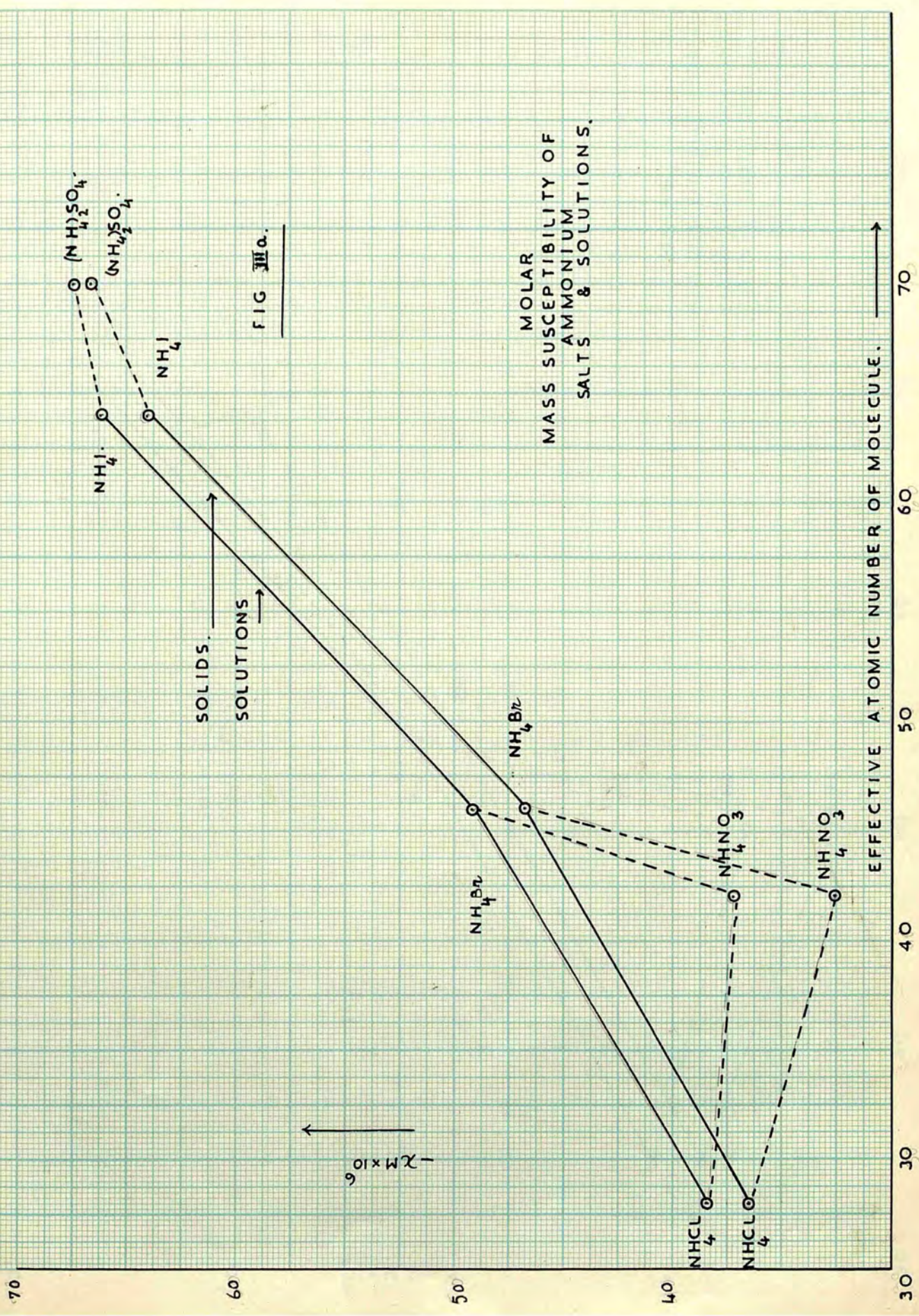
In 1932, Kido measured the magnetic susceptibility of certain alkali and ammonium salts. He noted a linear relationship between molecular magnetic susceptibility and number of electrons in the cation for the series of alkali salts with the same anions, and a similar relationship for the halide series with the same cation. From these results he deduced values for the ionic mass

susceptibility of alkali and halide ions without, however, making any allowance for the co-ordination number in the salts concerned. Some of his measurements were on salts in the solid state and some in solution. Later Brindley and Hoare (44) carried out a systematic investigation of the diamagnetic susceptibility of the alkali halides. In a later paper they showed that slightly higher values for the susceptibility of salts were obtained in the dissolved state than in the crystalline state. It may be said somewhat empirically, that the deforming actions which the ions have on each other when packed into a crystal lower their susceptibility. Brindley and Hoare found that with the exception of lithium and caesium chlorides, bromides and iodides, the susceptibility of other crystalline salts were additive within the limits of experimental error. They suggest reasons for the non additivity in the lithium salts. In lithium halides there is a small cation and relatively a large anion. The anion approaches closely, and the greater electrostatic repulsion which occurs produces larger interatomic distances than would be expected. The caesium halides on the other hand have different crystal structures from the other alkali halides which have the sodium chloride structure, and this is responsible for the deviation from strict additivity here. These workers also explained the higher value of the susceptibility of salts in solution as due to the reduction in the co-ordination number; this finding is also confirmed by the investigation of Bedwell, Spencer and Trew on ammonium (11)

compounds. The change in susceptibility on dissolution has been explained by Brindley & Hoare as due to a change in co-ordination number of the ions. <sup>(46)</sup> Begnal and Fowler had earlier pointed out that for the ions in solution the co-ordination number is lower than in the solid state. The electronic field of an ion is thus more restricted in the solid state than in the solution, with a consequent lowering of the diamagnetism. <sup>(47)</sup> Lee has also shown that the transfer of an ion from the crystalline solid to solution involves two factors, one an increase in susceptibility due to a release of the ion from a strong field in which mutual deformation occurs, and also a counter effect of a deformation of some of the water molecules due to the introduction of an ion into their vicinity, which will lower the susceptibility of the solution. <sup>(48)</sup> Frivold <sup>(49)</sup> and Fahlenbrach <sup>(14)</sup> and Prasad have also reported higher values for the susceptibility of salts in solution, and all these earlier results are fully confirmed by the present results. The exception of magnesium ammonium sulphate may possibly be due to too large a value for the experimental susceptibility in the solid state and a slightly too low value in the dissolved state.

Certain systematic relationships exist between the susceptibilities of salts containing ions of related series which are best shown graphically. These relationships are shown in figures III(a) and (b) for the halide salts of potassium and ammonium. In these graphs the molar susceptibility of the

salts is plotted against the number of electrons in the salt for both the salts in solution and in the crystalline state. Figure (IV) shows the similar relationships for the magnesium and zinc salts investigated. In the case of hydrated salts it was necessary, in order to obtain values for <sup>the</sup> anhydrous salts to subtract a constant amount for the susceptibility of the water combined in the molecule. (i.e. 12.96 susceptibility units for every water molecule present, assuming as is usual in this instance, that the water is additively attached). The values so obtained for the anhydrous salts, plotted in Figure (IV) are then comparable with the values for ammonium and potassium. A similar type of curve is obtained for both sets of results, and the curves for the values in solution are roughly parallel to those in the crystalline state over the corresponding linear section. Similarly the graphs for the magnesium and zinc salts show distinct relationships with those for potassium and ammonium, having the same pattern over the comparable sections. This type of parallelism has already been shown to exist by Trew <sup>(13)</sup> in the values of Brindley and Hoare for the alkaline halides, and for the ammonium halides by Bedwell, Spencer and Trew <sup>(11)</sup>. The present values are in good agreement with this behaviour. The theoretical <sup>(12)</sup> basis of this type of curves has been shown both by Klemm and <sup>(13)</sup> Trew to be in the electronic arrangement of the ions. A change in the slope of the graph results when an increase in the number of electrons occurs due to the beginning of the d and f orbitals within the ions. This will influence the size of the



70

60

50

40

30

$-\chi_M \times 10^6$

SOLIDS.  
SOLUTIONS

FIG IIIa.

MOLAR  
MASS SUSCEPTIBILITY OF  
AMMONIUM  
SALTS & SOLUTIONS.

EFFECTIVE ATOMIC NUMBER OF MOLECULE.

70

60

50

40

30



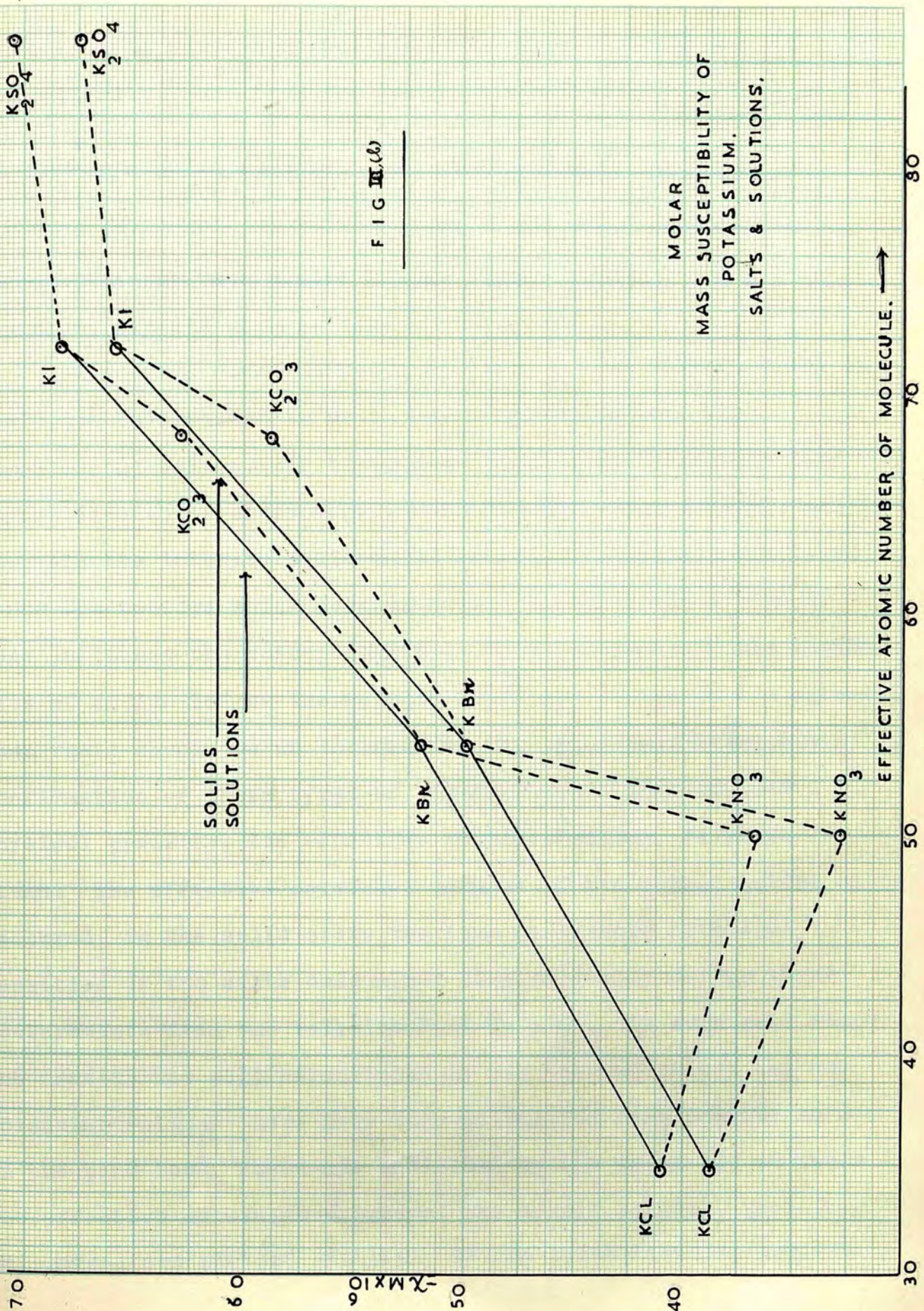


FIG III (b)

MOLAR  
 MASS SUSCEPTIBILITY OF  
 POTASSIUM  
 SALTS & SOLUTIONS.

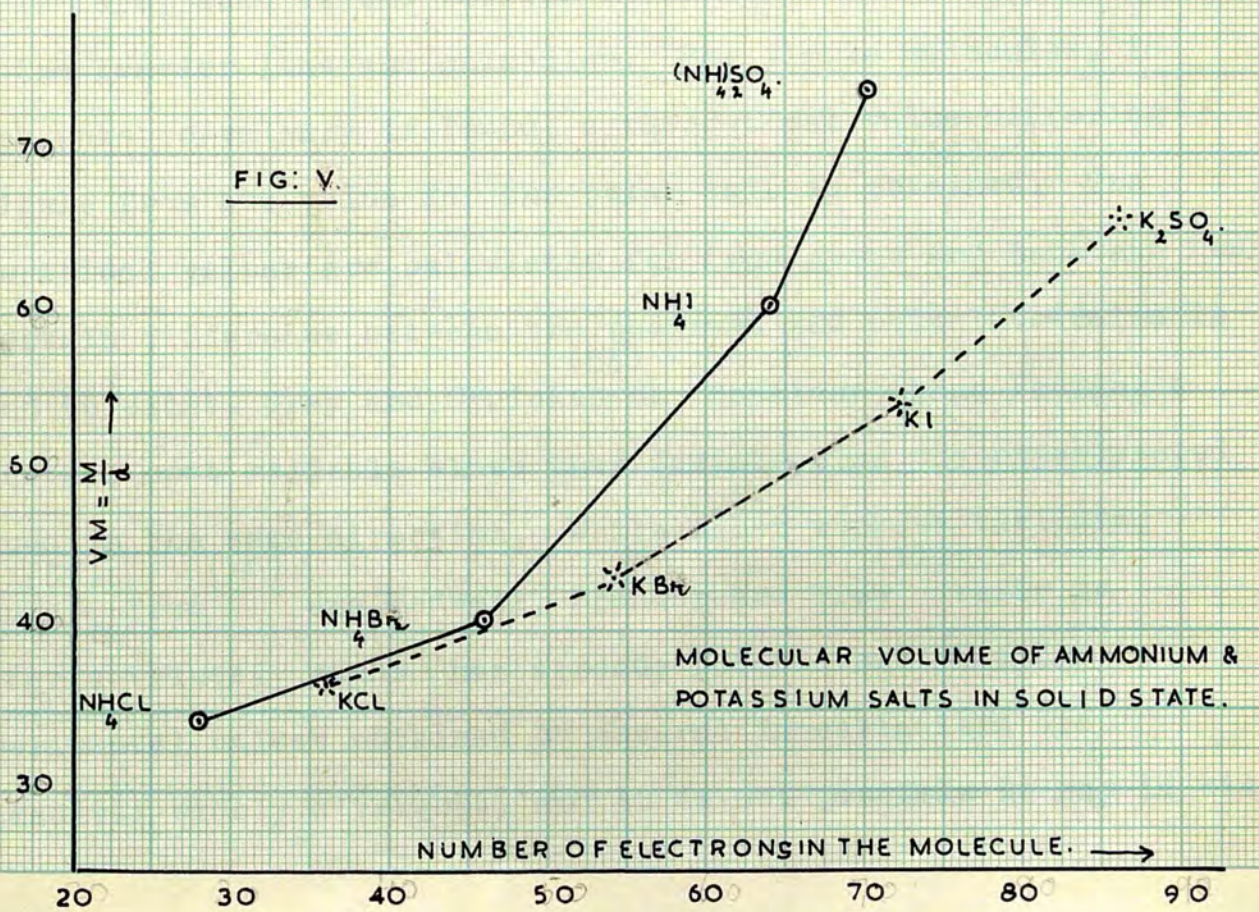
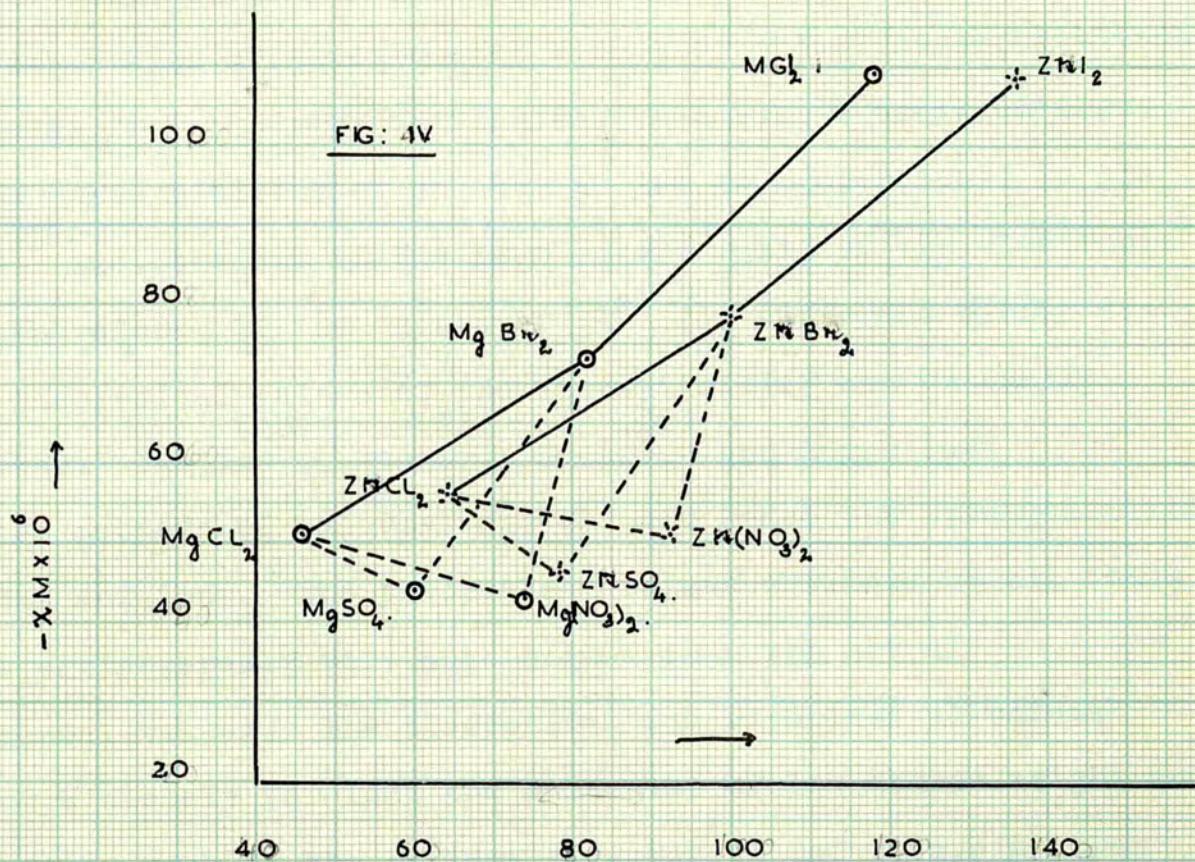
ionic radii. For a spherical ion the susceptibility may be theoretically found from the Langevin's equation:-

$$-10^6 \chi_A = \frac{e^2 L}{6 m c^2} \times \sum \bar{r}^2 = 2.83 \times 10^{-10} \sum_n \bar{r}^2$$

Where  $\sum_n \bar{r}^2$  is the mean square radius summed over all the  $n$  orbits within the atom or ion.

Since this equation holds only for a spherical free ion it would not be expected to be in exact agreement with the experimental values. It is evident from Langevin's theory that the susceptibility of an atom or ion is proportional to  $\sum \bar{r}^{-2}$ , and in crystals the interionic distances depend on the ionic radii and hence the factors which determine such distances in a crystal must influence the susceptibility. If an increase in the packing size of an ion led to increase in  $\sum \bar{r}^{-2}$  for an ion in the crystal, then there should be an increase in the molar mass susceptibility. Confirmation of these types of zig-zag curves from another physical property, the effective molecular volume, is to be found. The effective molecular volumes of the alkali halide salts measured in the solid state, has been calculated from the densities of the salts determined very carefully during these measurements from the relationships  $V_M = \frac{M}{d}$ . In some case where the density was well established it was not determined and the molecular volumes here have been calculated from density values in the hand-book. These are indicated by the index (6) in Table I. The effective molecular volumes of the alkali halides, including sulphates, are plotted similarly to the susceptibility against

the number of electrons in the molecule. The graph, Figure (V) shows approximately the same zig-zag curve as that of the susceptibility curves of Figure III (a) and (b) and (IV) for the ammonium, potassium, zinc and magnesium salts measured, but the effect of change in the co-ordination number is more obvious. The graph for the ammonium salts is not parallel to that for the potassium salts due to the difference in co-ordination number of the salts. Ammonium iodide and potassium iodide have the same co-ordination number, i.e. a co-ordination<sup>number</sup> of six. Ammonium bromide and chloride have a co-ordination number of eight at room temperature, having the body-centred caesium chloride structure, while potassium chloride and iodide have the rock salt structure, with co-ordination number six. These differences are shown clearly in the molecular volumes, and in Figure (V). While ammonium iodide has a higher molecular volume than potassium iodide, ammonium bromide and ammonium chloride have lower molecular volumes than the corresponding potassium salts. This is shown in Figure (V) where the curve for the ammonium salts shows a much greater slope between the bromide and iodide than does that for the potassium bromide and iodide, and the curves between the chloride and bromide while parallel to that for the potassium salts lies rather closer to it than would be the case if the co-ordination number was the same. The rather low value for the molecular volume of potassium sulphate is also significant as is mentioned later on, and may be due to the occurrence of resonance in the sulphate ion. The high value for the molecular volume of ammonium sulphate relative to the

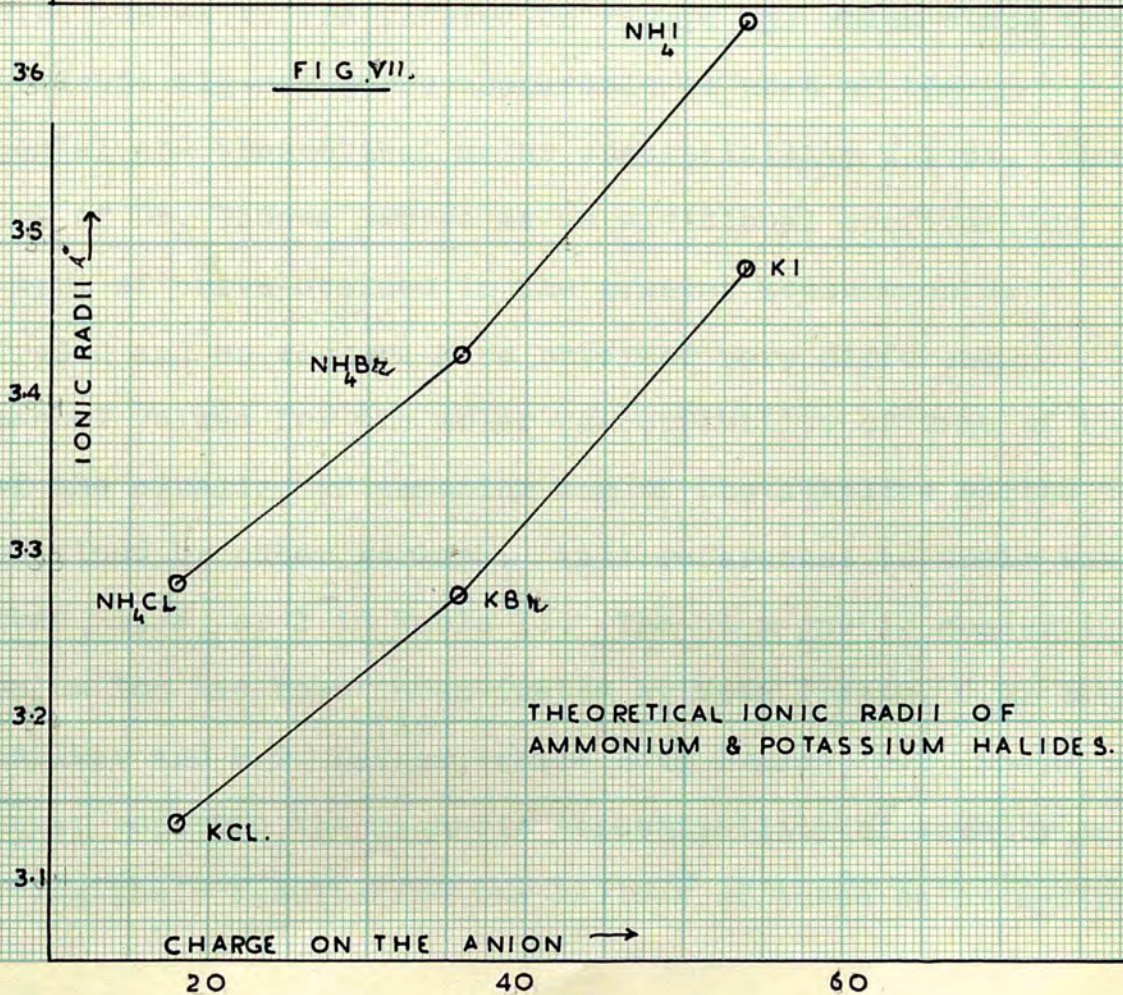
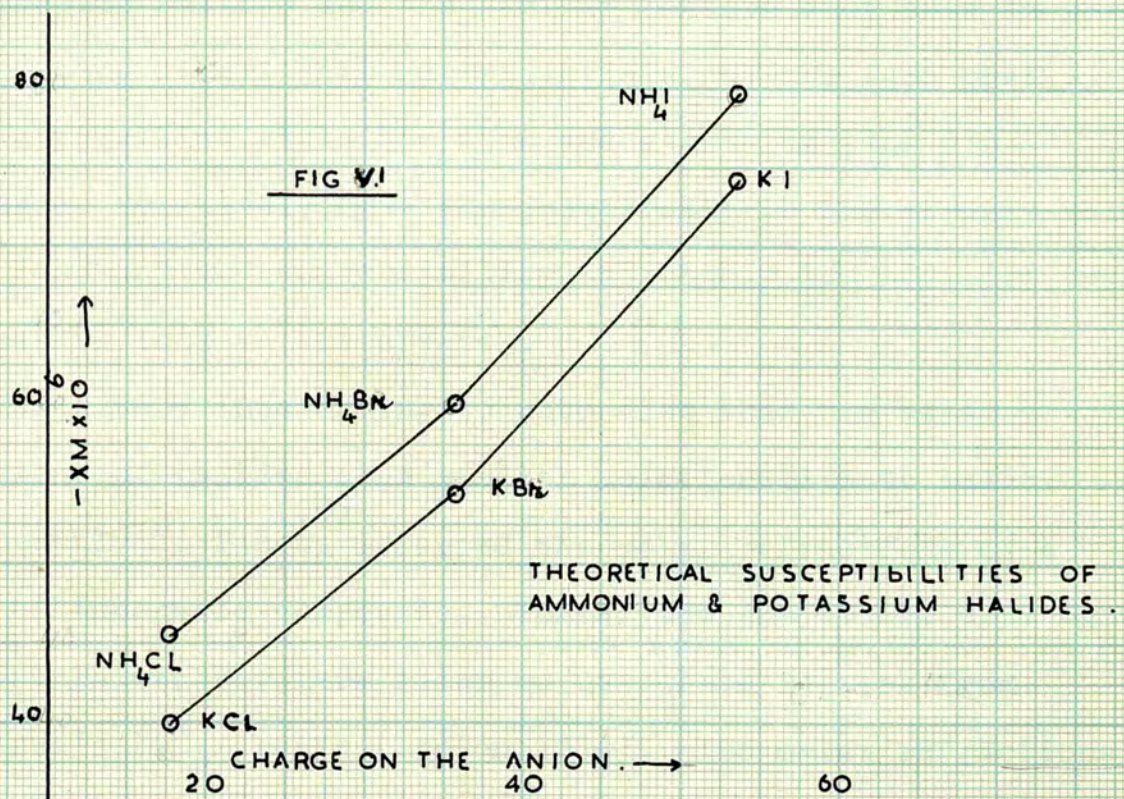


potassium sulphate is not easy to explain.

Comparison of experimental with theoretical susceptibilities can be made from the present figures. Langevin's equation shows that the susceptibility of an atom or ion is proportional to the term  $\sum \bar{r}^{-2}$  i.e. the sum of the mean square radii of the electronic orbits therefore, if the values of  $\bar{r}^{-2}$  for different orbits are known, theoretical values of the susceptibility can be easily calculated. Pauling<sup>(50)</sup>, Stoner<sup>(51)</sup>, Slater<sup>(52)</sup>, and Angus<sup>(53)</sup> have evaluated methods of calculating  $\sum \bar{r}^{-2}$  and hence the susceptibilities for atoms and ions. The theoretical values obtained by all these methods are generally very much higher than the actual experimental values. The theoretical and experimental values agree more closely for ions and molecules of low atomic weight and simple form, such as the halides of ammonium and potassium than for the heavier ions and molecules. For simple molecules, in which pure co-valency is found, a theoretical value differing a little from the value for the polar salt is obtained. The theoretical values are calculated for free atoms and ions and hence a certain difference between the observed and calculated value is bound to exist. Gray and Cruickshank<sup>(56)</sup> consider that Pauling's values are most reliable since they deviate from the experimental values in the same direction. While other workers including Ananta<sup>(57)</sup>, Trew<sup>(13)</sup> and Bedwell<sup>(11)</sup>, Spencer and Trew<sup>(58)</sup> refer to Slater's values. Angus has already pointed out that the experimental values obtained by several investigators are themselves widely divergent, and it is not possible to say in his

opinion which theoretically method, therefore gives the most reliable values. Pauling's values are greater than those of Slater which are slightly higher than those of Angus' ~~susceptibilities~~. The latter in general agree more closely with the experimental values for salts in the solid state, although Slater's figures are more commonly accepted and used as they are valid for other properties than the susceptibility. For comparison the <sup>Slater (52)</sup> theoretical susceptibilities (the sum of the ions in the ammonium and potassium salts measured) are plotted against the charge on the anion in Figure (VI). This graph shows a shape comparable to that for the experimental molecular susceptibility of the halide salts of ammonium, potassium, zinc and magnesium. The similarity of the comparable part of the graphs in Figure V and Figures III (a) and (b) and (IV) shows that there is a theoretical basis for the type of experimental susceptibility curves obtained. For further confirmation the sum of the Pauling theoretical ionic radii <sup>(59)</sup> of the ions forming the salts were plotted against the number of electrons in the anion on figures ~~(VII & VIII)~~ <sup>VII & VIII</sup> which again show a similar type of curve.

It should be noted that the present experimental molar susceptibility values of the magnesium and zinc halides in the anhydrous form show a type of slope similar to that found for the alkali metals. These are also comparable with the ionic radii curves for the magnesium and zinc halides calculated similarly to the potassium and ammonium ones from Pauling's values for the crystal radii. The similarity between these curves for the zinc

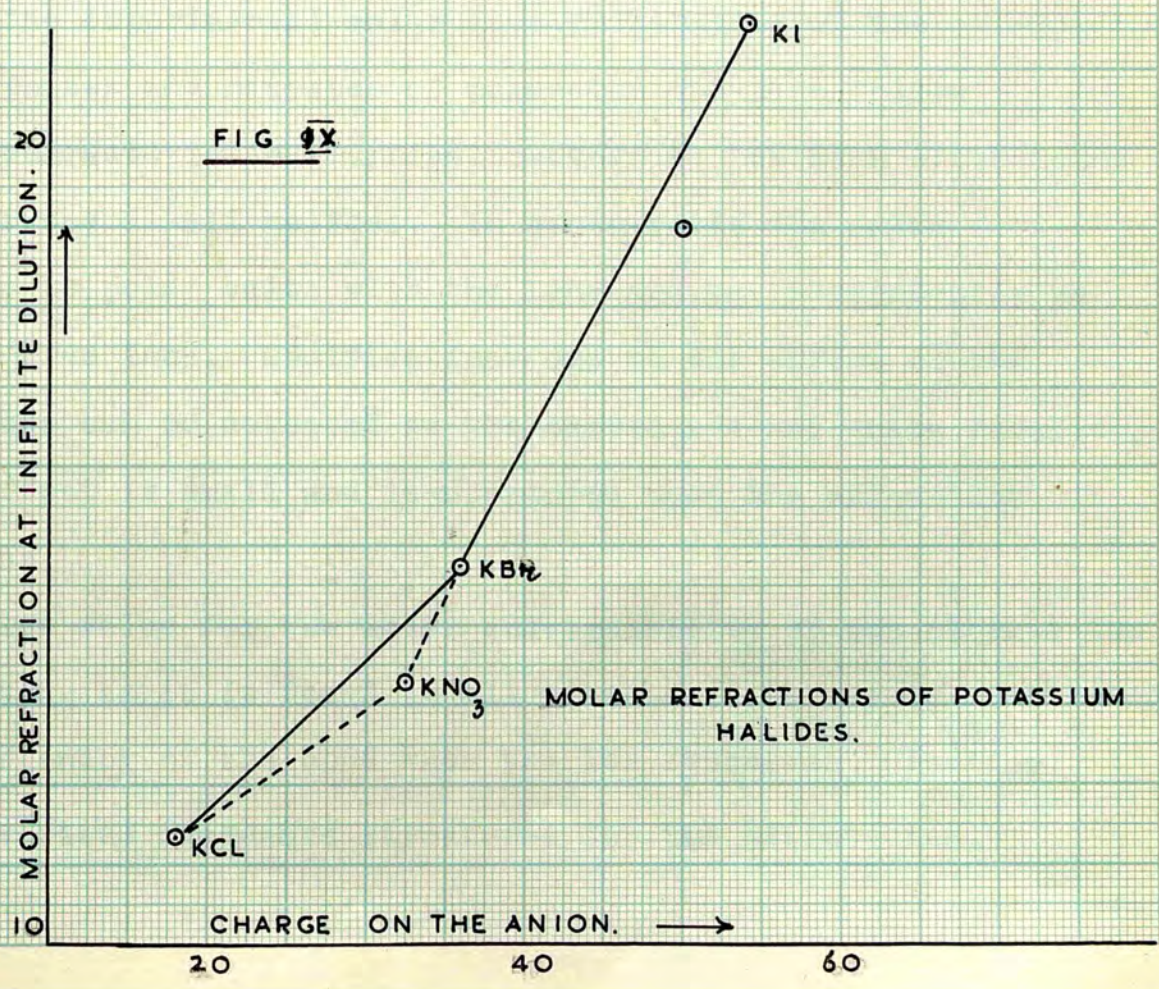
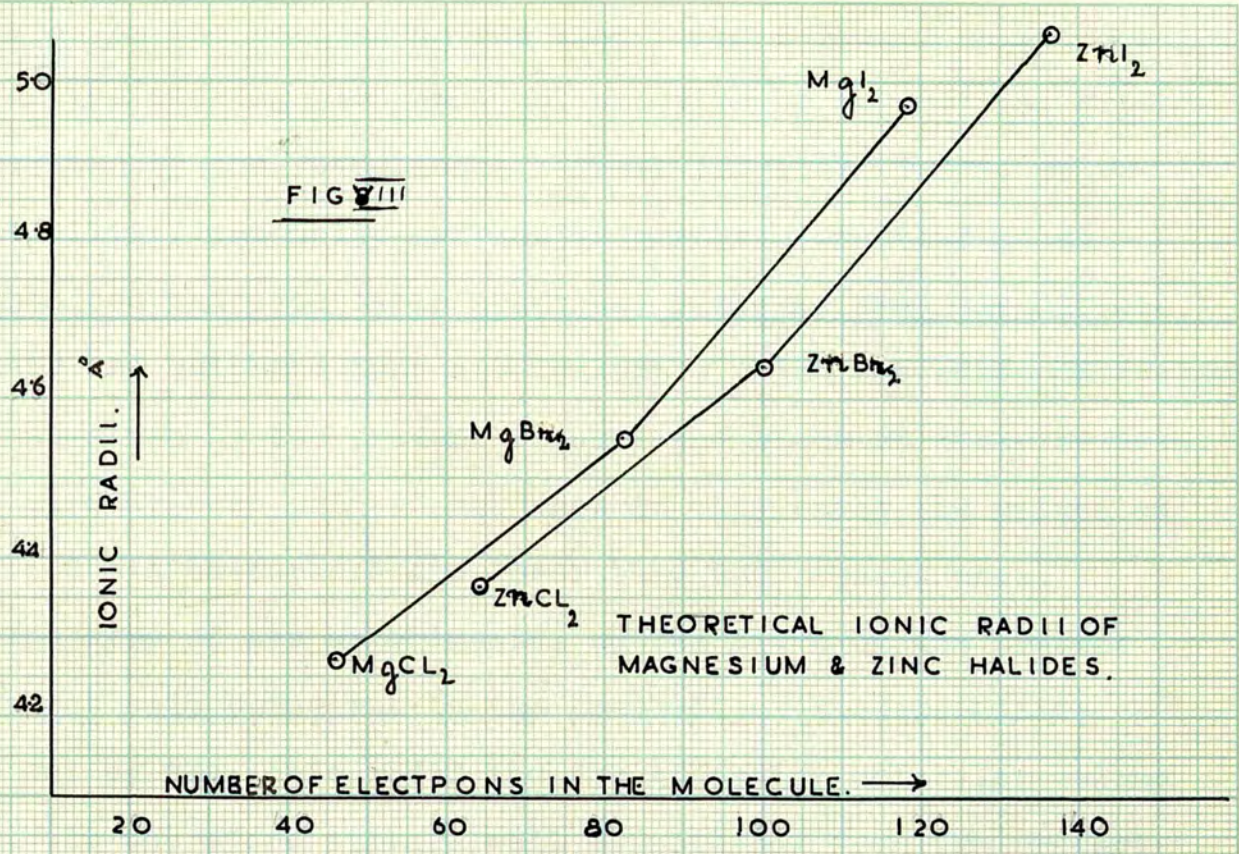


and magnesium halides and the similar pattern they show to the corresponding alkali salt curves, brings out the fact that in the crystalline state the zinc and magnesium ions are behaving as relatively free ions comparable to the strongly polar alkali ions and the susceptibility is roughly the additive sum of the separate ions in the crystal.

It is very interesting to note also that the molar refractions of halides show similar relationships to exist. (60)  
Very recently I. Padowa measured the molar refractions of a number of inorganic compounds. Thanks are due to Dr. C.E. Smith and Dr. I Padowa for permission to use these figures from Dr. Padowa's Ph.D. thesis (London 1954). The molar refractions for the halide salts are plotted on figure (8) which shows the characteristic zig-zag curve comparable to that of the experimental and theoretical molar susceptibility curves. Thus this work of Dr. Padowa serves as an additional confirmation of the type of curve obtained in the present measurements.

(14)  
Prasad and co-workers have obtained very different experimental values for the molar susceptibility of some of the salts of the alkalis, of ammonium and of the alkaline earths to those obtained by other workers. (All references to their work are marked, 14, 15, or 17 in Table I). The diamagnetic susceptibility of ammonium ion has been investigated by Mata Prasad, C.R. Kanekar, D.D. Khodlkar and M.G. Dattar, while Mata Prasad, S.S. Dharmatti and Kanekar reported the magnetic susceptibility of some hydrates. (15)  
On plotting their results for the halides of these salts against

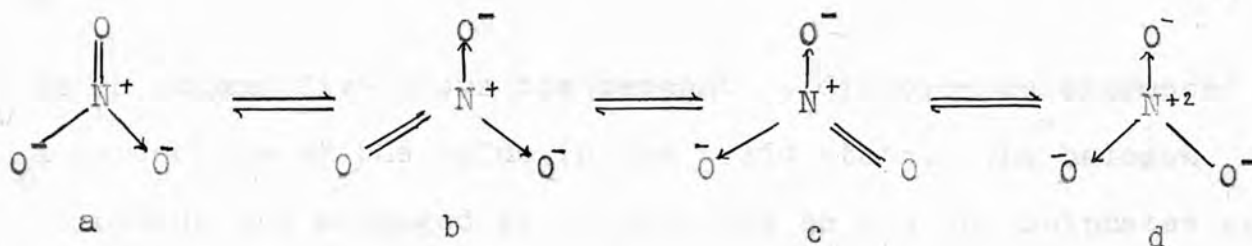




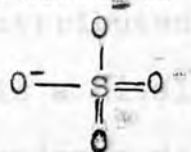
the charge on the various anions they found a linear relationship where as the zig-zag plot would be expected on theoretical grounds as indicated by the resemblance between the ionic radii, molar susceptibility, and molar refraction graphs. In other cases they obtained characteristic graphical patterns when the nitrate, carbonate and sulphate ions are included, which are rather different from that given by the present figures and those of other workers. It has already been pointed out that in many cases the values of Prasad and his co-workers are lower than the present ones.

The type of the experimental curves given by the present work is not only borne out by the theoretical susceptibility curves but by the ionic radii and the effective molecular volume curves. It therefore appears well established from the present work that the experimental molar susceptibilities of the halides, sulphates and nitrates of magnesium and zinc follow a similar characteristic graphical pattern as had been established earlier for the alkali halides. In other words the salts approximate to polar salts with the ions acting independently as relatively free ions. Modifications due to the effect of the adjacent ions can be detected as the curves are not quite parallel, but this effect is small and is superposed upon the effect due to free ions.

The low value for the molar susceptibility of the nitrate ion is interesting as it is found in all nitrates. It may be attributed to the shortening of the bond when the ion resonates. Pauling gives the various resonance structures for the nitrate ion.



Of these a, b and c would have the same susceptibility and d a different susceptibility due to the different bonds present. A similar anomaly is found in the case of the sulphate and carbonate ions. This low value for the sulphate and carbonate ion may be explained as due to the bond shortening phenomenon in the various resonance structures of <sup>the</sup> sulphate and carbonate ions. In the case of the sulphate ion the possibility of shortening of these bonds is due to the fact that the ions resonate among a number of structures involving double bonds for example :-



A lower experimental susceptibility for

nitrates, sulphates and carbonates than might be expected from a simple formula with no resonance was found from the results of the present work as is shown in figures 1 (a) and (b) and (V), in which the susceptibilities for the salts containing these ions fall below the positions which might be expected from the value of the total electronic charge of the salts. // As already noted the susceptibility of salts in solution is greater than that of the same salts in the solid state. It was thought that there might be some regularities in these changes in susceptibility on solution of the salt and so the percentage difference between the susceptibility of the salts investigated in the solid state and in solution was calculated. These values are in Table II in

which column five shows the percentage differences expressed as a percentage of the value in the solid state. The halogen compounds are arranged as a group and so are the sulphates and nitrates. A certain general trend can be noted among these percentages. The percentage differences between the susceptibility in solution and <sup>in</sup> the solid state, for the chloride, bromide and iodide, of ~~the~~ ammonium and potassium salts are of the same order. In the case of magnesium salts the differences are smaller, i.e. for the chloride, bromide and iodide they are of the order of 1%. In the zinc halides the percentage is of the same order in the three halides but the value is much larger than for magnesium. This can be attributed to the fact that the zinc in the solid halides is a divalent unhydrated ion and hence will more readily undergo deformation effects than the magnesium ion which is hexa-hydrated in the halides and so protected by a water sheath. All nitrates show greater percentage differences on solution than do the corresponding halides and sulphates. This may be due to the nitrate ion, which is known to be abnormal with respect to other properties. This discrepancy also appears to be shown in the bond lengths for the nitrate ion. Pauling's calculated bond length for this ion, even allowing for resonance, does not agree with that observed by experiment, which is smaller than the calculated. (Wells p. 409). Table II seems therefore to show the following regularities:-

Table II

Differences of Molar Susceptibilities of salts in the solid state and in solution.

Salt	Composition g/100 g of sol. <sup>21</sup>	Molar Mass Susceptibility -10 <sup>6</sup> XM		Percentage Difference
		solid	solution	
NH <sub>4</sub> Cl	24.74	36.73	38.47	4.7
KCl	22.45	38.89	40.94	5.2
* ZnCl <sub>2</sub>	29.31	55.72	64.6	16%
MgCl <sub>2</sub> ·6H <sub>2</sub> O	17.73	128.56	130.47	1.48
NH <sub>4</sub> Br	41.76	46.96	49.18	4.7
KBr	24.68	49.84	52.09	4.5
* ZnBr <sub>2</sub>	25.03	78.96	88.10	11.5
MgBr <sub>2</sub> ·6H <sub>2</sub> O	65.62	150.65	152.14	.99
NH <sub>4</sub> I	24.68	64.07	66.39	3.6
KI	14.31	65.84	68.40	3.8
* ZnI <sub>2</sub>	20.23	108.72	112.65	3.6
MgI <sub>2</sub> ·8H <sub>2</sub> O	16.96	213.37	215.36	.93
* CdI <sub>2</sub>	29.98	112.58	138.77	23.2

Salt	Composition g/100 g of sol. <sup>n</sup>	Molar Mass Susceptibility -10 <sup>6</sup> .X <sub>M</sub>		Percentage Difference
		solid	solution	
NH <sub>4</sub> NO <sub>3</sub>	18.20	32.60	38.75	18.8
KNO <sub>3</sub>	15.62	32.83	36.74	11.9
NaNO <sub>3</sub>	23.04	25.33	27.61	9.0
* AgNO <sub>3</sub>	25.09	46.49	53.41	14.6
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	12.50	120.67	125.36	3.9
Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	29.61	103.23	114.21	<b>10.5</b>
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	37.57	67.06	67.70	.95
K <sub>2</sub> SO <sub>4</sub>	8.645	67.47	70.50	4.5
MgSO <sub>4</sub> ·7H <sub>2</sub> O	28.44	134.95	139.41	3.3
ZnSO <sub>4</sub> ·7H <sub>2</sub> O	46.90	136.39	143.63	5.3
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	35.29	337.33	344.19	2.0

\* The values in solution for the zinc halides were taken from the measurements in the last section of the thesis. A 20% or 29% composition was selected as being comparable with the concentrations for the alkali salts.

(1) The percentage differences on solution for the corresponding halides of potassium and ammonium are almost identical, and are of about the same order of magnitude (<sup>i.e. for</sup> chloride, bromide and iodide). This would indicate a similar change in the forces affecting the molar susceptibility for all these salts on solution.

(2) The percentage difference on solution for all the magnesium salts measured tends to be definitely lower than for the alkali salts. This may be ascribed to the hydrated state of the magnesium ion.

(3) The percentage difference on solution for zinc salts tend to be higher than for the alkali salts measured. This is especially so for the zinc salts in which the zinc ion is unhydrated in the solid state e.g. chloride, bromide and iodide. The difference in the case of the sulphate, in which the hexahydrated zinc ion occurs in the solid state, is more normal.

(4) All nitrates show considerably greater percentage differences on solution to that shown by the other salts. This may be due to some modification of the forces affecting the structure of the nitrate ion in the dissolved state to that in the solid state.

(4) Additivity Relationships of double salts in the crystalline state and in solution

Another aspect of the present work was to test the additivity relationships of the diamagnetic susceptibility of some double salts, in aqueous solution and in the crystalline state. For this purpose a series of measurements has been made on some double salts of potassium and ammonium with magnesium and zinc, measurements being made in the solid state and in solution. The experimental results for the solid measurements are shown in Table III. In column two the values for the molar magnetic susceptibility of the univalent component is given. Column three gives the molar susceptibility of the poly-valent component of the double salt as the required hydrate. In the fourth and fifth columns respectively, (assuming strict additivity) the calculated molar susceptibility and the experimental molar susceptibility of the double salts are given, for example:-

← in the case of magnesium ammonium chloride the calculated value of the molar susceptibility can be regarded as the sum of the experimental values for ammonium chloride and that for magnesium chloride hexa-hydrate as given in Table I. The values for these salts are shown respectively in the first line in columns (2) and (3) of Table III, and added give the value in column (4). Where necessary, as in the case of magnesium iodide octahydrate and magnesium sulphate hepta-hydrate, the values for the molar susceptibility of two and one molecules of water respectively were subtracted from the values obtained.



Table III

## Additivity Relationships in Double salts in the solid state.

(Double salts of magnesium and zinc with ammonium &amp; potassium)

Double salts	molar susceptibilities of:				Difference
	Univalent Component	poly valent component + H <sub>2</sub> O	Calculated	Observed	
MgCl <sub>2</sub> NH <sub>4</sub> Cl.6H <sub>2</sub> O	36.73	128.56	165.29	168.62	+ 3.33
MgBr <sub>2</sub> NH <sub>4</sub> Br.6H <sub>2</sub> O	46.96	150.65	197.61	198.53	+ .92
MgI <sub>2</sub> NH <sub>4</sub> I.6H <sub>2</sub> O	64.07	187.45	251.52	252.17	+ .65
MgCl <sub>2</sub> KCl.6H <sub>2</sub> O	38.89	128.56	167.45	166.87	- .58
MgBr <sub>2</sub> KBr.6H <sub>2</sub> O	49.84	150.65	200.49	194.07	- 6.42
KGI <sub>2</sub> KI.6H <sub>2</sub> O	65.84	187.45	253.29	251.84	- 1.45
MgSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .6H <sub>2</sub> O	67.06	121.99	189.05	193.98	+ 4.93
MgSO <sub>4</sub> K <sub>2</sub> SO <sub>4</sub> .6H <sub>2</sub> O	67.47	121.99	189.46	181.92	- 7.64
ZnSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .6H <sub>2</sub> O	67.06	123.43	190.49	194.32	+ 3.83
ZnSO <sub>4</sub> K <sub>2</sub> SO <sub>4</sub> .6H <sub>2</sub> O	67.47	123.43	190.90	194.87	+ 3.97

in Table I to get the figures <sup>in Table</sup> III, column 3 (i.e. 12.96 units of susceptibility per mole of water). The last column gives the difference  $\Delta \chi_M = \chi_{M, \text{Expt}} - \chi_{M, \text{calc}}$ . In Table IV similar values are given for the substances in solution.

The question of additivity is then tested by comparing the sums of the molar susceptibilities of the univalent and polyvalent components which form the double salt (calculated) with the experimental values for the double salt.

Considering first Table IV, the values of the molar susceptibilities of the double salts in solution show in almost all cases an additive relationship, the experimental value agreeing with the calculated within the experimental error. The maximum difference is about one percent in the case of magnesium ammonium chloride, magnesium potassium chloride and zinc ammonium sulphate. This deviation may be due to the possibility considered in the later part of the work of the susceptibility of <sup>a</sup> salt in solution varying with the concentration. The deviation from additivity is much greater in the case of alums, measurements for which are given in the Appendix, but not included in the Tables as only a few salts were measured.

Deviations from additivity in the crystalline double salts (Table III) are rather larger than in the dissolved state. Since the theoretical susceptibility calculated by Langevin's equation, as given in section (3) during the discussion of single salts, was originally deduced for the magnetic mass susceptibility of the polar compounds consisting of two uni-nuclear spherically symmetrical ions such as  $\text{Na}^+$  and  $\text{Cl}^-$ , it cannot strictly apply

Table IV

Additivity Relationships in Double Salts in solution.

Double salts.	Molar susceptibilities				
	Univalent Component	poly-valent component +H <sub>2</sub> O-	Calculated	Observed	Difference
MgCl <sub>2</sub> NH <sub>4</sub> Cl·6H <sub>2</sub> O	38.47	130.47	168.94	170.34	+1.40
MgBr <sub>2</sub> NH <sub>4</sub> Br·6H <sub>2</sub> O	49.18	152.14	201.32	200.71	-0.61
MgI <sub>2</sub> NH <sub>4</sub> I·6H <sub>2</sub> O	66.39	189.44	255.83	225.68	-0.15
MgCl <sub>2</sub> KCl·6H <sub>2</sub> O	40.94	130.47	171.41	172.70	+1.29
MgBr <sub>2</sub> KBr·6H <sub>2</sub> O	52.09	152.14	204.23	203.70	-0.53
MgI <sub>2</sub> KI·6H <sub>2</sub> O	68.40	189.44	257.84	257.97	+0.13
MgSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	67.70	126.45	194.15	193.62	-0.53
MgSO <sub>4</sub> K <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	70.50	126.45	196.95	196.86	-0.09
ZnSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	67.70	130.67	198.37	197.34	-1.03
ZnSO <sub>4</sub> K <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	70.50	130.67	201.17	200.64	-0.53

to any other type of compounds since, as already indicated, the number of ions co-ordinated around any particular ion will modify its susceptibility. An increase in co-ordination will decrease the susceptibility and vice versa. In hydrated compounds the co-ordination of water may affect the anion or cation, since it changes the radius of the molecule. The attraction of the water molecules by the central atom causes the molecule to contract, although the net effect is an increase in the radius due to the water shell, the individual ionic susceptibility will be affected, since, it depends on the ionic radius. Therefore a certain difference between the observed and calculated value is likely to exist. A comparison of the susceptibility with the size of the ions in the crystalline salt as given by the molar volume is therefore of interest. The results of such a comparison are tabulated in Tables (VI & VII). From the measured, or known, densities of the salts the molar volumes in Table I were obtained. Thus for the crystalline double salts, calculated values for the molar volumes ( $\frac{M}{d_4}$ ) were derived in exactly the same way as just described for the molar susceptibilities, by adding the values of the molar volumes of the single salt components. The results are tabulated in Table VI which shows the experimental and calculated values and their differences for both the molar susceptibility and the molar volumes of the salts measured. In comparing the molar susceptibility of the double salts

Table VI

Comparison of calculated and Experimental Molar susceptibilities and Molar Volumes  
 of <sup>Crystalline</sup> Double Salts.

Double salts	Molar Susceptibilities			Molar Volume		
	$-\chi_M \times 10^6$ Experimental	$-\chi_M \times 10^6$ calc	$\Delta \chi_M \times 10^6$ Expt-calc	VM Expt	VM calc	$\Delta VM$ Expt:-Calc
$MgCl_2 \cdot NH_4Cl \cdot 6H_2O$	168.6	<u>165.3</u>	+ 3.3	175.9	<u>162.9</u>	+ 13.0
$MgBr_2 \cdot NH_4Br \cdot 6H_2O$	198.5	<u>197.6</u>	+ 0.9	196.1	<u>182.2</u>	+ 13.9
$MgI_2 \cdot NH_4I \cdot 6H_2O$	252.2	<u>251.5</u>	+ 0.7	226.6	<u>225.7</u>	+ 0.9
$MgSO_4(NH_4)_2SO_4 \cdot 6H_2O$	194.0	<u>189.0</u>	+ 5.0	212.1	<u>202.5</u>	+ 9.6
$ZnSO_4(NH_4)_2SO_4 \cdot 6H_2O$	194.3	<u>190.5</u>	+ 3.8	211.5	<u>202.2</u>	+ 9.3
$MgCl_2 \cdot 2KCl \cdot 6H_2O$	166.9	<u>167.4</u>	- 0.5	172.0	<u>165.5</u>	+ 6.5
$MgBr_2 \cdot 2KBr \cdot 6H_2O$	194.1	<u>200.5</u>	- 6.4	192.6	<u>185.9</u>	+ 6.7
$MgI_2 \cdot 2KI \cdot 6H_2O$	251.8	<u>253.3</u>	- 1.5	218.3	<u>223.5</u>	- 5.2
$MgSO_4 \cdot 4K_2SO_4 \cdot 6H_2O$	181.9	<u>189.9</u>	- 8.0	188.0	<u>193.9</u>	- 5.9
$ZnSO_4 \cdot 4K_2SO_4 \cdot 6H_2O$	194.9	<u>190.5</u>	+ 4.4	197.6	<u>193.6</u>	+ 4.0

with its molar volume it is seen that in the case of double salts containing the ammonium ion the experimental molar volume and molar susceptibility are both larger than calculated and so differ from the calculated in the same direction. The increase in the size of the ions is for these salts also accompanied by an increase in the susceptibility. There is a fair correlation between the magnitude of the deviation for the two properties, except in the case of magnesium ammonium bromide where the difference in the susceptibility is very low when compared with the difference in the molar volume. It was expected that a similar difference would show in both the properties because of the  $\sum r^{-2}$  term in the equation for the diamagnetic susceptibility. A larger difference is shown in the molar volumes of the chloride and bromide than in the iodide. The molar susceptibility difference is similar for the chloride and iodide but the very low difference for the magnesium ammonium bromide is unexpected. The experimental value seems to be low as there is no correlation with the differences in molar volumes.

In the case of potassium double salts the correlation is less obvious but with the exception of the chloride and bromide, once again both properties change in the same direction. It may be that small errors of individual experimental values have added up in the case of magnesium potassium chloride <sup>and bromide</sup> to make the experimental value fall below the theoretical value. A comparison of differences between the susceptibilities of the double salts of magnesium potassium chloride, bromide and iodide in the solid

states and in the solution i.e. the values in Table V indicates that the experimental value for magnesium potassium bromide may be 3 - 4 units low.

Table V

	Salts	solid $-X_M \times 10^6$	differ- ence $-X_M \times 10^6$	solu- tion $-X_M \times 10^6$	differ- ence $-X_M \times 10^6$	remark
(1)	Magnesium Chloride hexa-hydrate	128.6	22.0	130.5	21.6	the difference is normal
	Magnesium bromide hexa-hydrate	150.6		152.1		
(2)	Potassium chloride	38.9	10.9	40.94	11.2	the difference is normal
	Potassium bromide	49.8		52.9		
	Magnesium Potassium chloride $6H_2O$ .	166.9	27.2	172.7	31.0	difference seems 3 - 4 units low for the solid.
	Magnesium Potassium Bromide $6H_2O$ .	194.1		203.7		

This is however still not sufficient to explain why in the case of this salt and the chloride the molar volume shows a greater value than the calculated, while the molar susceptibility is lower. Some modification of the charge distribution on the ions may be influencing the susceptibility in these cases. Another interesting point which can be considered from the present figures is the relationship between the susceptibilities of the ammonium ion in its salts and of the potassium ion in its salts.

For easy comparison Table VII gives the molar susceptibilities and molar volumes of the single and double salts of ammonium

and potassium which have been arranged in pairs, with the differences in the two properties found on passing from the potassium to the ammonium salt. The figures in the table show that in the case of the double salts the molar susceptibility of the ammonium double salt is always larger than that of the potassium double salt, *except for the zinc double sulphate*. This relationship was expected to be such, as the theoretical ionic radii of ammonium is greater than that of potassium and the theoretical ionic susceptibility is also in the same direction as shown by the following figures.

	$\text{NH}_4^+$	$\text{K}^+$
Pauling crystal radii	= 1.48	1.33
$-10^6 \chi$ calculated susceptibility ion (Slater)	= 15.0	14.4

For single salts the relationships are much more complicated and the change in co-ordination number in the different crystals seems important here. The co-ordination number in ammonium chloride and bromide at room temperature is 8. ( $\text{CsI}$  structure) while for all the other halides it is 6. (rock salt structure). The change from 6 to 8-fold co-ordination is sufficient to bring the molar volume in the case of ammonium chloride and bromide below the potassium value as shown in table VII. This is also shown as noted earlier on the graph figure 5, whereas in the iodides, in which no change in co-ordination number occurs, the ammonium salt has the larger molar volume. In the case of the susceptibility the chloride and bromide show a similar effect to that of the molar volume. The lower values of the susceptibility for the



Table VII

Comparison of Molar Volumes and molar susceptibilities of potassium and ammonium salts and Double salts.

Single salt.	Susceptibility		Molar Volume Experimental		Double salt	Susceptibility		Molar Volume Experimental	
	$-10^6 \chi_m$	$\Delta$ K-NH <sub>4</sub>	VM	$\Delta$ K-NH <sub>4</sub>		$-10^6 \chi_m$	$\Delta$ K-NH <sub>4</sub>	VM	$\Delta$ K-NH <sub>4</sub>
NH <sub>4</sub> Cl	36.73	+2.16	34.9	+2.5	MgCl <sub>2</sub> ·NH <sub>4</sub> Cl. 6H <sub>2</sub> O	168.6	-1.7	175.9	-3.9
KCl	38.89		37.4		MgCl <sub>2</sub> ·KCl. 6H <sub>2</sub> O	166.9		172.0	
NH <sub>4</sub> Br	47.0	+2.8	40.6	+3.7	MgBr <sub>2</sub> ·NH <sub>4</sub> Br. 6H <sub>2</sub> O	198.5	-4.4	196.1	-3.5
KBr	49.8		44.3		MgBr <sub>2</sub> ·KBr. 6H <sub>2</sub> O	194.1		192.6	
NH <sub>4</sub> I	64.1	+1.7	58.0	-3.3	MgI <sub>2</sub> ·NH <sub>4</sub> I. 6H <sub>2</sub> O	253.2	-0.6	226.6	-8.3
KI	65.8		54.7		MgI <sub>2</sub> ·KI. 6H <sub>2</sub> O	251.8		218.3	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	67.06	+0.41	74.4	-8.6	MgSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	194.0	-12.1	212.1	-24.1
K <sub>2</sub> SO <sub>4</sub>	67.47		65.8		MgSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub> 6H <sub>2</sub> O	181.9		188.0	
MgSO <sub>4</sub> ·7H <sub>2</sub> O	134.9	+1.5	146.2	-0.3	ZnSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	194.3	+ 0.6	211.5	-13.9
ZnSO <sub>4</sub> ·7H <sub>2</sub> O	136.4		145.9		ZnSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub> 6H <sub>2</sub> O	194.9		197.6	

ammonium salt may therefore be attributed to the change in the co-ordination number. In the case of ammonium iodide the susceptibility of the salt is closer to that of potassium iodide than is the case for the chloride and bromide, but is still below the potassium salt value.

To explain this lower susceptibility of the ammonium ion in the iodide it can be said somewhat empirically that some additional factors other than the molar volume must be acting here, possibly a factor due to a different degree of polarisability of the ammonium and potassium ions. In ammonium and potassium sulphates the same problem arises.

The molar volume of potassium sulphate is less than that of ammonium sulphate as might be expected, but the susceptibility is slightly higher, although only by a small amount.

In the case of the hepta-hydrated zinc and magnesium sulphates (single salts) it is not clear why the zinc salt has a smaller molar volume than the magnesium salt. It has a larger molar susceptibility as would be expected from the position of the two ions magnesium and zinc in the periodic system.

The magnesium double sulphates show a normal relationship between the molar volume and susceptibility, the values for both properties being higher for the ammonium salt than for the potassium as in the halide double salts. Once again, the zinc double sulphates seem anomalous. Zinc potassium sulphate has a slightly higher susceptibility than the zinc ammonium salt. This difference is very slight and may be due to the accumulative effect of experimental error.

5. Investigations into the variation of susceptibility with concentration of solution

(Univalent salts with values at different concentrations showing linear relationships)

In the previous sections it has been shown that in solution the more polar salts studied show values for the molar magnetic susceptibility only a few percent higher than those in the solid state, the difference probably being due to a change in the ionic atmosphere surrounding the ions. In a few cases, however, the differences were considerably higher, i.e., in the case of the nitrates, the zinc salts studied, and the alums. Similarly when considering the additivity relations of double salts it was found that in solution, while most double salts showed a molar susceptibility which was almost exactly the sum of the single salts, in the case of zinc ammonium chloride and the alums and to a less extent in magnesium ammonium chloride and magnesium potassium chloride and zinc ammonium sulphate rather larger departures from additivity were found. It was therefore thought useful to investigate whether any marked variation of the susceptibility of salts in

solution with change in concentration could be detected. Even small variations might explain the fact that in Table IV the values of the susceptibility of double salts in solution fall, in general, slightly below the additive values for the single salts from which they are formed. In addition, in the case, for example, of zinc and cadmium salts more marked variation of molar susceptibility with concentration might be expected owing to the possibility of the existence of complex ions in solutions containing these cations. There is also a possibility of interaction with the solvent, which is likely to be more marked for divalent ions.

The additive law has often been used in calculating the magnetic susceptibility of a salt from the susceptibility of the solution and the solvent, but very few workers have investigated the strict validity of this law in solutions containing diamagnetic ions. The systematic investigation of diamagnetic compounds in solution has been undertaken by the following investigators. Reicheneder investigated the susceptibilities of halogen acid solution. Farquharson along with the halogen acids measured the variation of the susceptibilities of sulphuric acid solutions with concentration and found departures from linearity in the curves. Varadachari has also measured sulphuric acid

(73)  
solutions. Ranganadham and Qureshi have measured the susceptibility of nitric acid solutions and have reported a departure from linearity in the curves of nitric acid corresponding to four hydrates. Blair and Scott (74) investigated the solutions of hydrochloric acid and lithium chloride and noted the variation of susceptibility with concentration in lithium chloride solutions to be non-uniform over the entire range. On the other hand they considered the variation of hydrochloric acid to be quite normal. Ikenmeyer is the other investigator who has measured lithium chloride solutions, and found the variation to be quite normal. Very recently Nayar, Pande and Srivastava (76) investigated the possibility of complex formation in the solutions of potassium nitrate and lead nitrate. Prasad, Dharmatti, Kanekar and (14) Biraxdar have also measured the susceptibility of some hydrates in solution at different concentrations. Their figures also appear to show a linear relationship. Conclusions of the various investigators seem therefore to be at variance even as regards one substance.

This section of the present work was carried out mainly to see whether the susceptibility shows any change with the concentration of the solution, or is constant

for all concentrations. As in the earlier part of this work it was necessary to include measurements on single salts as well as complex salts to obtain comparative measurements.

A series of measurements on the solutions of simple salts i.e. potassium chloride, ammonium chloride and potassium iodide were made at different concentrations, as well as on the acids, hydro-chloric acid, hydrobromic acid, hydriodic acid and acetic acid. These acids were included as it was found necessary to add them to suppress hydrolysis of zinc salts in certain cases.

The results are tabulated in the Tables VIII to XIV. These show that for ammonium chloride and hydrogen iodide solutions the specific and molar susceptibilities of the salts or acid in solution is constant over the range of concentrations studied, within the limits of the experimental error. The hydrogen bromide solutions show, on taking an average of the figures, an almost constant susceptibility for the acid but possibly with a very slight indication of a fall with increasing concentration. There would be a definite fall if it were not for the high result obtained in one set of measurements.

In the case of potassium chloride solutions there also seems to be a slight fall in the susceptibility of the salt with increased concentration. In potassium iodide,

Table VIII

Susceptibilities of hydriodic acid solutions.

HI g/100 ml. Solution	HI g/100g. of solution	Mean $-10^6 \chi$ solution	$-10^6 \chi$ HI.	$-10^6 \chi$ M HI
12.13	11.17	.68540	.4103	52.48
6.065	5.83	.70184	.4086	52.36
1.213	1.205	.71620	.4047	51.78
0.6065	0.604	.71810	.4055	51.87
0.3032	0.303	.7191	.4200	53.71
0.1213	0.121	.7194	Too dilute to be accurate	

Preparation of solution

A stock solution of approximately 57% HI was used. From a gravimetric determination, as silver iodide, the concentration of HI in this acid was found to be 54.49g/100g of solution. A small trace of free iodine was present, but was considered negligible. The original acid was then diluted to give the strongest solution above. From gravimetric measurements the weight of HI in the first solution measured = 12.13g/100 ml. The subsequent solutions were made by dilution in this case and in the case of the other solutions studied in the subsequent sections. In most of the following experiments two and sometimes more completely different sets of solutions were made up and measured. Good agreement was found in most cases for the measurements on solutions of the same concentrations as the Tables show.

Table IX  
Ammonium Chloride Solution  
 Susceptibility of solution and salt.

Percentage g/100g of sol.	Molality	Mean $-10^6 \times \chi$ solution	$-10^6 \cdot \chi$ salt	$10^6 \cdot \chi_M$ salt
5.10	1.004	.71995	.7191	38.47
10.12	2.104	.71981	.7181	38.41
15.08	3.319	.71984	.7189	38.46
15.12	3.319	.71977	.7186	38.44
20.01	4.675	.71983	.7191	38.47
21.46	5.10	.71960	.7181	38.41
23.01	5.586	.71991	.7196	38.49
24.82	6.170	.71972	.7188	38.45



Table X

Susceptibilities of hydrobromic acid solution.

approximate normality	g/100 g. of sol.	Mean $-10^6 \cdot \bar{X}$ solution	$-10^6 \cdot \bar{X}$ HBr	$-10^6 \cdot \bar{X}_M$ HBr
	31.35	.62347	.4120	33.33
N/1	7.702	.69632	.4124	33.37
.5N	3.96	.70786	.4133	33.34
.2N	1.61	.71507	.4142	33.51
	31.35	.62267	.4095	33.13
N/1	7.751	.69673	.4196	33.95
.5N	3.971	.70783	.4136	33.46
.2N	1.611	.71508	.4149	33.57

Table XI a

Potassium chloride solution.

Composition g/100 g sol.	Molality	Mean $-10^6 \chi$ Solution	$-10^6 \chi$ Salt	$-10^6 \chi_M$ Salt
5.11	.7207	.71147	.5530	41.23
10.10	1.506	.70304	.5520	41.15
15.11	2.387	.69446	.5510	41.10
15.12	2.389	.69440	.5506	41.05
18.11	2.966	.68925	.5502	41.04
18.20	2.984	.68874	.5482	40.87
21.44	3.66	.68352	.5499	41.02
22.45	3.88	.68189	.5492	40.95

Table XI b

Potassium chloride Solution

(X - Z) = .166 *Calculation of True Molality and Hydration number*  
*(See page 83.)*

Molality	$\chi_{\text{solvent}} - \chi_{\text{sol.}}$	True Wt. Fraction	True Molality	hydration number.
.7207	.0086	.05181	.7320	1.19
1.506	.0171	.1030	1.540	1.25
2.387	.0257	.1548	2.456	.654
2.389	.0257	.1548	2.456	.654
2.966	.0309	.1861	3.067	.613
2.984	.0314	.1909	3.164	1.06
3.66	.0366	.2204	3.792	.53
3.88	.0382	.2301	4.008	.457

Table XII

Potassium iodide solution

Susceptibility of solution and salt.

Percentage g/100 g. of sol.	Molality	Mean $-10^6 \chi$ solution	$-10^6 \chi$ salt	$-10^6 \chi_M$ salt
15.11	1.072	.67348	.4121	68.41
20.11	1.516	.65806	.4120	68.40
30.08	2.591	.62729	.4118	68.36
40.11	4.033	.59593	.4106	68.16
50.06	6.037	.56462	.4095	67.97



Table XIV

Susceptibilities of Acetic acid solution

Normality	g/100 g of sol.	Mean $-10^6 \cdot X$ sol.	$-10^6 \cdot X$ HAc	$-10^6 \cdot XM$ HAc.
.503	3.01	.71603	.5885	35.33
.5031	3.01	.71601	.5877	35.28
1.006	6.01	.71013	.5821	34.94
1.046	6.233	.71079	.5719	34.33
1.046	6.233	.71088	.5733	34.42
1.980	11.71	.70006	.5497	33.00
2.0125	11.89	.69999	.5517	33.12
2.0925	12.34	.69960	.5547	33.30
original	99.01	.53283	.5381	32.30

Calculation of the Limiting Values

The 'ideal' limiting values for the graph of the susceptibility of the mixture plotted against the concentration, in which the susceptibility of one part is assumed to be constant with changing concentration was calculated as follows:

from the mixture law for solutions.

$$X_{\text{solution}} = X_{\text{solvent}} + X_{\text{solute}}$$

$$X_{\text{sol}} = X_{\text{HAc}} + X_{\text{solvent}}$$

hydrogen chloride, and acetic acid solutions the fall in the susceptibility of the salt or acid is slightly more marked, although in all the cases the graphs, Figure 3 X a-g, show that there is a linear relationship between the specific susceptibility of the solution and the concentration (g. salt per 100 g. of solution). Such a linear relationship does not inevitably mean a constant value for the susceptibility of the salts in solution. Only one definite slope to the graph will be found if the susceptibility of the salt or acid is constant, and a slightly increased slope over this value may be obtained when there is a slight fall in susceptibility of the salt with increasing concentration.

#### Calculation of the Limiting Slope

The 'ideal' limiting slope for the graph of the susceptibility of the solution plotted against the concentration, in which the susceptibility of the salt is assumed to be constant with changing concentration was calculated as follows:-

From the mixture law for solutions.

$$\chi_{\text{solution}} = \chi_{\text{solvent}} (1-p) + p \chi_{\text{salt}}$$

$$\chi_{\text{sol}} = \chi_0 - \chi_{\text{op}} + \chi_{\text{sp}}$$

where  $\chi_{\text{sol}}$  = susceptibility of solution i.e. measured susceptibility,

$\chi_0$  = susceptibility of solvent and

$\chi_s$  = Ideal susceptibility of salt, constant with change in concentration.

$p$  = weight fraction of salt.

$$\chi_{\text{sol}} - \chi_0 = p (\chi_s - \chi_0) \text{----- (1)}$$

If the susceptibility of the solution varies linearly with the concentration the graph showing its variation with concentration is of the form:-

$$\chi_{\text{sol}} = \chi_0 + a p$$

where  $\chi_0$  = susceptibility of solvent and  $a$  is a constant;  $p$  is the weight fraction as before.

$$\therefore \chi_{\text{sol}} - \chi_0 = a p \text{----- (2)}$$

whence from (1) and (2) it follows that

$$a = (\chi_{\text{salt}} - \chi_0) \text{----- (3)}$$

or the ideal limiting slope for the graph of susceptibility of solution with concentration, when this is changing linearly, is given by the difference between the susceptibility of the solvent and the extrapolated susceptibility ( $\chi_{\text{salt}}$ ) of the salt. For the graphs in this section where the

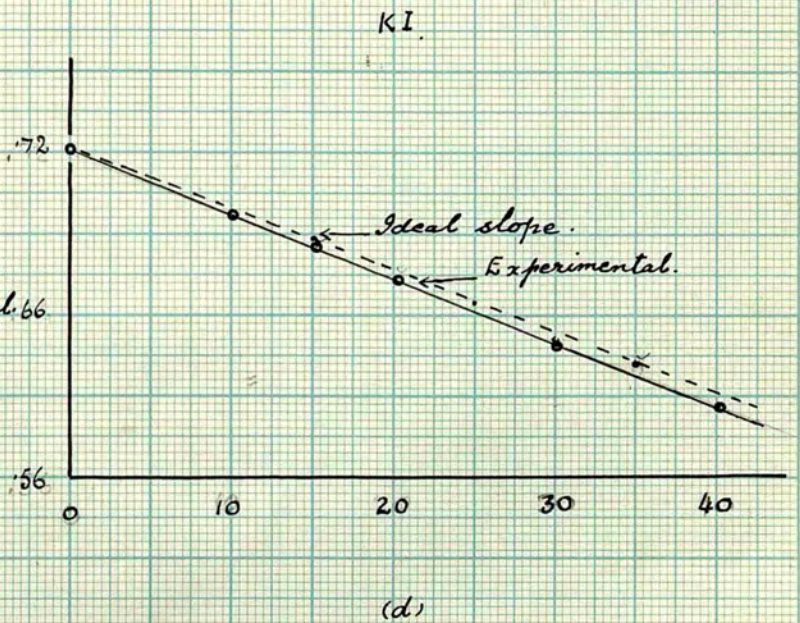
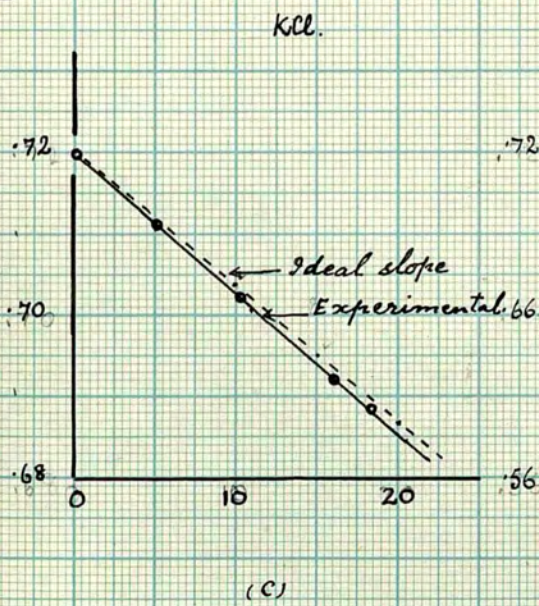
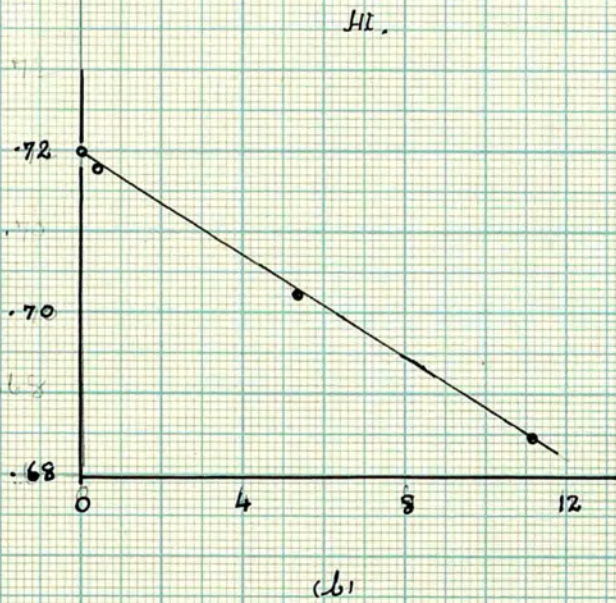
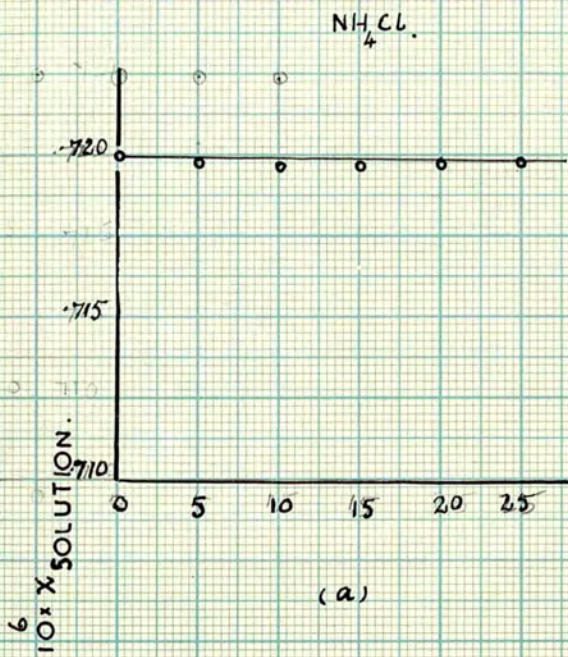


susceptibility of the solution does vary linearly,  $\chi_{\text{salt}}$  can be obtained by extrapolation of the experimental susceptibilities of the salt to infinite dilution and hence a the ideal limiting slope can be calculated and plotted on the graphs. In the case of hydriodic acid, and ammonium chloride the ideal slope seems to coincide with the experimental slope, within the limits of the experimental error.

In the case of potassium chloride, potassium iodide, hydrochloric acid, hydrobromic acid and acetic acid a slight fall in the susceptibility of the salt with increasing concentration was noted. The figures for the specific susceptibility of the salt (see Table XI a) for potassium chloride extrapolate to a value of  $-10^6 \chi = .554$ . The slope calculated from this is shown by the dotted line in the graph figure (X C). Similarly for potassium iodide the ideal slope was calculated and plotted in figure (X d). The values in Table XII gave an extrapolated value for potassium iodide =  $-10^6 \chi = .4124$ .

The extrapolated value for hydrochloric acid =  $-10^6 \chi = .658$  from the data tabulated in Table XIII. The ideal and experimental curves are shown in figure X e. The ideal slope for hydrobromic acid is shown in figure X f.

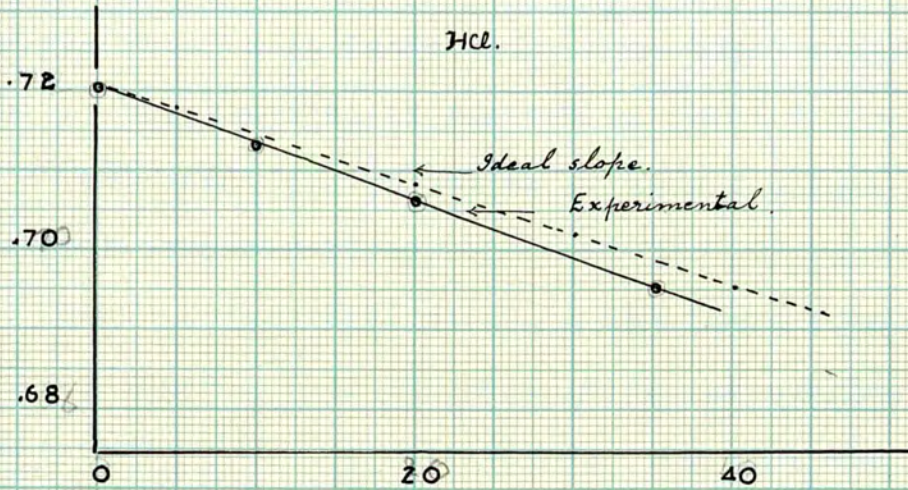
FIG. X (a-d).



PERCENTAGE CONCENTRATION

FIG X (e-g)

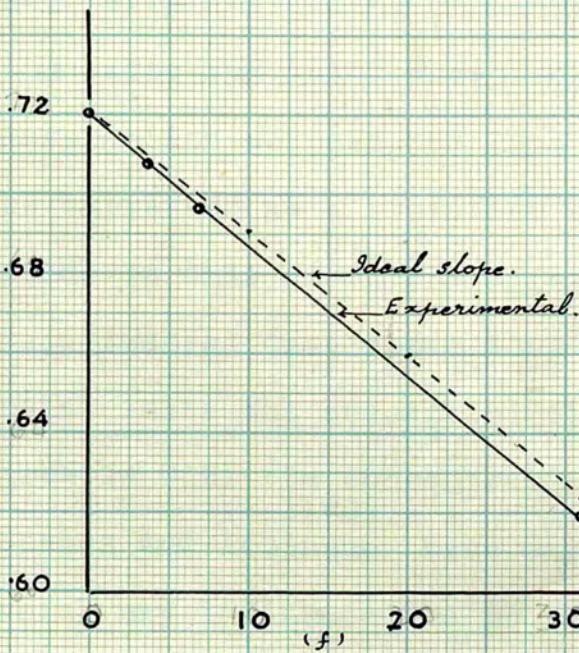
HCl.



(c)

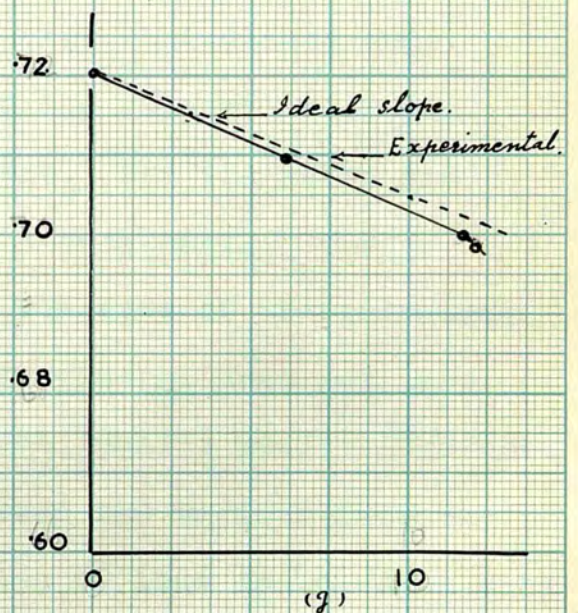
$-10^6 X \text{ SOLUTION}$

HBr



(f)

CH<sub>3</sub>COOH



(g)

PERCENTAGE CONCENTRATION

by a dotted line, calculated from the mean  $\chi \times 10^6 = -.4150$ .  
*extrapolated*  
 (salt)  
 In the case of acetic acid the ideal slope was calculated  
 $\chi \cdot 10^6 = .589$   
 from the results in Table XIV. The ideal slope along  
 with the experimental is plotted on <sup>the</sup> graph figure X, g.  
 The experimental curves begins to show a slight curvature  
 at higher concentrations.

Since polar salts exist in the ionic form even in the solid state, they can be regarded as completely ionized at all reasonable concentrations. The ions are not however necessarily free to move independently since oppositely charged ions will affect each other as a result of electrostatic attractions and the ions may interact with the solvent (water).

The slight fall in specific susceptibility of the salt with increasing concentration, shown by certain of the salts and acids measured, appears to indicate some interaction between the ions and the solvent which can be expressed as a hydration effect. For the salts and acids in this group the effect is only small. The experimental data shows that in the case of uni-univalent polar salts the susceptibility in general does not vary greatly with the concentration but remains nearly constant.

(78)

Stokes and Robinson have expressed the various factors which may influence the properties of ions in solution, such as ion-ion interaction either between ions of the solute

or between those of the solute and solvent, in terms of a hydration number.

In their attempt to explain the experimental activity co-efficient data in terms of ionic hydration, they found that the hydration number values were greater than the values they expected to find on current ideas of hydration, which were largely based on the treatment (46) by Bernal and Fowler of apparent molar volumes in dilute solution. According to the latter authors' view the large anions  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  are unhydrated, <sup>and</sup> therefore the hydration number depends on the cations.

Having accepting this idea that it is the cation rather than the anions which are hydrated, Stokes and (loc-cit) Robinson emphasize, however that the hydration number is not the same thing as the conventional number of water molecules in the first layer round the ion. They suggest that it is rather a number introduced to allow for the average effect of all ion-solvent interaction and may therefore very well contain contributions from solvent molecules outside the first layer. They have explained the increase of hydration number with increasing anion size, for a given cation as follows. In a concentration range considered, the water molecules are not bound simply by the fields of isolated ions, but rather by the resultant field of an ion, and its neighbours, which of course

depends on their dimensions.

The work of Stokes & Robinson showed that as the concentration of solutions of even univalent polar salts such as potassium chloride increases, the hydration as expressed by the hydration number falls off. This appears to be in line with the <sup>trend of the</sup> susceptibility results and it was therefore thought of interest to attempt to calculate hydration numbers from the susceptibility results to see if any agreement is found with those of Stokes and Robinson. As this effect was more prominent for bivalent salts in solution it is discussed in the next section.

On the basis of the investigation of recent years into activity co-efficients of salts it may be regarded as certain that the union of ions whether to form molecules, ion pairs, or complex ions in the solution is always accompanied by more or less extensive changes in osmotic coefficients, activity coefficients, conductivities and transport numbers. Such changes are particularly marked in the salts of poly-valent ions, and especially so in those cases where complex ion formation can occur. Similar variations, can also be detected in the susceptibility measurements of solutions of the salts in this section which show a systematic deviation from strict additivity. Series of measurements

6. Measurements showing non-linear relationships with concentration.

In the first part of this thesis, in the study of additivity relationships of double salts in solution, it was noted that in the results recorded for zinc and cadmium salts and the alums, the deviations from additivity were rather large. This deviation might be caused by the variation of the susceptibility of the ions forming the salt with the concentration of the solution.

On the basis of the investigation of recent years into activity co-efficients of salts it may be regarded as certain that the union of ions whether to form molecules, ion pairs, or complex ions in the solution is always accompanied by more or less extensive changes in osmotic coefficients, activity coefficients, conductivities and transport numbers. Such changes are particularly marked in the salts of poly-valent ions, and especially so in those cases where complex ion formation can occur. Similar variations, can also be detected in the susceptibility measurements of solutions of the salts in this section which show a systematic deviation from strict additivity. Series of measurements

were made on aqueous solutions of silver nitrate and some electrolytes of 2:1 valency type, extending over as wide a range of concentration as the solubility of the salt permitted. The purpose of this part of the investigation was to show whether the magnetic measurements, like other physico-chemical measurements, could be used in the investigation of complex ion formation, or other complex solvent effects. The results can be considered in several groups:-

(1) Silver nitrate solutions ranging from	5% - 70%
(2) Cadmium Iodide .. .. .	10% - 45%
(3) Zinc Iodide .. .. .	5% - 55%
(4) Zinc Chloride .. .. .	5% - 63%
(5) Zinc bromide .. .. .	5% - 59%
(6) Zinc iodide 1 Eq. of potassium iodide	5% - 54.55%
(7) Zinc iodide 2 Eq. of potassium iodide	5% - 54%
(8) Zinc Chloride 1 Eq. Ammonium chloride	5% - 66%
(9) Zinc Chloride 2 Eq. Ammonium chloride	5% - 59%

The study of silver nitrate solutions was not in the original programme but while the work on solutions was in progress Professor C.W. Davies and <sup>D.C. (79)</sup> Morgan reported at a meeting of the Chemical Society (in February 1954) that they had obtained some interesting anomalous results in measurements on the solubility

\* Eq = equivalent.



of silver salts. The solubility varied with change in concentration in a manner which indicated the existence of an  $\text{Ag}_2^{++}$  ion.

The recorded data for several properties of silver salts in aqueous solution show a number of anomalies. The equivalent conductivity of silver nitrate is abnormal, and so are the transport number results for this salt. The solubility of silver acetate in solutions of other salts was found by MacDougall and his collaborators to show unusual features. Schwarzenbach and Prue, in their studies of metal complexes with poly amines, found that silver was unique among the metals investigated in forming compounds containing two metal atoms. Ion pairs and complex ions have been evoked to explain some of these results, but a generally satisfactory explanation on such lines does not seem possible.

It seemed interesting therefore to include this salt in the series studied. // The results are recorded in Table XV. The results are also depicted by the curve in figure XIa, in which the susceptibility of the solution is plotted against concentration. It will be observed that the variation of the susceptibility is not linear with the concentration but deviates from additivity showing a 'sigmoid' type of curve. The curve shows a progressive fall in susceptibility below a linear slope (through the values at lowest concentration)

up to a certain concentration and then a less rapid fall in susceptibility with concentration occurs, thus giving rise to the 'sigmoid' type of curve. A plot of the susceptibility of the salt (calculated from the measurements in solution, assuming the mixture law as in the earlier cases) against percentage concentration shows that the susceptibility of the salt appear to fall with concentration, to pass through a minimum and then rise again. (see graph figure XI, 6).

In order to investigate these effects further, the nature of the sigmoid curve was studied. It is theoretically possible to fit an equation of the type  $p = p_0 + ac + \beta c^2 + \gamma c^3 + \dots$  etc to a curve of this kind where  $p$  is the property considered  $a$  and  $\beta$  and  $\gamma$  are constants of either positive or negative sign and  $c$  is the concentration of the solution. The second term on the right hand side will be dominant for the most dilute solutions, (where  $c^2$  and  $c^3$  are negligible) which are of most interest but for which the experimental measurements tend to be least accurate. If the constant  $a$  can be evaluated it gives the limiting slope over the dilute solution range where the variation with concentration is linear, and hence enables the value of the property at infinite dilution to be calculated. In this type of

curve the sign of  $\alpha$  is negative. The third term on the right hand side if  $\beta$  is of negative sign, as was found to be the case, indicates an increasing curvature over the linear slope, as was just becoming apparent for acetic acid in the previous group. This term becomes significant over the intermediate range of concentrations. The fourth term and the constant  $\gamma$  if of positive sign will explain the upward curvature at higher concentration i.e. the type of curve is fitted by an equation:-

$$p = p_0 - \alpha c - \beta c^2 + \gamma c^3 + \dots \text{higher terms if required.}$$

Applying this to the susceptibility it follows

$$\chi_{\text{solution}} = \chi_{\text{solvent}} - \alpha c - \beta c^2 + \gamma c^3$$

(All susceptibilities in this discussion are in C.G.S. units  $\times (-10^6)$ ).

The constants  $\alpha$ ,  $\beta$  and  $\gamma$  can be solved for the silver nitrate solution as follows.

$$\chi_1 - \chi_0 = \alpha c + \beta c^2 + \gamma c^3$$

$$\text{For 20\% solution: } 0.2\alpha + 0.04\beta + 0.008\gamma = -.0801 \dots\dots\dots \text{I}$$

$$\text{For 40\% solution: } 0.4\alpha + 0.16\beta + 0.064\gamma = -.1727 \dots\dots\dots \text{II}$$

$$\text{For 60\% solution: } 0.6\alpha + 0.36\beta + 0.216\gamma = -.2671 \dots\dots\dots \text{III}$$

Equation I is multiplied by 2 and then  
Equation II is subtracted.

$$\begin{aligned} .4a + .08\beta + .016\gamma &= -.1602 \\ .4a + .16\beta + .064\gamma &= -.1727 \\ -.08\beta - .048\gamma &= .0125 \\ .08\beta + .048\gamma &= -.0125 \dots \dots \dots \text{IV} \end{aligned}$$

Eq II is multiplied by 3 and Eq III by 2 and subtracted.

$$\begin{aligned} (1) \quad 1.2a + .48\beta + .192\gamma &= -.5181 \\ (2) \quad 1.2a + .72\beta + .432\gamma &= -.5342 \\ (3) \quad -.24\beta + .240\gamma &= -.0161 \\ 24\beta + .240\gamma &= -.0161 \dots \dots \dots \text{V} \end{aligned}$$

From Equation IV and V:-

$$.24\beta + .240\gamma = -.0161$$

$$.24\beta + .144\gamma = -.0375$$

$$.096\gamma = .0214$$

$$\gamma = \frac{.0214}{.096}$$

$$= .223$$

Substituting the value for  $\gamma$  we get.

$$.08\beta + (.048 \times .223) = -.0125$$

$$.08\beta = -.0125 - .0107$$

$$= -.0232$$

$$\beta = -.290$$

For  $\alpha$  using the same eq:-

$$.4\alpha + .08\beta + .016\gamma = -.1602$$

$$.4\alpha + (.08 \times .29) + (.016 \times .223) = -.1602$$

$$.4\alpha - .0232 + .003568 = -.1602$$

$$.4\alpha = -.1406$$

$$\alpha = -.3515$$

$$(1) \alpha = -.3515$$

$$(2) \beta = -.290$$

$$(3) \gamma = .223.$$

Thus the equation to the curve in Figure XIa, for silver nitrate is  $X = X_0 - .3515e^{-.290c^2} + .223c^3$  where  $X_0 = .7201$ , the susceptibility found for the solvent water when  $X = .7023$ .

Benzene

The equation was further tested by calculating the susceptibilities for 15% and 45% of the salt and gave values in <sup>fair</sup> agreement with the experimental ones. At the highest concentrations less close agreement was found, an effect which is more marked in some of the other cases studied, owing to the neglect of higher terms. The equations with the constants  $\alpha$ ,  $\beta$  and  $\gamma$  for <sup>most of</sup> the other salts studied are summarised below.

- (1)  $\text{AgNO}_3$ ,  $\chi = .7201 - .3515C - .290C^2 + .2230C^3$
- (2)  $\text{CdI}_2$ ,  $\chi = .7201 - .278C - .2691C^2 + .166C^3$
- (3)  $\text{ZnI}_2$ ,  $\chi = .7201 - .3336C - .2234C^2 + .2333C^3$
- (4)  $\text{KCl}$ ,  $\chi = .7201 - .166C \dots \dots \dots$  Linear
- (5)  $\text{KI}$ ,  $\chi = .7201 - .3104C$
- (6)  $\text{ZnI}_2 + 1 \text{ eq KI}$ ,  $\chi = .7201 - .3104C - .1850C^2 + .113C^3$
- (7)  $\text{ZnI}_2 + 2 \text{ eq KI}$ ,  $\chi = .7201 - .3104C - .130C^2 + .150C^3$

From the value of the constant  $a$ , for the different salts the limiting slope at low concentrations, could be calculated as in the previous section, since <sup>at low concentration</sup> here the variation <sub>of susceptibility</sub> with concentration is linear. In figures XIa — XVa this ideal limiting slope is shown by the dotted line, and gives the slope which would be shown if the susceptibility of the salt remained constant. The limiting slope enables the susceptibility of the salt at infinite dilution to be calculated as before, i.e.

$$a = \chi_{\text{solute}} - \chi_0$$

$$\text{i.e. } \chi_s = \chi_0 + a, \text{ and } a = -.3515$$

$$\begin{aligned} X_s &= .7201 - .3515 \\ &= .3686 \end{aligned}$$

This value is obviously in good agreement with the extrapolated value for the susceptibility of silver nitrate in Figure XI b although, as already pointed out, this extrapolation cannot be made very accurately. Therefore for silver nitrate  $X_0$ , the ideal susceptibility of the salt at infinite dilution = .3686. The molalities, moles salt per 1000 g water, of the solutions measured were also calculated from the concentration in grams salt per 100 grams solution. Knowing  $X_0$  ideal, the (loc-cit) hydration number as defined by Stokes and Robinson was calculated as follows:-

Calculation of true molalities and hydration number.

To find the true molality and 'hydration number' of an ion, it was assumed for the purposes of calculation that any deviation of the susceptibility from the limiting value for the salt is all ascribed to hydration. The limiting value has already been calculated just above. Now, if the susceptibility had shown complete additivity and no change in hydration with change in concentration then.

$$\chi_{\text{sol}} = (1-p') \chi_{\text{solvent}} + p' \chi_{\text{salt (lim)}}.$$

Where  $\chi_{\text{sol}}$  = the susceptibility of the solution measured in c.g.s. units  $\times (-10^6)$ ;  $\chi_{\text{solvent}}$  = susceptibility of solvent, i.e. water, or in some cases dilute acetic acid or hydriodic acid etc, and  $p'$  is the true weight fraction of the salt or 'ideal' weight fraction; representing the weight fraction of the salt and any associated water and  $(1-p')$  is the true weight fraction of the water that is acting as true solvent and not associated with the ion. The above equation could be written like this:-

$$y = (1-p') x + (p' \times Z).$$

$$\text{or } y = x - p' x + p' Z.$$

$$(x-y) = p' (x-Z).$$

$$p' = \frac{x-y}{x-Z}$$

Where  $x = \chi_{\text{solvent}}$ , frequently  $\chi_{\text{H}_2\text{O}} = .7201$

$y =$  susceptibility of solution measured

$Z =$  extrapolated susceptibility of salt or  $\chi_{\text{salt (lim)}}$

The quantity  $p'$  which is the true weight fraction, allows



for some of the water associated with the ions as water of hydration or solvation and therefore it will enable the true molality  $m'$  to be calculated.

i.e. if  $p'$  = the number of grams salt per 100 g solution after allowance for the hydration of the ion.

$$(100-p') = \text{weight of water acting as solvent}$$

$$\left(\frac{p' \times 1000}{100 - p'}\right) = \text{weight of salt per 1000 g of water}$$

$$\left(\frac{p' \times 1000}{(100 - p')M}\right) = \text{moles of salt per 1000 g of water}$$

$$= m' \text{ the true molality.}$$

If there were no hydration then 55.51 moles of water (1000 g) are present per  $m$  moles of salt. Where  $m$  is the weight of the salt weighed out. If  $n$  moles of water per one mole of salt is the 'hydration number'. Then  $(55.5 - n \times m)$  moles of water are acting as true solvent to give a true molality  $m'$ .

$$\text{Hence } \frac{m'}{m} = \frac{55.51}{(55.51 - nm)}$$

$$\text{or } n = \frac{(m' - m)}{(.018 \times m \cdot m')}$$

where  $n$  is the hydration number,  $m$  is the molality calculated from the weight weighed out, and  $m'$  the true

molality calculated from  $p'$  the true weight fraction. The hydration number so obtained was calculated for each of the silver nitrate solutions measured and for the salts studied, and compared with values by other workers, where such were available.

Table <sup>s</sup>~~XV~~ a - XIXa show, for the salts studied, the molalities of the solutions, calculated from the compositions made up, and the susceptibilities and molar susceptibilities of the salt, calculated on the assumption of additivity, and not allowing for the hydration effect. ~~the~~ Tables XVI b - XIXb show the values for the true molalities and the hydration numbers calculated as indicated above for the salts studied in this section.

The corresponding graphs are plotted in Figures XI, - XV. The Figures with suffix (a) show the graphs of susceptibility of solution plotted against concentration (g /100 g solution). Those with suffix (b) show the apparent susceptibility of the salt, calculated on the linear mixture law plotted similarly, while those with suffix (c) show apparent molar susceptibility of the salt plotted against the apparent molality (i.e. molality calculated from the concentration of the solution). A graph of change in hydration number with molality of the solution is shown in Figure XVI for the four salts studied.

Table XV (a)  
Silver nitrate solution.

Susceptibility of solution and salt.

Composition g/100g. sol.	Molality	Mean $-10^6 \chi$ Solution	$-10^6 \chi$ Salt	$-10^6 \chi_M$ Salt.
5.0	.3098	.70215	.3631	61.69
5.0	.3098	.70214	.3629	61.65
9.991	.563	.68293	.3489	59.27
10.09	.660	.68238	.3471	58.97
10.09	.6605	.68241	.3482	59.16
10.09	.660	.68249	.3482	59.16
10.11	.661	.68228	.3469	59.15
10.11	.661	.68243	.3484	59.19
15.12	1.04	.66162	.3339	56.73
15.03	1.04	.66232	.3362	57.12
20.08	1.48	.64015	.3223	54.76
20.09	1.47	.64012	.3225	54.79
20.12	1.48	.64000	.3224	54.77
25.04	1.97	.61820	.3136	53.28
25.09	1.97	.61825	.3144	53.41
30.06	2.53	.59459	.3027	51.42
30.07	2.53	.59456	.3028	51.44
30.09	2.53	.59464	.3033	51.53
35.01	3.17	.57159	.2963	50.34
35.01	3.17	.57159	.2960	50.29
40.00	3.92	.54744	.2884	48.99

Table X v a continued.

Composition g/100g. sol.	Molality	Mean $-10^6 \chi$ Solution	$-10^6 \cdot \bar{\chi}$ Salt	$-10^6 \cdot \bar{\chi}_M$ Salt.
40.08	3.94	.54736	.2892	49.13
44.99	4.81	.52410	.2845	48.33
45.04	4.82	.52348	.2836	48.18
45.05	4.82	.52375	.2843	48.29
45.05	4.82	.52404	.2847	48.37
50.04	5.89	.49969	.2796	47.50
50.06	5.90	.49969	.2799	47.55
50.06	5.90	.49951	.2795	47.48
50.12	5.91	.49849	.2787	47.35
54.88	7.15	.47746	.2767	47.01
54.91	7.17	.47665	.2768	47.02
55.10	7.22	.47587	.2768	47.02
55.10	7.22	.47621	.2775	47.14
60.10	8.866	.45304	.2758	46.85
60.12		.45303	.2759	46.87
61.59	9.47	.44750	.2775	47.14
64.33	10.61	.43574	.2780	47.22
64.92	10.89	.43980	.2784	47.30
69.51	13.42	.41930	.2874	48.82
70.12	13.81	.41796	.2892	49.13

NB. The values in column 4 are obtained by assuming the additive law to hold as on page 43. Values of approximately the same composition were made up independently.

Table XVI(a)

Cadmium Iodide Solutions.

Composition g/100 gm. sol.	Molality	Mean $-10^6 \cdot X$ solution	$-10^6 \cdot X$ Salt	$-10^6 \cdot X_M$ Salt
10.10	.3067	.68982	.4211	154.23
10.11	.307	.68978	.4211	154.23
15.08	.485	.67326	.4102	150.24
15.09	.485	.67346	.4115	150.71
20.08	.682	.65506	.3965	145.22
20.11	.6872	.65495	.3965	145.22
25.10	.9149	.63602	.3853	141.12
29.98	1.169	.61777	.3789	138.78
30.10	1.175	.61720	.3784	138.59
30.60	1.204	.61479	.3761	137.75
30.84	1.217	.61391	.3760	137.71
35.01	1.471	.59736	.3697	135.40
35.08	1.38	.59663	.3683	134.89
35.10	1.476	.59638	.3677	134.67
35.11	1.477	.59619	.3671	134.45
35.12	1.478	.59594	.3667	134.30
37.46	1.635	.58695	.3636	133.17
38.70	1.724	.58223	.3639	133.28
39.79	1.804	.57781	.3626	132.80
40.02	1.82	.57680	.3621	132.62
40.05	1.824	.57630	.3612	132.29

Table XVI a. continued.

Composition g/100 gm. sol.	Molality	Mean $-10^6 \cdot \chi$ solution	$-10^6 \cdot \chi$ Salt	$-10^6 \cdot \chi M.$ Salt
43.61	2.111	.56317	.3603	131.96
44.95	2.229	.56042	.3649	133.64
45.16	2.248	.56076	.3673	134.52

14.21	0.580	.56214	.35901	114.20	0.0172
17.21	0.711	.56148	.35885	117.05	0.0169
20.25	0.844	.56315	.35905	112.65	0.0162
25.51	1.074	.56281	.35875	114.20	0.0170
28.54	1.205	.56215	.35870	110.24	0.0160
30.52	1.256	.56195	.35862	107.75	0.0152
31.59	1.273	.56115	.35775	107.74	0.0154
35.21	1.402	.56309	.35875	106.21	0.0155
36.85	1.428	.56702	.35956	106.43	0.0157
40.82	1.616	.56962	.35885	104.50	0.0153
45.87	1.846	.56770	.35862	104.50	0.0157
49.09	2.021	.56074	.35241	105.46	0.0157
49.26	2.04	.56261	.35289	106.25	0.0152
55.00	2.283	.56935	.35394	105.54	0.0152

Table XVII a

Zinc iodide solution.

Composition g/100gm. sol.	Molality	Mean $-10^6 \cdot X$ solution	$-10^6 \cdot X$ Salt	$-10^6 \cdot XM$ Salt	Normality of Solvent.
5.10	.1683	.70278	.38422	122.65	0.0019
10.12	.3527	.68464	.37273	118.98	0.0040
14.84	.5458	.66619	.35901	114.60	0.0062
15.21	.5619	.66448	.35665	113.85	0.0065
20.23	.7944	.64543	.35289	112.65	0.0080
23.93	.9854	.63041	.3474	110.90	0.0105
23.54	.9854	.63130	.3474	110.9	0.0102
30.22	1.356	.60483	.34061	108.73	0.0148
31.99	1.473	.59715	.3375	107.74	0.0164
35.21	1.702	.58309	.33273	106.21	0.0183
36.86	1.828	.57702	.3336	106.49	0.0197
40.82	2.16	.55962	.3286	104.90	0.0225
43.87	2.448	.54770	.32862	104.90	0.025
49.09	3.021	.54074	.3241	103.46	0.035
49.26	3.04	.52851	.33285	106.25	0.0382
55.00	3.83	.50993	.3394	108.34	0.0402

Table XVIII a

Susceptibilities of zinc chloride solutions.

Percentage g/100g sol.	Normality of sol.	$\chi \times 10^{-6}$ solvent from graph	Mean $-10^6 \cdot \chi$ solution	$-10^6 \cdot \chi$ salt
5.11	.0157N	.71995	.70947	.5149
10.07	.01678N	.71992	.69776	.4998
10.70	.0172N	.71992	.69647	.5007
10.65	.0171	.71992	.69647	.4997
19.83	.0170	.71991	.67419	.4893
20.11	.0169	.71991	.67389	.4910
29.31	.0181	.71990	.64788	.4740
30.11	.0168	.71991	.64668	.4766
30.07	.018	.7199	.64665	.4893
35.10	.0188	.7199	.63167	.4684
39.13	.0269	.7198	.62008	.4648
39.98	.0262	.7198	.61868	.4667
39.99	.0221	.7198	.61841	.4663
40.13	no acid		.61836	.4667
45.10			.60405	.4627
45.11			.60333	.4614
50.01			.59030	.4606
50.10			.59025	.4610
50.10			.59029	.4610
50.11	.0557	.71979	.59016	.4611



Table XVIII a continued.

Percentage g/100g sol.	Normality of sol.	$X \times 10^{-6}$ solvent from graph	Mean $-10^6 \cdot X$ solution	$-10^6 \cdot X$ salt
50.11			.58994	.4604
55.05			.57737	.4607
55.12			.57658	.4597
55.13	.0647	.7197	.57620	.4611
57.60			.56942	.4585
59.38			.56651	.4615
59.98			.56384	.4596
60.65	.074	.7196	.56242	.4605
61.05			.56173	.4607
63.34			.56047	.4681

Table XIX a

Susceptibilities of zinc bromide solution

in N/1 hydrogen bromide				
Percentage g/100 g sol.	Normality	$-10^6 \cdot X$ solution	$-10^6 \cdot X$ solvent graph	$-10^6 \cdot X$ salt
5.11	N/1	.67829	.6910	.4424
5.11	"	.67833	"	.4432
10.07	"	.66468	"	.4296
10.09	"	.66417	"	.4301
15.09	"	.64960	"	.4166
20.09	"	.63412	"	.4079
20.10	"	.63421	"	.4085
25.03	"	.61597	"	.3912
25.10	"	.61576	"	.3912
30.07	"	.59657	"	.3769
30.08	"	.59650	"	.3768
35.00	"	.57754	"	.3668
35.03	"	.57732	"	.3664
40.05	"	.55669	"	.3556
40.05	"	.55669	"	.3556
45.08	"	.53878	"	.3533
45.09	"	.53874	"	.3533
50.01	"	.52287	"	.3548
50.09	"	.52223	"	.3540
55.12	"	.50896	"	.3607

Table XIX a continued.

Percentage g/100 g sol.	Normality	$-10^6 \cdot X$ solution	$-10^6 \cdot X$ solvent graph	$-10^6 \cdot X$ salt
79.10	N/1	.50001	.6910	.3678
59.33	"	.49812	"	.3656

1.04	.0565	.1654	1.026	1.026
1.04	.0573	.1673	1.026	1.026
1.48	.0800	.2275	1.475	1.475
1.47	.0800	.2275	1.475	1.475
1.49	.0801	.2278	1.475	1.475
1.97	.1019	.2979	1.975	1.975
1.97	.1019	.2979	1.975	1.975
2.53	.1255	.3574	2.535	2.535
2.53	.1255	.3574	2.535	2.535
2.53	.1255	.3574	2.535	2.535
3.17	.1685	.4824	3.175	3.175
3.17	.1685	.4824	3.175	3.175

Table XV (b)

Silver Nitrate Solutions.Calculation of True Molality and Hydration Number

(X - Z) = .3515				
Molality	$X_{\text{solvent}} - X_{\text{Sol}}$	True Wt. Fraction	True Molality	hydration number
.3098	.0180	.0512	.3176	4.588
.3098	.0180	.0512	.3176	4.588
.563	.0372	.1058	.6963	6.18
.660	.0378	.1072	.7067	5.50
.6605	.0377	.1072	.7045	5.36
.660	.0377	.1072	.7067	5.50
.661	.0378	.1075	.7089	5.58
.661	.0377	.1072	.7067	5.62
1.04	.0585	.1664	1.174	5.23
1.04	.0578	.1638	1.152	6.11
1.48	.0800	.2275	1.733	5.74
1.47	.0800	.2275	1.733	5.74
1.48	.0801	.2278	1.736	5.54
1.97	.1019	.2899	2.403	5.08
1.97	.1019	.2899	2.403	5.08
2.53	.1255	.3570	3.267	4.96
2.53	.1255	.3570	3.267	4.96
2.53	.1255	.3570	3.267	4.96
3.17	.1485	.4224	4.304	4.62
3.17	.1485	.4224	4.304	4.62

Table XV b. continued.

Molality	$\chi_{\text{solvent}} - \chi_{\text{sol}}$	True Wt. Fraction	True Molality	hydration number
3.92	.1727	.4913	5.684	4.399
3.94	.1727	.4913	5.684	4.327
4.81	.1960	.5576	7.418	4.062
4.82	.1966	.5593	7.470	4.08
4.82	.1964	.5578	7.424	4.04
4.82	.1961	.5587	7.452	4.07
5.89	.2204	.6270	9.894	3.82
5.90	.2204	.6275	9.915	3.82
5.90	.2206	.6270	9.894	3.80
5.91	.2316	.6304	10.04	3.87
7.15	.2426	.6901	13.107	3.533
7.17	.2435	.6927	13.27	3.563
7.22	.2442	.6947	13.39	3.54
7.22	.2439	.6938	13.34	3.53
8.866	.2671	.7598	18.61	3.28
8.866	.2671	.7598	18.61	3.28
9.47	.2726	.7755	20.33	3.138
10.61	.2844	.8091	24.95	2.88
10.89	.2812	.7974	23.16	2.70
13.42	.3008	.8557	34.90	2.55
13.81	.3022	.8594	35.98	2.47

Table XVI (b)

Cadmium Iodide Solution

$(\chi - \bar{\chi}) = .278$

Molality	$\chi_{\text{solvent}} - \chi_{\text{sol.}}$	True Wt. Fraction	True Molality	hydration number
.3067	.0303	.1089	.3336	14.94
.307	.0303	.1089	.3336	14.77
.485	.0468	.1683	.5524	14.04
.485	.0466	.1676	.5497	13.47
.682	.0650	.2338	.8331	14.28
.6872	.0651	.2345	.8363	14.47
.9149	.0841	.3025	1.184	13.86
1.169	.1023	.3679	1.589	12.57
1.175	.1029	.3701	1.604	12.65
1.204	.1053	.3787	1.664	12.77
1.217	.1062	.3820	1.69	12.73
1.471	.1227			
1.38	.1235	.4442	2.18	13.09
1.476	.1237	.4449	2.19	12.27
1.477	.1239	.4456	2.194	12.29
1.478	.1242	.4467	2.204	12.38
1.635	.1331	.4791	2.511	11.83
1.724	.1379	.4956	2.682	11.51
1.804	.1423	.5118	2.862	11.38
1.82	.1433	.5154	2.903	11.37
1.824	.1438	.5172	2.924	12.22

Table XVI b. continued.

Molality	$\chi_{\text{solvent}} - \chi_{\text{sol.}}$	True Wt. Fraction	True Molality	hydration number
2.111	.1569	.5643	3.536	10.63
2.229	.1597	.5744	3.684	9.844
2.248	.1593	.5730	3.663	9.547

Table XVII. b

Zinc iodide

$(X - Z) = .3336$

Composition g/100 gm.sol.	Molality	$\chi_{\text{solvent}} - \chi_{\text{sol.}}$	True Wt. Fraction	True Molality	hydration number.
5.10	.1683	.01712	.05187	.174	11.9
10.12	.3527	.03512	.1065	.380	11.5
14.84	.5458	.05353	.1625	.620	11.8
15.21	.5619	.05522	.1666	.626	10.15
20.23	.7944	.07419	.2239	.9037	8.46
23.93	.9854	.08901	.2688	1.151	8.25
23.54	.9854	.08815	.2661	1.135	7.50
30.22	1.356	.11443	.3456	1.654	7.35
31.99	1.473	.1221	.3687	1.829	7.42
35.21	1.702	.136	.4106	2.182	7.21
36.86	1.828	.1421	.4289	2.35	6.74
40.82	2.16	.1594	.4811	2.904	6.59
43.87	2.448	.17123	.5167	3.349	6.08
49.09	3.021	.1779	.5377	3.643	3.14
49.26	3.04	.18995	.5743	4.226	5.12
55.00	3.83	.20847	.6300	5.33	4.100



Table XVIIIb

Zinc chloride solutionCalculation of True Molality and Hydration Number

(see page 83).

$$(X - Z) = .207$$

Molality	$X$ solvent- $X$ sol.	True wt. Fraction	True Molality	Hydration Number
.395	.0106	.0512	.3958	.285
.879	.0222	.1073	.8819	.208
.879	.0234	.1132	.9366	3.89
.874	.02345	.1132	.9366	4.25
1.814	.0457	.2208	2.079	3.90
1.846	.04602	.2223	2.097	3.63
1.846	.04602	.2223	2.097	3.63
3.042	.07202	.3479	3.914	4.07
3.15	.07326	.3539	4.018	3.82
3.16	.07323	.3537	4.01	3.72
3.97	.08823	.4262	5.45	3.8
4.89	.1011	.4884	7.004	3.42
4.918	.1015	.4903	7.058	3.42
6.027	.1161	.5608	9.368	3.28
6.029	.1168	.5642	9.499	3.36
7.232	.1298	.6270	12.33	3.17

Table XVIIIb continued

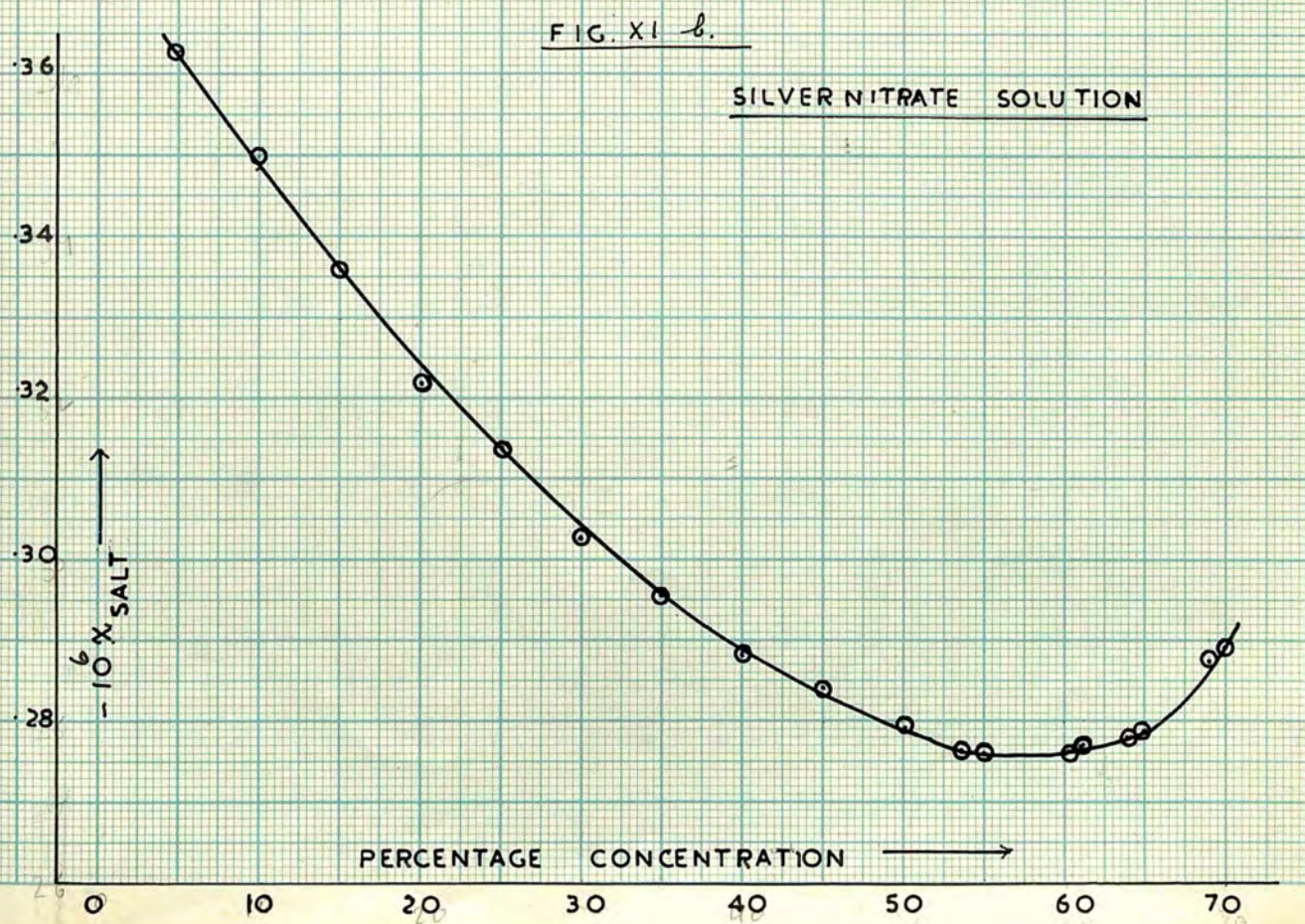
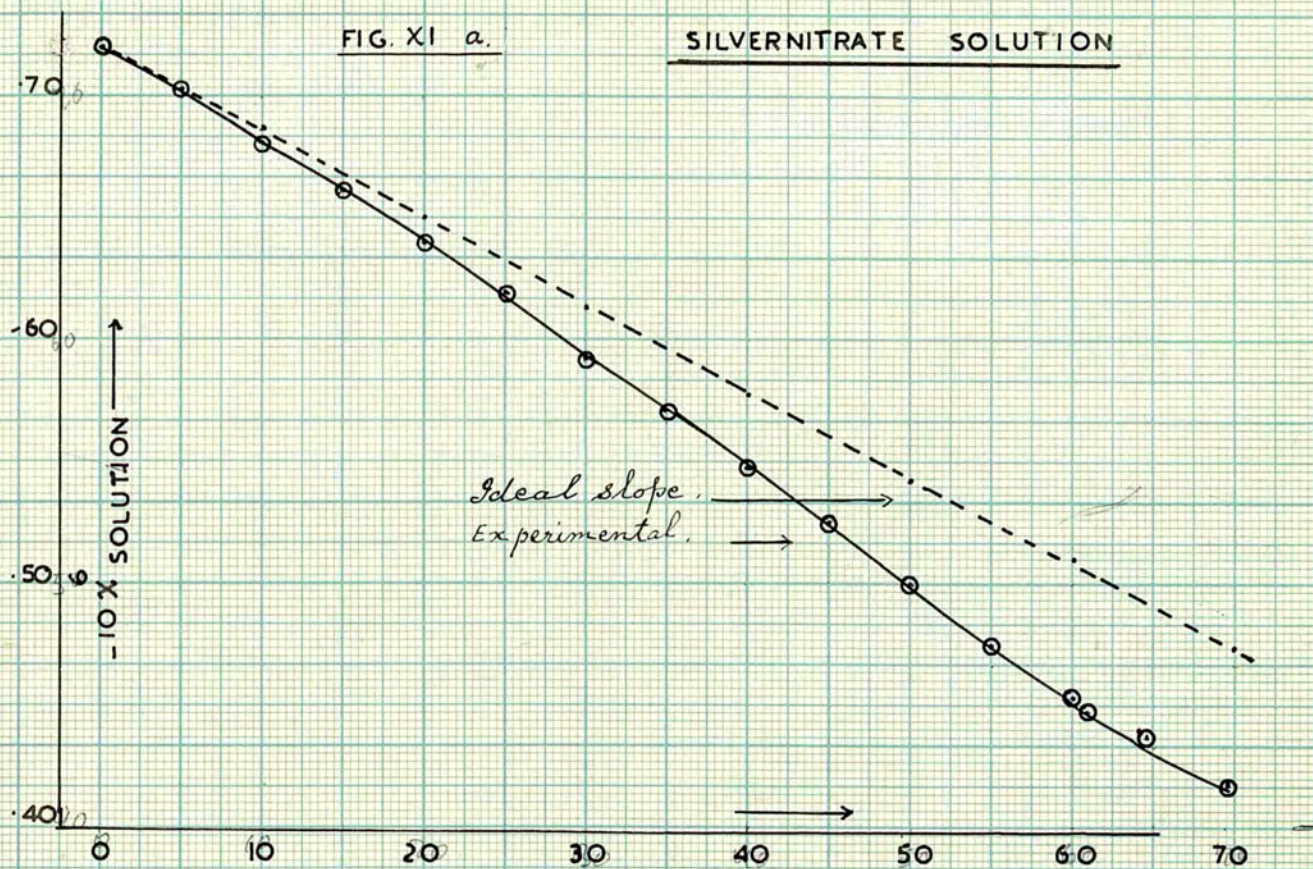
Molality	X solvent- X sol.	True wt. Fraction	True Molality	Hydration Number
7.369	.1302	.6289	12.43	3.07
7.369	.1299	.6275	12.36	3.04
7.366	.1299	.6275	12.36	3.05
9.015	.1439	.6951	16.72	2.84
8.98	.1427	.6893	16.27	2.71
11.31	.1577	.7618	23.46	2.54
12.68	.1596	.7710	24.70	2.13

Table XIXb

Zinc bromide solution.

(X-Z) = .2359 Calculation of True Molality and hydration  
number (see page 83)

Molality	X solvent -X solution	True wt. Fraction	True Molality	hydration number
.2391	.0127	.0538	.2525	(18.40)
.497	.0263	.1114	.5569	12.22
.789	.0814	.1754	.9449	11.63
1.116	.0569	.2412	1.412	10.45
1.482	.0569	.2412	1.412	10.45
1.482	.0750	.3179	2.070	10.28
1.487	.0752	.2187	2.078	10.62
1.909	.0944	.4001	2.962	10.35
1.910	.0945	.4005	2.967	10.36
2.39	.1135	.4811	4.118	9.76
2.394	.1137	.4819	4.132	9.76
2.966	.1343	.5693	5.872	9.27
3.644	.1522	.6451	8.075	8.37
3.646	.1523	.6456	8.092	8.37
4.442	.1681	.7125	11.00	7.45
4.456	.1688	.7155	11.17	7.49
5.453	.1821	.7719	15.04	6.49
6.416	.1910	.8096	18.88	5.71
6.477	.1929	.8177	19.92	5.79



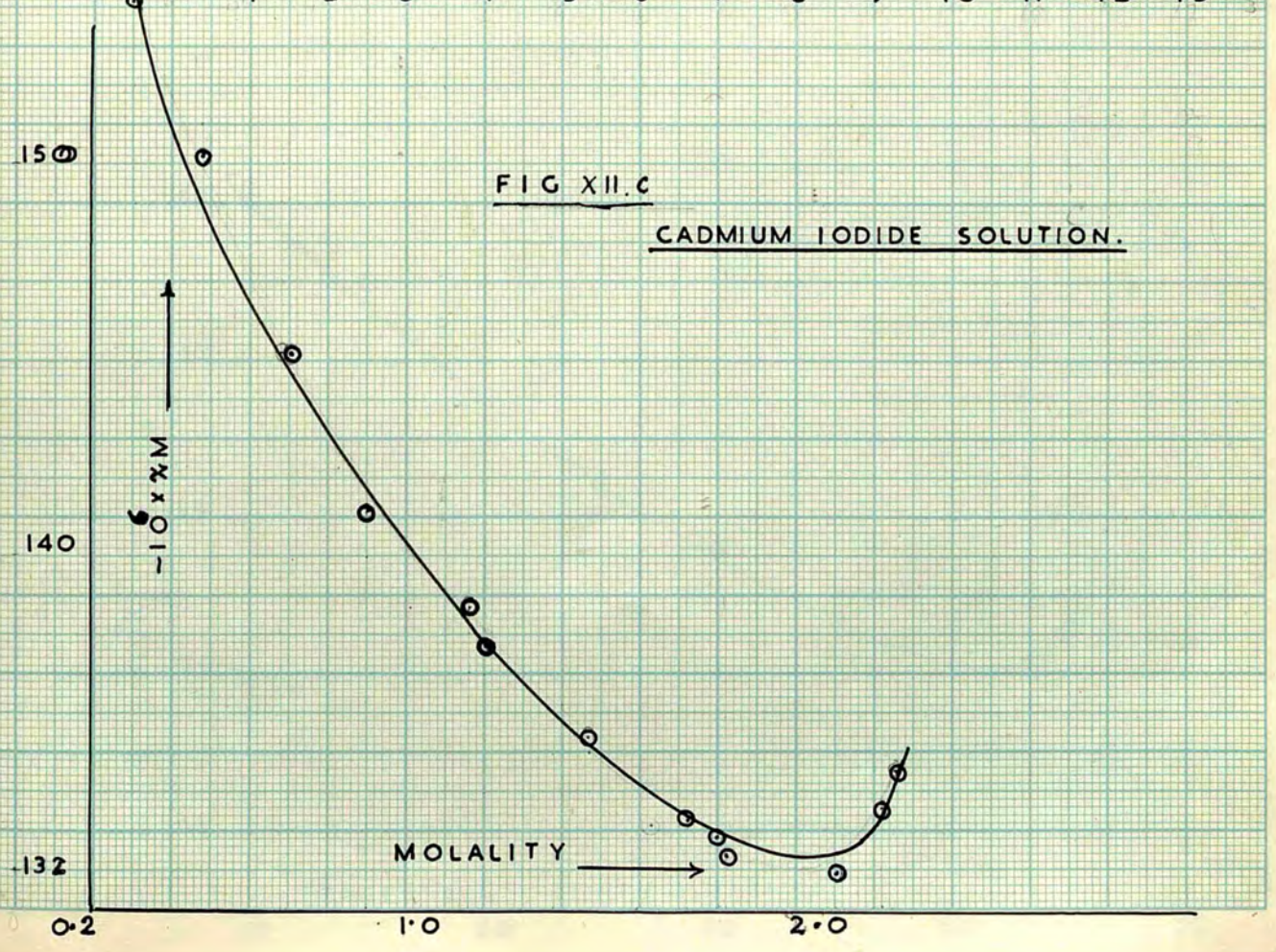
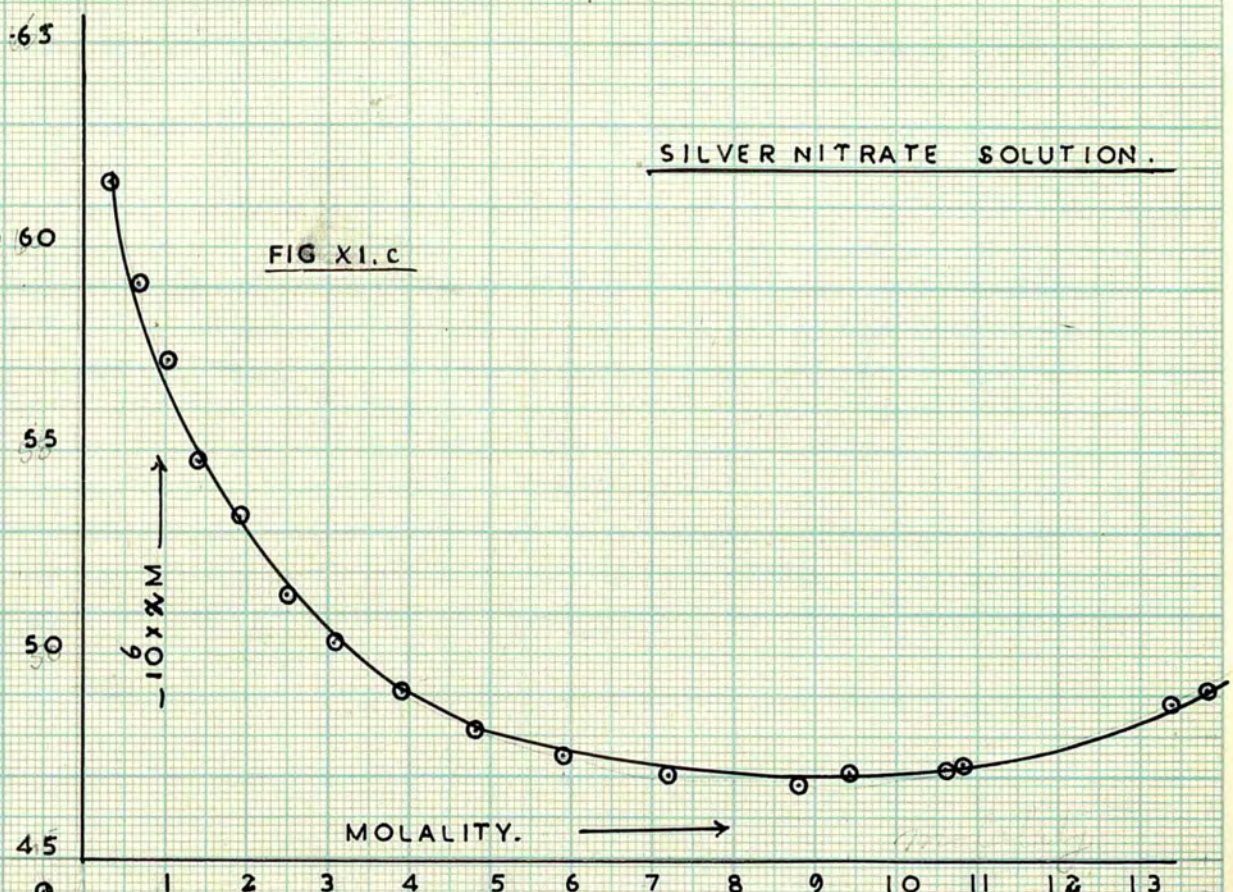


FIG XII a.

CADMIUM IODIDE SOLUTION

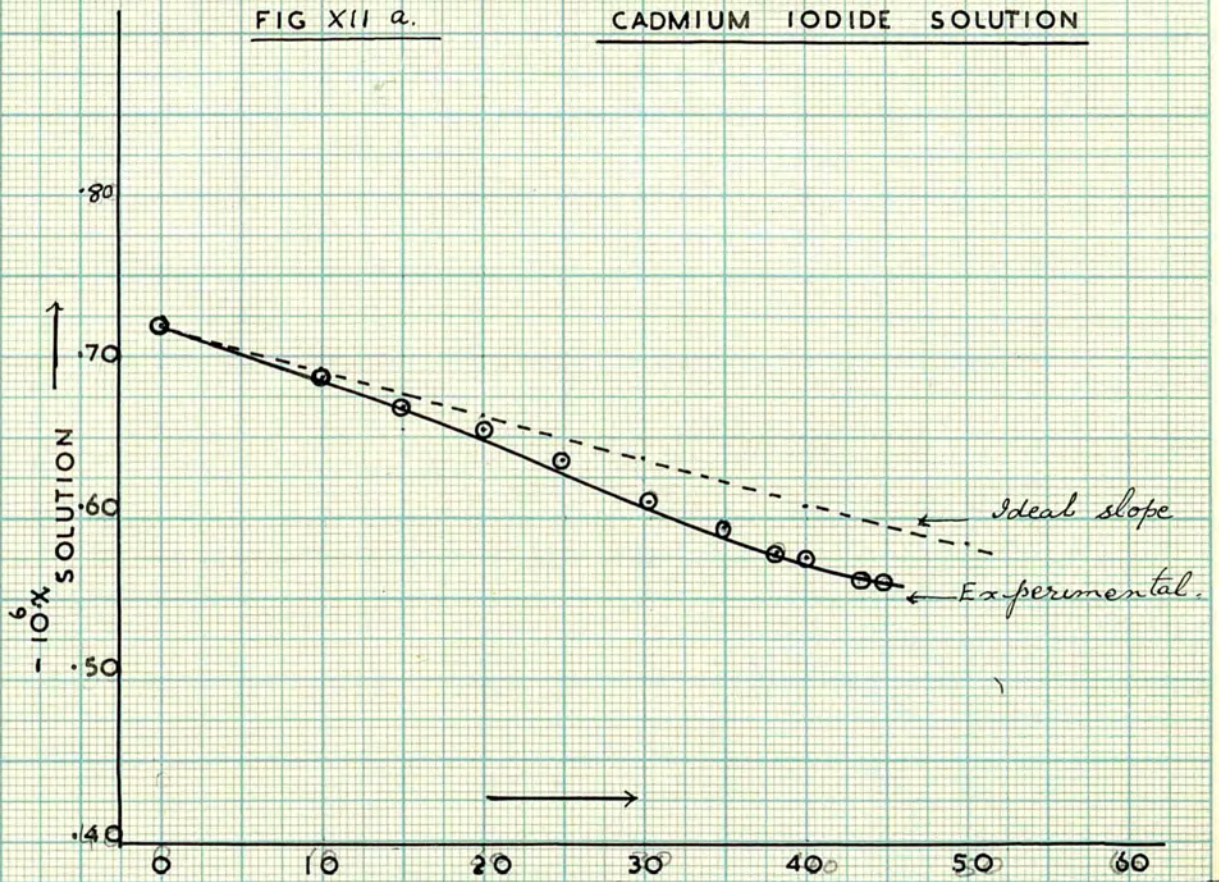


FIG XII b.

CADMIUM IODIDE SOLUTION

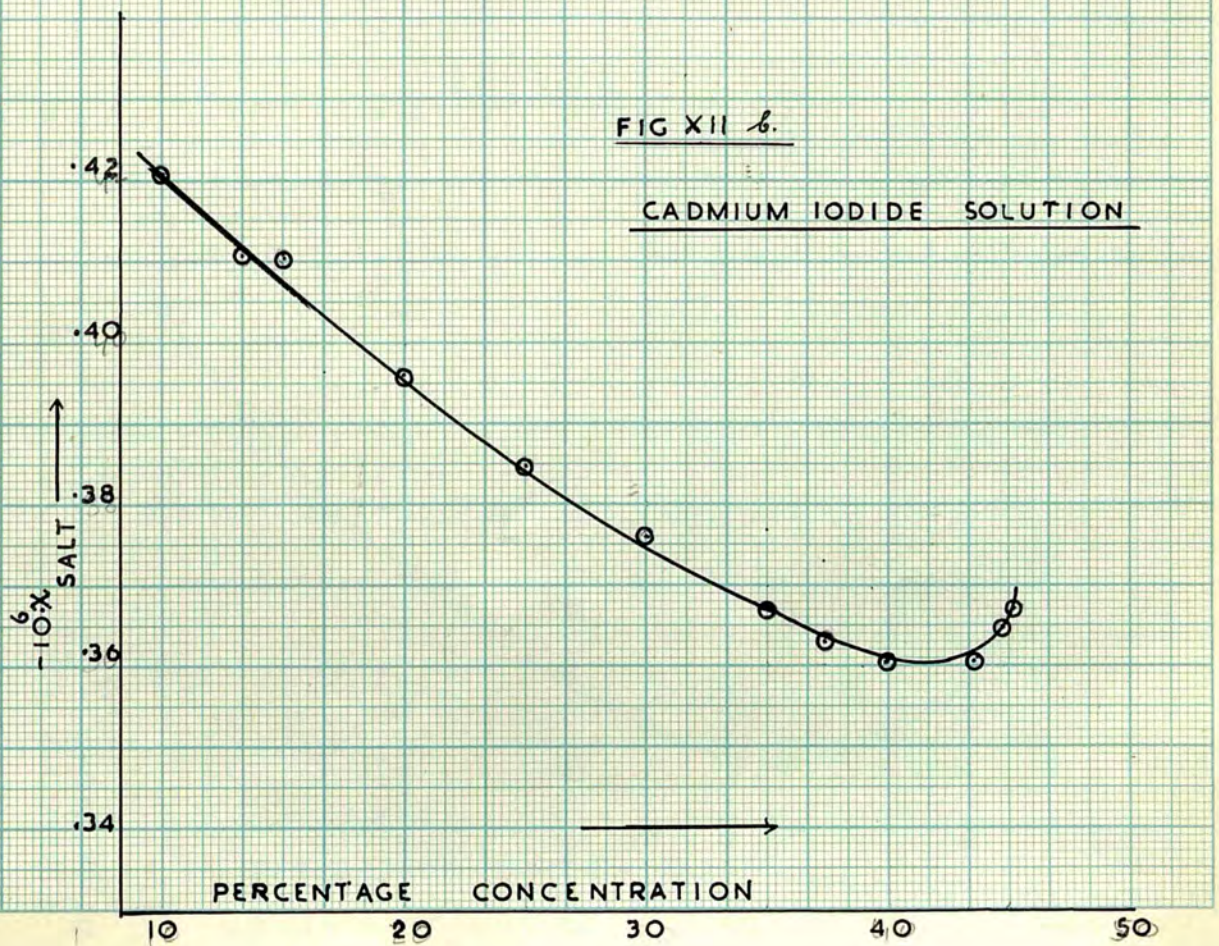


FIG XIII a

ZINC IODIDE SOLUTION

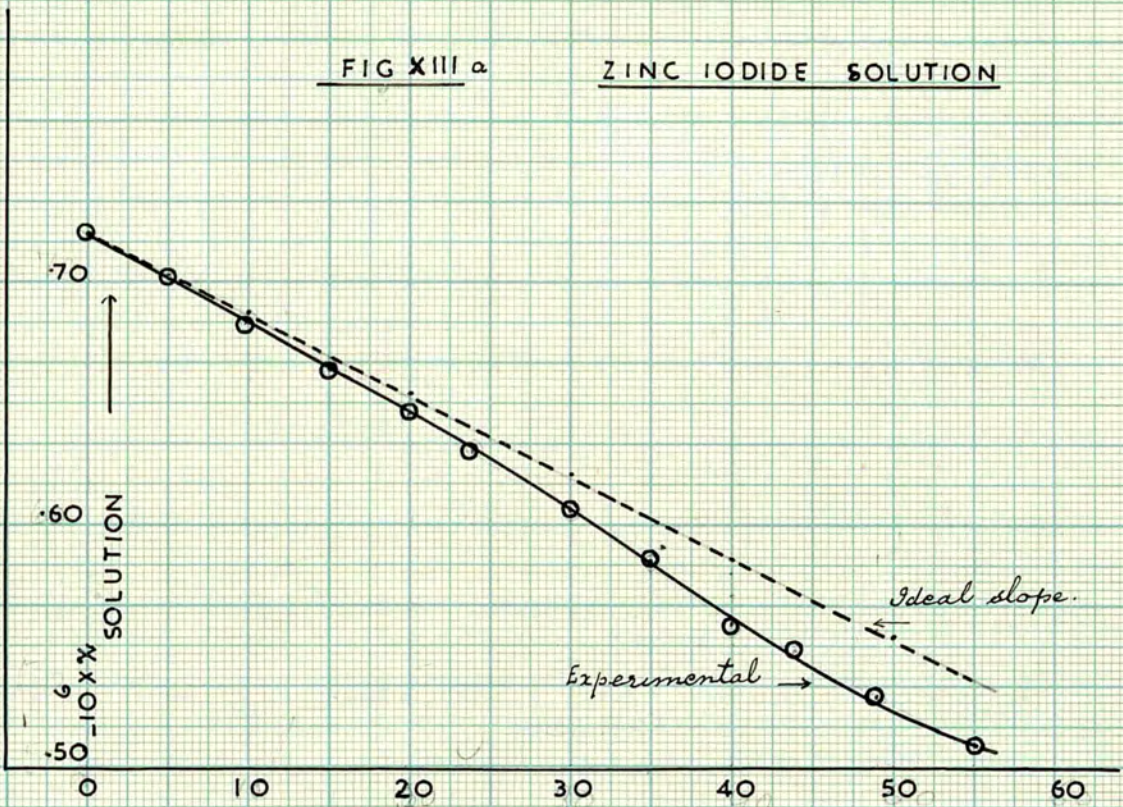


FIG. XIII b.

ZINC IODIDE SOLUTION

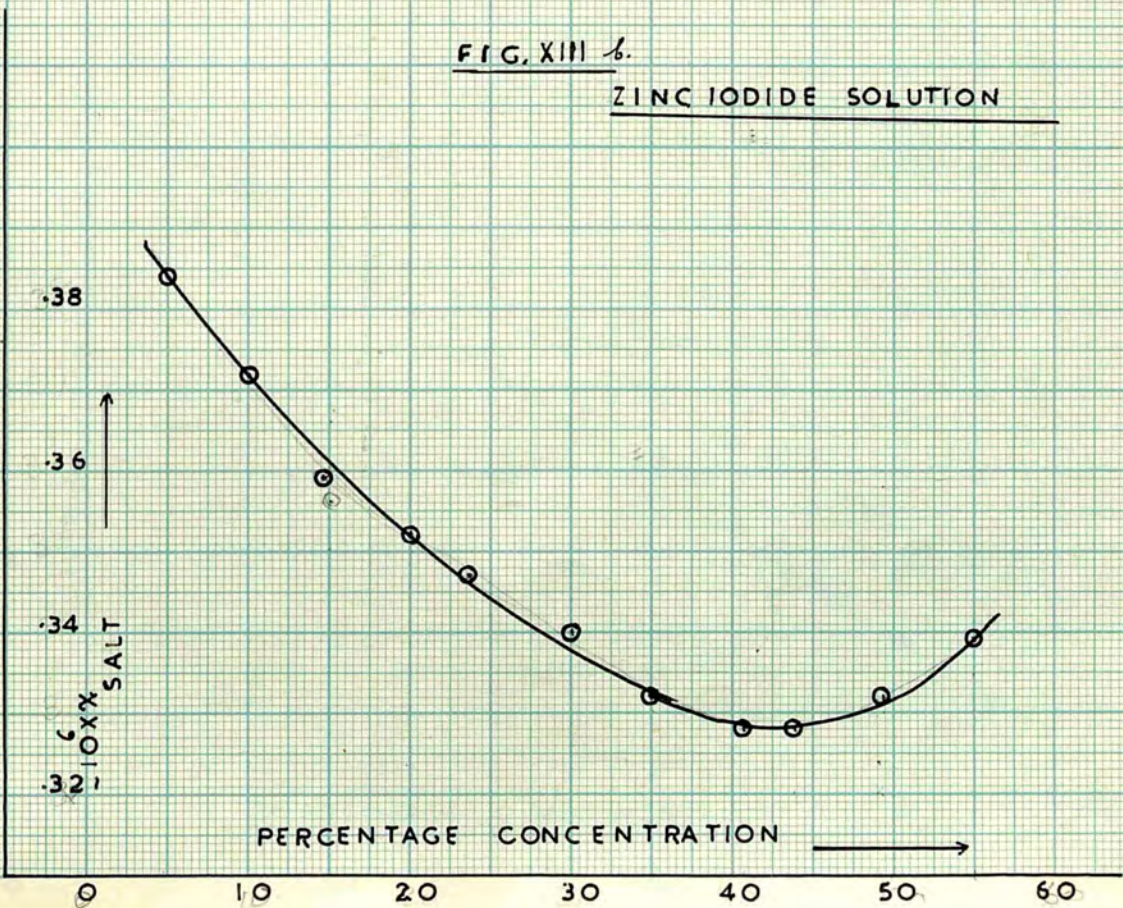


FIG XIII c.

ZINC IODIDE SOLUTION

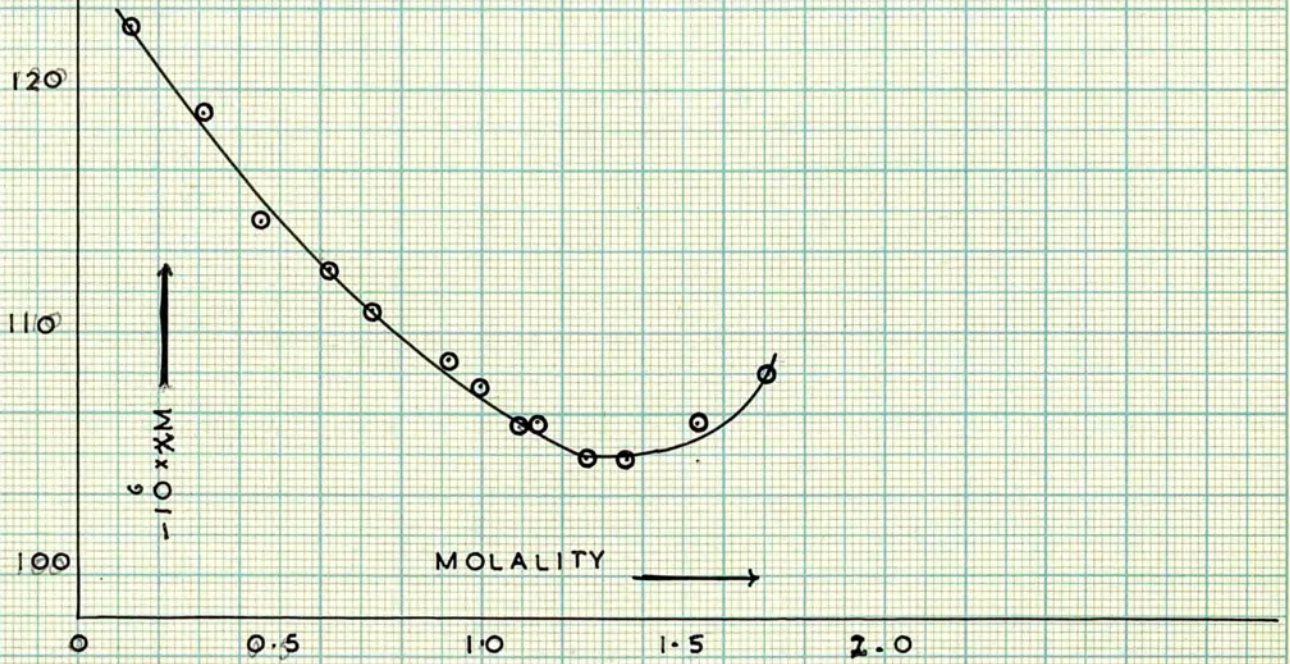
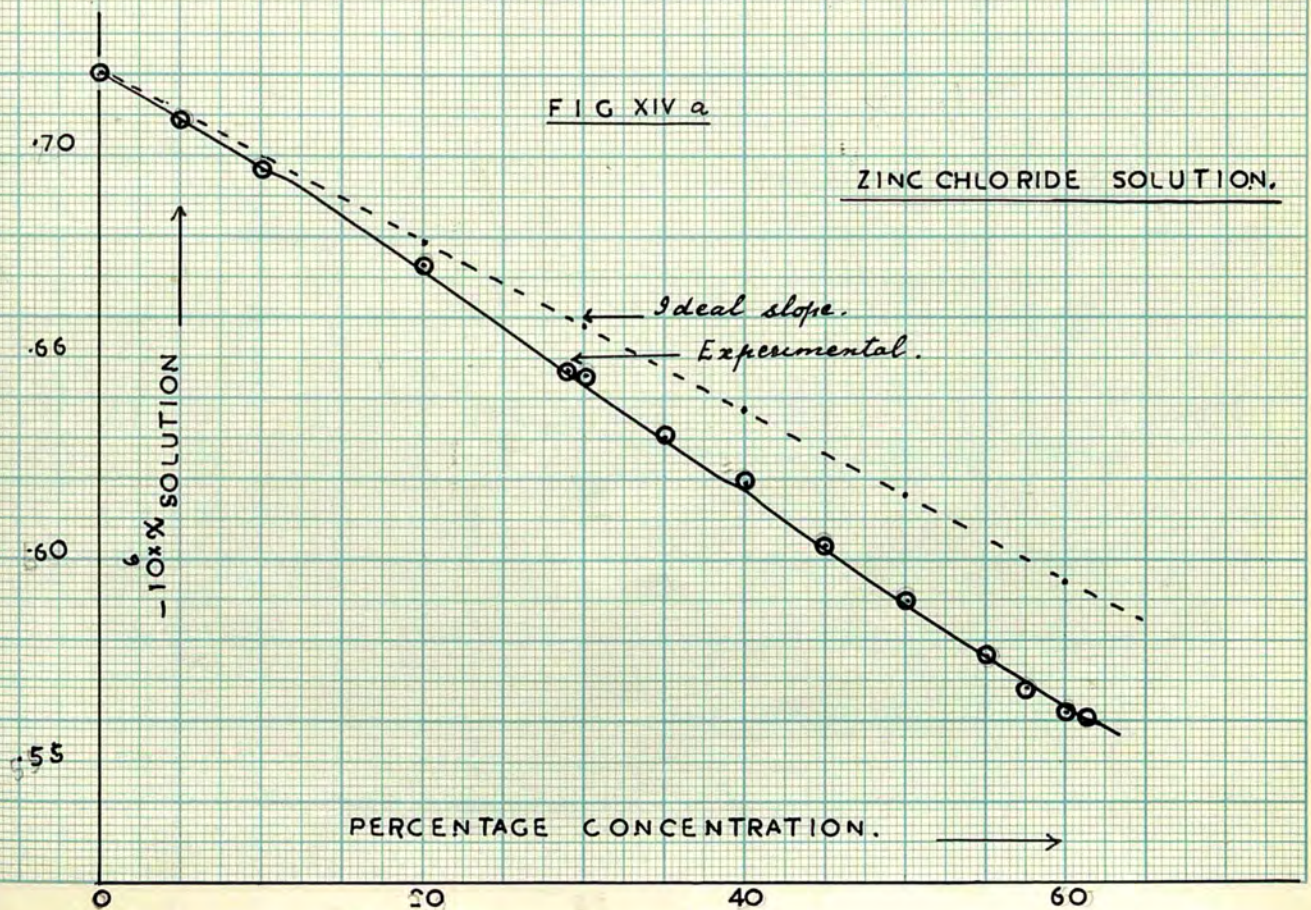
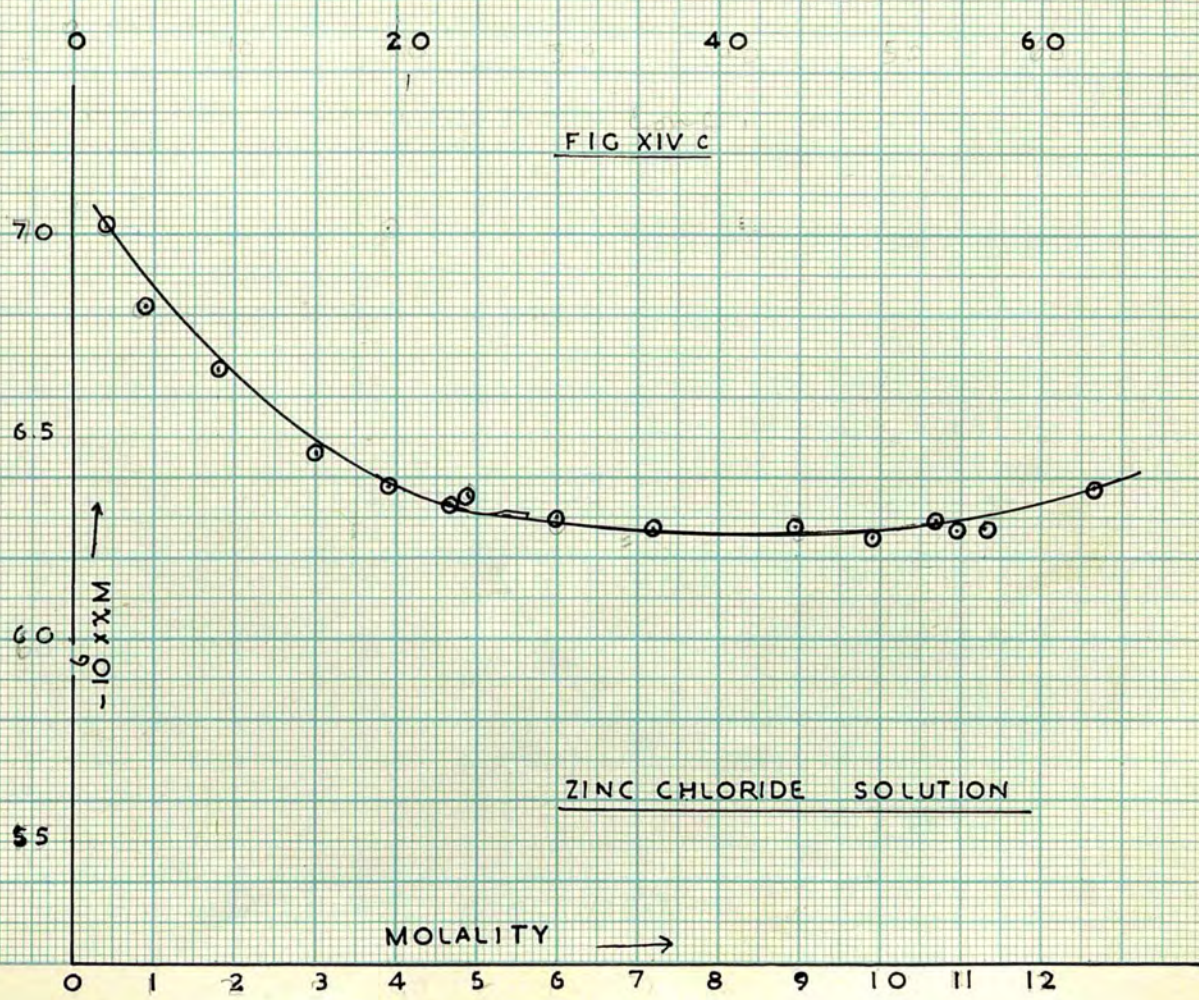
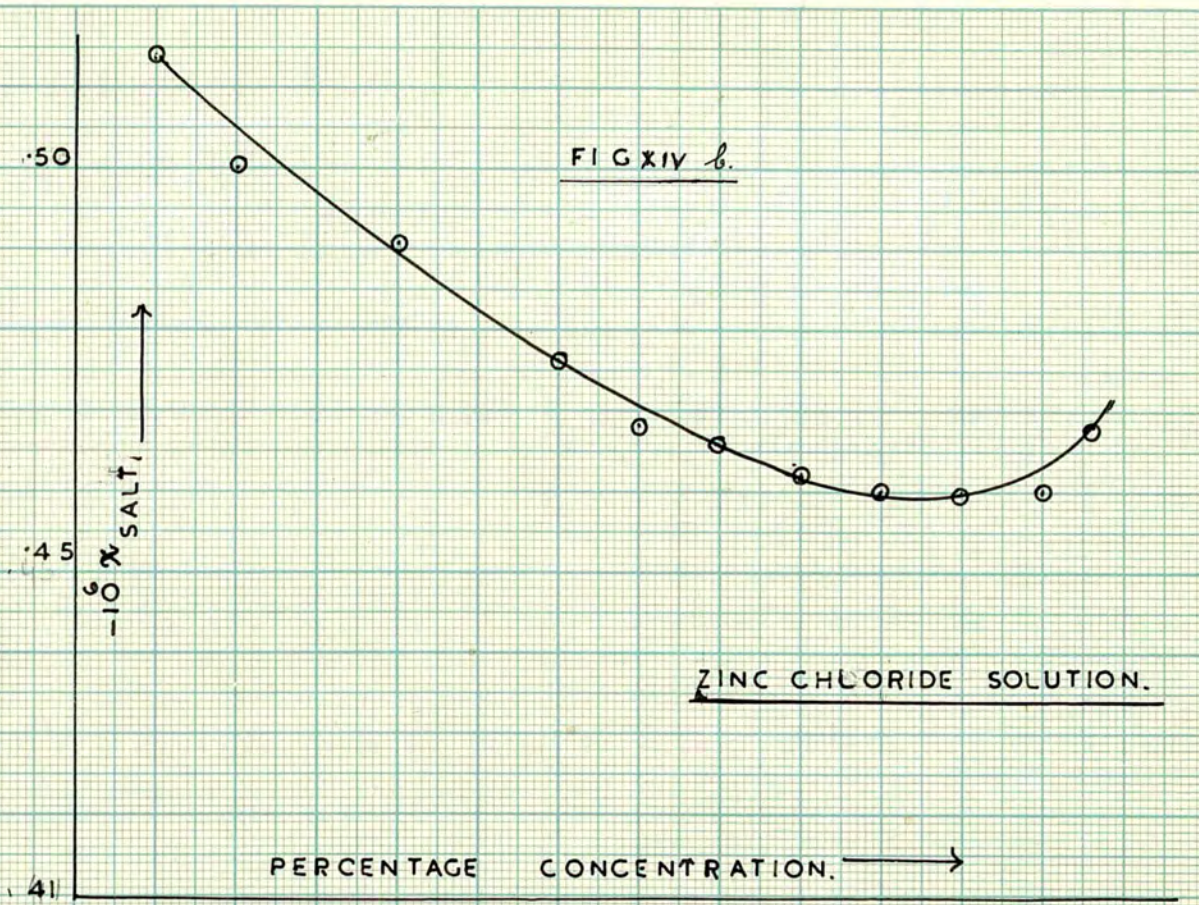


FIG XIV a

ZINC CHLORIDE SOLUTION.







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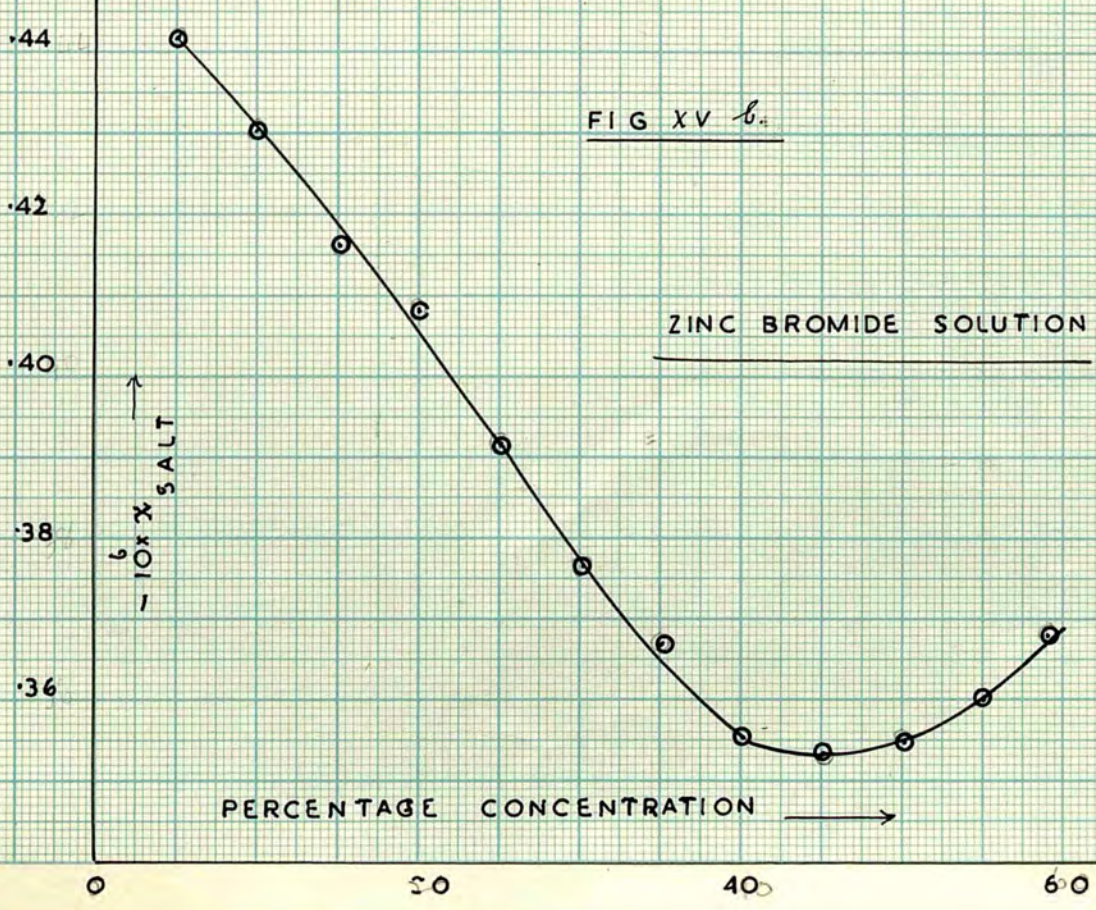
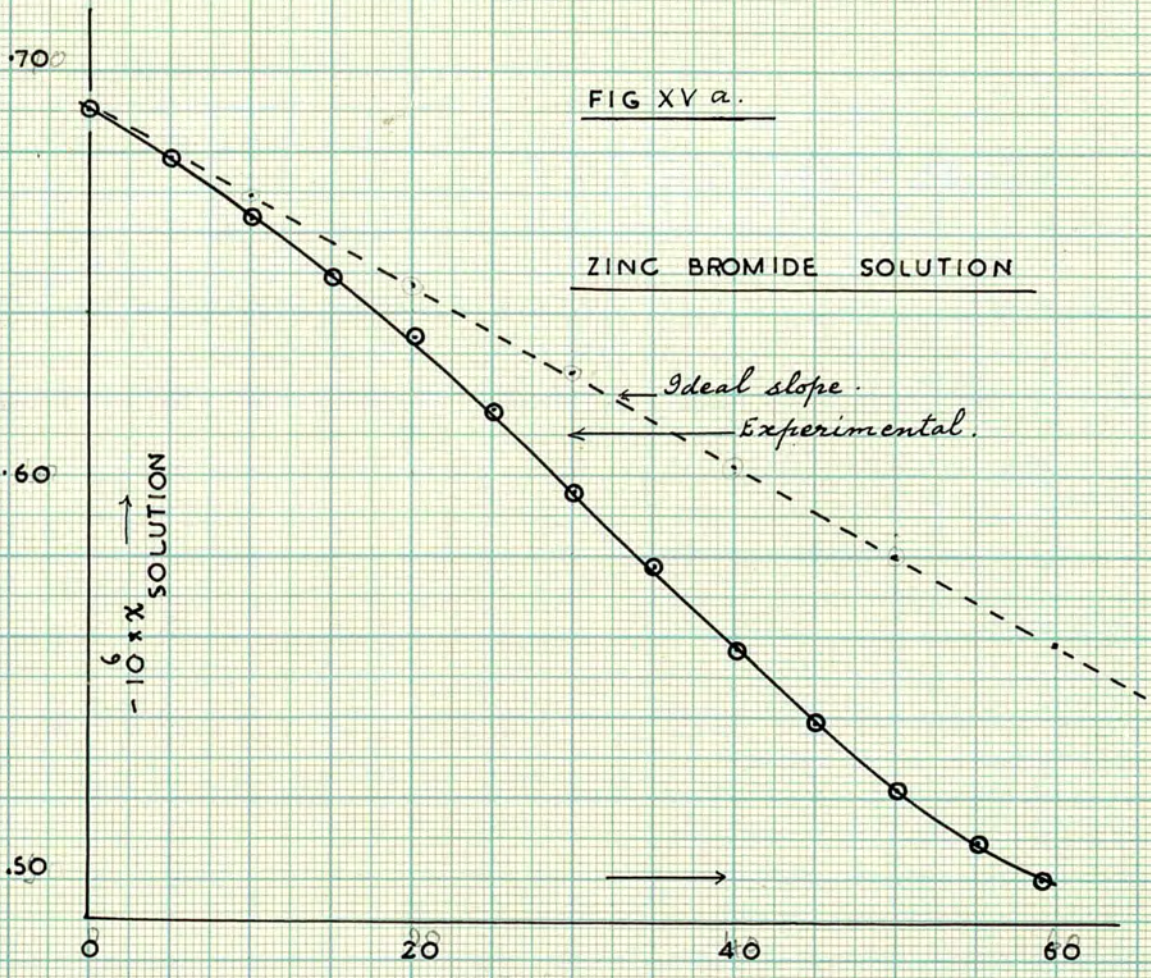
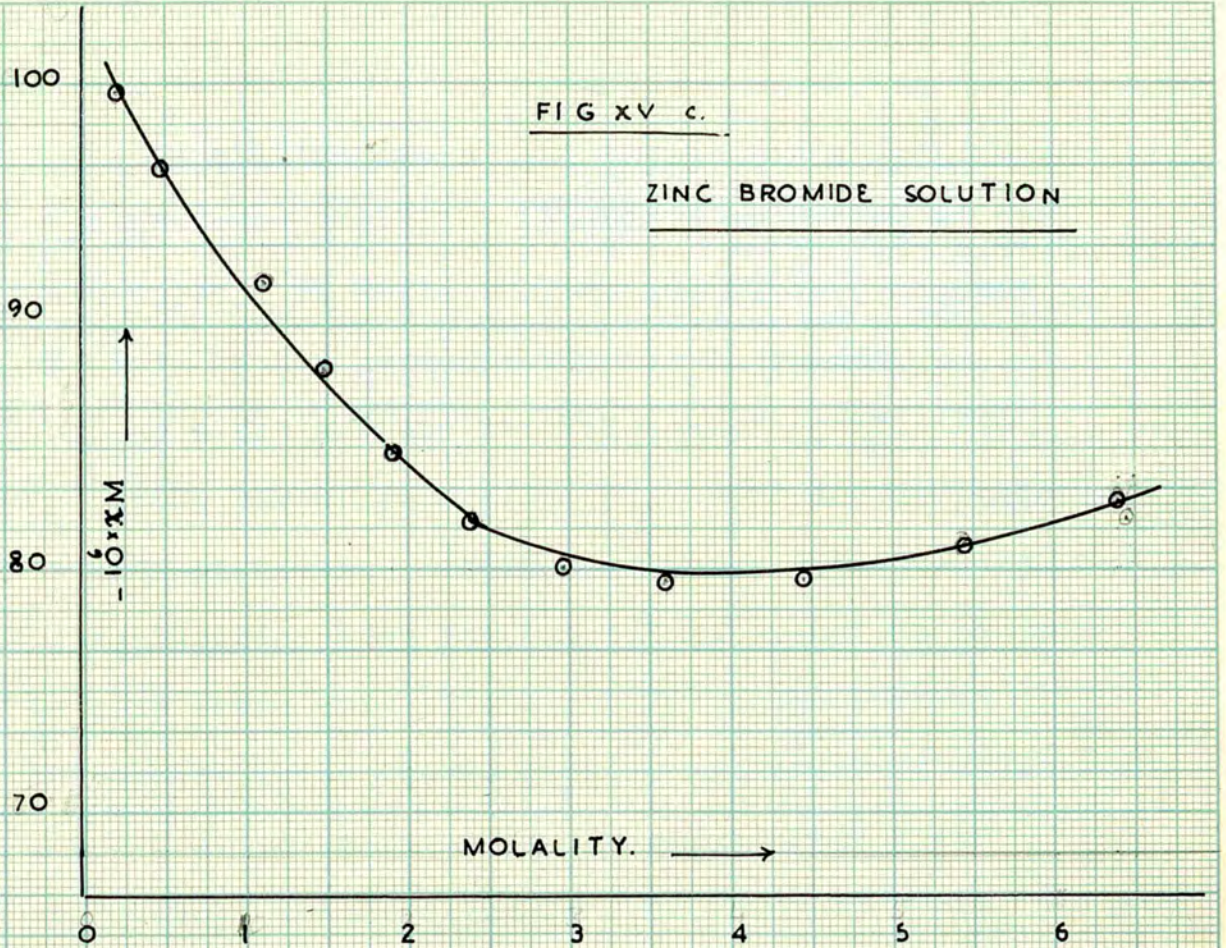


FIG XV c.

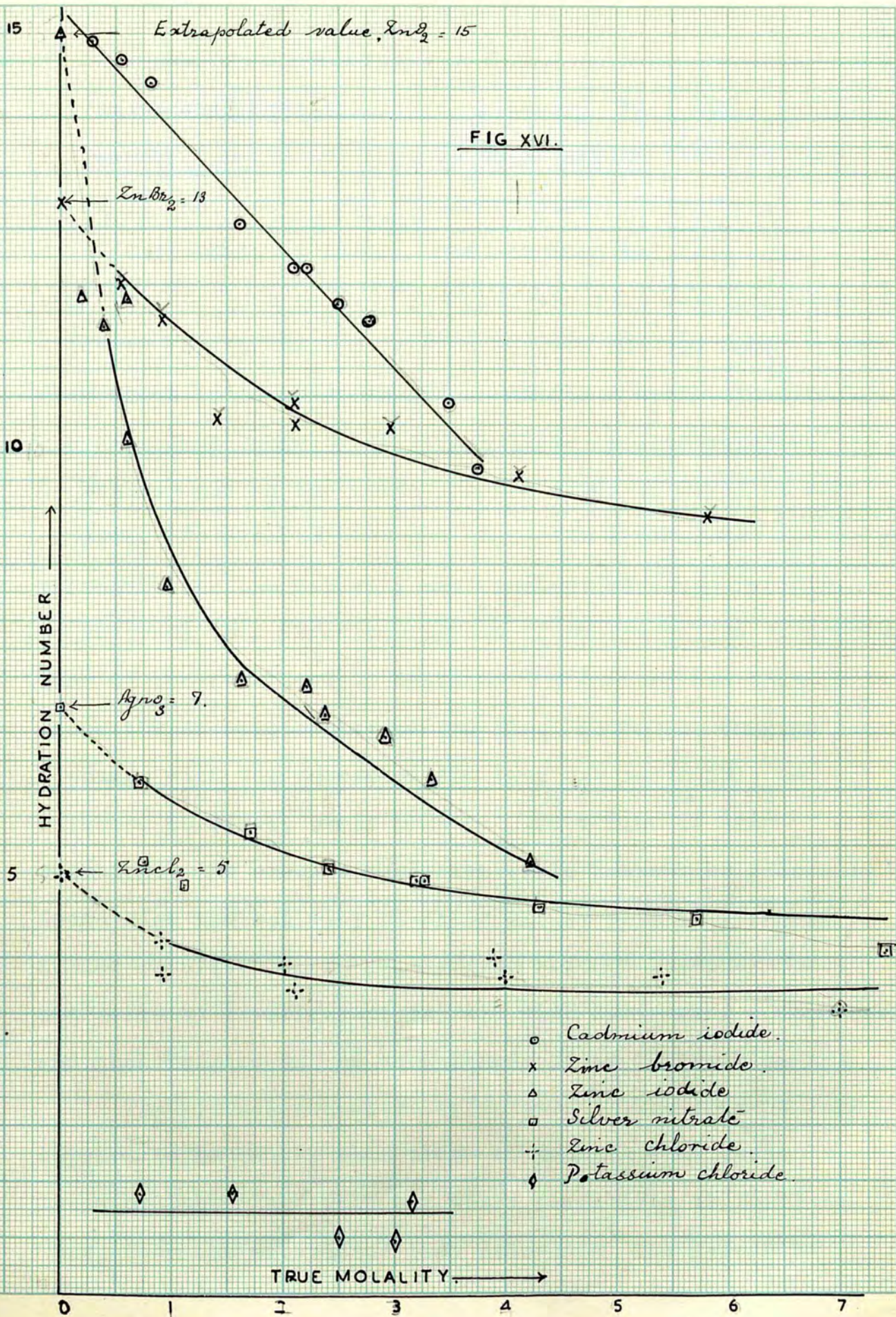
ZINC BROMIDE SOLUTION



An examination of the Tables and graphs shows that the susceptibility (specific or molar) of the salt appears to deviate from additivity, decreasing at first as the concentration is increased, passes through a minimum and then increases again. The hydration number generally falls with increasing molality or concentration. Little weight was given to the irregularities seen for the dilute solutions, since in this range very slight errors in the experimental susceptibilities become greatly magnified in calculating the hydration number. A more marked fall with increasing concentration in the apparent susceptibility of the salt, and in the hydration number, is observed for the salts which tend to form complex ions.

The tendency towards the formation of complex ions or ion pairs, which will have been included in the deviation of the hydration number, seems therefore to show a marked influence on the susceptibility.

It seems better to express the results in this section in terms of the concept of hydration number as calculated above, rather than to consider them in terms of an actual fall in susceptibility of the salt with concentration. Figures XI - XVI seem to indicate that the zinc and cadmium salts undergo more marked changes in the hydration number as the concentration



increases than does the silver nitrate, <sup>with the exception of zinc chloride.</sup> This would be in agreement with the tendency to form complex ions and ion pairs in the case of the divalent salts.

(80)

Very recently Stokes has reported the anomalous behavior of these salts. Robinson has also obtained some evidence for ion-pair formation between  $\text{Cd}^{++}$  and  $\text{CdX}_4^{--}$  from unpublished measurements on  $\text{CdCl}_2 - \text{CaCl}_2$  mixtures. The anomalous behavior of zinc halides is also reported

(80)

by Stokes during the thermodynamic study of bivalent metal halides. He also pointed out that with increasing concentration the activity coefficient decreases rapidly.

(80)

He suggests this behaviour is due to the formation of complex ions of the type  $\text{ZnCl}_4^{--}$ . Whatever the factors are that cause the susceptibility of the zinc halides to undergo a change with the concentration they may reasonably be expected to affect other physical properties of the solutions. No exact correlation could however be generally found with the activity co-efficient or with the transport number results. There is, however a rough tendency for the activity co-efficient to fall with increasing concentration and then to rise in the same manner as in figures XIc - XVc.

The hydration numbers calculated in the present work appears to be of the same order of magnitude as those found by Stokes and Robinson where comparison is possible.

(78)

Thus, from the activities they calculated the hydration

number at infinite dilution for potassium in the chloride to be 1.9, compared with the maximum value of 1.2 from the susceptibilities. They give no figures which will enable a comparison to be made for silver nitrate. For zinc and zinc perchlorate solutions they give a value of 20.0. The <sup>maximum</sup> value calculated from the susceptibility results on zinc iodide is of the order 12-15 and in the case of the chloride 4-5 and bromide 13-14 (neglecting the high first value).

These values are of the same order, as that in the perchlorate, but the hydration of the zinc ion will be modified by the nature of the anion which, even if itself unhydrated, will influence the ionic atmosphere of the cation.

(loc cit)

Stokes has pointed out in considering activity co-efficient data that the effect of the anion is consistent with its being unhydrated but influencing the mean effective diameter of the ions.

Although interpreting the susceptibility results in terms of a hydration effect it must be recognised that this includes the alternative explanation of complex ion formation. Stokes has, as indicated above, shown that this would explain the anomalous character of the activity co-efficient data in the case of zinc and cadmium halides. In the case of zinc salts there is a tendency to form  $ZnCl_4^{--}$ ,  $ZnBr_4^{--}$  and  $ZnI_4^{--}$  ions in the

solution while cadmium tends to form similar  $\text{CdX}_4^{--}$  ions. The formation of these ions in the solution would tend to lower the diamagnetic susceptibility owing to the closer approach of the halogen to the central metal atom in the co-ordinated complex ion to that in the purely polar halide. The apparent fall in the diamagnetic susceptibility of the zinc and cadmium halides with increasing concentration is therefore consistent with such complex ion formation. The effect of increasing concentration is considerably more marked for these two cations than for potassium chloride and silver nitrate solutions, as is shown by the hydration number - concentration graph. This would support such an interpretation in the case of the susceptibility results.

Some series of measurements were made of the susceptibility of solutions of zinc halides with the addition of equivalent proportions of univalent electrolytes, to see whether the effect of complex-ion formation could be further studied.

Tables XX and XXI give the results for the susceptibilities of solution of zinc halides with one equivalent and two equivalents of alkali salts added. The two sets of families of curves for zinc iodide-potassium iodide solutions, and zinc chloride - ammonium chloride solutions, are plotted on the same graphs. These curves of the susceptibility of the solution, plotted against concentration (Figure XVII. a & b).



Table XX a

Zinc iodide solutions with 1 Eq of KI

g/100g of sol Double salt	Mean -10 <sup>o</sup> .X sol.	Mean <sub>6</sub> -10 <sup>o</sup> .X *D.salt	Composition of the solution		
			Zn I <sub>2</sub>	KI	Wt. of the Final sol.
5.11	.70428	.4125	1.2710	.6610	37.7440
14.97	.67008	.3865	3.1992	1.6602	32.4609
20.12	.65044	.3743	3.055	1.590	23.0862
29.95	.61506	.3695	3.1992	1.6602	16.2006
30.11	.61231	.3623	4.010	2.084	20.2336
40.09	.57213	.3511	4.871	2.533	18.4658
44.98	.55123	.3447	5.054	2.628	17.0766
50.11	.53401	.3488	5.166	2.685	15.6672
54.55	.51947	.3523	5.263	2.737	14.6632

\*D salt = Double salt.

Table XXI

Zinc iodide solution with 2 Eq: of KI

g/100 g sol. Double salt	Mean <sub>6</sub> -10 <sup>6</sup> .X solution	Mean <sub>6</sub> -10 <sup>6</sup> .X D.salt	Composition of the solution		
			ZnI <sub>2</sub>	KI	Final wt. of sol.
5.11	.70517	.4301	.4124	.4305	16.4648
15.09	.67171	.4000	1.245	1.292	16.8088
15.11	.6754	.3993	1.350	1.402	18.2152
15.85	.66795	.3981	2.297	2.387	29.5402
20.08	.65353	.3889	1.671	1.898	17.7698
25.12	.63671	.3883	2.652	2.769	21.5804
25.49	.63403	.3827	1.7717	1.8428	14.1776
29.97	.61533	.3707	2.395	2.491	16.2975
30.06	.61842	.3820	3.170	3.294	21.4974
39.96	.57987	.3693	3.279	3.425	16.7816
40.13	.58147	.3748	3.057	3.177	15.5338
45.01	.56043	.3642	3.361	3.510	15.2640
45.10	.56242	.3705	6.3842	6.6408	28.8756
45.29	.56124	.3694	3.1922	3.3204	14.3792
50.03	.54336	.3669	3.432	3.583	
54.92	.52965	.3741	4.4043	4.5957	16.3856

Table XXI a

Zinc chloride solution with 1 Eq of  $\text{NH}_4\text{Cl}$ .

g/100 g of solution	Mean $-10^6 \times X$ Solution	Mean $-10^6 X$ Double Salt	Composition of the solution		
			$\text{ZnCl}_2$	$\text{NH}_4\text{Cl}$	Final wt. of the solution
5.11	.71329	.5888	.8582	.3368	23.3812
5.11	.71325	.5881	.7949	.3119	21.6294
9.973	.70645	.5839	.20174	7.918	28.1677
10.10	.70645	.5839	.20174	7.918	28.1677
10.10	.70624	.5836	4.0940	1.606	56.4268
10.11	.70607	.5826	3.8279	1.5025	52.7176
20.07	.68864	.5637	5.1592	2.0252	35.7832
20.08	.66935	.5515	5.3848	2.1137	24.9236
20.09	.68851	.5632	2.8390	1.1144	19.6734
20.10	.68842	.5628	5.7253	2.2474	39.6532
25.11	.67931	.5577	2.9885	1.1730	16.5698
30.02	.66952	.5518	3.5584	1.3968	16.5048
30.08	.66935	.5515	5.3848	2.1137	24.9236
30.11	.66921	.5513	6.9933	2.7451	32.3346
30.12	.66977	.5530	6.3205	2.4810	29.2190
35.10	.65833	.5442	4.2387	1.6638	16.8122
40.03	.64728	.5383	7.1657	2.8128	24.9260
40.05	.64726	.5383	6.2378	2.4485	21.6864
40.42	.64626	.5375	4.4204	1.7352	15.2290

Table XXI a continued

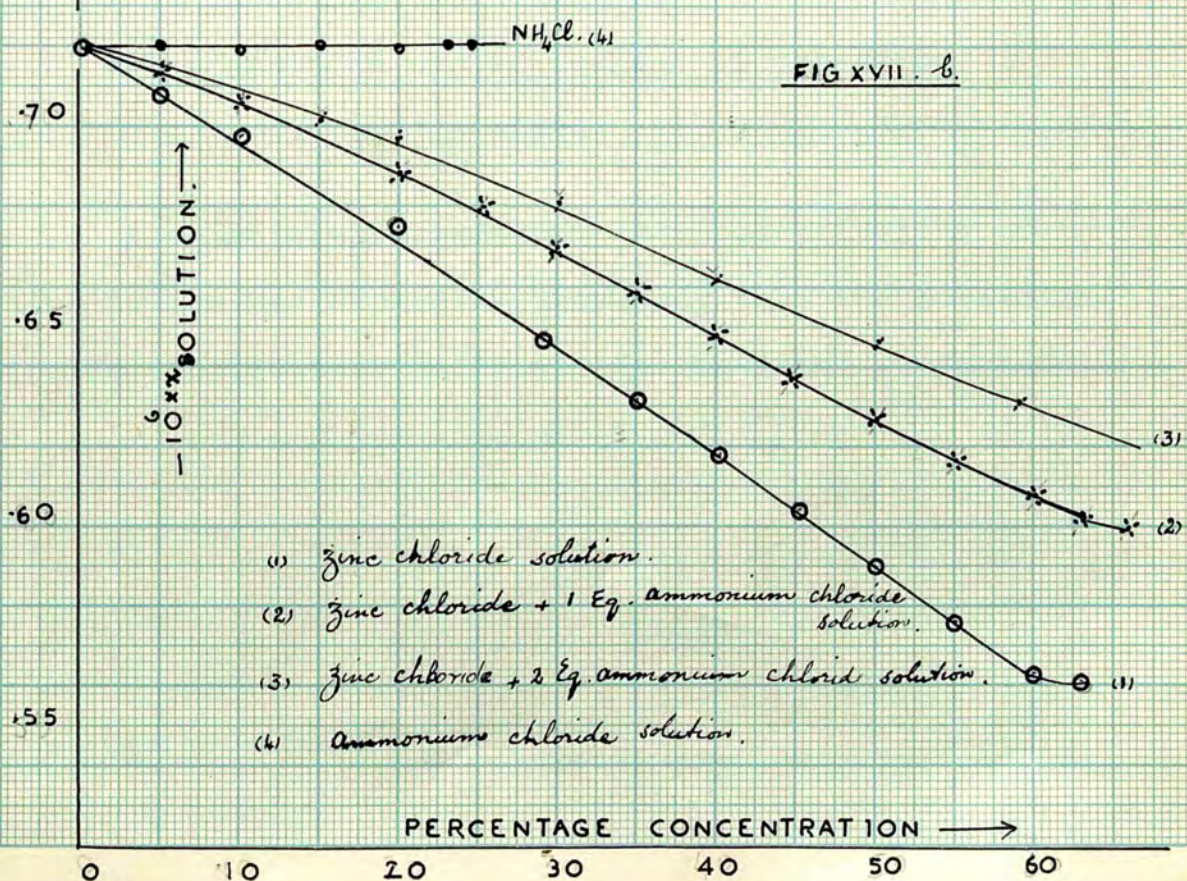
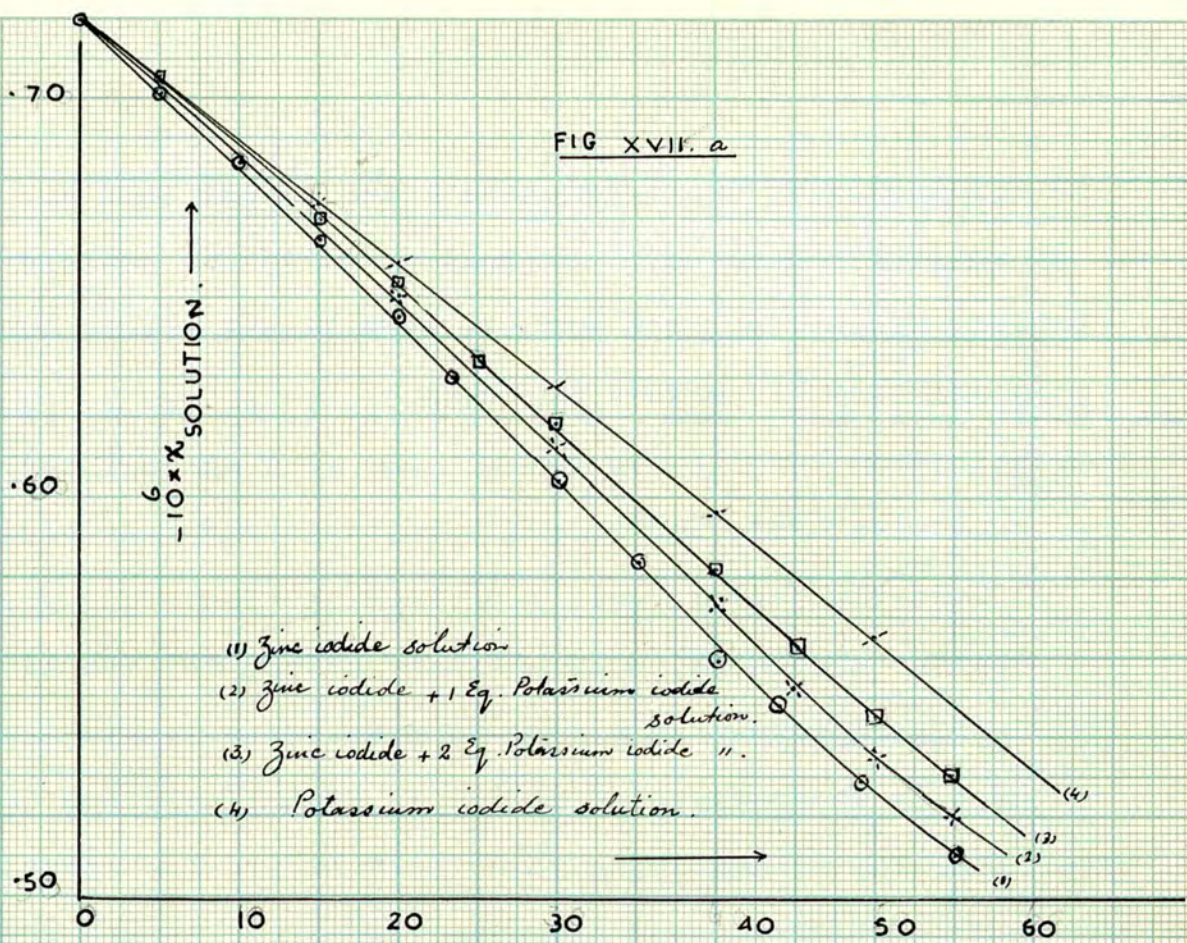
g/100g of solution	Mean $-10^6 \cdot X$ solution	Mean $-10^6 \cdot X$ Double Salt	Composition of the solution		
			ZnCl <sub>2</sub>	NH <sub>4</sub> Cl	Final wt. of the sol.
40.08	.64714	.5382	7.8546	3.0832	27.2884
44.84	.63739	.5357	5.3653	2.1060	16.6623
50.02	.63739	.5357	5.3653	2.1060	16.6623
50.02	.62688	.5338	6.4742	2.5414	18.0244
50.05	.62678	.5337	11.8086	4.635	32.8503
50.11	.62592	.5322	14.8974	5.8479	41.3924
50.13	.62642	.5332	7.3363	2.8798	20.3792
55.12	.61662	.5324	7.6828	3.0158	19.4084
60.11	.60867	.5347	19.8757	7.8021	46.0446
60.11	.60779	.5332	9.9427	3.9029	23.0300
60.15	.60765	.5332	11.0438	4.3351	25.5842
63.81	.60368	.5376	13.6290	5.35	29.7406
66.00	.60099	.5396	12.0512	4.7306	25.4248
66.24	.60045	.5394	14.1792	5.5659	29.8048
66.46	.60056	.5402	22.9686	9.0162	48.1258

Table XXI b

Zinc chloride solution with

2 Eq of  $\text{NH}_4\text{Cl}$

g/100g of Solution	Mean $-10^6 \cdot X$ Solution	Mean $-10^6 \cdot X$ Double Salt	Composition of the solution		
			$\text{ZnCl}_2$	$\text{NH}_4\text{Cl}$	Final wt. of the sol.
5.127	.71488	.6202	8.2970	.6513	28.8831
15.08	.70310	.6079	1.8420	1.4460	21.7908
20.00	.69610	.6027	2.5526	2.0039	22.7142
20.06	.69636	.6021	2.2336	1.7535	19.8664
29.82	.68090	.5889	4.6247	3.6307	27.6798
30.06	.68077	.5896	3.1110	2.0039	22.7142
39.98	.66356	.5796	5.3270	4.1821	23.7810
49.85	.64587	.5712	6.4758	5.0840	23.1888
50.05	.64661	.5733	5.9597	4.6789	21.2542
59.44	.63028	.5690	8.8780	6.9700	26.6598
59.65	.63108	.5709	10.4102	8.1728	31.1504



show that the magnetic susceptibility relationships in solution are quite systematic. The susceptibility of

the single alkali salt and the zinc halide are plotted on the same graph to show the systematic relationship.

Calculations from the figures at selected concentrations

show that the susceptibility of the mixed solutions

are not truly strictly additive as was indicated in

the earlier section dealing with the double salts.

The alkali salts tend to modify the susceptibility

of the zinc iodide, i.e. the susceptibility of zinc

iodide calculated from these solutions is not additively

the sum of the actual measured susceptibilities for

the salts concerned, for example:-

Solutions with one equivalent of potassium

iodide added.

A calculated figure for the susceptibility of zinc iodide was worked out assuming that the potassium iodide contributes additively to the total susceptibility.

Zn I<sub>2</sub> solutions with one equivalent of KI

added:

Composition g/100 g sol.	-10 <sup>6</sup> .X Double salt	Contribu- tion of KI	-10 <sup>6</sup> .X Zn I <sub>2</sub> Calculated	-10 <sup>6</sup> .X Zn I <sub>2</sub> Experimental
15%	.3865	.1409	.3735	.3566
20%	.3743	.1409	.3547	.3529
30%	.3699	.1409	.3482	.3406
40%	.3511	.1400	.3174	.3286
50%	.3488	.1398	.3231	.3329

It will be noticed that in the more dilute solutions the susceptibility for zinc iodide calculated from the double salt measurements is higher than that measured directly in a very dilute solution of hydrogen iodide

(.02N). In the dilute solutions there will be little tendency to form ion-pairs or complex ions and it appears that here the effect of the added electrolyte is merely to increase the ionisation of the zinc iodide i.e. to promote the existence in solution of polar ions rather than a covalent molecule. As the solutions become more concentrated, however, the figure, calculated from the



double salt measurements, falls below the experimental one from the nearly neutral solution. This could be interpreted as due to a greater tendency for complex ions to be formed in the presence of the 1:1 electrolyte, than in the more nearly neutral solution in which the complex would have to be of the type  $Zn^{++} ZnI_4^{--}$  (80).

This somewhat complex behaviour would explain the nature of the deviations in Tables III & IV, *in section 2.* An exactly similar result is shown in Figure XVII b for the zinc chloride and ammonium chloride solutions.

These curves thus indicate the possibility of detecting the formation of complex ions in solution by systematic magnetic susceptibility measurements. Had time permitted a further study of this aspect of the work would have been of interest.

Appendix

Specific susceptibility of solid compounds

Volume of tube = 8.564 c.c.  
 Thrust of tube = .36 mgm.  
 Wt. of benzene = 7.46475 gm.  
 Thrust of benzene = 6.60 mgm.

NH<sub>4</sub>Cl

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture - $\bar{X}_t$ x 10 <sup>6</sup>	Susceptibility Salt - $\bar{X}_s$ x 10 <sup>6</sup>
8.52 mgm.	9.87445 gm.	5.779 gm.	4.0965	.69277	.6860
8.53 mgm.	9.87443 gm.	5.7781 gm.	4.0963	.69362	.6874

Mean value = .6867 x 10<sup>6</sup>

Volume of Tube = 8.564 c.c.  
 Thrust of Tube = 0.36 mgm.  
 Wt. of benzene = 7.46475 gm.  
 Thrust of benzene = 6.60 mgm.

NH<sub>4</sub>Br

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture $-\bar{X}_t \times 10^6$	Susceptibility Salt $-\bar{X}_s \times 10^6$
9.46 mgm.	14.20840 gm.	10.5549 gm.	3.6535 gm.	.53652	.4791
9.46 mgm.	14.25449 gm.	10.6862 gm.	3.5682 gm.	.53479	.4788
9.48 mgm.	14.25440 gm.	10.6864 gm.	3.5683 gm.	.53597	.4804

Mean Value = .4794 x 10<sup>-6</sup>

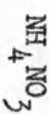
NH<sub>4</sub>I.

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mg.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mg.

Mean total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture $-X_t \times 10^6$	Susceptibility Salt $-X_s \times 10^6$
9.20 mgm.	13.51971 gm.	10.6594 gm.	2.8603 gm.	.49676	.4416
9.43 mgm.	14.01198 gm.	11.3416 gm.	2.6703 gm.	.49170	.4421
9.43 mgm.	14.01205 gm.	11.3616 gm.	2.6504 gm.	.49170	.4425

Mean Value = .4420 x 10<sup>-6</sup>

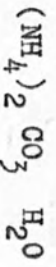
Volume of Tube = 7.705 c.c.  
 Thrust of Tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.



Mean Total Thrust on Salt	Total Wt. Salt + Benzene	Wt. of Salt Packed.	Wt. of Benzene	Susceptibility of Mixture $\bar{X}_t \times 10^6$	Susceptibility of Salt $\bar{X}_s \times 10^6$
6.83 mgm.	9.53459 gm.	5.9878 gm.	3.5467 gm.	.51681	.4069
6.84 mgm.	9.94807 gm.	6.9556 gm.	2.9924 gm.	.49609	.4073
6.94 mgm.	10.16395 gm.	7.2214 gm.	2.9425 gm.	.49292	.4077

Mean Value =  $.4073 \times 10^{-6}$

Volume of the tube = 7.703 c.c.  
 Thrust of the tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.



Mean Total Thrust of Salt + $\text{C}_6\text{H}_6$	Total Wt. Salt + $\text{C}_6\text{H}_6$	Wt. of Salt Packed	Wt. of $\text{C}_6\text{H}_6$	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_s \times 10^6$
7.24 mgm.	7.83145 gm.	2.7168 gm.	5.1146 gm.	.66872	.6055
7.40 mgm.	8.12531 gm.	3.5640 gm.	4.5610 gm.	.65939	.6045
7.57 mgm.	8.35905 gm.	3.8798 gm.	4.4792 gm.	.65630	.6032

Mean Value =  $.6044 \times 10^{-6}$

Volume of tube = 7.705 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_g \times 10^6$
7.58 mgm.	9.40442 gm.	5.6566 gm.	3.7478 gm.	.58415	.5058
7.88 mgm.	9.97275 gm.	6.5860 gm.	3.3867 gm.	.57357	.5073
8.00 mgm.	10.19521 gm.	6.9972 gm.	3.1980 gm.	.56993	.5094

Mean Value =  $.5075 \times 10^{-6}$

Volume of tube = 7.705 c.c.  
 Thrust of tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

KCl

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_s \times 10^6$
8.88 mgm.	11.35395 gm.	8.3666 gm.	2.9873 gm.	.57026	.5231
8.94 mgm.	11.49155 gm.	8.5678 gm.	2.9237 gm.	.56737	.5214
8.98 mgm.	11.55380 gm.	8.6399 gm.	2.9110 gm.	.56692	.5215

Mean Value = .5216 x 10<sup>-6</sup>



Volume of the tube = 7.703 c.c.  
 Thrust of the tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

KBr.

Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{x}_t \times 10^6$	Susceptibility Salt $\bar{x}_s \times 10^6$
8.59 mgm.	12.49501 gm.	8.8768 gm.	3.6182 gm.	.50127	.4193
8.75 mgm.	13.09152 gm.	9.9498 gm.	3.1417 gm.	.48708	.4192
8.78 mgm.	13.19325 gm.	10.0886 gm.	3.1046 gm.	.48505	.4181

Mean Value = .4188  $\times 10^{-6}$

Volume of tube = 7.705 c.c.  
 Thrust of tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

KI.

Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $-X_L \times 10^6$	Susceptibility Salt $-X_S \times 10^6$
9.66 mgm.	15.30149 gm.	12.0560 gm.	3.2454 gm.	.46160	.3968
9.72 mgm.	15.42896 gm.	12.2056 gm.	3.2233 gm.	.46073	.3969
9.72 mgm.	15.56225 gm.	12.4622 gm.	3.1000 gm.	.45726	.3963

Mean Value =  $.3966 \times 10^{-6}$

Volume of tube = 7.703 c.c.  
 Thrust of tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

$\text{KNO}_3$

Mean Total Thrust Salt + $\text{C}_6\text{H}_6$	Total Wt. Salt + $\text{C}_6\text{H}_6$	Wt. of Salt Packed.	Wt. of $\text{C}_6\text{H}_6$	Susceptibility Mixture $\text{C}_6\text{H}_6$ $-X_t \times 10^6$	Susceptibility Salt $-X_s \times 10^6$
6.74 mgm.	10.5098 gm.	6.6688 gm.	3.8410 gm.	.46240	.3242
6.87 mgm.	11.47570 gm.	8.2128 gm.	3.2629 gm.	.43203	.3246
6.90 mgm.	11.68244 gm.	8.5552 gm.	3.1272 gm.	.42632	.3254

Mean Value = .3247  $\times 10^{-6}$

Volume of tube = 7.705 c.c.  
 Thrust of tube + 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

$K_2CO_3$

Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $-X_t \times 10^6$	Susceptibility Salt $-X_s \times 10^6$
7.60 mgm.	10.12773 gm.	5.8686 gm.	4.2591 gm.	.54392	.4289
7.93 mgm.	11.11590 gm.	7.4990 gm.	3.6169 gm.	.51797	.4290
7.97 mgm.	11.12350 gm.	7.5893 gm.	3.5352 gm.	.52034	.4272

Mean Value =  $.4285 \times 10^{-6}$

Volume of tube = 8.564 c.c.  
 Thrust of tube = 0.36 mgm.  
 Wt. of benzene = 7.46475 gm.  
 Thrust of benzene = 6.60

$K_2SO_4$

Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_s \times 10^6$
9.12 mgm.	16.61111 gm.	13.7354 gm.	2.8757 gm.	.44188	.3873
9.20 mgm.	16.86116 gm.	14.0632 gm.	2.7979 gm.	.43931	.3869
9.20 mgm.	16.80350 gm.	14.0632 gm.	2.7871 gm.	.43956	.3874

Mean Value =  $.3872 \times 10^{-6}$

Volume of Tube = 7.703 c.c.  
 Thrust of Tube = 0.27  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mg.

MgCl<sub>2</sub> 6H<sub>2</sub>O

Mean Total Thrust on Material	Total Wt. of Salt + Benzene	Wt. of Salt Packed in gm.	Wt. of Benzene in gm.	Susceptibility of Mixture $\bar{X}_t$ 10 <sup>-6</sup>	Susceptibility of Salt $\bar{X}_s$ 10 <sup>-6</sup>
7.99 mgm.	8.69833 gm.	4.6172 gm.	4.0811 gm.	.66714	.6360
8.44 mgm.	9.36620 gm.	6.0726 gm.	3.2936 gm.	.65582	.6306
8.69 mgm.	9.70718 gm.	6.7702 gm.	2.9369 gm.	.65223	.6305

Mean value = .6323 x 10<sup>-6</sup>

Volume of Tube = 7.703 c.c.  
 Thrust of Tube = 0.27 mgm.  
 Wt. of Benzene = 6.7256 gm.  
 Thrust of Benzene = 6.59 mg.

MgBr<sub>2</sub> · 6H<sub>2</sub>O

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture - X <sub>t</sub> x 10 <sup>6</sup>	Susceptibility Salt - X <sub>s</sub> x 10 <sup>6</sup>
8.67 mgm.	11.11470 gm.	8.0010 gm.	3.1137 gm.	.56636	.5134
8.72 mgm.	11.17256 gm.	8.0804 gm.	3.0921 gm.	.56686	.5150
8.79 mgm.	11.26330 gm.	8.2904 gm.	2.9730 gm.	.56690	.5185

Mean Value = .5155 x 10<sup>-6</sup>

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

MgI<sub>2</sub> 8H<sub>2</sub>O

Mean Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture -K <sub>t</sub> x 10 <sup>6</sup>	Susceptibility Salt -K <sub>s</sub> x 10 <sup>6</sup>
8.61 mgm.	11.35937 gm.	8.6030 gm.	2.7563 gm.	.55205	.5039
9.33 mgm.	12.83390 gm.	11.2646 gm.	1.5693 gm.	.53095	.5070
9.52 mgm.	13.34212 gm.	12.2340 gm.	1.1081 gm.	.52148	.5051

Mean Value = .5053 x 10<sup>-6</sup>



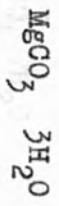
Volume of Tube = 7.703 c.c.  
 Thrust of Tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

Mg (NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O

Mean Total Thrust on Salt	Total Wt. Salt + Benzene	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture $\chi_t \times 10^6$	Susceptibility Salt $\chi_s \times 10^6$
7.13 mgm.	8.93806 gm.	4.8448 gm.	4.0932 gm.	.57664	.4704
7.34 mgm.	9.62443 gm.	6.2628 gm.	3.3616 gm.	.55198	.4713
7.42 mgm.	9.85598 gm.	6.6746 gm.	3.1813 gm.	.54514	.4702

Mean Value .4706 x 10<sup>-6</sup>

Volume of tube = 7.703 c.c.  
 Thrust of tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.



Mean Total Thrust on Salt	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{x}_t \times 10^6$	Susceptibility Salt $\bar{x} \times 10^6$
6.52 mgm.	7.15550 gm.	1.7229 gm.	5.4180 gm.	.65596	.5158
6.64 mgm.	7.40472 gm.	2.1864 gm.	5.2183 gm.	.64612	.5120
6.70 mgm.	7.48849 gm.	2.3460 gm.	5.1424 gm.	.64493	.5192

Mean Value =  $.5156 \times 10^{-6}$

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

Mean Total Thrust Salt + $\text{C}_6\text{H}_6$	Total Wt. Salt + $\text{C}_6\text{H}_6$	Wt. of Salt Packed.	Wt. of $\text{C}_6\text{H}_6$	Susceptibility Mixture $-\chi_t \times 10^6$	Susceptibility Salt $-\chi_s \times 10^6$
7.683 mgm.	9.07819 gm.	5.1978 gm.	3.8803 gm.	.61371	.5475
7.963 mgm.	9.5730 gm.	6.0858 gm.	3.4877 gm.	.60403	.5477
8.02 mgm.	9.68645 gm.	6.3084 gm.	3.3780 gm.	.60143	.5474

Mean Value = .5475  $\times 10^{-6}$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.7356 gm.  
 Thrust of Benzene = 6.59 mgm.

ZnSO<sub>4</sub> 7H<sub>2</sub>O

Mean total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_s \times 10^6$
8.14 mgm.	10.95139 gm.	7.9386 gm.	3.0127 gm.	.53840	.4762
8.40 mgm.	11.57685 gm.	8.9068 gm.	2.6700 gm.	.52620	.4734
8.41 mgm.	11.58441 gm.	8.9206 gm.	2.6638 gm.	.52651	.4740

Mean Value = .4745 x 10<sup>-6</sup>

Volume of tube = 7.705 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.7356 gm.  
 Thrust of Benzene = 6.59 mgm.

ZnO<sub>2</sub>

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_s \times 10^6$
9.90 mgm.	15.75636 gm.	13.0962 gm.	2.6601 gm.	.45823	.4086
9.91 mgm.	15.75635 gm.	13.0980 gm.	2.6583 gm.	.45870	.4092
9.93 mgm.	15.82635 gm.	13.1990 gm.	2.6273 gm.	.45763	.4089

Mean Value = .4089 x 10<sup>-6</sup>

Volume of tube = 7.705 c.c.  
 Thrust of tube = .27 m.g.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of " = t.56 m.g.

ZnBr<sub>2</sub>

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility of Mixture -X <sub>t</sub> x 10 <sup>6</sup>	Susceptibility Salt -X <sub>s</sub> x 10 <sup>6</sup>
11.12 mgm.	20.59560	17.9440	2.6516	.39645	.3512
11.29 mgm.	21.08597	18.5356	2.5503	.39331	.3507
11.29 mgm.	21.09590	18.5469	2.5490	.39312	.3506

Mean value = .3508 x 10<sup>-6</sup>

Volume of tube = 7.703 c.c.  
 Thrust " " = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust " " = 6.56 mgm.

ZnI<sub>2</sub>

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility of Mixture $\bar{X} \times 10^6$	Susceptibility of salt $\bar{X}_s \times 10^6$
10.75 mgm.	19.32710	15.7326	3.5945	.40802	.3407
11.26 mgm.	20.83601	17.5892	3.2468	.39695	.3405
11.28 mgm.	20.90220	17.6922	3.2100	.39641	.3406

Mean value =  $.3406 \times 10^{-6}$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.7356 gm.  
 Thrust of Benzene = 6.59 mgm.

$\text{NaNO}_3$

Mean total Thrust Salt + $\text{C}_6\text{H}_6$	Total Wt. Salt + $\text{C}_6\text{H}_6$	Wt. of Salt Packed	Wt. of $\text{C}_6\text{H}_6$	Susceptibility Mixture $\chi_t \times 10^6$	Susceptibility Salt $\chi_s \times 10^6$
6.71 mgm.	11.83979 gm.	8.6142 gm.	3.2255 gm.	.40716	.296
6.78 mgm.	12.16715 gm.	9.1193 gm.	3.0478 gm.	.40052	.299
6.78 mgm.	12.18993 gm.	9.1493 gm.	3.0406 gm.	.40015	.299

Mean Value = .298  $\times 10^{-6}$



Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.7356 gm.  
 Thrust of Benzene = 6.59 mgm.

Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub> 18H<sub>2</sub>O.

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture -K <sub>t</sub> x 10 <sup>6</sup>	Susceptibility Salt -K <sub>s</sub> x 10 <sup>6</sup>
7.60 mgm.	9.41073 gm.	5.6926 gm.	3.7181 gm.	.58339	.5057
7.84 mgm.	9.87099 gm.	6.4480 gm.	3.4229 gm.	.57447	.5066
7.96 mgm.	10.03524 gm.	6.6324 gm.	3.4211 gm.	.57406	.5063

Mean Value = .5062 x 10<sup>-6</sup>

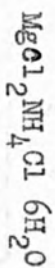
Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust " = 6.56 mgm.

CdI<sub>2</sub>

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of salt Packed	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility of Mixture -X <sub>f</sub> x 10 <sup>6</sup>	Susceptibility salt -X <sub>s</sub> x 10 <sup>6</sup>
13.15 mgm.	27.90278	25.0180	2.8847	.34752	.3066
13.36 mgm.	28.46136	25.6768	2.7845	.34628	.3076
13.45 mgm.	28.89146	26.2994	2.59206	.34347	.3081

Mean value = .3074 x 10<sup>-6</sup>

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mg.  
 Wt. of Benzene = 6.7356 gm.  
 Thrust of Benzene = 6.59 mgm.



Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{x}_t \times 10^6$	Susceptibility Salt $\bar{x}_s \times 10^6$
7.70 mgm.	8.16743 gm.	3.7016 gm.	4.4658 gm.	.68140	.6562
7.91 mgm.	8.41625 gm.	4.1334 gm.	4.2828 gm.	.68002	.6569
8.00 mgm.	8.52577 gm.	4.3140 gm.	4.2117 gm.	.67922	.6568

Mean Value = .6566  $\times 10^6$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

$MgI_2 \cdot NH_4 I \cdot 6H_2O$ .

Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $-x_f \times 10^6$	Susceptibility Salt $-x_s \times 10^6$
8.85 mgm.	11.98001 gm.	8.6160 gm.	3.3640 gm.	.53920	.4746
8.48 mgm.	13.31566 gm.	10.6714 gm.	2.6442 gm.	.52025	.4751
9.47 mgm.	13.31588 gm.	10.6735 gm.	2.6421 gm.	.51967	.4744

Mean Value =  $.4747 \times 10^{-6}$

Volume of Tube = 7.703 c.c.  
 Thrust of Tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 gm.

MgCl<sub>2</sub> KCl. 6H<sub>2</sub>O.

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture -X <sub>t</sub> x 10 <sup>6</sup>	Susceptibility Salt -X <sub>s</sub> x 10 <sup>6</sup>
7.72 mgm.	8.51670 gm.	3.7680 gm.	4.7487 gm.	.65744	.6009
8.11 mgm.	9.09839 gm.	4.8692 gm.	4.2291 gm.	.64776	.6004
8.20 mgm.	9.24592 gm.	5.2146 gm.	4.0313 gm.	.64477	.6003

Mean Value = .6005 x 10<sup>-6</sup>

Volume of tube = 7.705 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

$\text{MgBr}_2 \cdot \text{KBr} \cdot 6\text{H}_2\text{O}$

Mean Total Thrust Salt + $\text{C}_6\text{H}_6$	Total Wt. Salt + $\text{C}_6\text{H}_6$	Wt. of Salt Packed.	Wt. of $\text{C}_6\text{H}_6$	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_s \times 10^6$
8.40 mgm.	10.93686 gm.	6.7626 gm.	4.1743 gm.	.55880	.4702
8.81 mgm.	11.75809 gm.	7.9656 gm.	3.7924 gm.	.54616	.4718
8.96 mgm.	12.03303 gm.	8.3882 gm.	3.6448 gm.	.54309	.4739

Mean Value = .4719

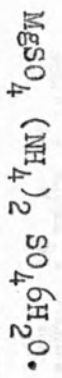
Volume of Tube = 7.703 c.c.  
 Thrust of Tube = 0.27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

$MgI_2 \cdot 6H_2O$

Mean Total Thrust on Salt	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{X}_L \times 10^6$	Susceptibility Salt $\bar{X}_S \times 10^6$
8.76 mgm.	12.43595 gm.	9.5020 gm.	2.9339 gm.	.51335	.4550
9.12 mgm.	12.92340 gm.	9.8234 gm.	3.1000 gm.	.51502	.4559
9.16 mgm.	13.0330 gm.	10.0121 gm.	3.0212 gm.	.51299	.4558

Mean Value = .4555  $\times 10^{-6}$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647  
 Thrust of Benzene = 6.56 mgm.



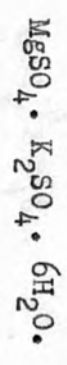
Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_s \times 10^6$
8.00 mgm.	9.97620 gm.	6.4200 gm.	3.5562 gm.	.59436	.5379
8.136 mgm.	10.02220 gm.	6.8840 gm.	3.1382 gm.	.59001	.5388
8.223 mgm.	10.22925 gm.	7.2960 gm.	2.9332 gm.	.58449	.5371

Mean Value =  $.5379 \times 10^{-6}$

MEAN VALUE = .5379 x 10<sup>-6</sup>



Volume of tube = 7.705 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.



Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_s \times 10^6$
8.75 mgm.	12.67697 gm.	10.1306 gm.	2.5463 gm.	.50300	.4529
8.76 mgm.	12.75777 gm.	10.2512 gm.	2.5065 gm.	.50040	.4510
8.70 mgm.	12.69050 gm.	10.2512 gm.	2.4393 gm.	.51733	.4512

Mean Value = .4517  $\times 10^{-6}$

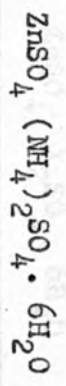
Volume of Tube = 8.480 c.c.  
 Thrust of Tube = 0.36 mgm.  
 Wt. of Benzene = 7.46079 gm.  
 Thrust of Benzene = 6.60 mgm.

$ZnCl_2 \cdot 4NH_4Cl$ .

Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $10^{-6} -X_t$	Susceptibility Salt $10^6 -X_s$
8.70 mgm.	11.65432 gm.	8.0221 gm.	3.5002 gm.	.59944	.6544
8.76 mgm.	11.70667 gm.	8.6522 gm.	3.0544 gm.	.60103	.5652
8.87 mgm.	11.89953 gm.	8.900 gm.	2.9095 gm.	.59897	.5655

Mean Value =  $.5650 \times 10^{-6}$

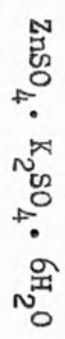
Volume of tube = 7.705 c.c.  
 Thrust of tube = .27 mg.  
 Wt. of Benzene = 6.7356 gm.  
 Thrust of Benzene = 6.59 mgm.



Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of Salt Packed.	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture -X <sub>t</sub> x 10 <sup>6</sup>	Susceptibility Salt -X <sub>s</sub> x 10 <sup>6</sup>
8.42 mgm.	11.50667 gm.	9.0032 gm.	2.5034 gm.	.53072	.4830
8.43 mgm.	11.58244 gm.	9.1823 gm.	2.3691 gm.	.52790	.4846
8.52 mgm.	11.70107 gm.	9.3198 gm.	2.3812 gm.	.52833	.4838

Mean Value = .4838 x 10<sup>-6</sup>

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

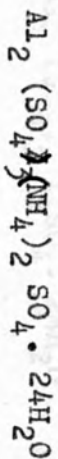


Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{X}_t \times 10^6$	Susceptibility Salt $\bar{X}_g \times 10^6$
8.88 mgm.	13.27430 gm.	10.8492 gm.	2.4251 gm.	.48775	.4397
8.68 mgm.	12.71277 gm.	9.9040 gm.	2.8087 gm.	.49743	.4393
8.82 mgm.	13.10748 gm.	10.5296 gm.	2.5778 gm.	.49052	.4386

Mean Value = .4392  $\times 10^{-6}$

Mean Value = .4386

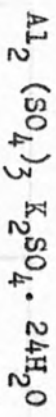
Volume of tube = 7.705 c.c.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.  
 Thrust of tube = .27 mgm.



Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\times 10^6$	Susceptibility Salt $\times 10^6$
8.00 mgm.	9.54730 gm.	6.3542 gm.	3.1730 gm.	.60860	.5615
8.07 mgm.	9.65802 gm.	6.5582 gm.	3.0998 gm.	.60705	.5620
8.10 mgm.	10.09878 gm.	7.0855 gm.	2.7297 gm.	.58285	.5601

Mean Value = .5612.

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.



Mean Total Thrust Salt + $C_6H_6$	Total Wt. Salt + $C_6H_6$	Wt. of Salt Packed.	Wt. of $C_6H_6$	Susceptibility Mixture $\bar{K}_t \times 10^6$	Susceptibility Salt $\bar{K}_s \times 10^6$
8.36 mgm.	10.56950 gm.	7.5215 gm.	3.0450 gm.	.57545	.5241
8.41 mgm.	10.85922 gm.	8.4286 gm.	2.4306 gm.	.56358	.5235
8.43 mgm.	10.96188 gm.	8.6082 gm.	2.3536 gm.	.55968	.5207

Mean Value =  $.5227 \times 10^{-6}$

Volume of tube = 7.703 c.c.  
 Thrust of " = .27 m.g.  
 Wt. of Benzene = 6.72647 g.  
 Thrust of " = 6.56 m.g.

AgNO<sub>3</sub>

Mean Total Thrust Salt + C <sub>6</sub> H <sub>6</sub>	Total Wt. Salt + C <sub>6</sub> H <sub>6</sub>	Wt. of salt Packed	Wt. of C <sub>6</sub> H <sub>6</sub>	Susceptibility Mixture $-\bar{X}_t \times 10^6$	Susceptibility salt $-\bar{X}_s \times 10^6$
9.58 mg.	20.75280 gm.	17.6209gm.	3.1319	.33744	.2725
10.09 mg.	22.82202 gm.	20.1942 "	2.6278	.32371	.2744
10.18 mg.	23.19792 gm.	20.6461 "	2.5518	.32139	.2743

Mean value = .2737 x 10<sup>-6</sup>

Appendix (Solutions in section 3.)

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27  
 Wt. of benzene = 6.7356 gm.  
 Thrust of benzene = 6.59 mgm.

$\text{NH}_4\text{Cl}$  (sol) 24.74% w/w

Thrust Negative Tube + Material	Mean Total Thrust Material	Weight of Material	$-\bar{X} \times 10^6$ Solution	$-\bar{X} \times 10^6$ Solute
8.44 mgm. 8.43 " 8.43 "	8.163 mgm.	8.21652 gm.	.7197	.7190
8.44 mgm. 8.42 " 8.46 "	8.17 mgm.	8.22347 gm.	.7197	.7190
8.42 mgm. 8.44 " 8.46 "	8.17 mgm.	8.22347 gm.	.7197	.7190
8.44 mgm. 8.44 " 8.44 "	8.17 mgm.	8.22345 gm.	.7198	.7194

Mean Value  $-\bar{X}_{\text{solute}} = .7191 \times 10^6$

$\text{NH}_4\text{Br}$  (sol) 41.76% w/w

8.82 mgm. 8.86 " 8.84 "	8.57 mgm.	9.88754mgm.	.6289	.5019
8.85 mgm. 8.86 " 8.85 "	8.583 "	9.90297 "	.6290	.5021
8.85 " 8.83 " 8.87 "	8.58 "	9.89627 "	.6292	.5025

Mean Value  $-\bar{X}_{\text{solute}} = .5021 \times 10^6$



Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgn.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust " = 6.56 mgn.

NH<sub>4</sub>I (sol.) 24.68% <sup>w</sup>/<sub>w</sub>

Thrust Negative Tube + Material	Mean total Thrust, Material	Wt. of material	$-\bar{x} \times 10^6$ solution	$-\bar{x} \times 10^6$ solute
8.44 mgn. 8.43 " 8.46 "	8.173 mgn.	9.06383 gm.	.6554	.4582
8.44 mgn. 8.46 " 8.43 "	8.17 mgn.	9.06292 gm.	.6553	.4578
8.45 mgn. 8.42 " 8.46 "	8.173 mgn.	9.06399 gm.	.6554	.4580

Mean Value  $-\bar{x}_{\text{solute}} = .4580 \times 10^6$

K<sub>2</sub>CO<sub>3</sub> (sol.) 13.31% <sup>w</sup>/<sub>w</sub>

8.37 mgn. 8.35 " 8.36 "	8.09 mgn.	8.58650 gm.	.68462	.4549
8.35 mgn. 8.36 " 8.37 "	8.09 mgn.	8.58512 "	.68474	.4551
8.36 mgn. 8.36 " 8.36 "	8.09 mgn.	8.58612 "	.68465	.4544

Mean Value  $-\bar{x}_{\text{solute}} = .4548 \times 10^6$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgn.  
 Wt. of benzene = 6.7356 gm.  
 Thrust of benzene = 6.59 mgn.

Kel (sol.) 22.45%

Thrust Negative Tube + Material	Mean total Thrust of Material	Weight of Material	$-\bar{X} \times 10^6$ solution	$-\bar{X} \times 10^6$ solute
8.59 mgn. 8.59 " 8.60 "	8.323 mgn.	8.852530 gm.	.68160	.5492
8.60 mgn. 8.60 " 8.61 "	8.333 mgn.	8.86315 gm.	.68163	.5493
8.61 mgn. 8.60 " 8.60 "	8.333 mgn.	8.86324 gm.	.68162	.5493

Mean Value  $-\bar{X}_{\text{solute}} = .5492 \times 10^6$

$(\text{NH}_4)_2 \text{SO}_4$  (sol.) 37.57% w/w

8.55 mgn. 8.55 " 8.54 "	8.276 mgn.	9.34267 gm.	.6420	.5126
8.56 mgn. 8.53 " 8.55 "	8.276 mgn.	9.3444 gm.	.6419	.5123

Mean Value =  $-\bar{X}_{\text{solute}} = .5124 \times 10^6$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

KBr (sol.) 24.68% w/w

Thrust Negative Tube + Material	Mean total Thrust of Material	Wt. of Material	$\bar{x} \times 10^6$ solution	$\bar{x} \times 10^6$ solute
8.54 mgm. 8.52 " 8.53 "	8.26 mgm.	9.23915	.6501	.4367
8.58 mgm. 8.55 " 8.52 "	8.28 mgm.	9.26029	.6503	.4376
8.55 mgm. 8.54 " 8.56 "	8.28 mgm.	9.25549	.6506	.4388

Mean Value  $\bar{x}_{\text{solute}} = .4377 \times 10^6$

KI (sol.) 14.31% w/w

8.08 mgm. 8.09 " 8.08 "	7.813 mgm.	8.58045 gm.	.66074	.4116
8.09 mgm. 8.10 " 8.10 "	7.826 mgm.	8.59421 gm.	.66083	.4122
8.09 " 8.10 " 8.10 "	7.826 mgm.	8.59385 gm.	.66086	.4122

Mean Value  $\bar{x}_{\text{solute}} = .4120 \times 10^6$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

$\text{KNO}_3$  (sol.) 15.62% w/w

Thrust Negative Tube + Material	Mean total Thrust Material	Weight of Material	$-X \times 10^6$ solution	$-X \times 10^6$ solute
8.00 mgm. 8.04 " 8.08 "	7.77 mgm.	8.48191 gm.	.66459	.3649
8.02 mgm. 8.03 " 8.04 "	7.76 mgm.	8.47373 gm.	.66435	.3636
8.02 mgm. 8.06 " 8.04 "	7.77 mgm.	8.48638 gm.	.66404	.3617

Mean Value  $-X$  solute =  $.3634 \times 10^6$

$\text{NaNO}_3$  (sol.) 23.04% w/w

8.07 mgm. 8.05 " 8.09 "	7.80 mgm.	9.00410 gm.	.62856	.3231
8.05 mgm. 8.06 " 8.04 "	7.78 mgm.	8.96990 gm.	.62928	.3262
8.07 mgm. 8.09 " 8.05 "	7.80 mgm.	8.99650 gm.	.62909	.3254

Mean Value  $-X$  solute =  $.3249 \times 10^6$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 gm.

$\text{NH}_4\text{NO}_3$  (sol.) 18.20% w/w

Thrust Negative Tube + Material	Mean total Thrust Material	Weight of Material	$\bar{x} \times 10^6$ solution	$\bar{x} \times 10^6$ solute
7.98 mgm. 7.99 " 8.00 "	7.72 mgm.	8.27009 gm.	.67706	.4840
8.00 mgm. 7.97 " 8.00 "	7.72 mgm.	8.26967 gm.	.67709	.4842
7.99 mgm. 7.99 " 7.99 "	7.72 mgm.	8.26977 gm.	.67709	.4842

Mean Value  $\bar{x}_{\text{solute}} = .4841 \times 10^6$

$\text{K}_2\text{SO}_4$  (sol.) 8.645%

8.12 mgm. 8.13 " 8.11 "	7.85 mgm.	8.22432 gm.	.69275	.4050
8.11 mgm. 8.10 " 8.09 "	7.83 mgm.	8.20436 gm.	.69269	.4039
8.10 mgm. 8.10 " 8.10 "	7.83 mgm.	8.19218 gm.	.69270	.4050

Mean Value  $\bar{x}_{\text{solute}} = .4046 \times 10^6$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of benzene = 6.72647 gm.  
 Thrust of benzene = 6.56 mgm.

ZnCl<sub>2</sub> (sol.) 12.17% W/w

Thrust Negative Tube + Material	Mean total Thrust of Material	Weight of Material	-X x 10 <sup>6</sup> solution	-X x 10 <sup>6</sup> solute
8.36 mgm. 8.37 mgm. 8.35 mgm.	8.09 mgm.	8.56270 gm.	.68653	.4450
8.35 mgm. 8.38 " 8.35 "	8.09 mgm.	8.56389 gm.	.68643	.4442
8.35 mgm. 8.36 " 8.36 "	8.086 mgm.	8.56200 gm.	.68623	.4425

Mean Value -X<sub>solute</sub> = .4439 x 10<sup>6</sup>

Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> 18H<sub>2</sub>O (sol.) 35.29% W/w ; Wt of Benzene = 6.7356g  
 Thrust " " = 6.59 mg.

8.60 mgm. 8.60 " 8.61 "	8.333 mgm.	9.32131 gm.	.6482	.5165
8.60 mgm. 8.61 " 8.60 "	8.333 mgm.	9.31975 gm.	.6482	.5165
8.62 mgm. 8.60 " 8.60 "	8.336 mgm.	9.32323 gm.	.6482	.5165

Mean Value -X<sub>solute</sub> = 5165 x 10<sup>6</sup>

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27  
 Wt. of Benzene = 6.7356 gm.  
 Thrust of Benzene = 6.59 mgm.

MgSO<sub>4</sub> · 7H<sub>2</sub>O (sol.) 28.44% w/w

Thrust Negative Tube + Material	Mean total Thrust Material	Weight of Material	$-X \times 10^6$ solution	$-X \times 10^6$ solute
8.66 mgm. 8.64 " 8.65 "	8.38 mgm.	8.99114 gm.	.6759	.5650
8.64 mgm. 8.68 " 8.60 "	8.37 mgm.	8.97592 gm.	.6761	.5657
8.62 mgm. 8.63 " 8.64 "	8.36 mgm.	8.94937 gm.	.6772	.5661

Mean Value  $-X_{\text{solute}}$  = .5656 x 10<sup>6</sup>

ZnSO<sub>4</sub> · 7H<sub>2</sub>O (sol.) 46.90% w/w

9.00 mgm. 8.99 " 8.98 "	8.72 mgm.	10.26646 gm.	.6167	.4997
8.99 mgm. 8.99 " 8.99 "	8.72 mgm.	10.26691 gm.	.6167	.4997
8.99 mgm. 8.98 " 9.00 "	8.72 mgm.	10.26796 gm.	.6167	.4997

Mean Value  $-X_{\text{solute}}$  = .4997 x 10<sup>6</sup>

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgn.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgn.

MgCl<sub>2</sub> 6H<sub>2</sub>O (sol.) 17.73% w/w

Thrust Negative Tube + Material	Mean total Thrust Material	Weight of Material	$-X \times 10^6$ solution	$-X \times 10^6$ solute
8.28 mgn. 8.28 " 8.28 "	8.01 mgn.	8.24116 gm.	.70598	.6409
8.27 mgn. 8.27 " 8.27 "	8.00 mgn.	8.22618 gm.	.70635	.6430
8.27 mgn. 8.28 " 8.28 "	8.006 mgn.	8.23628 gm.	.70604	.6412

Mean Value  $-X_{\text{solute}} = .6417 \times 10^6$

MgI<sub>2</sub> 8H<sub>2</sub>O (sol.) 16.96% w/w

8.24 mgn. 8.28 " 8.20 "	7.97 mgn.	8.45728 gm.	.68438	.5100
8.23 mgn. 8.23 " 8.25 "	7.966 mgn.	8.45352 gm.	.68433	.5100
8.23 mgn. 8.25 " 8.24 "	7.97 mgn.	8.45820 gm.	.68430	.5100

Mean Value  $-X_{\text{solute}} = .5100 \times 10^6$



Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgn.  
 Wt. of Benzene = 6.7356 gm.  
 Thrust of Benzene = 6.59 mgn.

MgBr<sub>2</sub> 6H<sub>2</sub>O (sol.) 65.62% w/w.

Thrust Negative Tube + Material	Mean total Thrust Material	Weight of Material	$-X \times 10^6$ solution	$-X \times 10^6$ solute
9.46 mgn. 9.44 " 9.45 "	9.18 mgn.	11.33651 gm.	.58910	.5205
9.48 mgn. 9.47 " 9.49 "	9.21 mgn.	11.37141 gm.	.5893	.5208

Mean Value  $-X$  solute =  $.5206 \times 10^6$

MgCl<sub>2</sub> NH<sub>4</sub>Cl 6H<sub>2</sub>O (sol.) 24.25% w/w.

9.01 mgn. 9.01 " 9.01 "	7.94 mgn.	8.13385 gm.	.7064	.6639
9.02 mgn. 9.00 " 9.01 "	7.94 mgn.	8.13466 gm.	.7063	.6635
8.19 mgn. 8.20 " 8.18 "	7.92 mgn.	8.11720 gm.	.7061	.6626

Mean Value  $-X$  solute = .6633

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

Mg (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (sol.) 12.50% W/w

Thrust Negative Tube + Material	Mean total Thrust of Material	Weight of Material	-X x 10 <sup>6</sup> solution	-X x 10 <sup>6</sup> solute
8.04 mgm. 8.05 mgm. 8.06 mgm.	7.78 mgm.	8.16730 gm.	.69112	.4889
8.07 mgm. 8.03 mgm. 8.05 mgm.	7.78 mgm.	8.16722 gm.	.69113	.4890
8.05 mgm. 8.05 mgm. 8.05 mgm.	7.78 mgm.	8.16720 gm.	.69113	.4890

Mean Value  $\bar{X}_{\text{solute}} = .4889 \times 10^6$

MgBr<sub>2</sub> · KBr 6H<sub>2</sub>O. (sol.) 19.82% W/w.

8.50 mgm. 8.50 " 8.50 "	8.23 mgm.	8.85707 gm.	.67570	.4968
8.50 mgm. 8.51 " 8.52 "	8.24 mgm.	8.87294 gm.	.67530	.4949
8.50 mgm. 8.49 " 8.51 "	8.23 mgm.	8.86298 gm.	.67520	.4944

Mean Value  $\bar{X}_{\text{solute}} 10^6 \times .4953$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.7356  
 Thrust of Benzene = 6.59 mgm.

MgCl<sub>2</sub> KCl 6H<sub>2</sub>O (sol.) 23.08% w/w

Thrust Negative Tube + Material	Mean total Thrust of Material	Weight of Material	$\bar{X} \times 10^6$ solution	$\bar{X} \times 10^6$ solute
8.81 mgm. 8.82 " 8.80 "	8.54 mgm.	8.88947 gm.	.69710	.6208
8.83 mgm. 8.84 " 8.82 "	8.56 mgm.	8.90716 gm.	.69740	.6221
8.80 mgm. 8.80 " 8.81 "	8.536 mgm.	8.88094 gm.	.69730	.6217

Mean Value  $\bar{X}$   
solute = .6215 x 10<sup>6</sup>

MgBr<sub>2</sub> NH<sub>4</sub>Br 6H<sub>2</sub>O. 45.52% w/w

8.96 mgm. 8.95 " 8.97 "	8.69 mgm.	10.06936 gm.	.6266	.5149
8.95 mgm. 8.96 " 8.96 "	8.686 mgm.	10.06703 gm.	.6264	.5144
8.95 mgm. 8.96 " 8.94 "	8.68 mgm.	10.05953 gm.	.6265	.5147

Mean Value  $\bar{X}$   
solute = .5146 x 10<sup>6</sup>

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647 gm.  
 Thrust of Benzene = 6.56 mgm.

MgI<sub>2</sub>(NH<sub>4</sub>)I. 6H<sub>2</sub>O (sol.) 22.54% w/w.

Thrust Negative Tube + Material	Mean total Thrust Material	Weight of Material	-X x 10 <sup>6</sup> solution	-X x 10 <sup>6</sup> solute
8.38 mgm. 8.39	8.115 mgm.	8.85509 gm.	.66598	.4803
8.38 mgm. 8.37 " 8.39 "	8.11 mgm.	8.84078 gm.	.66664	.4832
8.39 mgm. 8.38 " 8.39 "	8.116 mgm.	8.85497 gm.	.66608	.4807

Mean Value  $-X_{\text{solute}} = .4814 \times 10^6$

MgI<sub>2</sub>KI6H<sub>2</sub>O (sol.) 16.0% w/w

8.25 mgm. 8.27 " 8.29 "	8.00 mgm.	8.55260 gm.	.67940	.4662
8.28 mgm. 8.28 " 8.29 "	8.013 mgm.	8.56296 gm.	.67972	.4681
8.27 mgm. 8.27 " 8.28 "	8.003 mgm.	8.55302 gm.	.67963	.4675

Mean Value  $-X_{\text{solute}} = .4672 \times 10^6$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = t.7356 gm.  
 Thrust of Benzene = 6.59 mgm.

$MgSO_4 (NH_4)_2 SO_4 \cdot 6H_2O$ . (sol.) 19.64% w/w.

Thrust Negative Tube + Material	Mean total Thrust Material	Weight of Material	$-X \times 10^6$ solution	$-X \times 10^6$ solute
8.31 mgm. 8.33 " 8.30 "	8.043 mgm.	8.51264 gm.	.6440	.5371
8.30 mgm. 8.29 " 8.31 "	8.03 mgm.	8.50031 gm.	.6840	.5371
8.31 mgm. 8.32 " 8.32 "	8.046 mgm.	8.51897 gm.	.68395	.5366

Mean Value  $-X_{\text{solute}} = .5369 \times 10^6$

$ZnSO_4 (NH_4)_2 SO_4 \cdot 6H_2O$ . (sol.) 13.81% w/w.

8.17 mgm. 8.17 " 8.19 "	7.906 mgm.	8.30804 gm.	.6885	.4923
8.20 mgm. 8.20 " 8.20 "	7.93 mgm.	8.33556 gm.	.6884	.4916
8.10 mgm. 8.20 " 8.27 "	7.92 mgm.	8.32795 gm.	.6882	.4902

Mean Value  $-X_{\text{solute}} = .4913 \times 10^6$

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.72647  
 Thrust of Benzene = 6.56 mgm.

ZnSO<sub>4</sub> K<sub>2</sub>SO<sub>4</sub> 6H<sub>2</sub>O (sol.) 12.97% W/w.

Thrust Negative Tube + Material	Mean total Thrust of Material	Weight of Material	$\bar{x} \times 10^6$ solution	$\bar{x} \times 10^6$ solute
7.93 mg. 7.92 " 7.94 "	7.93 mgm.	8.40460 gm.	.6850	.4502
7.90 mg. 7.89 " 7.88 "	7.89 mgm.	8.35796 gm.	.6852	.4518
7.94 7.92 7.93	7.93 mgm.	8.39750 gm.	.68566	.4548

Mean Value  $\bar{x}$  solute = .4522

MgSO<sub>4</sub> K<sub>2</sub>SO<sub>4</sub> 6H<sub>2</sub>O (sol.) 15.88% W/w.

8.29 mgm. 8.30 " 8.28 "	8.02 mgm.	8.53055 gm.	.68292	.4867
9.31 mgm. 9.32 " 9.32 "	8.046 mgm.	8.55254 gm.	.68346	.4899
9.31 mgm. 9.31 " 9.32 "	8.043 mgm.	8.55012 gm.	.68339	.4899

Mean Value  $\bar{x}$  solute = .4888 x 10<sup>6</sup>

Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.7356  
 Thrust of Benzene = 6.59 mgm.

ZnCl<sub>2</sub> 4NH<sub>4</sub>Cl (sol.) 39.75% w/w.

Thrust Negative Tube + Material	Mean total Thrust Material	Weight of Material	$-X \times 10^6$ solution	$-X \times 10^6$ solute
8.76 mgm. 8.77 " 8.75 "	8.49 mgm.	9.14681 gm.	.6981	.6027
8.77 mgm. 8.75 " 8.79 "	8.50 mgm.	9.14604 gm.	.6742	.6047
8.74 mgm. 8.74 " 8.74 "	8.47 mgm.	9.13189 gm.	.6732	.6022

Mean Value  $-X$  solute =  $.6032 \times 10^6$

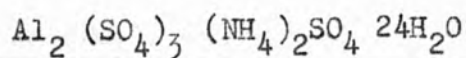
Volume of tube = 7.703 c.c.  
 Thrust of tube = .27 mgm.  
 Wt. of Benzene = 6.7356  
 Thrust of Benzene = 6.59 mgm.

Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> 5.80% w/w

8.26 mgm. 8.07 " 8.07 "	7.796 mgm.	8.09685 gm.	.70297	.5336
8.07 mgm. 8.07 " 8.07 "	7.80 mgm.	8.09175 gm.	.70251	.5336
8.07 mgm. 8.06 " 8.08 "	7.806 mgm.	8.09585 gm.	.70303	.5367

Mean Value  $-X$  solute =  $.5339 \times 10^6$

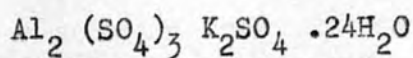
Volume of Tube = 7.703 c.c.  
 Thrust of " = .27 mg.  
 Wt. of Benzene = 6.7356g.  
 Thrust of Benzene = 6.59 mg.



Thrust Negative Tube + Material	Mean Total Thrust	Wt. of Material	$-\bar{x} \times 10^6$ solution	$-\bar{x} \times 10^6$ solute
8.15 mg. 8.15 " 8.14 "	7.876	8.67238	.7058	.5937
8.15 " 8.15 " 8.16 "	7.883	8.08177	.7056	.5920
8.15 " 8.15 " 8.15 "	7.88	8.07576	.7059	.5934

Mean Value  $-\bar{x}$  solute =  $.5934 \times 10^6$

Wt. of Tube = 7.703 c.c.  
 Thrust of Tube = .27 mg.  
 Wt. of Benzene = 6.72647 g.  
 Thrust of Benzene = 6.56 mg.

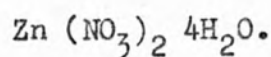


8.06 mg. 8.07 " 8.07 "	7.796	8.09685	.70297	.5356
8.07 " 8.07 " 8.07 "	7.80	8.05175	.70291	.5356
8.07 " 8.08 " 8.08 "	7.806	8.05685	.70303	.5367

Mean Value  $-\bar{x}$  solute =  $.5359 \times 10^6$



Volume of Tube = 7.703 c.c.  
 Thrust of Tube = .27 mg.  
 Wt. of Benzene = 6.72647 g.  
 Thrust of Benzene = 6.56 mg.



Thrust Negative Tube + Material	Mean Total Thrust	Wt. of Material	$\bar{X} \times 10^6$ solution	$\bar{X} \times 10^6$ solute
8.21 mg. 8.22 " 8.23 "	7.95	9.05529	.6358	.4358
8.24 " 8.20 " 8.22 "	7.95	9.05524	.6358	.4358
8.22 " 8.22 " 8.22 "	7.95	9.06615	.63676	.4389

Mean Value  $\bar{X}$  solute = .4368 x 10<sup>6</sup>

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