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Title THE APPARENT MOLAL VOLUME OF SALTS IN METHANOL -----  
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A study of the apparent molal volumes of salts in methanol solution was made in order to determine the universality of Masson's rule. Examination of the literature shows that the density determinations from which the apparent molal volume can be calculated are not sufficiently accurate in most cases to yield reliable results.

In this thesis has been presented a discussion of the experiments carried out in connection with the investigation of the apparent molal volumes of salts in methanol and their comparison with the values of the same salts in aqueous solutions.

1. The densities and apparent molal volumes for a number of salts in methanol have been experimentally determined.

2. The apparent molal volumes of additional methanol solutions have been calculated from data obtainable in the literature.

3. The apparent molal volumes of a number of salts in aqueous solution have been listed.

4. Curves have been drawn comparing the apparent molal volumes of the salts in methanolic and aqueous solutions.

5. Masson's rule is apparently obeyed to about the same extent in alcoholic solutions as it is in aqueous solutions.

THE APPARENT MOLAL VOLUME  
OF SALTS IN METHANOL SOLUTION

by

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A THESIS


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## TABLE OF CONTENTS

	Page
I--Introduction .....	1
II--Theoretical .....	4
III--Experimental .....	10
Figure I .....	10
Table I .....	16
Table II .....	17
Table III .....	18
Table IV .....	20
Figure II .....	21
Figure III .....	22
Figure IV .....	23
IV--Discussion of Results .....	24
V--Summary .....	28
VI--Bibliography .....	29

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PART I

INTRODUCTION

THE APPARENT MOLAL VOLUME  
OF SALTS IN METHANOL SOLUTION

PART I--INTRODUCTION

From the Debye-Hückel theory that properties of electrolytes in solution may be calculated on the basis of the inter-ionic attraction, may be derived various equations showing that the partial molal heat capacity, the partial molal expansibility, the partial molal volume, and other partial molal quantities are linear functions of the square root of the concentration. In the studies which have been stimulated by these theoretical predictions it has also developed that another type of quantity, the apparent molal properties, should behave in a similar manner.

This finding substantiated an empirical rule developed by Masson (10) in 1929 concerning the apparent molal volume. An unexpected result however is that Masson's equation for the relation between apparent molal volume and concentration seems to hold for relatively concentrated solutions. This would scarcely be expected because any equation that has been derived from the Debye-Hückel equation and the simple Debye-Hückel treatment is usually reliable only for quite dilute solutions.

When Masson first developed his rule it was thought to be fundamental for all salts in all solvents. The derivation from the Debye-Hückel theory lent support to



its fundamental character. Occasional measurements that were made in other than aqueous solvents seemed to bear this out. However as the number of investigations have increased recently, doubts have arisen as to its universality. The work of Scott (12) shows that the apparent molal volume of calcium nitrate in water solution is not a linear function of the square root of the concentration. More recent work by Gibson (3,4) on the apparent molal volume of salts both in water and alcoholic solutions has demonstrated that in many cases a distinct curvature is found. The belief of Gibson is that straight lines when obtained are fortuitous and that they should be S shaped curves. Some extremely accurate observations seem to bear out this belief. On the other hand there are many accurate observations that yield straight lines.

In view of the gradually accumulating evidence of the undoubted occurrence of both curvilinear and rectilinear relationships it would appear that no complete explanation of the cause has yet been attained.

Masson's equation was developed from the study of solutions of salts in water and the purpose of this investigation was to test the generality of the equation by examining its validity in other solvents than water. Methanol was chosen as the solvent because of the high solubility of many inorganic salts in it and its relative ease of purification.

There are to be found many data in the literature from which the apparent molal volume of salts in various solvents might supposedly be calculated, the necessary quantities being only the density and concentration at a given temperature.

Data were particularly desired for salts whose apparent molal volumes in methanol could be checked against existing data in the literature for water solutions. Examination of the data indicated however that new density determinations would have to be carried out since only a minor number of the measurements recorded in the literature are accurate enough for the necessary calculations. The density data should be accurate to the fourth place for concentrated solutions and accurate to the sixth place for very dilute solutions.

The salts finally chosen for the experimental work were potassium thiocyanate, ammonium nitrate, mercuric chloride, and calcium nitrate. Included in the discussion are calculations of the apparent molal volume of several salts whose density data from the literature were found to be sufficiently accurate to give reliable curves.

PART II  
THEORETICAL



PART II--THEORETICAL

The apparent molal volume is defined by any of the following equations:

$$\begin{aligned}\phi &= \frac{V_2 - n_1 v_1}{n_2} \\ \phi &= \frac{1000}{c} - \frac{1}{d_1} \left( \frac{1000d_1}{c} - M_2 \right) \\ \phi &= \frac{V_2 (d_1 - d_2) + g}{d_1 n_2}\end{aligned}$$

where  $V_2$  is the volume of the solution,  $v_1$  the volume of a mol of the solvent,  $n_1$  and  $n_2$  the number of mols of solvent and solute,  $d_1$  and  $d_2$  the densities of solvent and solution.  $M_2$  is the molecular weight of the solute,  $c$  is the concentration in mols per liter and  $g$  is the weight of salt used.

As pointed out in the introduction Masson (10) has shown that there is for many salts a direct linear relationship between the apparent molal volume and square root of the normality. This was determined from the calculation of the apparent molal volume of twenty-eight salts in aqueous solution. Twenty-four of the salts were strong electrolytes and of the twenty-four, twenty-two gave straight lines when the apparent molal volumes were plotted against the square root of the concentration. The relation was expressed by Masson in the form

$$\phi_c = \phi_0 + k\sqrt{c}$$

where  $\phi_c$  is the apparent molal volume at any concentration,  $\phi_\infty$  is the apparent molal volume at infinite dilution,  $k$  is a constant dependent on the salt and the solvent, and  $c$  is the concentration in moles per liter.

According to Masson the apparent molal volume might be considered from one standpoint as merely the volume occupied by the salt in the solution if we consider that there is no change in the volume of the solvent, but this assumption is probably not true. There is more than one way in which the volume of the solvent may be changed. In the first place the quantity of the solvent may be reduced by solvate formation. If this is the case there are two possibilities to be considered. Each solute molecule will combine with the solvent to form some definite solvate and thus destroy, as solvent, an amount of the solvent proportional to the concentration over the entire solubility range up to the point where the whole mixture has the composition of the solvate; or the average composition of the mixed solvates will vary continuously with the concentration. Second; as a result of the admixture the solvent may suffer changes in its physical properties other than the quantity change. If this is true all the properties of the solvent must alter with the concentration including not only its specific volume but its degree of association and other related characteristics. That is, the properties of the solvent in this case are dependent on

the concentration of the solute and at each concentration there is what might be called a new solvent since many of its properties are changed.

Masson found evidence from his results with the strong electrolytes in aqueous solution to support the theory that the change of volume occurring when a soluble substance is mixed with water is due to the sum of two changes. One of these is described above, and is due to the formation of a hydrate from the solute and water; the other is caused by the dilution of that hydrate with an excess of the solvent or with an excess of the solute. The former he called the chemical effect even though it included in most cases a volume change due to the passing of the salt from the solid to the liquid state; the second he called the physical effect. The chemical effect may result in either a contraction or an expansion, the former accompanied by heat evolution and the latter by heat absorption. The total effect could be either a contraction with rise in temperature or an expansion with a lowering in temperature.

The explanation then advanced for the large diminution of the apparent molal volume with a decrease in the square root of the concentration is that the hydrate exists in a greater and a lesser form. The greater is a hydrate containing a great number of molecules of water and the lesser is a hydrate containing a very few molecules of water. The



determination of the apparent molal volume is always a determination of a mixture of the two forms in proportion as determined by the concentration. It is postulated by Masson that the lesser form could exist by itself only if it were possible for the hydrate to exist by itself in the complete absence of solute. This would mean existence at infinite dilution. The larger form could exist by itself only if it were possible for the hydrate to exist at all in the complete absence of the solvent. Curvature sets in for the sulphuric acid curve at a point corresponding to the mono-hydrate. In the case of most salts this point is not reached because of low solubility. It appears that below this point the true solute molecular volume is that of a characteristic hydrate and is the sum of the apparent molecular volume and a quantity determined by the degree of hydration.

The derivation of the square root relationship from the Debye-Hückel theory by Redlich and Rosenfeld (11) postulates that all salts of one valence type have the same slope. This is not strictly true when we examine the plotted data but it is approximated in most cases.

Mention has been made above that the application of the Debye-Hückel theory is usually confined to very dilute solutions, whereas a number of the results indicate agreement in concentrated solutions. A very likely compromise could reasonably be made in this matter by agreeing with

Gibson that the straight lines in concentrated solutions are indeed fortuitous but that all curves including the S curves should be found to approach a straight line as the concentration approaches zero. The experimental accuracy required for such a test is entirely beyond the limit of the pycnometer method and it is questionable whether a sufficiently accurate method has yet been devised.

Vosburgh, Connell, and Butler (13) in an investigation of electrostriction of salts in alcohol solutions show that the electrostriction of the solvent produced by the salt is greater in methanol solutions than in water. If the electrostriction is greater the apparent molal volume at infinite dilution will be less. In all cases in which a comparison has been made this was found to be true.

Apparent molal volumes of alkali halides have been determined by Johnson (6) in liquid ammonia. Due to the fact that the experimental error is so great little reliance can be placed on the results obtained although they indicate that there is a linear relationship between the apparent molal volume and the square root of the density.

The apparent molal volumes of non-electrolytes in aqueous solution have been determined in only a few instances (10). The difficulty of developing a general theory is increased by the fact that the non-electrolytes seemingly exhibit a behavior similar to that of electro-

lytes. The amount of data however is insufficient to be certain that the behavior is general.



PART III

EXPERIMENTAL

PART III--EXPERIMENTAL

The experimental part of this investigation consisted in the determination at 25°C. of the densities of methanol salt solutions at a series of concentrations. Densities were determined by means of a special pyknometer with a volume of 25.1760 cc. The pyknometer was specially constructed to avoid any creeping and consequent loss of solution.

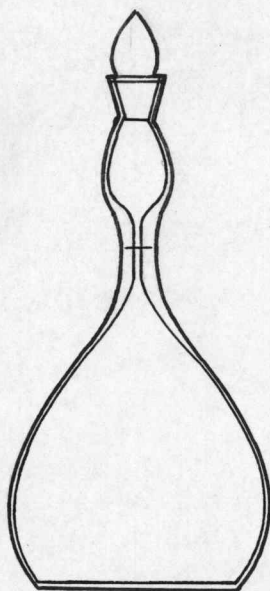
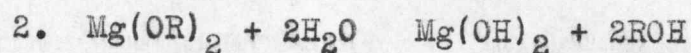
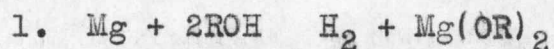


Fig. I

Considerable accuracy was desirable in determining densities since a small error in density is greatly magnified in the final calculation of apparent molal volumes. For example the density of a solution of potassium thiocyanate, 0.181 molar, was found to be 0.79964, from which the apparent molal volume was calculated to be 32.23 cc. An error in the density determination of one in the fourth

place would change the apparent molal volume to 31.52 cc. In more dilute solutions this error is magnified to a greater extent since the difference in density between the solvent and the solution is less. In addition any error in a basic measurement of density or weight of salt which would increase the apparent molal volume would act to decrease the magnitude of the square root of the concentration and vice versa. Probably the greatest difficulty in the manipulation was to prevent so far as possible the entrance of water during the transfer of the solution, from the volumetric flask in which it was made to the pyknometer. The salt was delivered to the volumetric flask from a stoppered weighing bottle in the presence of air which would enable a slight amount of moisture to be absorbed. The greatest difficulty was encountered with calcium nitrate which in particular is highly hygroscopic. The volume of the liquid was in every case adjusted to the mark on the pyknometer neck in a constant temperature bath at  $25 \pm 0.02^\circ\text{C}$ . This temperature was checked with a thermometer calibrated by the Bureau of Standards. The method of Lund and Bjerrum (9) was used for the purification of the methanol. It is based on the reactions:





Magnesium hydroxide is practically insoluble in alcohol, hence reaction two is practically complete and only a slight excess of magnesium is necessary at the start. The process should start with alcohol of a purity of 99% since the initial reaction does not proceed with sufficient rapidity if there is too much water present. Starting with about 50-75 cc. of 99% methanol, magnesium turnings (5 gr.) and iodine (0.5 gr.) were added. This mixture was refluxed until most of the iodine had reacted. When the iodine had disappeared stock alcohol (900cc.) was added and the mixture refluxed for a half hour. About two-thirds of the methanol was then distilled off using a fractionating column. The first batch of alcohol was also refluxed over anhydrous copper sulphate in addition to the above treatment but this did not appear to improve the purity of the product. To remove electrolytes one should distill the alcohol over tri-bromo-benzoic acid but as this was not available the step was omitted. The density of the methanol in various batches varied between 0.78666 and 0.78664 at 25°C. The density of highly purified methanol at 25°C. as determined by Jones and Fornwalt (7) is 0.786545. This indicates that a trace of water (approximately 0.03%) still remained in the alcohol.

The potassium thiocyanate used was Merck's best quality. It was dissolved in water and filtered to remove any insoluble material. It was recrystallized three times

from water, dried over potassium hydroxide and then over phosphorus pentoxide. After the material appeared dry it was heated in an oven to  $100^{\circ}\text{C}$ . to remove more water and then heated to  $70^{\circ}\text{C}$ . in a vacuum oven for two hours. The potassium thiocyanate was then analyzed by titration with silver nitrate and found to be 99.97% pure. This was considered sufficiently pure for the experimental work.

Baker's C. P. ammonium nitrate was dissolved in ethyl alcohol and filtered. It was then recrystallized three times from ethyl alcohol solution and dried over calcium chloride and phosphorus pentoxide. After this treatment it was dried for two hours at  $70^{\circ}\text{C}$ . in a vacuum oven.

The mercuric chloride used was Baker's C. P. It was dissolved in ethyl alcohol and filtered to remove insoluble material. It was then recrystallized three times from ethyl alcohol and dried over calcium chloride and phosphorus pentoxide. This preparation was not dried in an oven because of its high vapor pressure.

Merck's calcium nitrate was dissolved in ethyl alcohol and filtered to remove insoluble material. It was then recrystallized from ethyl alcohol and dried over calcium chloride and phosphorus pentoxide. After the material had dried in the desiccator it was heated for several hours in an oven at  $150^{\circ}\text{C}$ . This material was heated in the oven at frequent intervals to prevent the absorption of

moisture.

All the compounds were kept over phosphorous pentoxide in a vacuum desiccator for the duration of the experiment. The volume of the pyknometer was determined at 25°C. using distilled water. The salt used in the determinations was weighed in a glass stoppered weighing bottle and introduced into a standardized one hundred ml. volumetric flask. The flask was then filled nearly to the mark with methyl alcohol and immersed in the constant temperature bath. The flask remained in the bath twenty minutes and the volume of the solution was then brought up to the mark by the addition of the necessary alcohol. The solution was then transferred to a stock flask. Air pressure was used to force the solution from the stock flask through a capillary tube into the pyknometer. The pyknometer was filled above the mark and placed in the constant temperature bath. After the pyknometer had been in the bath for fifteen to twenty minutes the excess solution was carefully removed with cotton. The solution was then adjusted to the mark with a capillary medicine dropper and the upper part of the pyknometer redried. It was then removed from the bath, dried, and placed in the balance. Before weighing the pyknometer was redried using fine absorbent paper. Weighings were corrected to vacuum and for errors in weights. After the initial weighing a small



amount of solution was introduced and the process repeated. Any weighings which did not agree within 0.0004 grams were rejected and usually they agreed within 0.0002 grams. This constituted a variation of 0.02% error in the weight of the solutions.

TABLE I  
EXPERIMENTAL DETERMINATION OF APPARENT MOLAL VOLUMES  
OF SALTS IN METHANOL

Sol. no.	c mols/l.	<u>KONS</u>		ml.
		c	Density	
1	0.1811	0.426	0.79964	32.23
2	0.3438	0.586	0.80187	33.92
3	0.3918	0.626	0.81419	34.15
4	0.8307	0.911	0.84327	36.87
5	0.9545	0.977	0.85141	37.265
6	1.4999	1.225	0.88537	39.87
<u>NH<sub>4</sub>NO<sub>3</sub></u>				
1	0.2518	0.502	0.79959	36.40
2	0.4679	0.684	0.81011	37.99
3	0.7763	0.881	0.82468	39.47
4	0.8325	0.912	0.82730	39.67
5	0.9080	0.951	0.83083	39.89
<u>HgCl<sub>2</sub></u>				
1	0.1092	0.331	0.81264	42.60
2	0.2713	0.521	0.85120	42.69
3	0.3537	0.609	0.87070	42.62
4	0.6931	0.833	0.95145	42.89
5	0.8493	0.922	0.98862	42.83
<u>Ca(NO<sub>3</sub>)<sub>2</sub></u>				
1	0.1150	0.339	0.80831	25.49
2	0.3215	0.567	0.83230	28.06
3	0.5344	0.731	0.86163	30.22
4	0.5439	0.739	0.86281	30.58
5	0.7487	0.865	0.98063	32.02
6	1.086	1.042	0.93528	34.67
7	1.175	1.08	0.94724	34.82
8	1.563	1.25	0.99674	37.69
9	2.025	1.42	1.05430	39.71
10	2.045	1.43	1.05755	40.19

TABLE IIAPPARENT MOLAL VOLUMES OF SALTS IN METHANOL

(From Literature)

Sol. no.	C mols/l.	<u>KI</u> (7)	Density	ml.
		c		
1	0.01002	0.1001	0.788032	22.46
2	0.02715	0.1648	0.790538	24.09
3	0.04992	0.2234	0.793891	24.00
4	0.07525	0.2743	0.797520	25.66
5	0.10225	0.3166	0.801198	25.24
6	0.19933	0.4465	0.815356	27.31
7	0.34877	0.5906	0.836530	28.87
8	0.50192	0.7085	0.858108	29.81
9	0.60319	0.7767	0.872214	30.51

K Br (7)

1	0.01499	0.122	0.788174	13.17
2	0.03001	0.173	0.789793	13.72
3	0.05001	0.223	0.791920	14.68
4	0.08001	0.283	0.795098	15.41
5	0.10001	0.361	0.797237	15.41
6	0.11891	0.345	0.799295	14.99



TABLE III  
APPARENT MOLAL VOLUMES OF SALTS IN WATER

(From Literature)

Sol. No.	<u>KCNS</u> (5)		
	C mols/l.	c	ml.
1	0.1	0.316	48.67
2	0.2	0.447	48.82
3	0.5	0.707	49.67
4	1.0	1.000	50.07
5	2.0	1.414	50.67
6	4.0	2.000	51.87

<u>NH<sub>4</sub>NO<sub>3</sub></u> (4)			
1	0.125	0.354	47.906
2	0.635	0.796	48.358
3	1.297	1.14	48.720
4	1.984	1.41	49.013
5	2.700	1.64	49.273
6	3.444	1.855	49.514

<u>Ca(NO<sub>3</sub>)<sub>2</sub></u> (12)			
1	0.03212	0.179	44.14
2	0.25686	0.506	46.20
3	0.46906	0.684	47.10
4	1.2527	1.118	49.80
5	1.5048	1.227	50.36
6	1.8844	1.371	51.56
7	1.9739	1.402	51.83
8	2.1504	1.466	52.32
9	2.5379	1.590	53.16
10	3.2636	1.806	55.03
11	4.1146	2.024	56.96

<u>KBr</u> (1)			
1	0.228	0.477	34.75
2	0.457	0.676	35.01
3	0.919	0.959	35.60
4	2.295	1.515	36.68
5	4.60	2.145	37.90

TABLE III Continued

Sol. No.	C mols/l.	c	ml.
<u>KI</u> (1)			
1	0.275	0.525	46.13
2	0.553	0.744	46.47
3	1.112	1.054	47.00
4	2.776	1.666	47.96

TABLE IV  
COMPARISON OF THE APPARENT MOLAL VOLUMES OF SALTS  
IN WATER AND METHANOL

Salt	$\phi$ --Water	$\phi$ --Methanol	Difference
KCL	26.4 (1)	8.5    5.2 (3)	17.9   19.2
KBr	33.7 (1)	15.2   8.4 (7)	18.5   21.3
KI	45.2 (1)	22.0   19.2 (7)	23.2   26.0
KCNS	48.0 (5)	28.2	19.8
$\text{NH}_4\text{NO}_3$	47.5 (4)	32.6	14.9
$\text{Ca}(\text{NO}_3)_2$	43.3 (12)	21.0	22.3



Fig. III

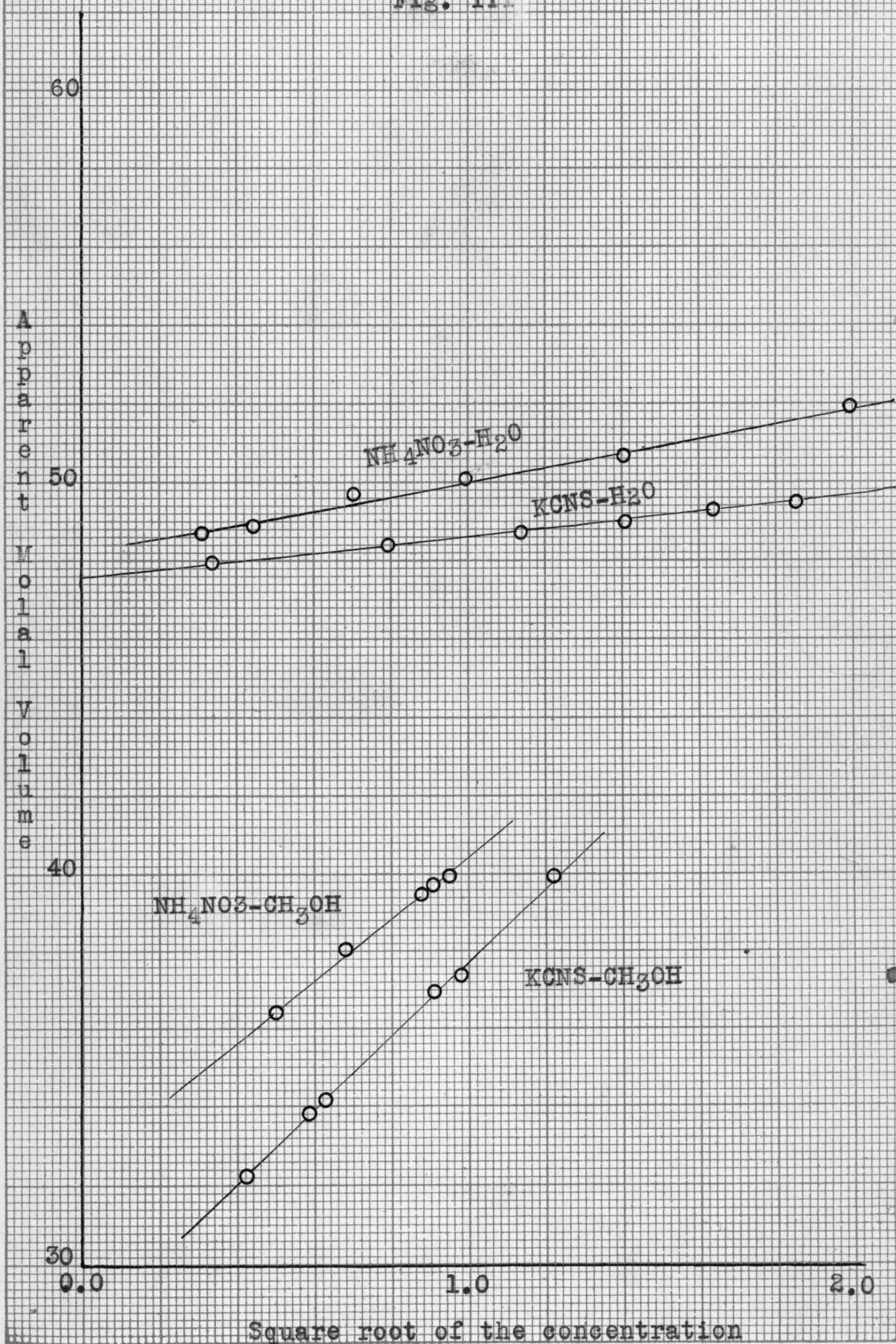


Fig. III

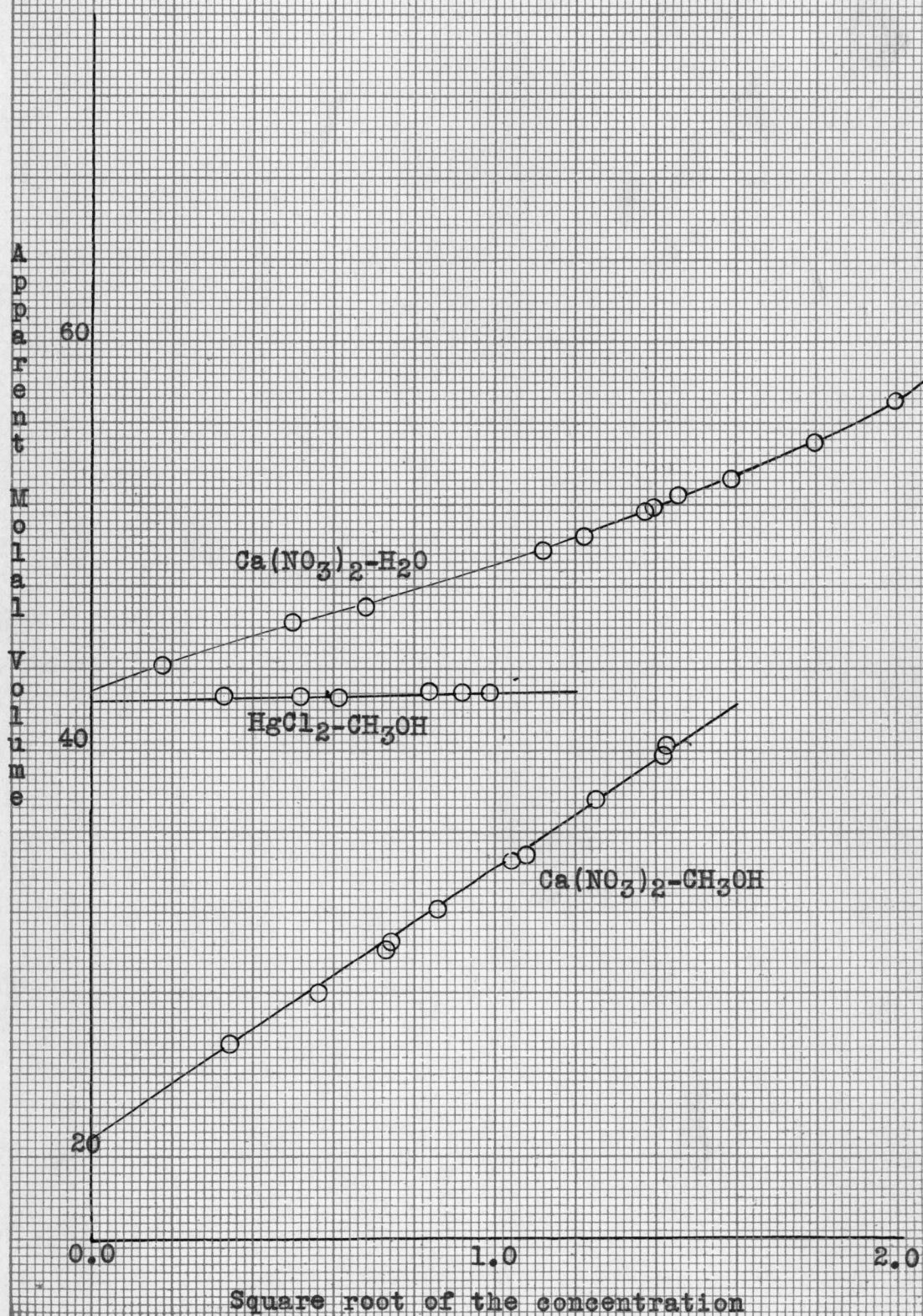
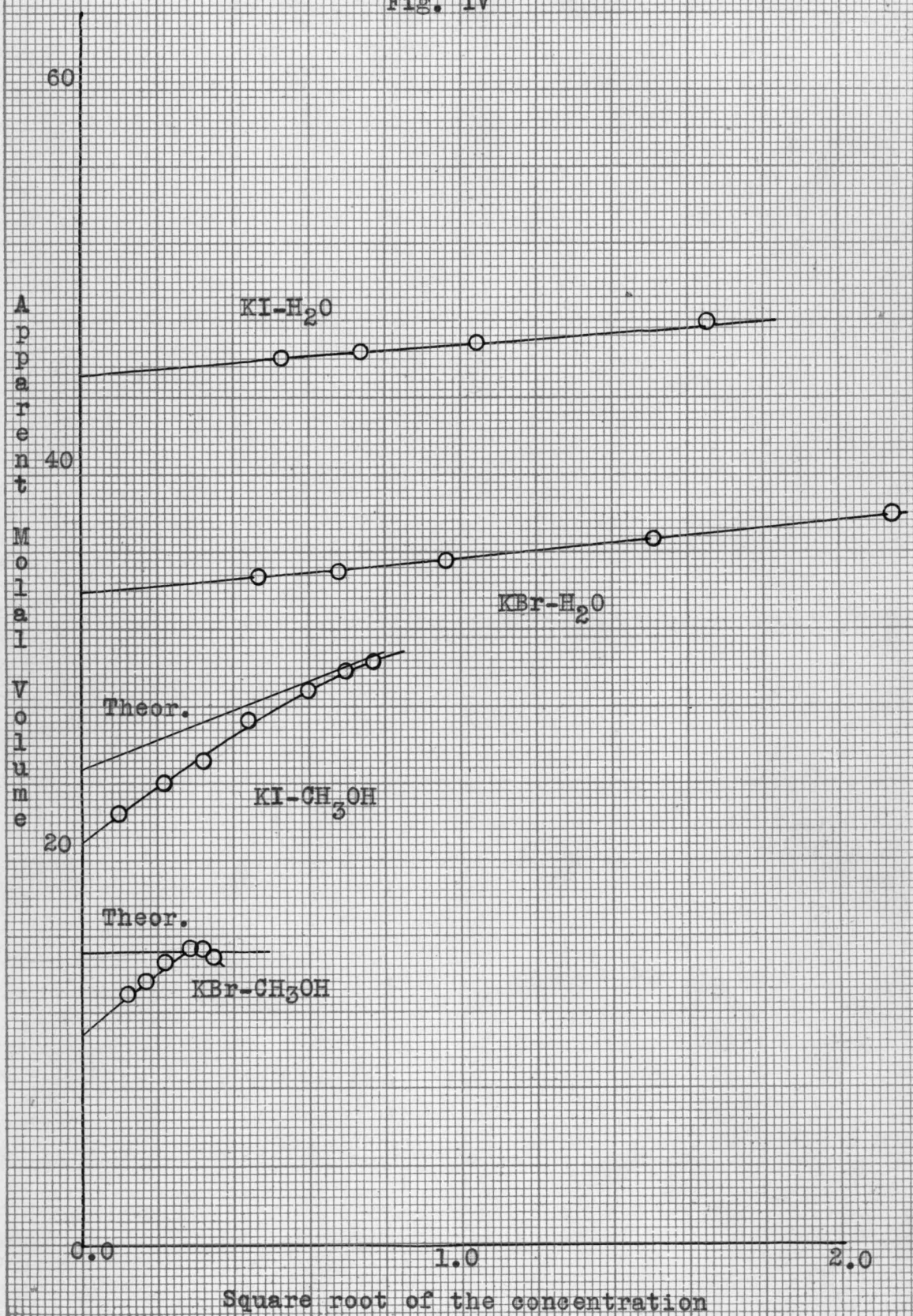




Fig. IV





PART IV  
DISCUSSION

#### PART IV--DISCUSSION

From the data given in the tables the apparent molal volume has been calculated and plotted against the square root of the concentration, and shown in Figures II, III, and IV. The difficulty inherent in the problem is very well illustrated by the cases of potassium iodide and bromide. The curves for these substances are shown in Figure II and are taken from the very exact measurements of Jones and Fornwalt (7). They estimate their densities to be accurate to 2 units in the sixth decimal place, and give also an equation for the smoothed density curve. When, now, the experimental data are plotted they give a smooth but indubitably curved line. On the other hand, data taken from their equation give a straight line of markedly different slope, as is shown in the figure. The measurements for this thesis were therefore confined to concentration for the most part higher than those of Jones and Fornwalt and where the deviations will consequently be smaller. Since the slopes of the curves calculated from the experimental densities of Jones and Fornwalt agree very closely with the slope of other univalent salts in alcohol it would appear possible that the density data is more accurate than the curve. It has been calculated (11) that the slope for salts of the same valence type should be the same, with that of bi-univalent

salts higher than that of uniunivalent. The first part of this relationship seems to be borne out by the results as may be seen from the curves. However some anomalies are evident. The slope of calcium nitrate in alcohol is of the same order as that for ammonium nitrate. Also the curve for mercuric chloride is essentially of zero slope. Some departure from normal behavior might be expected from the fact that mercuric chloride is a weak electrolyte. The curve for potassium bromide, taken from the equation of Jones and Fornwalt shows this same peculiarity, for which no explanation can be offered, except possibly the low solubility. It has been pointed out above that the experimental results (rather than the equation) actually show the expected slope.

Examination of the curve for ammonium nitrate indicates a linear relationship within the range of experimental error although it might almost as well be drawn as a curved line.

The curve for calcium nitrate in water is one which shows definite curvature. In alcohol likewise a similar curvature, though of lesser degree, seems possible. Here again the line is straight with the limits of experimental error.

When extrapolated to zero concentration the apparent molal volume becomes the thermodynamic quantity, the partial molal volume of the salt. A comparison of these



figures as shown in Table IV shows some interesting relations. In the series of potassium salts, Cl-Br-I-CNS the values in water solution show a gradual increase with size (or deformability) of the anion from 26.4 cc. for KCl to 48.0 for KCNS. The same regular rise is found in alcohol showing an increase from 5.2 cc. for KCl to 28.2 cc. for KCNS. The difference between the water value and alcohol value also for the same salt shows a regular progression for the halides increasing from 19.2 for KCl to 26.0 for KI. In this case however the KCNS does not maintain in the regular order falling slightly below the difference for KI.

Including next the nitrates in the comparison the wider variation between the values of different salts in alcohol becomes more obvious. While there is only approximately a 10% variation in water values for  $\text{Ca}(\text{NO}_3)_2$ -KI-KCNS-NH NO the values in alcohol run, apparently without much regularity, from 21.0 to 32.6 cc. Lacking complete data, except for the potassium series, it is difficult to generalize with certainty. The phenomena are definitely related to the dielectric constant of the solvent, the size and deformability of the ions, and according to Gibson (3) the compressibility of the solvent.

It may be safely concluded from the data presented that no greater regularity of the apparent molal volume--concentration relationship is to be found in alcohol than

in water solutions. On the other hand it is no less, as instances of definitely rectilinear curves are at hand.

PART V  
SUMMARY



PART VSUMMARY

In this thesis has been presented a discussion of the experiments carried out in connection with the investigation of the apparent molal volumes of salts in methanol and their comparison with the values of the same salts in aqueous solutions.

1. The densities and apparent molal volumes for a number of salts in methanol have been experimentally determined.

2. The apparent molal volumes of additional methanol *solutions* have been calculated from data obtainable in the literature.

3. The apparent molal volumes of a number of salts in aqueous solution have been listed.

4. Curves have been drawn comparing the apparent molal volumes of the salts in methanolic and aqueous solutions.

5. From the data it is a reasonable (though not proved) conclusion that the individual nature of the salts is of greater importance in alcoholic than in aqueous solution.

6. Masson's rule is apparently obeyed to about the same extent in alcoholic solutions as it is in aqueous solutions.

PART VI

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