The Temperatures of Maximum Density
and
Temperatures of Maximum Refractivity of Aqueous Solutions.

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by

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CONTENTS.

General Introduction.

Most liquids show a steady increase in density with fall of temperature, and similarly a steady increase in refractivity. Water, however, is known to be unusual in that at a certain temperature it reaches a maximum density, and below this temperature cooling produces a decrease in the density. The same phenomenon of a temperature maximum has been found to occur in the case of the refractivity of water. Temperatures of maximum density have also been observed in the case of aqueous solutions. The present thesis is in two parts dealing respectively with the Temperatures of Maximum Density, and the Temperatures of Maximum Refractivity of some aqueous solutions.

PART I.

The Temperatures of Maximum Density of Aqueous Solutions. Deviations from the Law of Despretz.

INTRODUCTION.

It has long been known that water, which like other liquids, normally increases in density with lowering of temperature, shows a maximum density at about 4°C, and that if the temperature is lowered beyond this point, the density decreases. Ice is known to be less dense than water, but as water does not freeze until it is cooled down to 0°C, this does not altogether explain the phenomenon of a density maximum occurring at 4°C. It has been assumed, however, that ice molecules must begin to be formed in the liquid at a temperature higher than that at which the liquid freezes entirely. The formation of these ice molecules of lower density will counteract the increase in density taking place in the liquid as a result of the temperature being lowered, and eventually their influence will predominate so that the total density begins to decrease. The temperature at which the rate of expansion due to the formation of ice molecules is just balanced by the rate of contraction of the rest of the liquid due to fall in temperature is that at which the maximum density will be found, and this occurs at 4°C. in the case of water.

HISTORICAL SURVEY.

A considerable amount of work has been done on the subject of the temperature of maximum density, and it has been found that aqueous solutions as a rule show a maximum density at temperatures lower than 4°C. Despretz (Ann. Chim. Phys., 70, 5, 49 (1839); 73, 29 (1840)) carried out a number of investigations on the effect on the temperature of maximum density of adding various solutes to water. As a result of these he concluded that the temperature of maximum density of water was lowered by the addition of a solute, and that the lowering was directly proportional to the concentration of the dissolved substance.

De Coppet [Ann. Chim. Phys., 3, 246, 268 (1894); Compt. rend., 125, 533 (1897); 128, 1559 (1899); 131, 178; 132, 1218 (1900); 134, 1208 (1902)] also carried out a great deal of research on the subject. He was particularly interested in the fact that the lowering produced by the addition of a solute to water was not dependent solely on the molecular concentration of the solute, but varied according to the nature of the solute. He measured the lowering of the temperature of maximum density produced by the addition of a gram molecule of various solutes in a litre of solution and found it to vary considerably according to the solute. In this respect it differs altogether from the lowering of the freezing point by the addition of a solute, as this depends solely on the molecular concentration. This shows that the lowering of the temperature of maximum density by a solute is not due simply to the fact that the addition of the solute has lowered the freezing point so that ice molecules are not formed until a much lower temperature is reached. Rosetti (Ann. Chim. Phys., 1867 (IV), 10, 461; 1869, 17, 370), having considered the early work done on the subject, tried to connect the two lowerings, but was not able to formulate a law which was generally applicable. Evidently some other factor must be taken into account, since the lowering varies with the nature of the substance.

De Coppet in the course of measuring the molecular lowering of the temperature of maximum density obtained the following results for the halides:

	Chloride	Bromide	Iodide
Rubidium	11·7	13·2	15·6
Potassium	11·6	12·8	15·4
Sodium	13·2	14·5	17·0
Lithium	6·0	7·0	8·3
Ammonium	7·2	8·7	11·1

He noticed that the iodide always produced the greatest effect, and the chloride the smallest, and concluded that "Le rapport entre les abaissements produit par le chlorure et le bromure (ou le bromure et le iodure) du même métal est sensiblement le même pour tous les métaux du groupe."

Wright (J. Chem. Soc., 115, 119 (1919)) came to the conclusion that, in the case of simple binary electrolytes, a specific effect could be attributed to each ion, and that the molecular lowering due to an electrolyte could be calculated if the lowering of certain similar compounds was known. He took the molecular lowering of hydrochloric acid as a standard, and was able to calculate the molecular lowering of any salt by adding to this standard the values due to the acidic and basic radicles of the salt. In this way he estimated the lowering for potassium nitrate to be 5·2 (hydrochloric acid) +

5·75 (potassium) + 7·2 (nitrate) = 18·15, and the actual value found was 18·0.

In the course of his studies on the variation in the lowering of the temperature of maximum density by various solutes, De Coppet (Compt. rend., 115, 652 (1892)) found the dilute solutions of the lower alcohols to be unusual in that they did not obey Despretz' law, although the salt solutions he investigated did, and also most of the solutions of organic substances. Ethyl alcohol is particularly interesting, and the values he obtained for it are given below.

Wt. of alcohol in 100 gms. of water.	T.M.D.	Lowering of T.M.D.
0·09	4·12* °C	-0·12°C
0·642	4·16	-0·16
1·346	4·29	-0·29
2·568	4·39	-0·39
3·943	4·02	-0·02
6·21	3·17*	+0·83
6·575	2·85	+1·15
7·408	2·25xx	+1·75
8·46	1·82*	+2·18
10·80	-0·19*	+4·19
17·12	-8·48*	+12·48

* indicates due to Rosetti, xx to Despretz.

In the case of very dilute solutions an actual rise in the temperature of maximum density may be observed, though as the solution becomes more concentrated a lowering is produced. McHutcheson (J. Chem. Soc., 129, 1899 (1926)) made a further study of the temperatures of maximum density of the alcohols, investigating five. His results are given below.

Temperatures of Maximum Density of Alcohol-Water Mixtures.

	2 M.	M.	M/2.	M/4.	M/8.	M/16.
Methyl alcohol	1·90°C	3·65	3·95	4·00	4·00	-
Ethyl alcohol	0·15	3·70	4·25	4·20	4·15	-
n-Propyl alcohol	-	1·50	3·30	3·80	4·15	4·10
iso- " "	-	2·65	3·70	4·00	4·00	-
n-Butyl "	-	-	-	3·10	3·90	3·90.

He found that, besides ethyl alcohol, n-propyl alcohol was the only one to give an elevation of the temperature of maximum density.

Ethyl ether does not follow Despretz' law either, but a rise in the temperature of maximum density cannot be seen, even in very dilute solutions.

Factors governing the lowering of the Temperature of Maximum Density.

In considering why these substances should form exceptions to Despretz' law, we must take into account three factors which affect the temperature of maximum density of solutions.

First, there is the lowering of the freezing point caused by the addition of a solute to water, as this involves the lowering of the temperature at which ice molecules would start to be formed. It has already been shown, however, that this factor, while it undoubtedly plays an important part in the lowering of the temperature of maximum density, cannot account for variations, as it should be the same for all solutions of equal molecular concentration. In the case of salt solutions the effect might be increased owing to ionisation of the solute, but certainly in the case of organic solutions the effect should be constant. In all cases, moreover, the addition of a solute to water lowers the freezing point, and with it the temperature of maximum density, so that in no way could this account for a rise in the temperature of maximum density such as is found with ethyl alcohol.

Another factor which must be of importance in the lowering of the temperature of maximum density is the coefficient of expansion of the liquid. If a liquid has a large coefficient of expansion, a greater number of ice molecules must be formed to counteract the effect of the greater contraction of the liquid with fall in temperature. This means that a lower temperature will be reached before the point of maximum density occurs. Aqueous solutions always have a greater coefficient of expansion than pure water, so the addition of a solute to water will always mean a lowering of the temperature of maximum density as far as this factor is concerned. The coefficient of expansion is also proportional to the concentration of the solute in dilute solutions.

The third factor which must be taken into account in connection with the temperature of maximum density of solutions is the density of the solution. If a solution has a density greater than that of water the formation of ice molecules and consequent increase in the concentration of the remaining solution will have opposite effects. The decrease in density due to the formation of the ice molecules will be counteracted by an increase in density due to the rest of the solution becoming more concentrated. This will tend to lower the temperature of maximum density. On the other hand, if the solution has a density less than water, both the formation of ice molecules and the consequent increase in concentration of the remainder of the solution will result in a decrease in density. The temperature of maximum density will therefore be arrived at more quickly on cooling, so that a higher temperature of maximum density will result.

From this it can be seen that the effect produced on the freezing point and on the coefficient of expansion by the addition of a solute to water will always tend to produce a lowering of the temperature of maximum density. The effect produced on the density, however, will vary in influence on the temperature of maximum density according to whether a solution is produced of greater or less density than water.

It appears then that the unusual results obtained in the case of the lower alcohols and ethyl ether are due to the fact that solutions of these have a smaller density than water. In the case of ethyl alcohol the coefficient of expansion for dilute solutions is very similar to that of water, and so for dilute solutions the factor due to the small density outweighs the slight effect due to increased coefficient of expansion, and to lowering of the freezing point. As the concentration becomes greater the increasing coefficient of expansion and lowering of the freezing point produce a lowering in the temperature of maximum density.

The three factors which control the lowering of the temperature of maximum density are all proportional to the concentration of the solute in dilute solutions, and so their combined effect should also be proportional to the concentration. This should result in the solution obeying the law of Despretz for dilute solutions at least. In the case of concentrated solutions these factors are usually so great that the temperature of maximum density is lower than the freezing point, and so not many have been investigated.

The molecular lowering, however, of hydrochloric acid and lithium chloride was calculated from the results obtained with dilute solutions to be about 6°C, and so it was decided to examine solutions of these two substances to see if Despretz' law was followed for concentrated solutions.

EXPERIMENTAL METHOD.

A dilatometer consisting of a glass bulb of approximately 50 c.c. volume and a stem of capillary tubing were used for these experiments. The contraction of the glass on cooling was compensated by the presence of the required amount of mercury inside the bulb. The contraction of the dilatometer bulb would tend to force the liquid higher up the stem, but the contraction of the mercury inside the bulb would tend to leave room for a greater volume of liquid in the bulb, and the amount of mercury used was calculated so that these two effects just balanced, and consequently only the expansion or contraction due to the liquid under investigation was seen. To find the amount of mercury necessary the dilatometer was weighed empty and then full of water to find its volume. Since the coefficient of mercury is about seven times that of glass, it was only necessary to add $\frac{1}{7}$th of this volume of mercury.

The dilatometer was filled with the required liquid by means of a dropping funnel and a water pump. A rubber stopper with a hole which fitted the stem of the dilatometer was placed in the funnel, after it had been half-filled with the liquid, and the dilatometer connected in this way. The other end of the funnel was connected to the pump. The funnel was then inverted and air sucked out of the dilatometer through the liquid in the funnel. Then the tap was closed and the apparatus disconnected from the pump, and when air was once more allowed into the funnel, the liquid ran into the dilatometer. This proceeding was repeated if necessary, and the final amount of air expelled by warming the dilatometer in a can of hot water.

In the case of subsequent experiments the dilatometer was emptied by slightly warming it first and then cooling to allow air into it, and then inverting so that the mercury ran out. The remaining liquid was then drawn out by means of the pump. The dilatometer was cleaned and rinsed with the fresh liquid before filling.

The compensated dilatometer was clamped inside a large Dewar flask, which was filled with water and to which ice or freezing mixture could be added as desired. This was kept stirred continually, and a thermometer hanging into it showed the temperature. The thermometer used was graduated in tenths of a degree, and ranged from 20°C to -20°C. The height of the liquid meniscus up the stem of the dilatometer was observed by means of a cathetometer. The cross-wire in the eye-piece of this was brought to the top of the meniscus and then the reading on the cathetometer scale and vernier recorded. The liquid in the Dewar flask was brought to the required temperature by adding ice and stirring, and the dilatometer was left to acquire this temperature throughout. Readings were then taken at intervals on the cathetometer, and when they became constant were recorded along with the temperature of the solution. More ice was added and the proceeding repeated. As the temperature of the solution became nearly that of its maximum density, the readings on the cathetometer became closer together, and in some cases it was hard to determine if any change had taken place or not. When the temperature of maximum density was passed the readings on the cathetometer began to move in the reverse direction. The turning point showed the temperature of maximum density of the solution.

EXPERIMENTAL RESULTS.

In the case of hydrochloric acid and lithium chloride twice normal, normal, and semi-normal solutions were examined, and the following results obtained:

	Concn.	T.M.D.	Lowering of T.M.D. of water.		Concn.	T.M.D.	Lowering of T.M.D. of water.
HCl	2N	-12·4°C	16·4°C	$LiCl$	2N	-8·5°C	12·5°C
	N	-2·9 C	6·9		N	-1·9 C	5·9
	N/2	1·1 C	2·9		N/2	1·3 C	2·7

The temperature of maximum density of water was also determined using this apparatus, and was found to be 4°C as was expected. The lowering of the temperature of maximum density produced by solutions was therefore calculated by subtracting their temperatures of maximum density from that of water, i.e., from 4°C.

On examining these results it is clear that Despretz' law is not obeyed in the more concentrated solutions.

It was therefore determined to investigate some other concentrated solutions if possible. On considering which substances would be most suitable, it was obvious that those which would not have temperatures of maximum density lower than their freezing points would be required. We have already seen that the property which tends to raise the temperature of maximum density of a solution is that of forming a solution less dense than water. In the case of solutions of organic compounds a smaller coefficient of expansion is generally found than with salt solutions, and no ionisation will take place so the freezing point will not be unduly lowered, and so fairly high temperatures of maximum density may be expected. Organic solutions less dense than water therefore appear to be the most suitable for investigation, but they must also be sufficiently soluble to give the required concentrated solutions. The alcohols have already been investigated, but the fatty amines, ammonia, acetone and aceto-nitrile were all examined in the present instance. The results are given below.

Temperatures of Maximum Density.

	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$
2N	-2·4 °C	-6·2°C	-	-7·1°C	-10·0°C approx.
N	+2·2	+1·4	-1·2	+0·8	-0·9
N/2	3·4	3·5	+2·85	2·85	+2·65
N/4	3·8	4·0	3·65	3·65	3·6
N/8	3·9	4·0	3·95	3·8	3·95

Temperatures of Maximum Density (Contd.).

	NH_3	$(CH_3)_2CO$	CH_3CN
2N	-1·2° C	-8·0°C approx.	below -10° C.
N	+1·6	-2·15	-3·35
N/2	2·85	+1·7	+0·7
N/4	3·6	3·0	2·45
N/8	3·8	3·6	3·15.

The lowering of the temperature of maximum density of water exerted by these substances was calculated by subtracting these figures from 4° C, and is as follows.

Lowering of the Temperature of Maximum Density of Water.

	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$.
2N	6·4°C	10·2 °C	-	11·1°C	14° approx.
N	1·8	2·6	5·2	3·2	4·9
N/2	·6	·45	1·15	1·15	1·35
N/4	·2	·0	·35	·35	·4
N/8	·1	·0	·05	·2	·05

	NH_3	$(CH_3)_2CO$	CH_3CN.
2N	5·2 °C	about 12°C	over 14° C
N	2·4	6·15	7·35
N/2	1·15	2·3	3·3
N/4	·4	1·0	1·55
N/8	·2	·4	·85

These figures show that the lowering due to the more concentrated solutions is much greater than would be expected by calculation from dilute solutions; i.e., that there is a deviation from the law of Despretz in the case of strong solutions.

Examination of Relative Densities.

Since the density of the solution plays such an important part in determining the temperature of maximum density, it was found at 5°C for all the solutions investigated. This temperature was chosen as being near that at which the main parts of the experiments were carried out, but yet far enough away from the temperature of maximum density and freezing point for no complications to occur through the formation of ice molecules. The densities obtained are given in the table following. They were determined in the ordinary way by means of a pyknometer.

Relative Densities at 5°C.

	CH_3NH_2	$(CH_3)_2NH$	$C_2H_5NH_2$	$(C_2H_5)NH$	$(CH_3)_3N$
2N	·9826	·9765	·9805	·9759	–
N	·9912	·9870	·9895	·9872	·9822
N/2	·9957	·9934	·9945	·9926	·9910
N/4	·9977	·9970	·9974	·9963	·9951
N/8	·9990	·9987	·9988	·9982	·9970

	NH_3	CH_3CN	$(CH_3)_2CO$	C_2H_5OH
2N	·9851	·9908	·9874	·9856
N	·9922	·9954	·9936	·9915
N/2	.9959	·9972	·9968	·9956
N/4	·9979	·9988	·9988	·9977
N/8	·9988	·9991	·9995	·9986

These densities when plotted against the concentrations give approximately linear graphs. Since the density thus varies directly with the concentration, even in concentrated solutions, this cannot be responsible for the deviation from Despretz' law which is found in strong solutions.

Examination of Coefficients of Expansion.

The coefficients of expansion of the various solutions were also examined. They were determined by means of the dilatometer used for finding the temperatures of maximum density, and were taken between the temperatures 12·5°C and 15°C. This temperature range was chosen simply because it was convenient, and also free from complications due to freezing. The coefficient of expansion was calculated from the formula

$$a = \frac{V_{15} - V_{12\cdot5}}{2\cdot5 \times V_{12\cdot5}}$$

where a = the coefficient of expansion

V_{15} = the volume of liquid at 15°C

and $V_{12\cdot5}$ = the volume of liquid at 12·5°C.

The 2·5 is the difference in temperature in °C.

In practice, the height of the liquid up the stem of the dilatometer at 15°C was noted by means of the cathetometer. The temperature was then lowered to 12·5° C and the height of the liquid at that temperature noted. The difference between the two readings of the cathetometer gave the fall of the column of liquid in centimetres. This was then multiplied by the area of the bore of the dilatometer stem to give the contraction of the liquid in cubic centimetres, and this figure divided by 2·5 times the volume at 12·5 °C to give the coefficient of expansion of the liquid.

The area of the bore of the dilatometer stem was determined by filling a portion of the stem with mercury, measuring the length of it, and then allowing it to run out and weighing it. Knowing the temperature at which the experiment was performed, and the density of mercury at that temperature, it was easy to find the volume of mercury used, and from this the area of the bore, since the length of the column was also known.

The coefficients of expansion obtained are given in the following table.

Coefficients of Expansion between 12·5° C and 15° C.

	CH_3NH_2	$(CH_3)_2NH$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	$(CH_3)_3N$
2N	·0002024	·0002450	·0002480	·0004037	-
N	1592	1690	1725	2043	·0002095
N/2	1432	1422	1447	1565	1574
N/4	1378	1360	1350	1358	1410
N/8	1360	1350	1350	1350	1375

	NH_3	CH_3CN	$(CH_3)_2CO$	C_2H_5OH
2N	·0002310	·0003260	—	·0001900
N	1610	2220	·0001953	1495
N/2	1480	1800	1670	1405
N/4	1415	1550	1440	1380
N/8	1375	1470	1363	1365

These coefficients of expansion when plotted against the concentration show excessive increase with increase of concentration. This is shown when the "molecular increase of coefficient of expansion" is worked out. This was calculated from the formula

$$i_m = \frac{a_s - a_w}{N}$$

where i_m = the molecular increase of coefficient of expansion,

a_s = the coefficient of expansion of the solution,

a_w = the coefficient of expansion of water,

N = the concentration of the solute in gram-molecules per litre.

If the increase in the coefficient of expansion was directly proportional to the concentration of the solute, then the molecular increase thus obtained should be a constant. The results obtained are given below, and it will be seen that in most cases the values obtained for concentrated solutions are much greater than those for the more dilute solutions.

Molecular Increase of Coefficient of Expansion.

	CH_3NH_2	$(CH_3)_2NH$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	$(CH_3)_3N$
2N	·0000337	·0000550	·0000565	·0001343	—
N	242	340	375	693	·0000645
N/2	164	150	294	430	448
N/4	112	40	000	32	240
N/8	80	00	000	00	200

	NH_3	CH_3CN	$(CH_3)_2CO$	C_2H_5OH
2N	·0000480	·0000905	–	·0000275
N	260	870	·0000600	145
N/2	260	900	640	110
N/4	260	800	360	120
N/8	200	960	104	120

This excessive increase in the coefficient of expansion in concentrated solutions would explain the deviations from Despretz' law, since they also occur in concentrated solutions. This theory is supported too by the fact that aceto-nitrile, which has a practically constant molecular increase of coefficient of expansion, obeys the law of Despretz. Ammonia also has a constant molecular increase of coefficient of expansion for solutions varying in strength from N to N/8 and for this range it obeys the law of Despretz. For the more concentrated 2N solution the molecular increase of coefficient of expansion is much greater, and here the lowering of the temperature of maximum density is also more than would be expected. In the case of ethyl alcohol the molecular increase of coefficient of expansion is practically constant, but the coefficient of expansion is so small that for dilute solutions it is outweighed by the other factors and the small density of the solution produces a rise in the temperature of maximum density as already suggested.

CONCLUSION.

We conclude that, as a rule, Despretz' law is obeyed in dilute solutions but not in concentrated solutions. The deviation shown in concentrated solutions is in the form of an increased lowering of the temperature of maximum density, and is due to the excessive increase in the coefficient of expansion of concentrated solutions.

PART II.

The Temperatures of Maximum Refractivity of Aqueous Solutions.

INTRODUCTION.

This subject was suggested by the previous study on the temperature of maximum density of aqueous solutions. The occurrence of a maximum on the curve showing the relation of density to fall in temperature was explained by the fact that ice is less dense than water and ice molecules are supposed to be formed above the freezing point. The lower density of these counteracts the increase in density due to fall in temperature of the liquid, and at a certain point produces a decrease in the density of the solution.

From this it appears that the existence of a temperature of maximum density depends on the fact that the change of density on freezing is in the opposite direction to the change in density produced by lowering the temperature of the liquid. With most of the other properties of liquids, such as viscosity or surface tension, the change on freezing continues to be in the same direction as that on lowering the temperature in the liquid state. It is clear then that these properties will show no maximum point when the liquid is subjected to a continuous rise or fall in the temperature - even over a range including the freezing point - but will continue to decrease or increase as the case may be. The property of refractivity, however, we find is analagous to that of density in that the refractive index of ice is less than that of water, (being 1·31 for ice, and 1·33 for water), although the refractive index of water increases with falling temperature. Here then we have a case where the change on freezing is in the opposite direction to that produced by fall of temperature in the liquid, and so we may expect to find the existence of a temperature of maximum refractivity for water.

HISTORICAL SURVEY.

On investigating the work previously done on this subject, we find that few measurements of refractivity have been made at low temperatures. Jamin however (Comptes rendus, 43, 1856) studied the relationship between refractive index and density of water, and took readings with his interferometer down to 0°C. Since the temperature of maximum density of water is 4°C, he expected to find a maximum refractive index at that point if the refractive index depended on the density. He did not find any change at 4°C when he raised the temperature progressively from 0°C to 30°C. But as the refractive index of ice is lower than that of water, he concluded there must be a maximum refractivity about 0°C, the ice molecules formed counteracting the increase due to lowering the temperature of the water. He thus concluded that there was an analogy between the temperature variation of refractive index and density, but that the maximum points occurred at different temperatures.

This difference seems easily explicable, assuming the theory of the formation of ice molecules above the freezing point, because the change of refractive index on freezing is only 1·5%, while the change of density is about 9%. It is therefore obvious that a greater concentration of ice molecules must be formed before their effect will become visible in the case of refractive index, and this means that the liquid will need to be cooled down to a lower temperature. This explains why the temperature of maximum refractivity of water is as low as 0°C, while the temperature of maximum density is at 4°C.

Pulfrich also measured the refractive index of water at low temperatures - his readings ranging from +10°C to -10°C. He found the maximum point to be even lower than that suggested by Jamin, being between -1°C and -2°C. As his work was most carefully carried out under very favourable conditions - he waited to take his readings till the temperature of the outside air was as cold as he required it - his results should be correct. Ketteler (Ann. der Physik, 33, 1888) also carried out some measurements on the refractive index of water, and though not many were at low temperatures, he obtained readings at -5°C and -10°C, which showed a distinct turning point in the curve.

Having thus established the fact that a point of maximum refractivity of water could be determined, it was decided to investigate the effect on it of the addition of solutes and to find if this produced a lowering which obeyed the same laws as the lowering of the temperature of maximum density.

EXPERIMENTAL METHOD.

In the first place the temperature of maximum refractivity of water was determined by means of a Zeiss Dipping Refractometer. Considerable difficulty was experienced at the beginning in the carrying out of this and the further experiments owing to the need for work at low temperatures and the difficulty in using a refractometer under such conditions. In the instruments used by Pulfrich and Jamin the temperature was hard to control and could not always be determined accurately. The present work was done by means of a Dipping Refractometer, which made the temperature regulation very simple. The liquid under investigation was contained in a small beaker or weighing bottle just large enough to enable the prism at the end of the refractometer to fit into it comfortably. This beaker was fixed on the end of the refractometer by means of a wide piece of rubber tubing, so that the junction was water-tight, although the beaker could easily be changed. The refractometer was then clamped so that it was held in a vertical plane with the small beaker dipping into a much larger one filled with water and used as a temperature regulator. The water or freezing mixture in this was kept stirred by a stream of air being constantly blown through, and the temperature was read off a thermometer hanging into it. This thermometer was graduated in tenths of a degree from -20°C to +20°C. A small inclined mirror was placed below the beaker and served to reflect the light from an electric lamp through the liquid under observation.

Direct readings can be made using the Dipping refractometer and for the present purpose did not need to be converted into actual refractive indices, as it was only necessary to see if the readings were becoming higher or lower, and to find the temperature where the change took place. The eyepiece contains a scale, and a micrometer screw enables tenths of this to be determined accurately. A variation of ± 0·1 of a scale division corresponds to a mean error of ±3·7 units of the fifth decimal place of the n_D value.

When the instrument was first used it was found to work very satisfactorily at ordinary temperatures, but when cooled down to low temperatures a film of moisture condensed on the top of the prism inside the instrument. This caused blurring, and the readings could not be taken with any accuracy. It was then attempted to keep any moist air from entering the refractometer by enclosing it in a tin case containing calcium chloride - only the top and bottom of the refractometer being allowed to project. This arrangement, however, was cumbersome and not very effective, and it was finally discovered that a small piece of calcium chloride wrapped in lead foil and placed on the upper surface of the prism was quite sufficient to absorb any moisture, and did not interfere with the observations as was at first anticipated.

Readings were then able to be taken without difficulty down to the point where the liquid froze.

Unfortunately it was found that, in the case of all solutions, freezing occurred before the temperature of maximum refractivity had been reached. To meet this difficulty the point of maximum refractivity was obtained by drawing graphs showing the change in refractivity per degree.

The change of refractive index per degree ($\frac{dr}{dt}$) decreases with fall of temperature till at the temperature of maximum refractivity - the turning point of the curve - it is equal to zero. If then the value of $\frac{dr}{dt}$ be plotted against temperature, and the curve so obtained exterpolated to determine the temperature at which the coefficient $\frac{dr}{dt}$ is of zero value, it follows that this temperature is the temperature of maximum refractivity.

The only defect in this method is that the line obtained is not straight but a curve, so that the point obtained by its exterpolation cannot be determined very accurately, but it appeared to be the most practical method, and the error should not be very great. The line drawn is nearly straight, and may be taken as such for the purpose of exterpolation.

A number of experiments were carried out in this way, and the temperature of maximum refractivity obtained for water and for $\frac{N}{2}$ and $\frac{N}{4}$ solutions of some of the common acids and their lithium, sodium, potassium and ammonium salts. The refractive indices were read off every 4°C down to a temperature where the change per degree was less than ·05 of a scale division at the mean temperature of the final range, or till the liquid froze. Each investigation was carried out twice in order to make sure that the experiment was sufficiently accurate, and it was found that the results obtained were fairly close together. In every case the instrument was kept at the required temperature for a quarter of an hour before a reading was taken, and then a second reading was taken five minutes later as a check on the first one.

EXPERIMENTAL RESULTS.

The results are given below:

Water.

Temperature in °C	10	6	2	-2	-3	-4	-5
Reading on refractometer	16·42 16·44	16·90 16·88	17·17 17·17	17·17 17·18	17·15 17·15	17·09	17·05
Refractive index	1·33370	1·33389	1·33424	1·33424	1·33416	1·33397	1·33385

These preliminary readings were taken direct, and the value of the refractive index obtained from tables supplied with the instrument. It can be seen that a maximum point occurs between 2° C and -2° C.

When it was found that the temperature of maximum refractivity of solutions had to be obtained by means of a graph, it was found for water in the same way.

As an illustration of the method of working, the complete set of figures obtained is shown below.

Temperature	Reading on scale.	∴ difference.	$\frac{dr}{dt}$	Mean temperature.
10°C	16·44 16·42			
		$\frac{\cdot 46}{4}$	= ·115	—— 8 °C
6° C	16·88 16·90			
2° C	17·17 17·17	$\frac{\cdot 28}{4}$	= ·07	—— 4°C
-2° C	17·17 17·18	$\frac{\cdot 01}{4}$	= ·002	—— 0°C

A graph drawn according to these figures shows the temperature of maximum refractivity to be -0·3°C.

The experiment was then repeated at different temperatures, and with a fresh sample of water.

Results:

Temperature	Reading on scale.	∴ difference.	$\frac{dr}{dt}$	Mean temperature.
8°C	16·67 16·68			
4°C	17·00 17·02	$\frac{\cdot 33}{4}$ =	·082 ——	6°C
0°C	17·17 17·18	$\frac{\cdot 17}{4}$ =	·042 ——	2°C
-4°C	17·12 17·12	$-\frac{\cdot 06}{4}$ =	·015 ——	-2°C

A graph drawn for these figures shows the temperature of maximum refractivity to be -0·5°C.

These graphs may be found appended at the back of the paper along with the others drawn for the various solutions.

The temperature coefficient of refractivity was also determined - being taken between the temperatures 20°C and 15°C. The results for water were:

Temperature	Reading on scale.	∴ difference.	$\frac{dr}{dt}$	Mean temperature.
20°C	14·59 14·59			
15°C	15·64 15·65	$\frac{1\cdot 06}{5}$ =	·214 ——	17·5°C

The temperature coefficient of refractivity at 17·5°C is therefore ·214 of the scale reading of the instrument.

Proceeding in this manner a complete series of acids and salts were examined at both $\frac{N}{2}$ and $\frac{N}{4}$ strengths. The figures for HCl and its lithium salt are given here. Those for the other acids and salts are all similar, and were obtained in the same way, so only the graphs drawn from them are given, and the final temperatures of maximum refractivity which were obtained.

(1)

$\frac{N}{2}$HCl Temperature	Reading on scale	Difference	$\frac{dr}{dt}$	Mean temperature.
20°C	24·98 29·99			
		$\frac{1\cdot10}{2}$	= ·22	17·5°C
15°C	26·08 26·09			
8°C	27·42 27·40			
		$\frac{\cdot56}{4}$	= ·14	6°C
4°C	27·95 27·98			
		$\frac{\cdot30}{4}$	= ·075	2°C
0°C	28·28 28·27			
		$\frac{\cdot12}{4}$	= ·03	-2°C
-4°C	28·38 28·39			

	Temperature	Reading on scale	Difference	$\frac{dr}{dt}$	Mean temperature.
(2)	20°C	24·99 24·98			
			$\frac{1\cdot02}{5}$ =	·20	17·5°C
	15°C	26·00 26·00			
	7°C	27·36 27·34			
			$\frac{\cdot44}{4}$ =	·11	5°C
	3°C	27·78 27·79			
			$\frac{\cdot25}{4}$ =	·06	1°C
	-1°C	28·04 28·04			
			$\frac{\cdot05}{4}$ =	·012	-3°C
	-5°C	28·09 28·09			

$\frac{N}{4}$ HCl

	Temperature	Reading on scale	Difference	$\frac{dr}{dt}$	Mean temperature.
(1)	20°C	19·88 19·90			
			$\frac{1\cdot14}{5}$ =	·208	17.5°C
	15°C	21·03 21·03			
	8°C	22·16 22·18			
			$\frac{\cdot33}{4}$ =	·082	6°C
	4°C	22·50 22·50			
			$\frac{29}{4}$ =	072	2°C

$\frac{N}{4}$ HCl (Contd.)

Temperature	Reading on scale	Difference	$\frac{dr}{dt}$	Mean temperature
0°C	22·80 22·78			
		$\frac{\cdot 03}{4}$ =	·001 —	-2°C
-4°C	22·82 22·82			
(2) 20°C	19·89 19·89			
		$\frac{1\cdot 11}{5}$ =	·22 —	17·5°C
15°C	21·00 21·00			
9°C	21·92 21·92			
		$\frac{\cdot 46}{4}$ =	·115 —	7°C
5°C	22·38 22·38			
		$\frac{\cdot 29}{4}$ =	·072 —	3°C
1°C	22·67 22·69			
		$\frac{\cdot 4}{4}$ =	·01 —	-1°C
-3°C	22·72 22·72			

$\frac{N}{2}$ LiCl.

	Temperature	Reading on scale	Difference		$\frac{dr}{dt}$	Mean temperature.
(1)	20°C	24·27 24·29				
			$\frac{1\cdot11}{5}$	=	·22	17·5°C
	15°C	25·39 25·40				
	7°C	26·09 26·10				
			$\frac{\cdot58}{4}$	=	·145	5°C
	3°C	26·68 26·68				
			$\frac{\cdot26}{4}$	=	·065	1°C
	-1°C	26·95 26·93				
			$\frac{\cdot09}{4}$	=	·022	-3°C
	-5°C	27·03 27·03				
(2)	20°C	24·37 24·37				
			$\frac{1\cdot01}{5}$	=	·20	17·5°C
	15°C	25·38 25·38				
	8°C	26·59 26·59				
			$\frac{\cdot41}{4}$	=	·102	6°C
	4°C	27·00 27·00				
			$\frac{\cdot30}{4}$	=	·075	2°C
	0°C	27·28 27 32 27 30				
			$\frac{\cdot08}{4}$	=	·020	-2°C
	-4°C	27 38 27 38				

$\frac{N}{4}$ LiCl

	Temperature	Reading on scale	Difference		$\frac{dr}{dt}$	Mean temperature.
(1)	20°C	18·85 18·84				
			$\frac{\cdot 98}{5}$	=	·196	17·5°C
	15°C	19·82 19·82				
	8°C	21·00 21·00				
			$\frac{\cdot 42}{4}$	=	·105	6°C
	4°C	21·40 21·44				
			$\frac{\cdot 22}{4}$	=	·055	2°C
	0°C	21·64 21·65				
			$\frac{\cdot 03}{4}$	=	·007	-2° C
	-4°C	21·67 21·68				
(2)	20°C	19·26 19·28				
			$\frac{1\cdot 07}{5}$	=	·214	17·5°C
	15°C	20·35 20·34				
	11°C	22·14 22·14				
			$\frac{\cdot 56}{4}$	=	·14	9° C
	7°C	21·58 21·58				
			$\frac{\cdot 37}{4}$	=	·092	5°C
	3°C	21·94 21·95				
			$\frac{\cdot 18}{4}$	=	·045	1° C
	1°C	22·13 22·15 22·11				

The temperatures of maximum refractivity obtained from these are as follows:

$\frac{N}{2}$ HCl	-4·2 °C -4·2° C	$\frac{N}{2}$ LiCl	-4·3° C -3·8° C
$\frac{N}{4}$ HCl	-2·1° C -2·1° C	$\frac{N}{4}$ LiCl	-2·3° C -2·5° C

The complete set of results is given below:

Temperatures of Maximum Refractivity.

	HCl	HBr	HI	HNO_3.
$\frac{N}{2}$	-4·2 -4·2	-2·8 -3·0	-3·5 -3·9	-6·5 -7·4
$\frac{N}{4}$	-2·1 -2·1	-2·1 -2·0	-3·0 -3·0	-3·5 -3·4
	NaCl	NaBr	NaI	$NaNO_3$.
$\frac{N}{2}$	-7·5 -9·8	-6·0 -7·0	-6·3 -6·8	-11·2 -10·9
$\frac{N}{4}$	-3·5 -3·6	-4·0 -3·9	-4·3 -4·2	-7·0 -6·6
	KCl	KBr	KI	KNO_3.
$\frac{N}{2}$	-6·5 -7·5	-7·8 -8·1	-8·3 -8·5	-10·0 -9·8
$\frac{N}{4}$	-3·5 -3·0	-3·5 -4·2	-4·5 -4·2	-6·2 -5·4

	LiCl	LiBr	LiI	$LiNO_3$.
$\frac{N}{2}$	-4·3 -3·8	-3·7 -3·8	-5·5 -5·3	-6·9 -6·8
$\frac{N}{4}$	-2·3 -2·5	-2·9 -2·3	-3·8 -3·5	-3·5 -2·5
	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3.
$\frac{N}{2}$	-4·9 -5·9	-4·9 -4·3	-5·5 -5·8	-7·6 -8·1
$\frac{N}{4}$	-3·7 -3·0	-2·5 -3·0	-3·0 -2·8	-5·1 -5·3

	H_2SO_4	H.COOH	CH_3.COOH	C_2H_5.COOH
$\frac{N}{2}$	-6·0 -6·4	-4·3 -4·6	-4·0 -4·5	-4·7 -4·8
$\frac{N}{4}$	-3·4 -3·4	-2·2 -1·7	-2·5 -2·6	-2·9 -2·7
	Na_2SO_4	H.COONa	CH_3COONa	C_2H_5COONa
$\frac{N}{2}$	12·6 12·0	-6·4 -6·0	-7·8 -8·0	-8·6 -8·4
$\frac{N}{4}$	5·6 5·0	-4·0 -4·4	-3·5 -3·3	-3·7 -4·2

CONSIDERATION OF RESULTS.

We may now examine these results to see what conclusions can be drawn from them.

In the first place we expected from analogy with density that they would obey Despretz' law, that the lowering due to a solute depends on its molecular concentration in the solution. The results bear out this law to a fair extent, though in most cases the lowering due to a semi-normal solution is not quite twice that of the $\frac{N}{4}$.

Below is given a table showing the lowering of the temperature of maximum refractivity - the value for water being taken as -0·5 °C.

Lowering of the Temperature of Maximum Refractivity.

	HCl	HBr	HI	HNO_3.
$\frac{N}{2}$	-3·7	-2·4	-3·2	-6·5
$\frac{N}{4}$	-1·6	-1·6	-2·5	-3·0
	$NaCl$	$NaBr$	NaI	$NaNO_3$
$\frac{N}{2}$	-8·1	-6·0	-6·0	-9·5
$\frac{N}{4}$	-3·1	-3·5	-3·8	-6·3
	KCl	KBr	KI	KNO_3.
$\frac{N}{2}$	- 6·5	-7·4	-7·9	-9·4
$\frac{N}{4}$	-2·7	-3·3	-3·8	-5·3

	$LiCl$	$LiBr$	LiI	$LiNO_3$.
$\frac{N}{2}$	-3·5	-3·3	-4.9	-6·3
$\frac{N}{4}$	-1·9	-2·1	-3·1	-2·5
	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3.
$\frac{N}{2}$	-4.9	-4.1	-5·2	-7·4
$\frac{N}{4}$	-2·8	-2·2	-2·4	-4·7

	H_2SO_4	$H.COOH$	CH_3COOH	C_2H_5COOH
$\frac{N}{2}$	-5·7	-4·0	-3·8	-4·3
$\frac{N}{4}$	-2·9	-1·4	-2·1	-2·3
	Na_2SO_4	$H.COONa$	CH_3COONa	C_2H_5COONa
$\frac{N}{2}$	-11·8	-5·7	-7·4	-8·0
$\frac{N}{4}$	-4·8	3·7	-2·9	-3·5

From these figures we can only say with certainty that the lowering increases with concentration. We cannot say that it depends directly on it. The method of determining the lowering of the temperature of maximum refractivity is perhaps not accurate enough to show a marked regularity - certainly it cannot be obtained with the same accuracy as that of density, where the following of Despretz' law was clearly shown.

The coefficient of expansion of the solution was found to influence the lowering of the temperature of maximum density, so the corresponding property was also investigated in the case of refractivity. The refractivity was measured at 20°C. and at 15°C., and the difference per degree calculated from the results. This gave the approximate increase in refractivity at the mean temperature, i.e., at 17·5°C. The temperatures taken were quite arbitrary, being selected as convenient, and sufficiently removed from the freezing point to ensure that there would be no interference due to formation of ice molecules.

The results are given on the following page:

Temperature Coefficients of Refractivity.

Water = ·21. The figures refer to scale readings of the refractometer.

	HCl	HBr	HI	HNO_3
$\frac{N}{2}$	·22 ·22	·22 ·22	·25 ·25	·26 ·27
$\frac{N}{4}$	·20 ·21	·22 ·22	·23 ·21	·24 ·24
	$NaCl$	$NaBr$	NaI	$NaNO_3$
$\frac{N}{2}$		·23 ·25	·27 ·27	·28 ·28
$\frac{N}{4}$		·22 ·23	·24	·23 ·25
	KCl	KBr	KI	KNO_3
$\frac{N}{2}$		·25 ·26	·25 ·27	·27 ·27
$\frac{N}{4}$		·23 ·20	·22 ·22	·23 ·24
	$LiCl$	$LiBr$	LiI	$LiNO_3$
$\frac{N}{2}$	·22 ·20	·21 ·22	·21 ·24	·26
$\frac{N}{4}$	·20 ·21	·21	·20	·21 ·22
	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3
$\frac{N}{2}$		·22	·25 ·24	·27
$\frac{N}{4}$		·19 ·20	·22 ·23	·24 ·22

	H_2SO_4	H.COOH	CH_3COOH	C_2H_5COOH
$\frac{N}{2}$	·26	·24	·24	·24
	·26	·25	·24	·24
$\frac{N}{4}$	·24		·22	·24
	·24	·22	·21	·20
	Na_2SO_4	H.COONa	CH_3COONa	C_2H_5COONa
$\frac{N}{2}$		·22		·26
		·22	·30	·22
$\frac{N}{4}$		·20	·23	·22
		·22	·22	·21

It can be seen by comparing these figures with those representing the lowering of the temperature of maximum refractivity, that as would be expected a high temperature coefficient is found for those solutions which show a marked lowering of the temperature of maximum refractivity, and vice versa.

In the case of the lowering of the temperature of maximum density a definite value was attributed to each ion. Following out the same idea for refractivity we get a somewhat similar result, although not so well-defined. The table on the following page shows the results obtained.

Lowering (in °C) of the Temperature of Maximum Refractivity caused by Replacement of Hydrogen by a Metal.

$\frac{N}{2}$ Solutions.	Cl	Br	I	NO_3	Mean
Li	-0·2	0·9	1·7	-0·2	·5
Na	4·4	3·6	2·8	3·0	3·5
K	2·8	5·0	4·7	2·9	3·9
NH_4	1·2	1·7	2·0	0·9	1·5

	SO_4	H.COO	CH_3COO	C_2H_5COO	Mean
Na	6·1	1·7	3·6	3·7	3·8

$\frac{N}{4}$ Solutions.	Cl	Br	I	NO_3	Mean
Li	·3	·5	·6	-0·5	·2
Na	1·5	1·9	1·3	3·3	2·0
K	1·1	1·7	1·3	2·3	1·6
NH_4	1·2	·6	0	1·7	·9

	SO_4	H.COO	CH_3COO	C_2H_5COO	Mean
Na	1·9	2·3	0·8	1·2	1·6

Comparing these figures we find that the lowering shown by a given ion is roughly twice as great in an $\frac{N}{2}$ solution as in an $\frac{N}{4}$ one, as would be expected. We are therefore able to calculate an approximate molecular value:

Li = ·9 K = 7·1
Na = 7·5 NH_4 = 3·3

If the lowering of hydrochloric acid is taken as a standard (as was done in the case of the lowering of the temperature of maximum density), the molecular lowering of any salt should be calculable by adding to the hydrochloric acid value the values corresponding to the acidic and basic radicles. Unfortunately the values obtained for the acidic radicles varied considerably, so standard values cannot be given here.

An interesting point is the resemblance of the figures obtained for the lowering of the temperatures of maximum refractivity to those previously obtained for the lowering of the temperature of maximum density (Wright, J.C.S., <u>115</u>, 119).

Lowering of temp. of maximum <u>refractivity</u> of $\frac{N}{2}$ solutions.

	<u>Cl</u>	<u>Br</u>	<u>I</u>	<u>NO_3</u>
H	3·7	2·4	3·2	6·5
Li	3·5	3·3	4·9	6·3
Na	8·1	6·0	6·0	9·5
K	6·5	7·4	7·9	9·4
NH_4	4·9	4·1	5·2	7·4

Lowering of temp. of maximum <u>density</u> of $\frac{N}{2}$ solutions.

	<u>Cl</u>	<u>Br</u>	*<u>I</u>	*<u>NO_3</u>
H	2·6	3·7	(4·4)	(6·2)
Li	2·8	3·8	(4·6)	(6·2)
Na	6·2	7·4	(8·0)	(10·0)
K	5·5	6·5	(7·4)	(9·0)
NH_4	3·6	4·7	(5·4)	(7·2)

*These values are calculated from $\frac{N}{4}$ results.

Effect on temp. of maximum refractivity in $\frac{N}{2}$ solutions of replacement of hydrogen by a metal.

	Cl	Br	I	NO_3	Mean
Li	·2	·9	1·7	·2	·5
Na	4·4	3·6	2·8	3·0	3·5
K	2·8	5·0	4·7	2·9	3·9
NH_4	1·2	1·7	2·0	·9	1·5

Effect on temp. of maximum density in $\frac{N}{2}$ solutions of replacement of hydrogen by a metal.

	Cl	Br	I	NO_3	Mean
Li	·2	·1	·2	0	·1
Na	3·6	3·7	3·6	3·8	3·7
K	2·9	2·8	3·0	2·8	2·9
NH_4	1·0	1·0	1·0	1·0	1·0

Lowering of temp. of maximum refractivity of $\frac{N}{4}$ solutions.

	Cl	Br	I	NO_3
H	1·6	1·6	2·5	3·0
Li	1·9	2·1	3·1	2·5
Na	3·1	3·5	3·8	6·3
K	2·7	3·3	3·8	5·3
NH_4	2·8	2·2	2·4	4·7

Lowering of temp. of maximum density of $\frac{N}{4}$ solutions.

	Cl	Br	I	NO_3
H	1·3	1·8	2·2	3·1
Li	1·4	1·9	2·3	3·1
Na	3·1	3·7	4·0	5·0
K	2·8	3·2	3·7	4·5
NH_4	1·8	2·3	2·7	3·6

Effect on temp. of maximum refractivity in $\frac{N}{4}$ solutions caused by replacement of hydrogen by a metal.

	Cl	Br	I	NO_3	Mean
Li	·3	·5	·6	-·5	·2
Na	1·5	1·9	1·3	3·3	2·0
K	1·1	1·7	1·3	2·3	1·6
NH_4	1·2	·6	0·	1·7	·9

Effect on temp. of maximum density in $\frac{N}{4}$ solutions caused by replacement of hydrogen by a metal.

	Cl	Br	I	NO_3	Mean
Li	·1	·1	·1	0	·1
Na	1·8	1·9	1·8	1·9	1·9
K	1·5	1·4	1·5	1·4	1·5
NH_4	·5	·5	·5	·5	·5

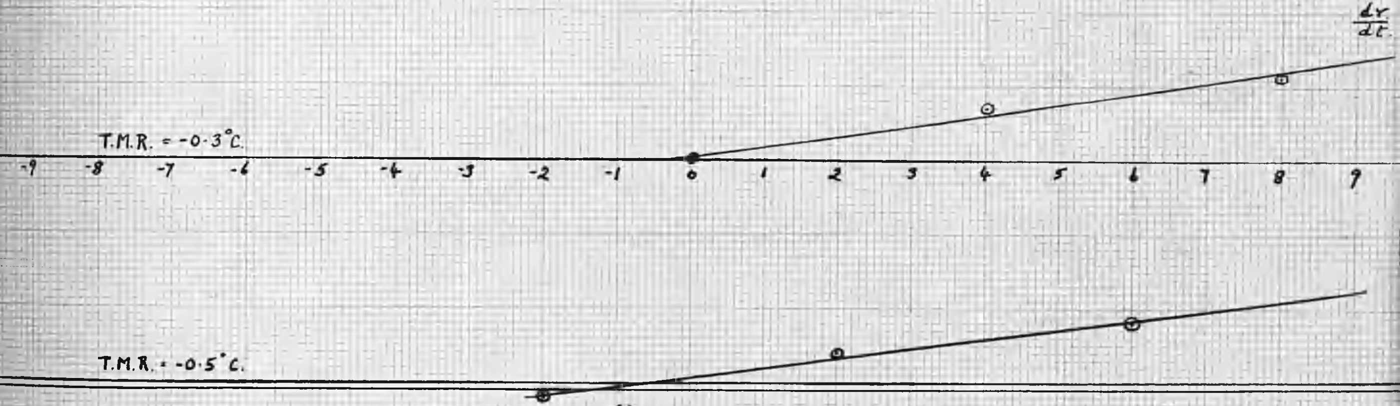
It can be seen that this is very close, and even more so if the average for each ion is taken across the series. This may be taken as a fair reading, as any inaccuracies should be approximately balanced and wiped out. The figures obtained in this way are very similar, which really shows that the lowering effect of any ion is similar for both the temperature of maximum density and the temperature of maximum refractivity.

CONCLUSION.

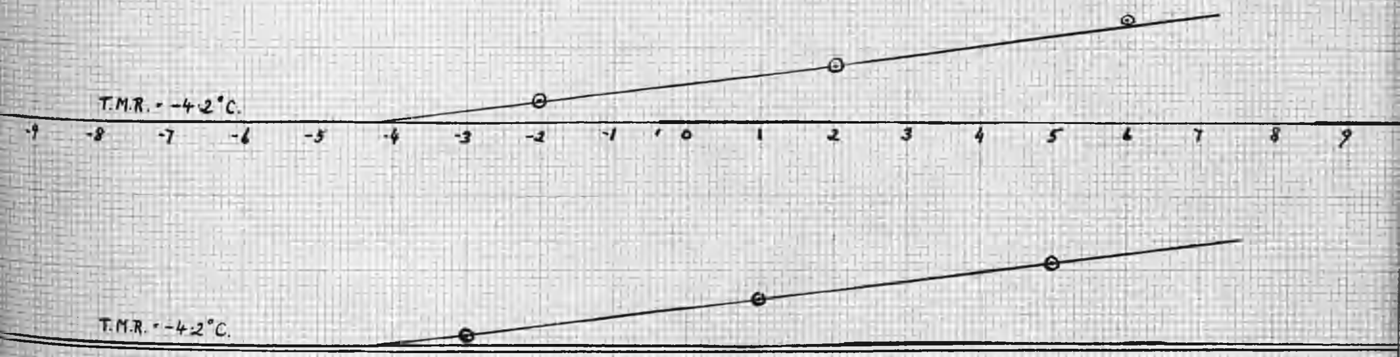
As a result of this study on refractivity we conclude that the temperature of maximum refractivity of water is lowered by the addition of solutes. This lowering is approximately proportional to the molecular concentration of the solute: certainly it increases with increasing concentration. As in the case of density, a greater lowering is found in solutions which show a high temperature coefficient. A definite lowering value can also be attributed to each ion, and these values are found to be very similar to those already obtained for the lowering of the temperature of maximum density.

Temperature Coefficient of Refractivity.

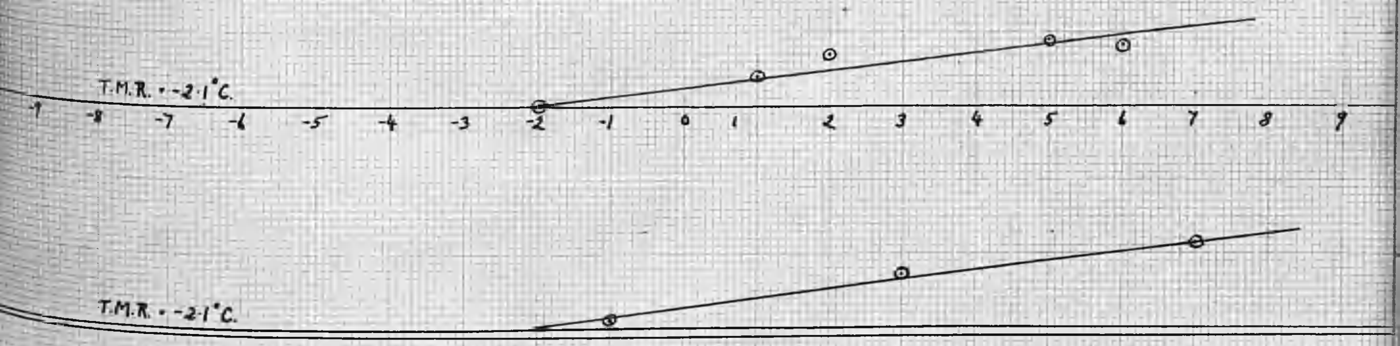
Water



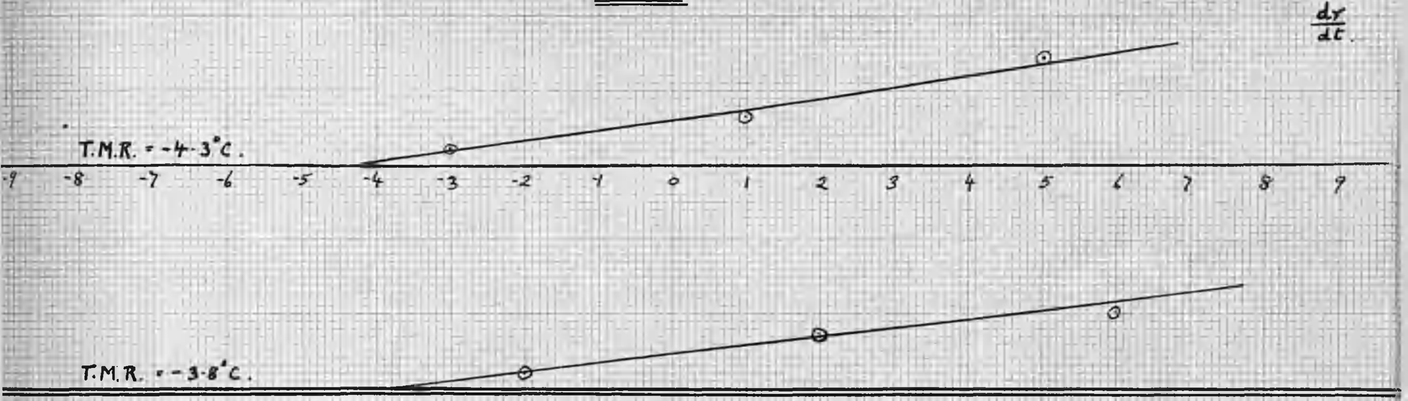
$\frac{N}{2}$ HCl.



$\frac{N}{4}$ HCl.



$\frac{N}{2}$ LiCl.



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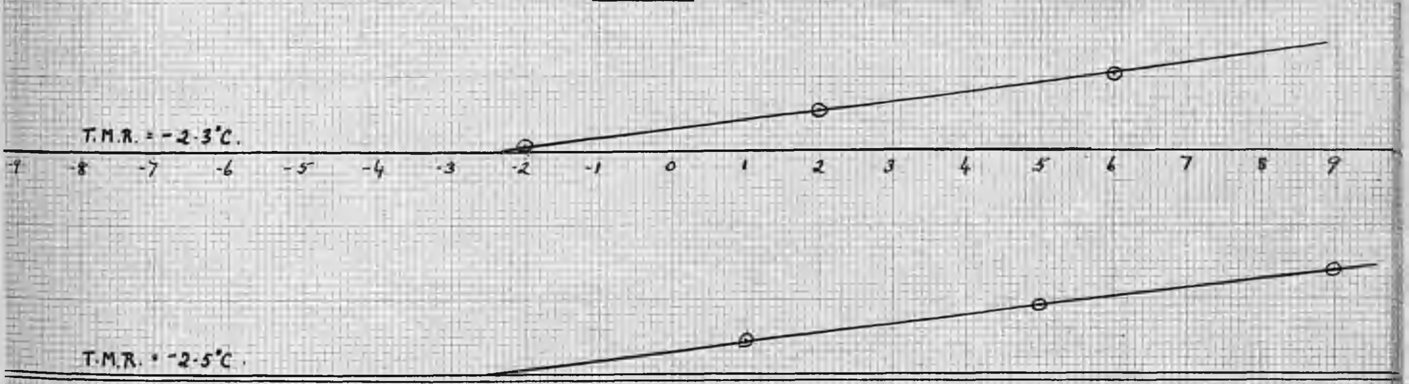

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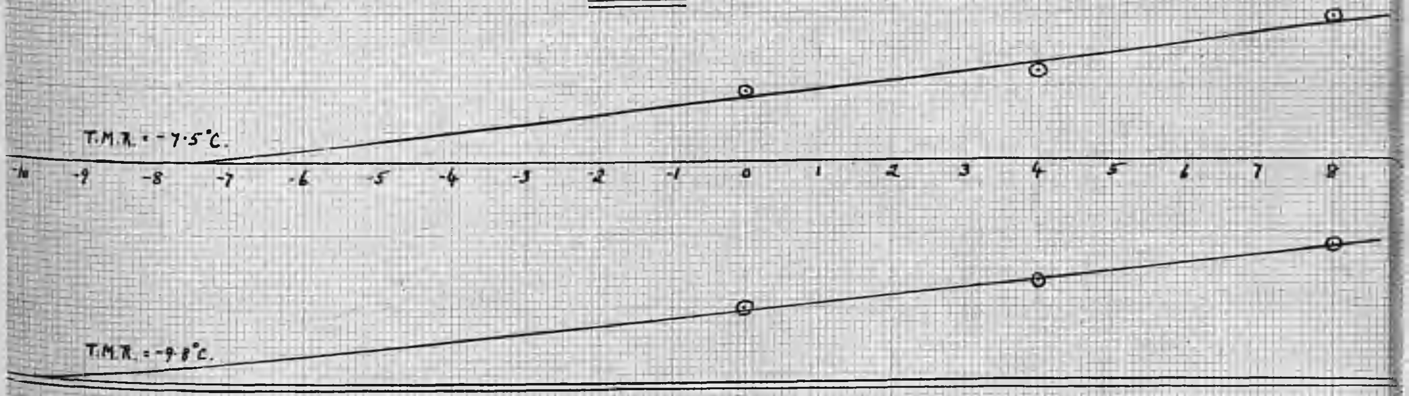

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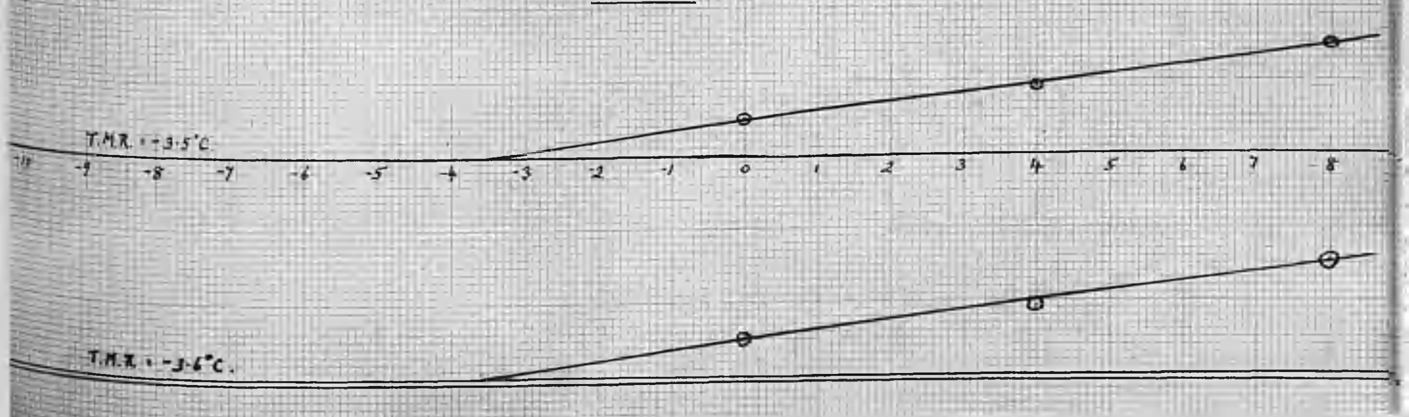

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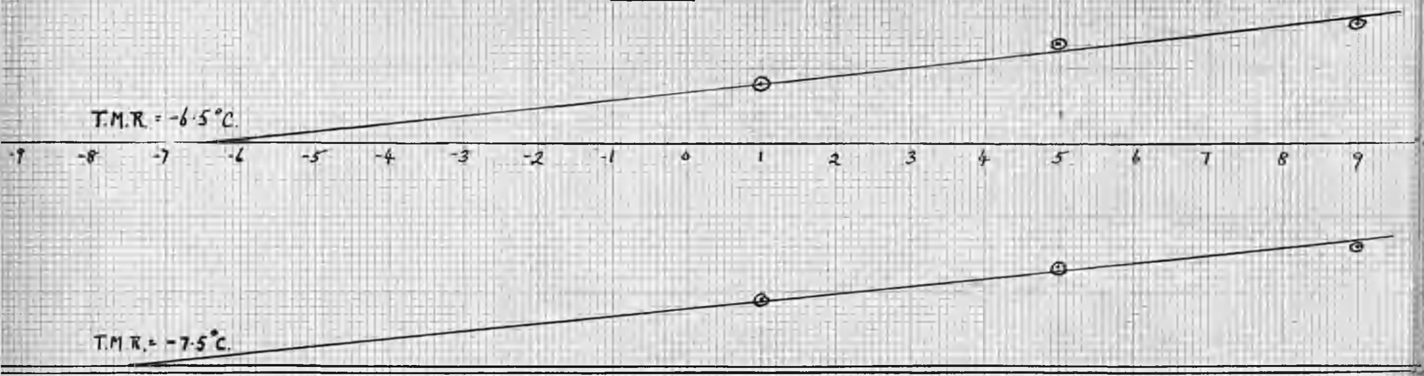

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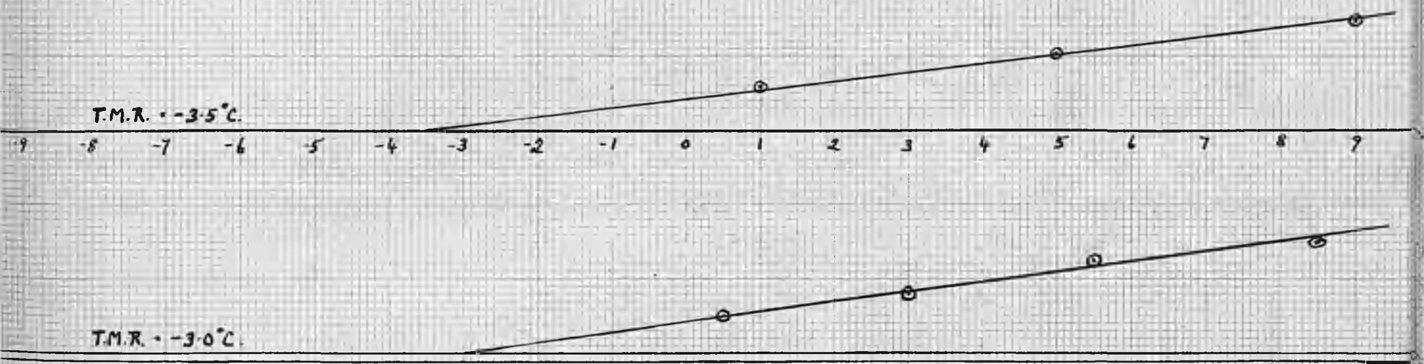

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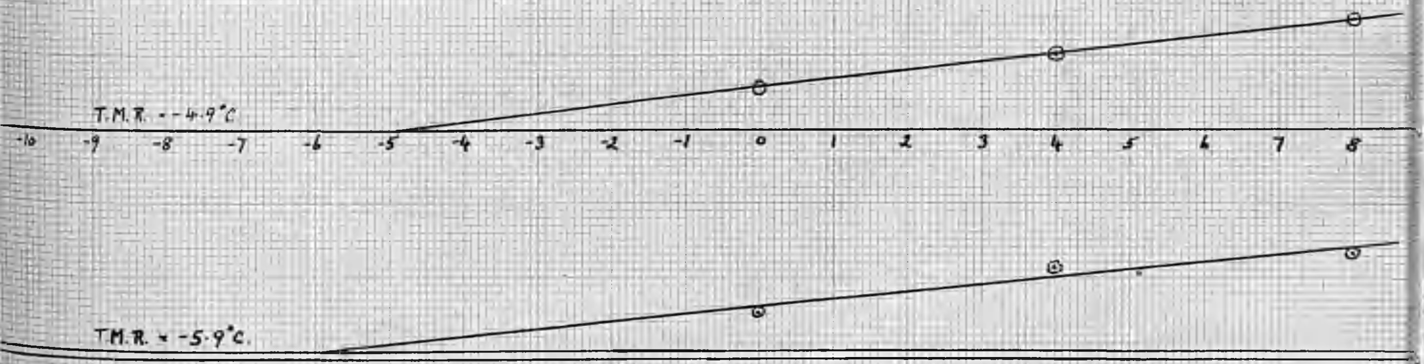

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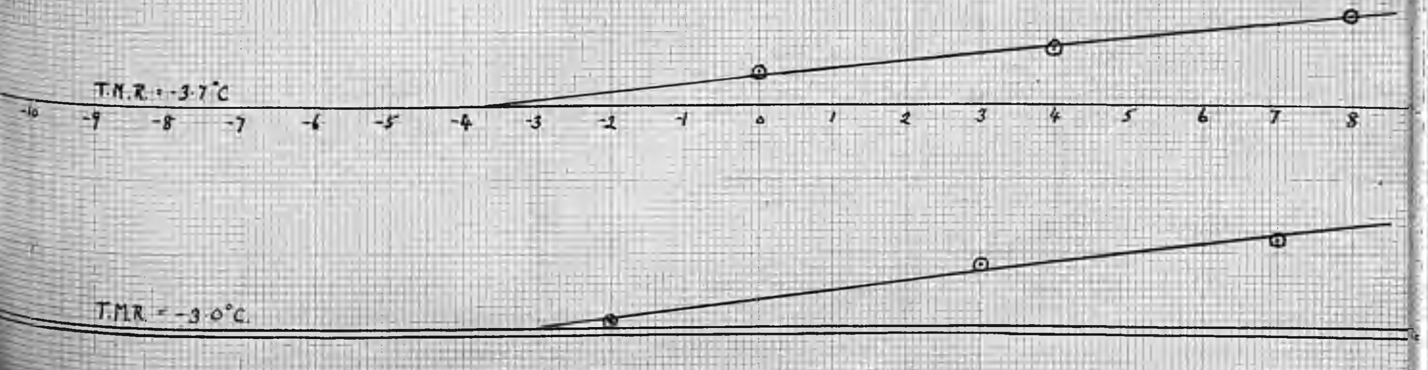
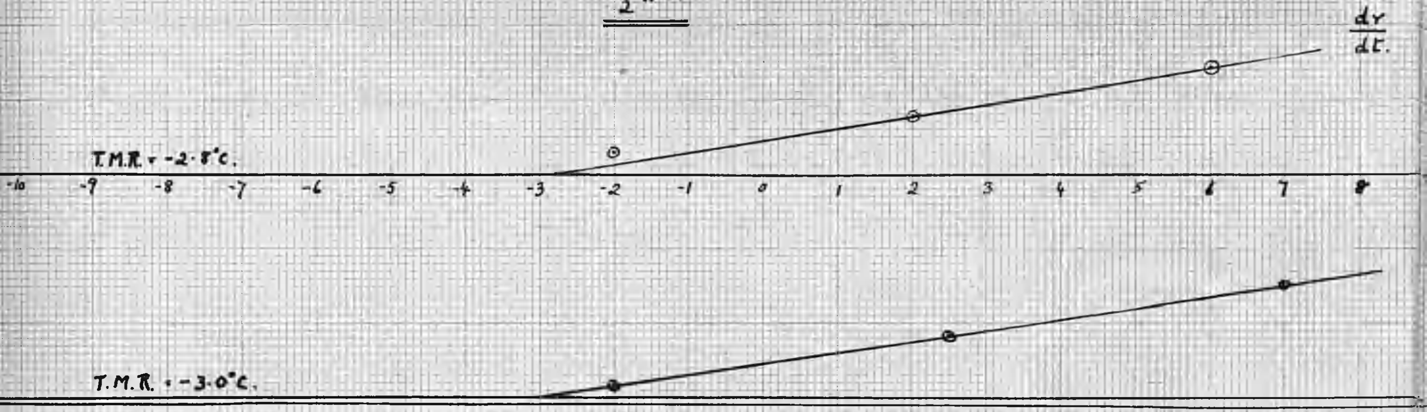
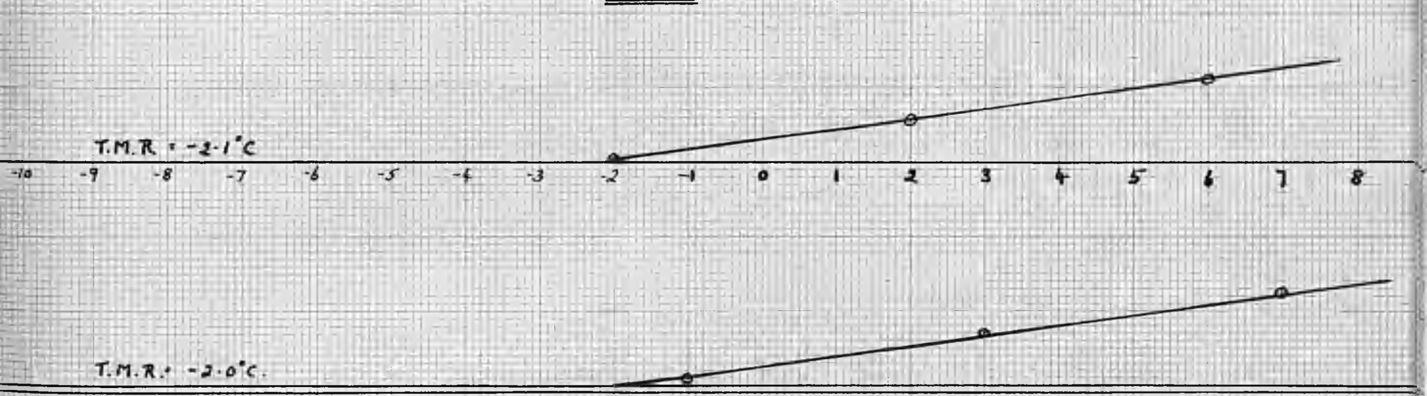


$\frac{N}{2}$ HBr



$\frac{N}{4}$ HBr.



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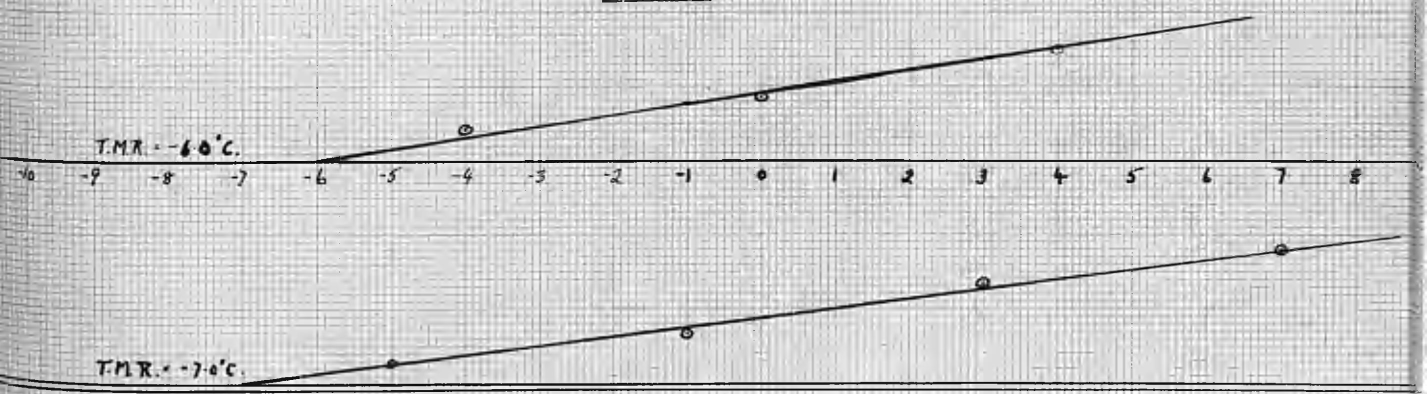

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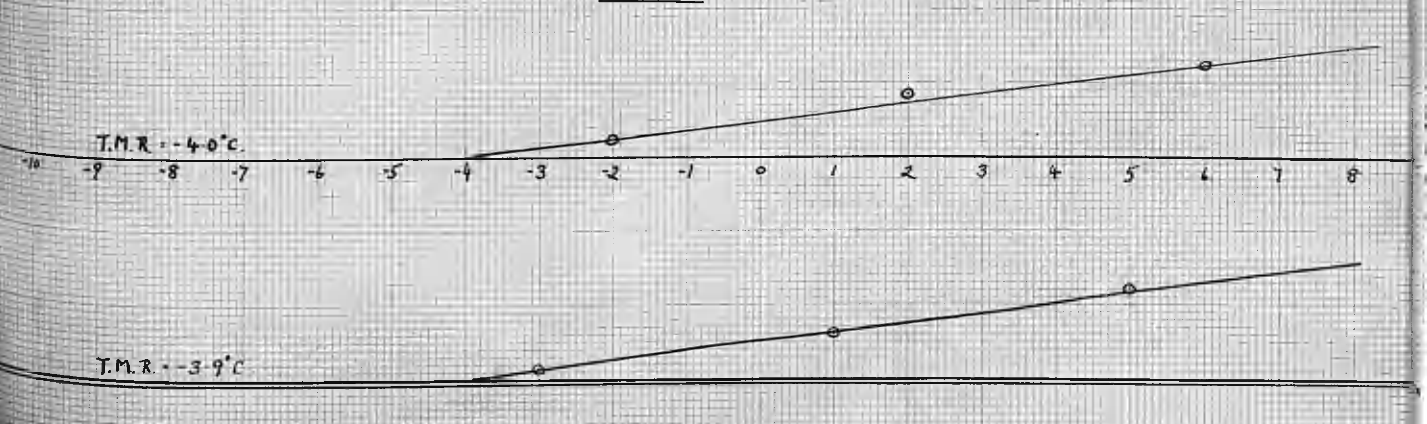
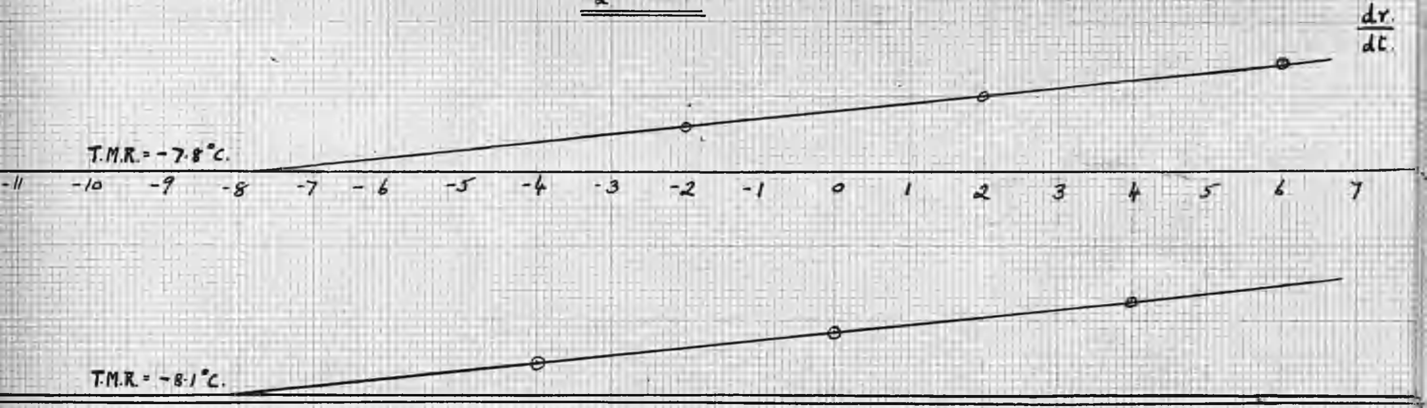


$\frac{N}{2}$ K.Br.



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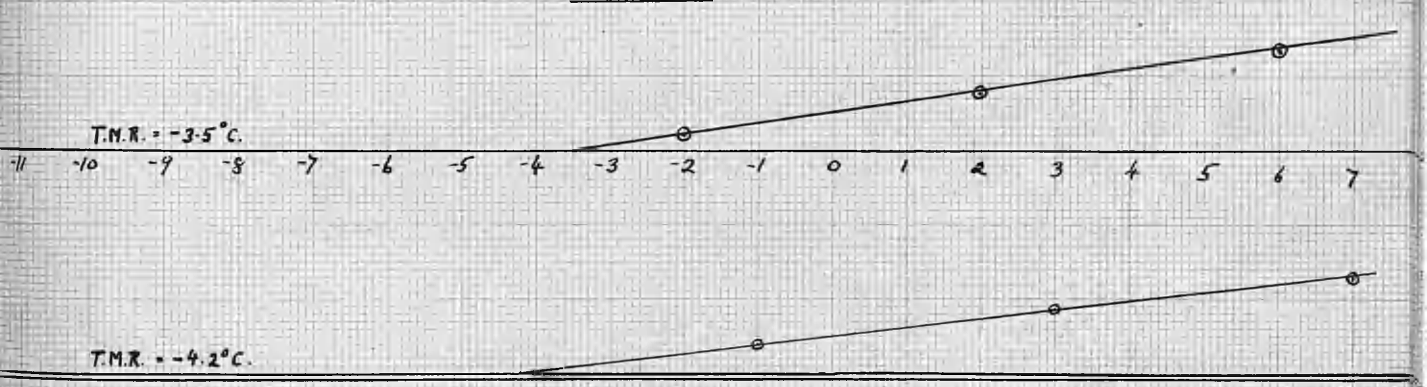
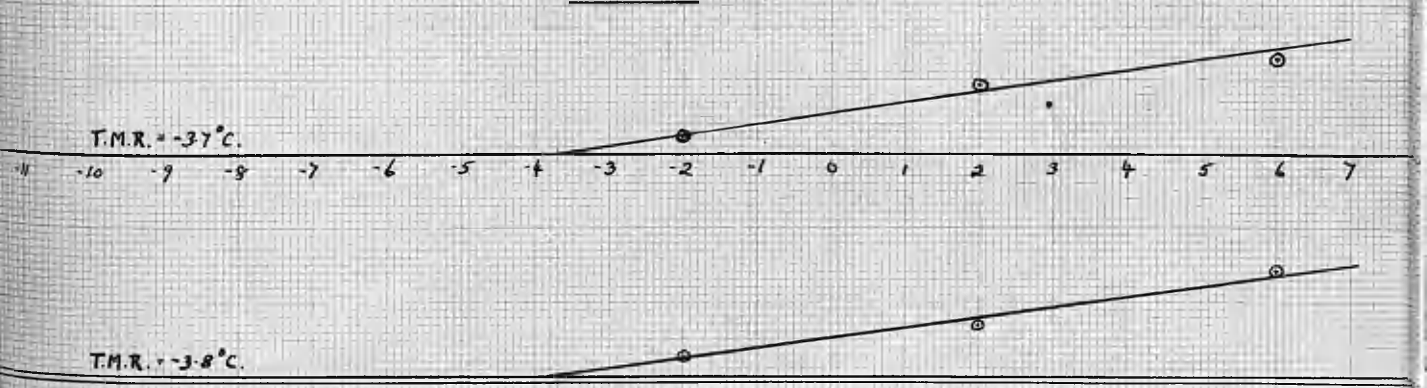
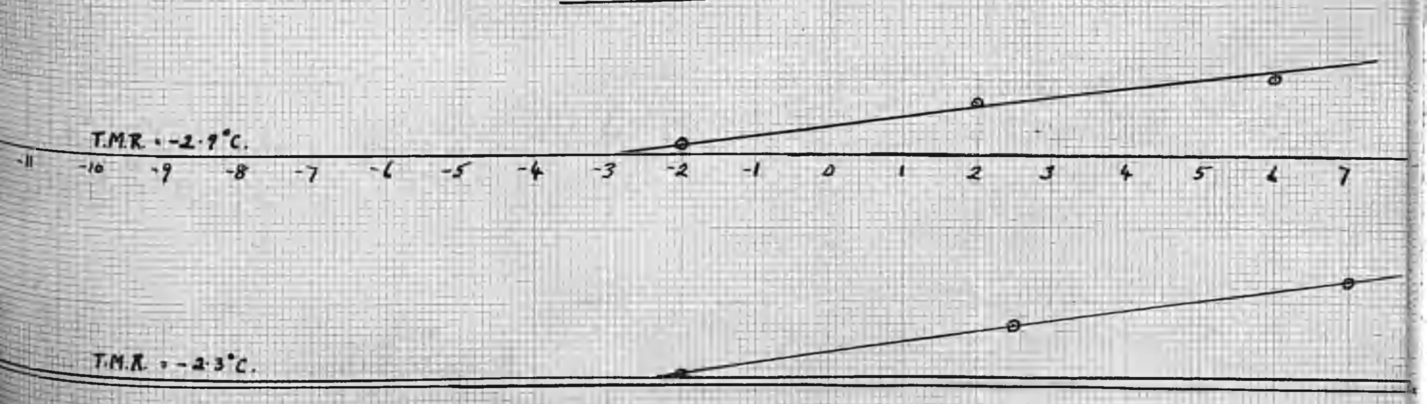


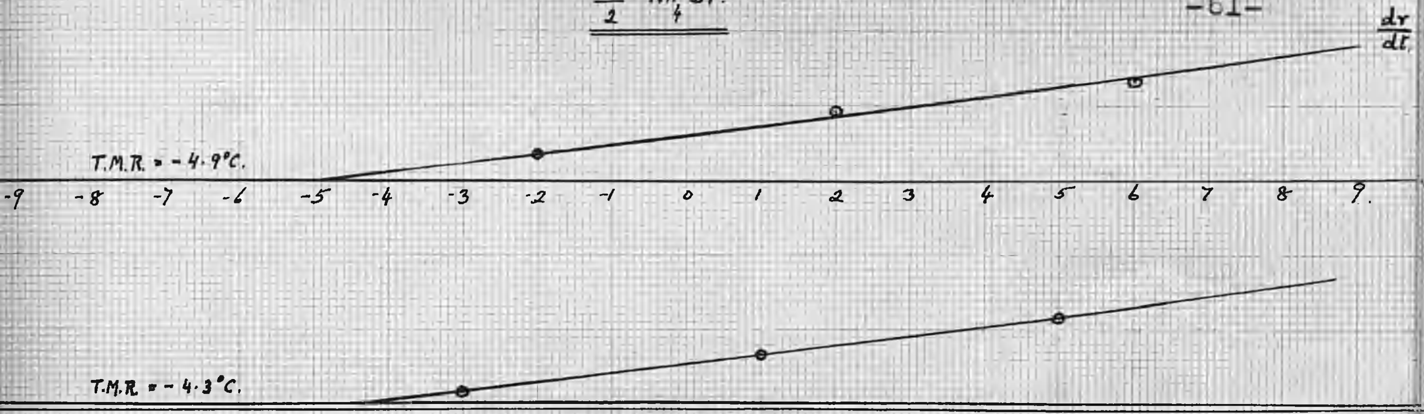
$\frac{N}{2}$ Li Br.



$\frac{N}{4}$ Li Br.



$\frac{N}{2}$ NH_4Br.



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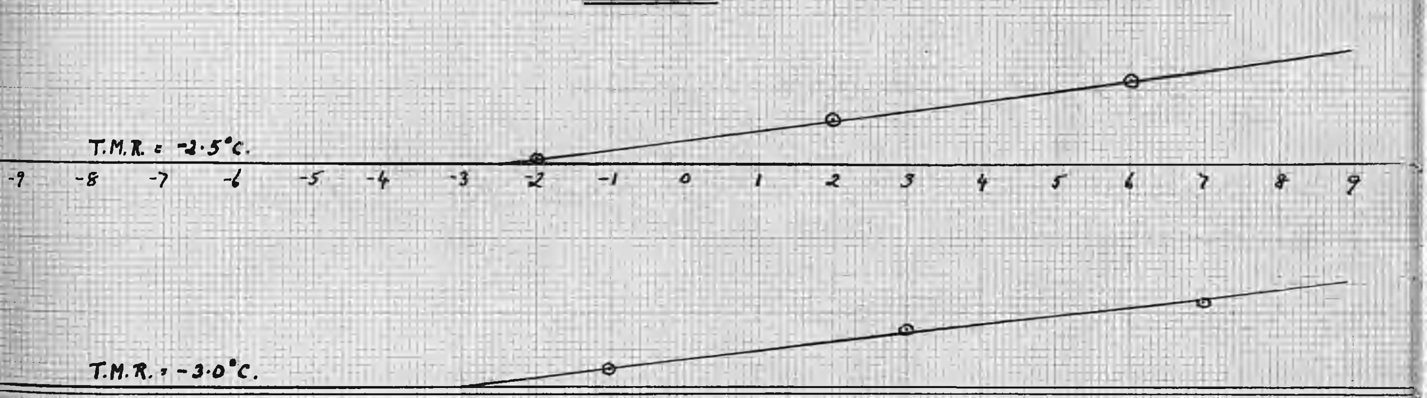
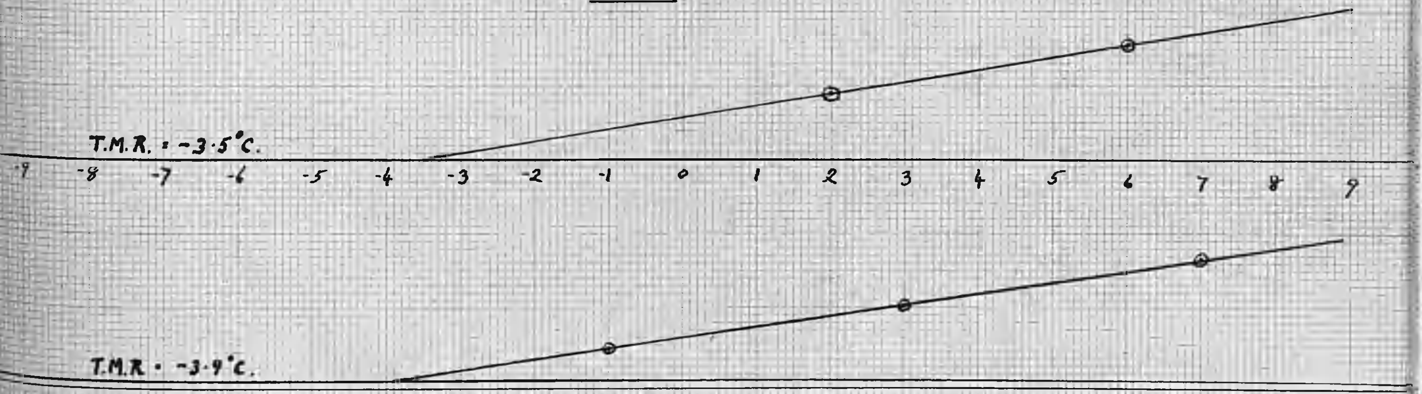
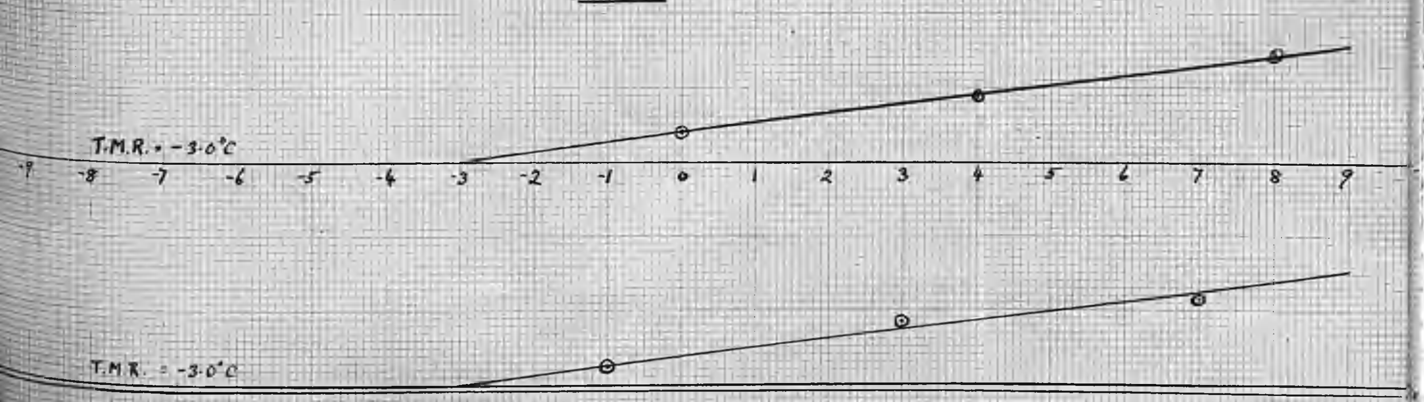


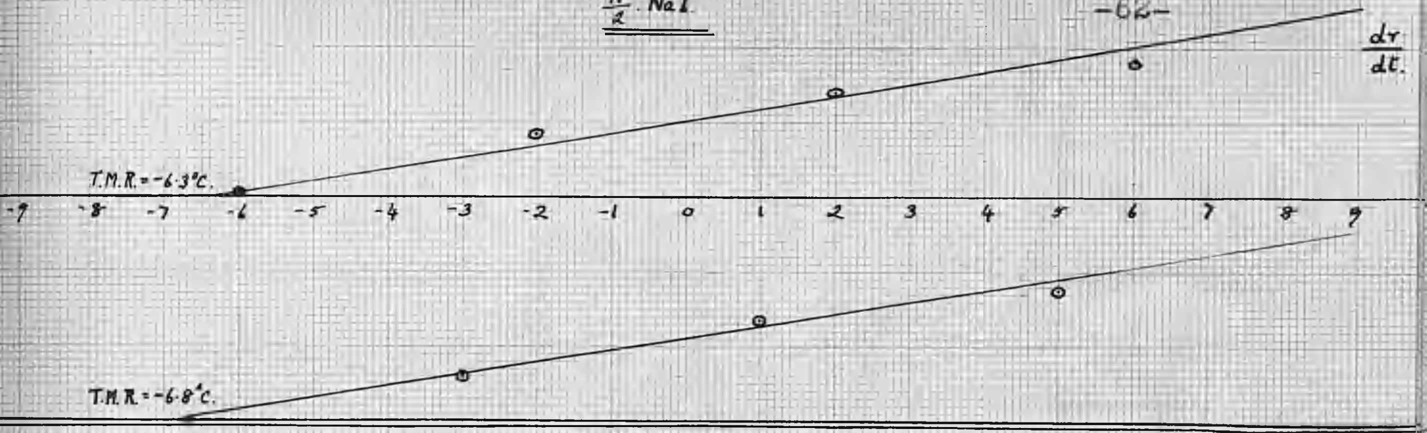
$\frac{N}{2}$ HI.



$\frac{N}{4}$ HI



$\frac{N}{2}$. NaI



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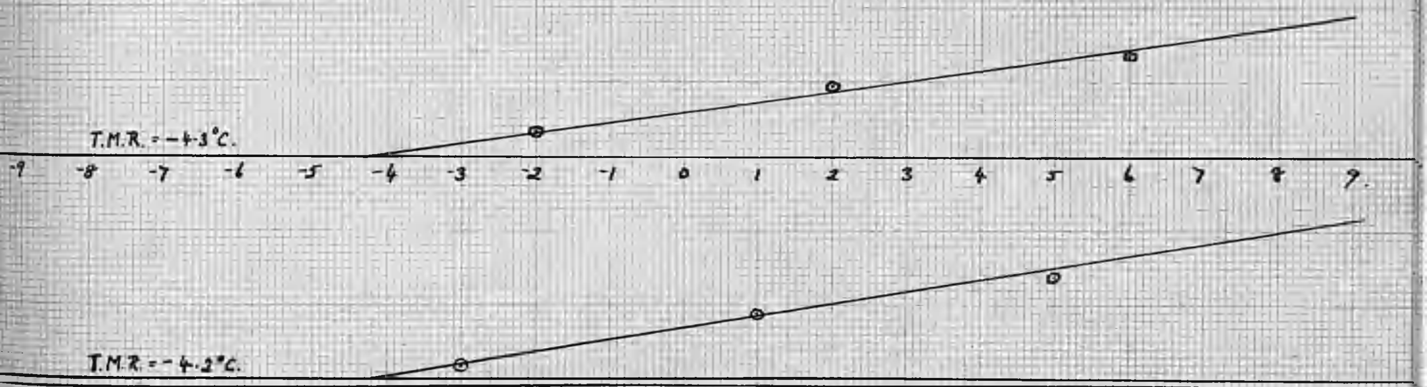

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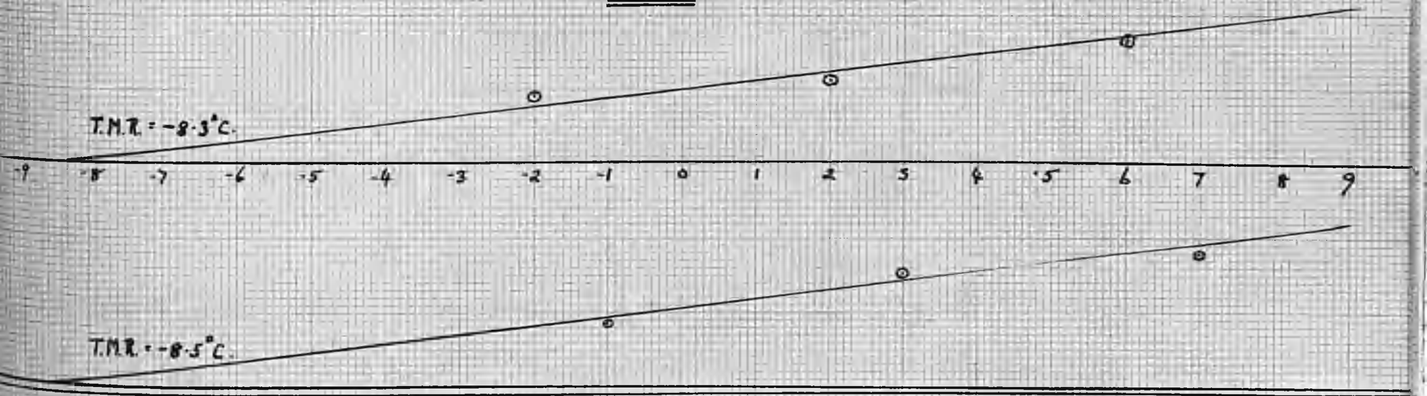

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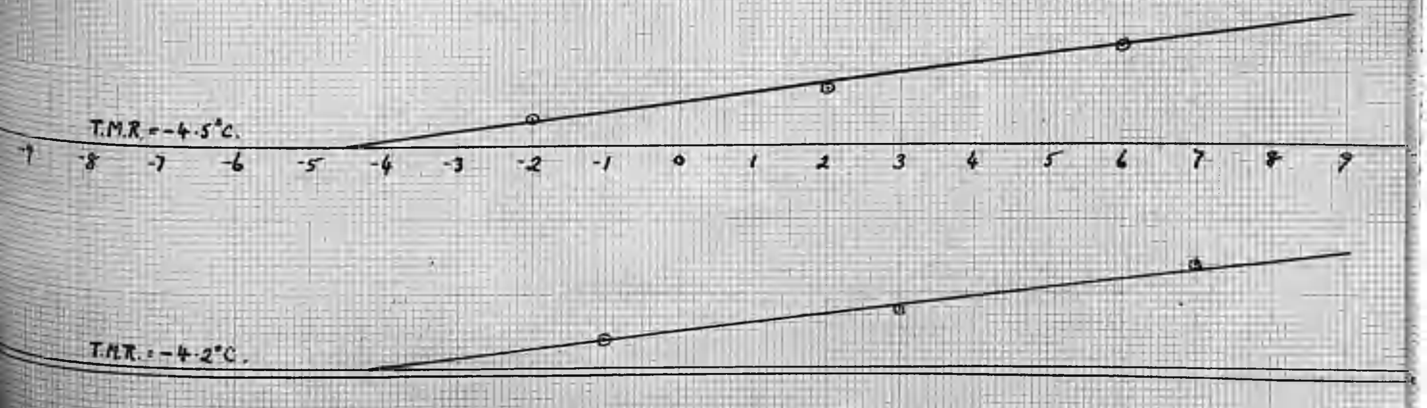

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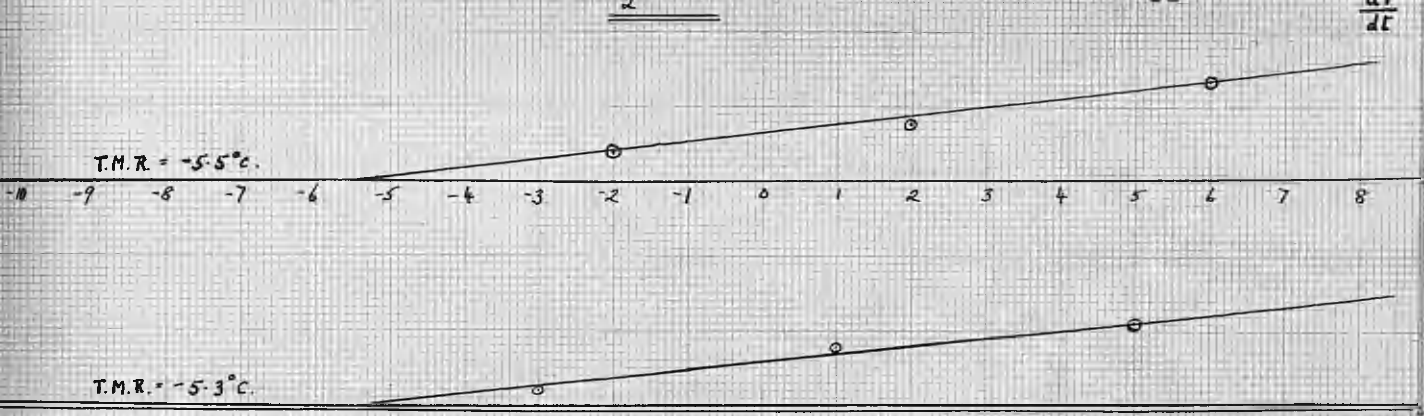

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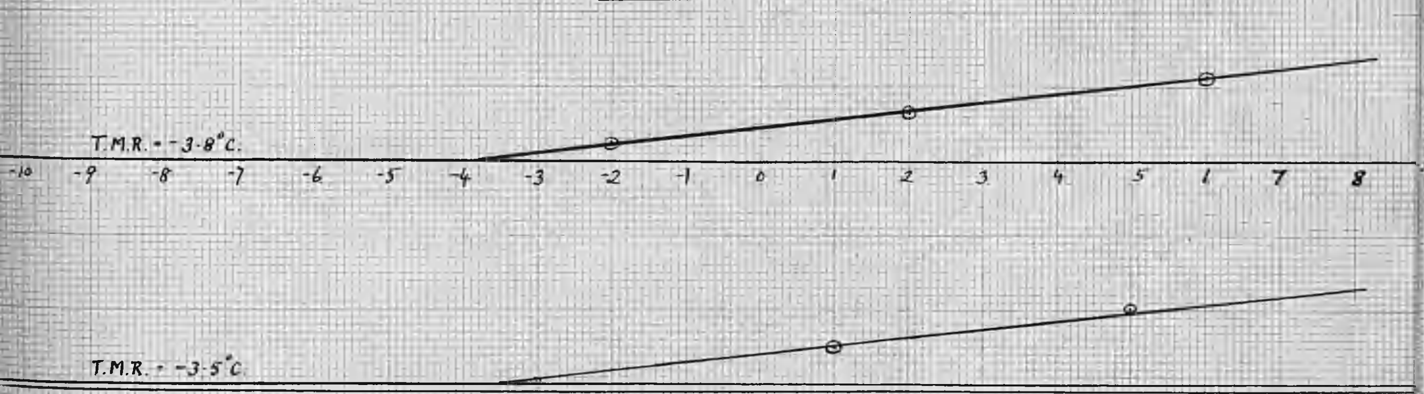
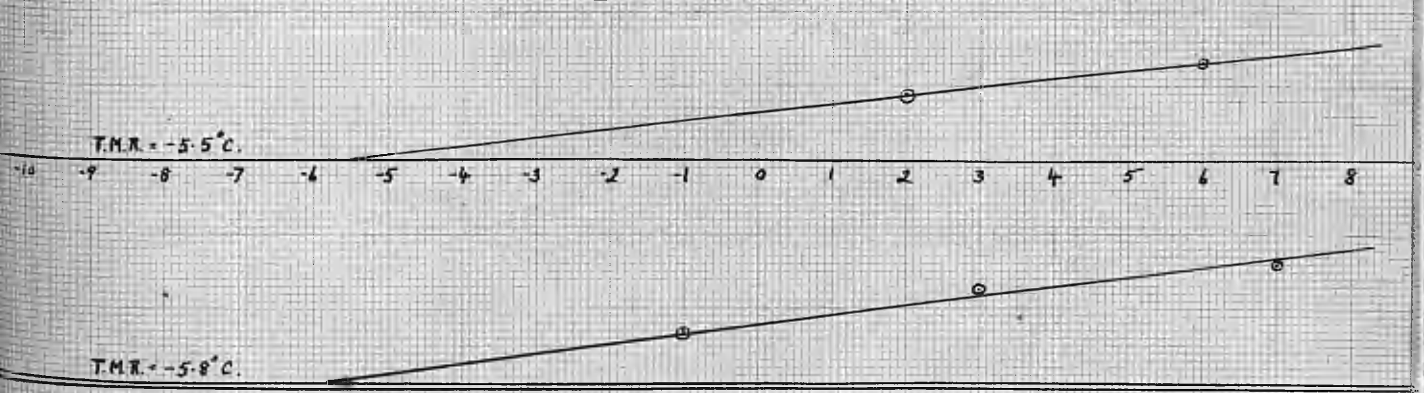


$\frac{N}{2}$ NH_4I.



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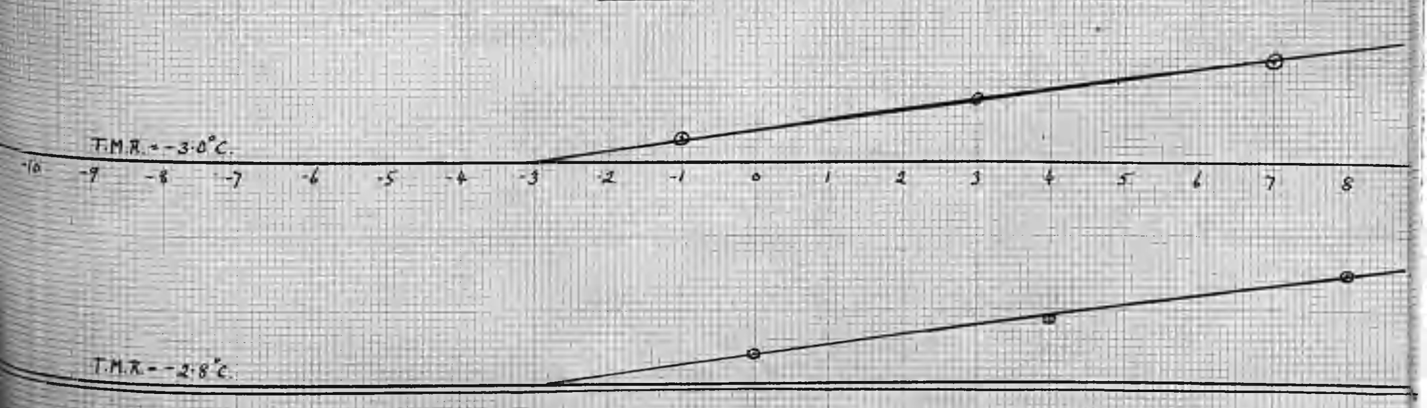
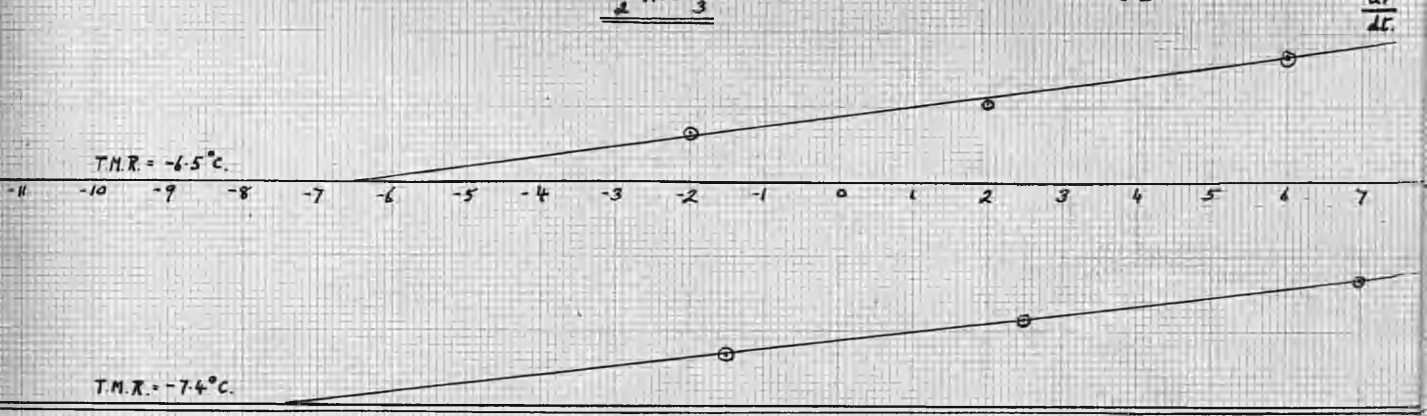
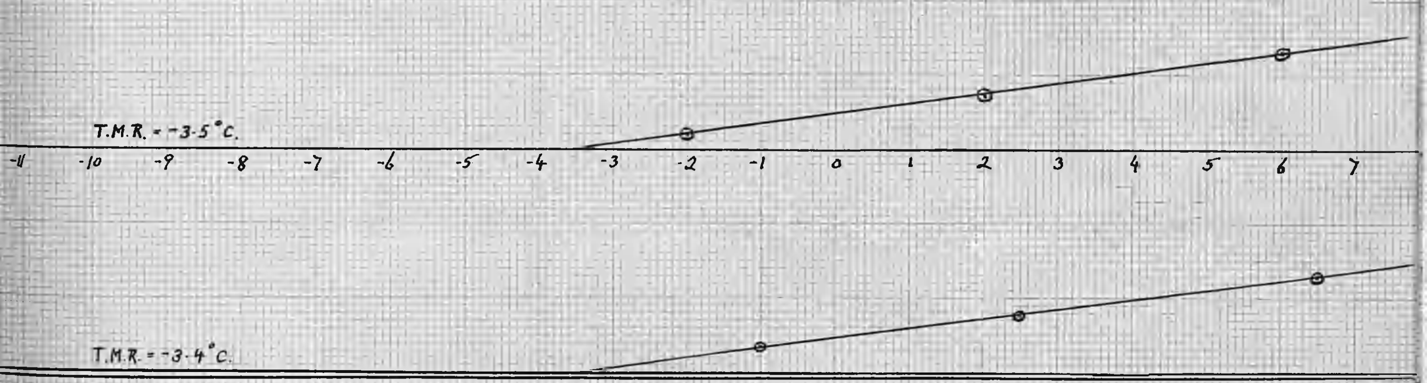


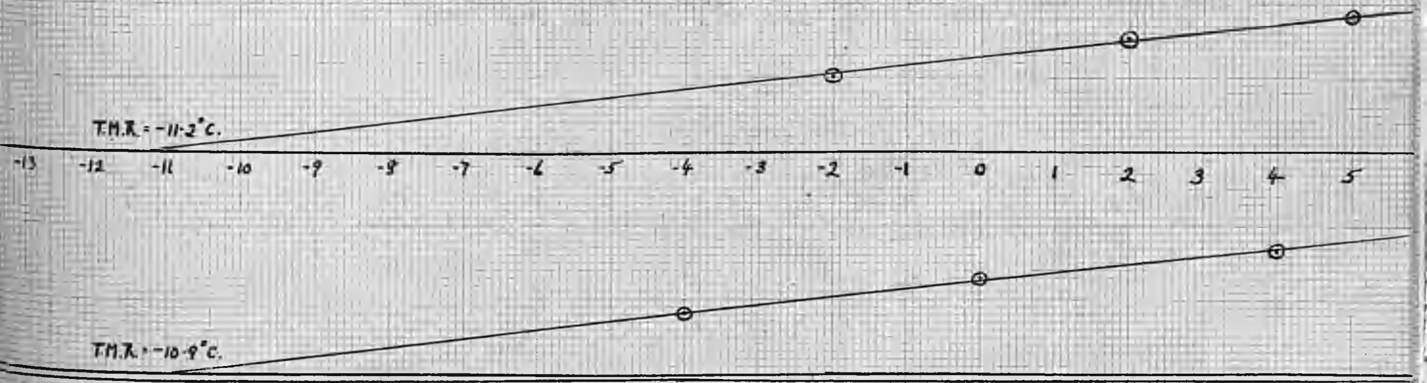
$\frac{N}{2}$ HNO_3



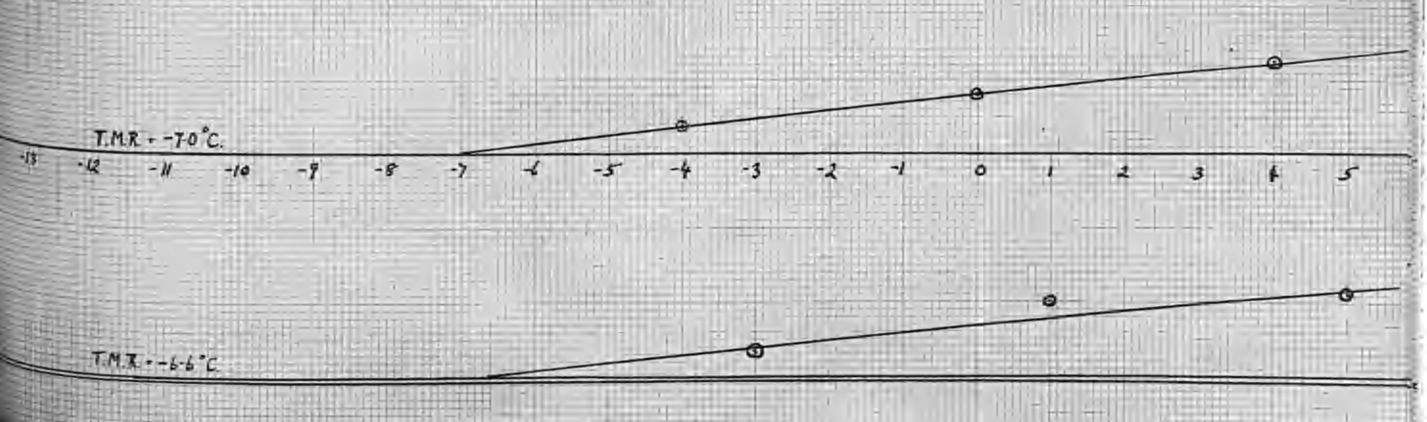
$\frac{N}{4}$ HNO_3



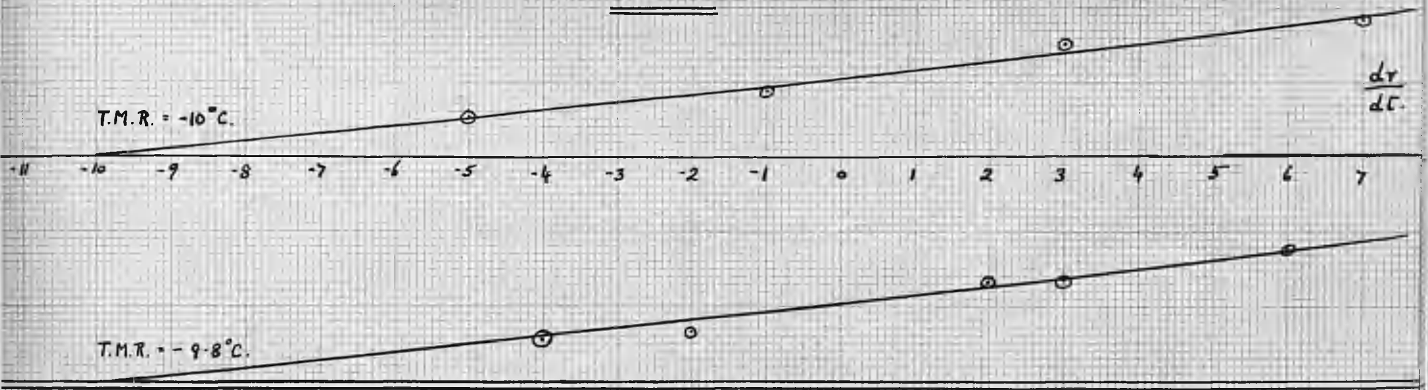
$\frac{N}{2}$ $NaNO_3$.



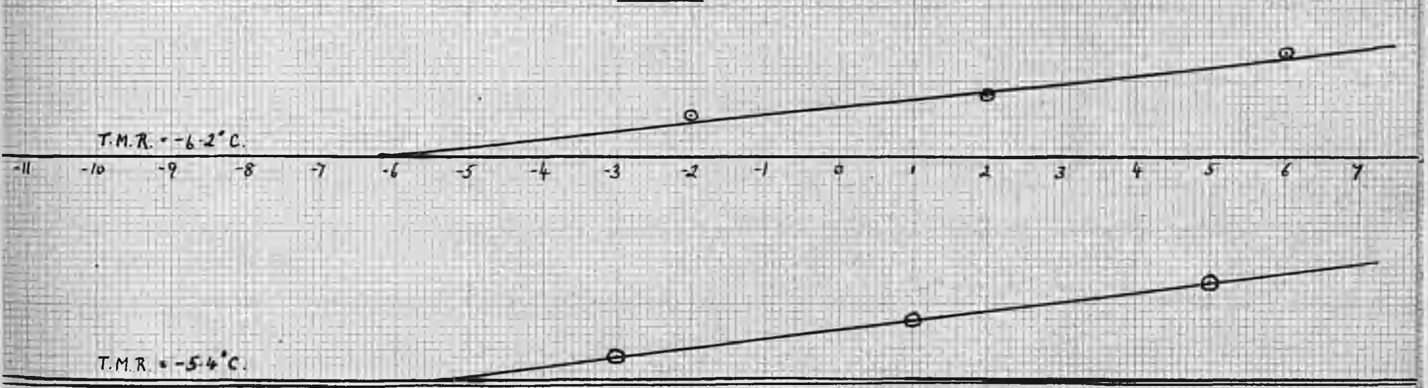
$\frac{N}{4}$ $NaNO_3$.



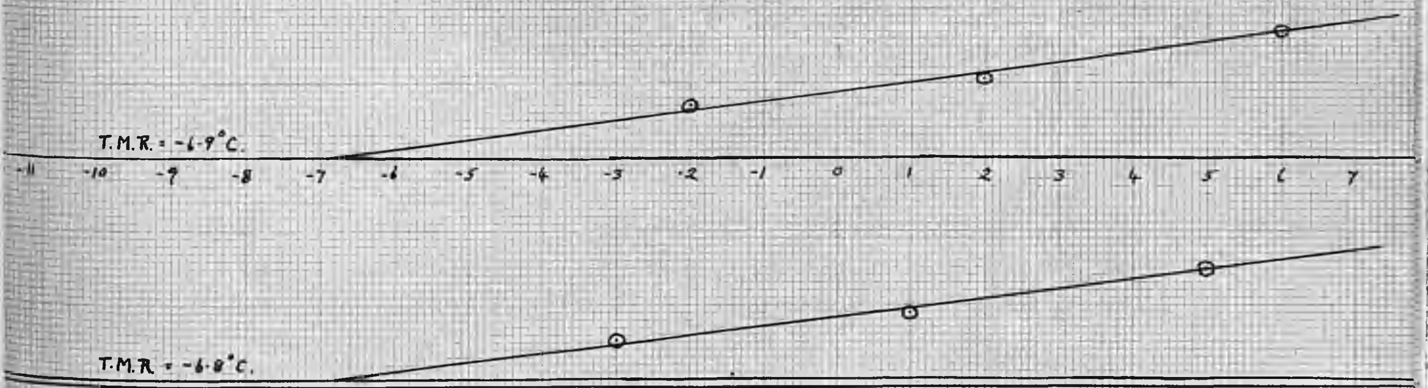
$\frac{N}{2}$ KNO_3



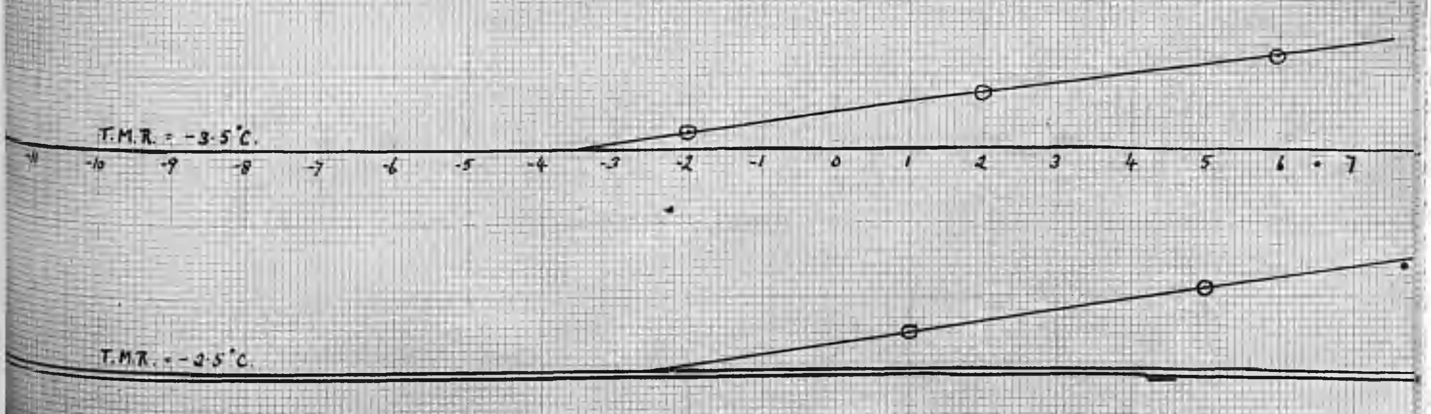
$\frac{N}{4}$ KNO_3



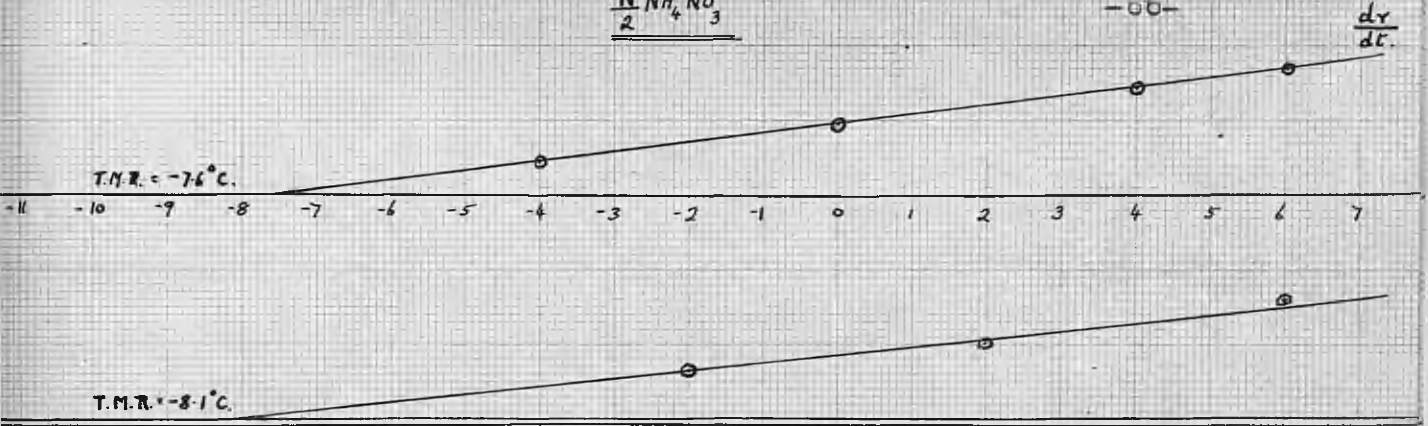
$\frac{N}{2}$ $LiNO_3$



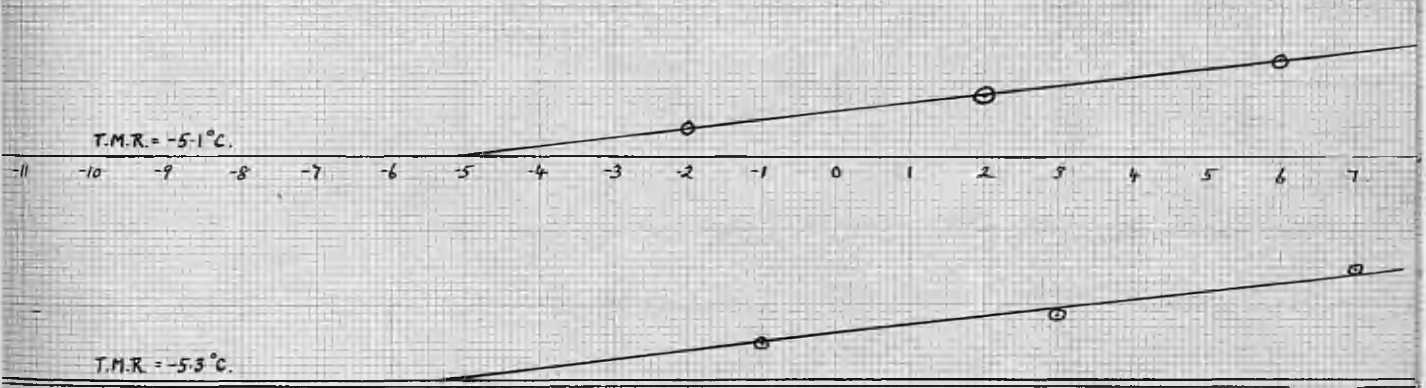
$\frac{N}{4}$ $LiNO_3$



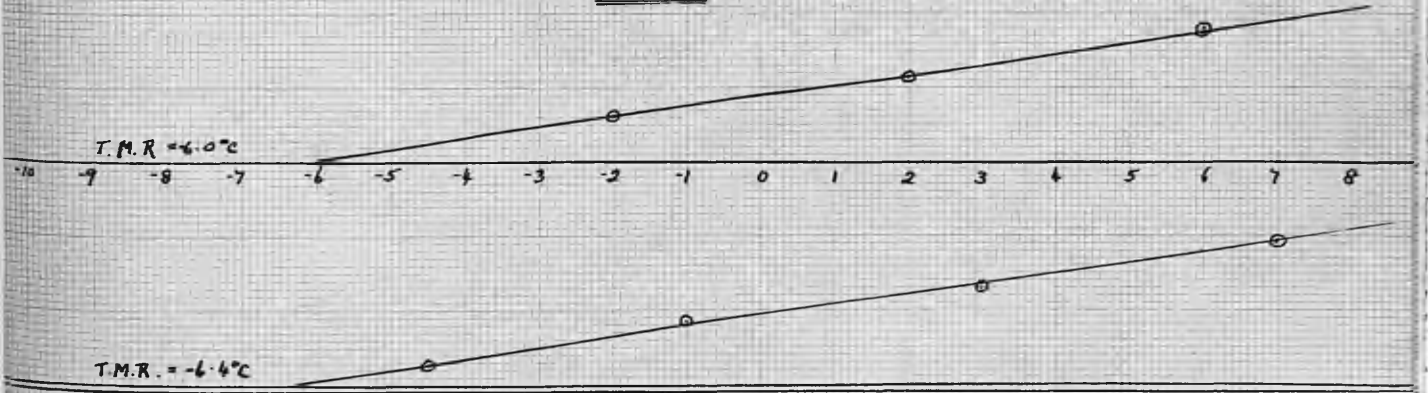
$\frac{N}{2}\ NH_4NO_3$



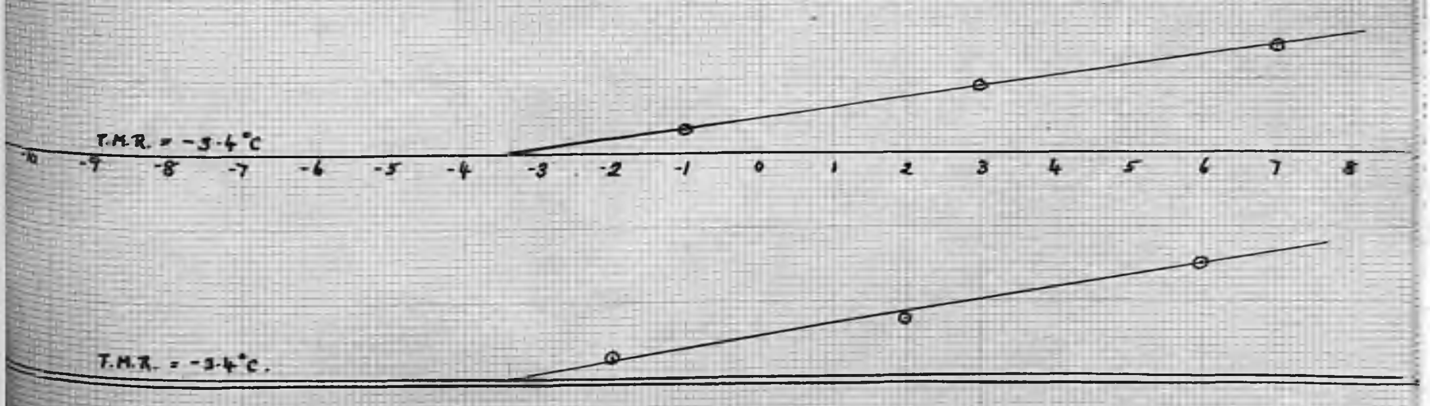
$\frac{N}{4}\ NH_4NO_3$



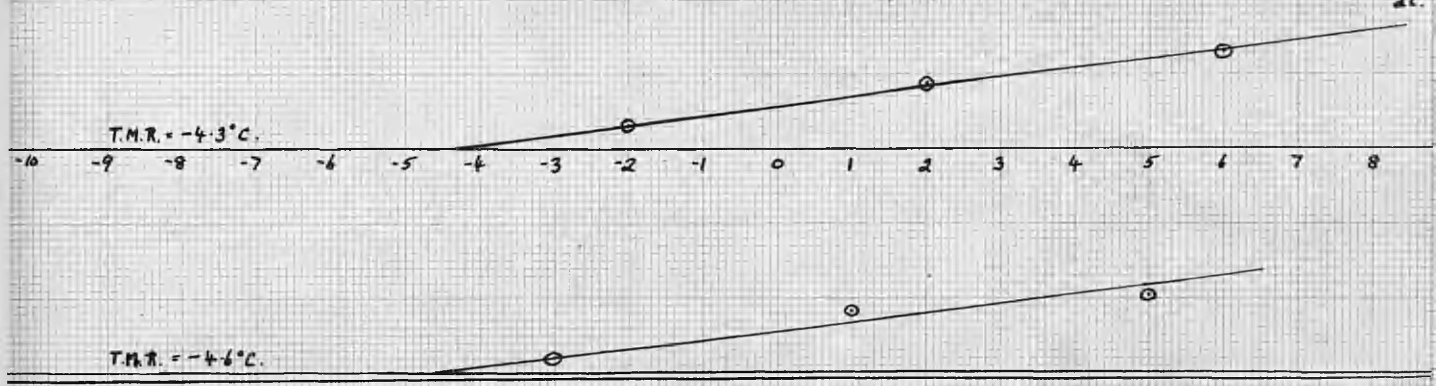
$\frac{N}{2}\ H_2SO_4$



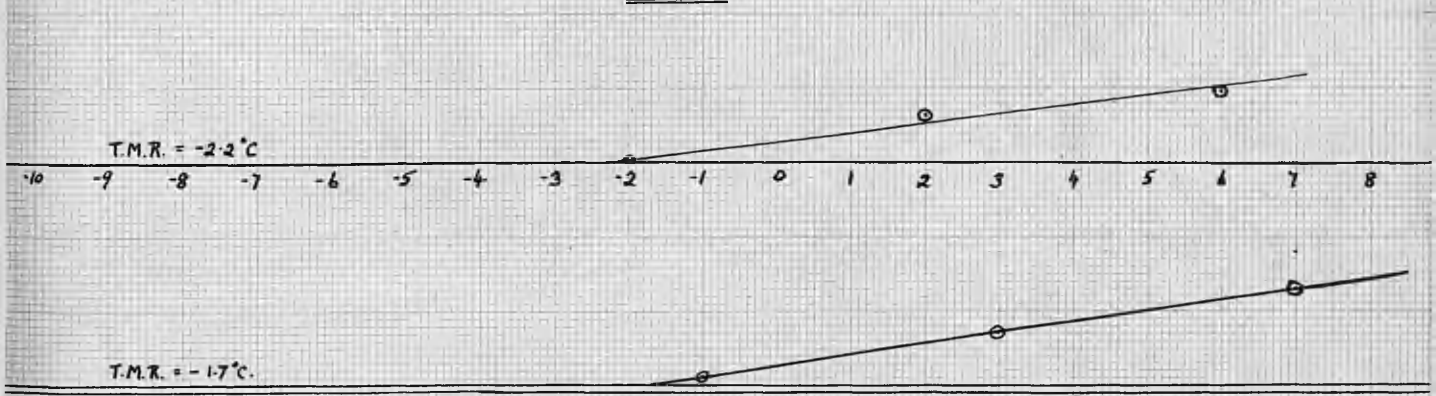
$\frac{N}{4}\ H_2SO_4$



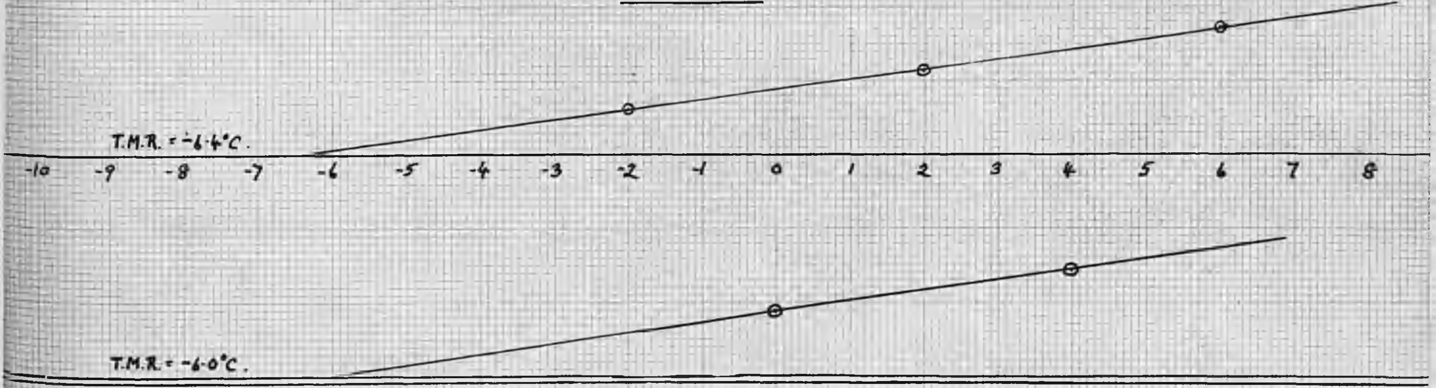
$\frac{N}{2}$ H.COOH



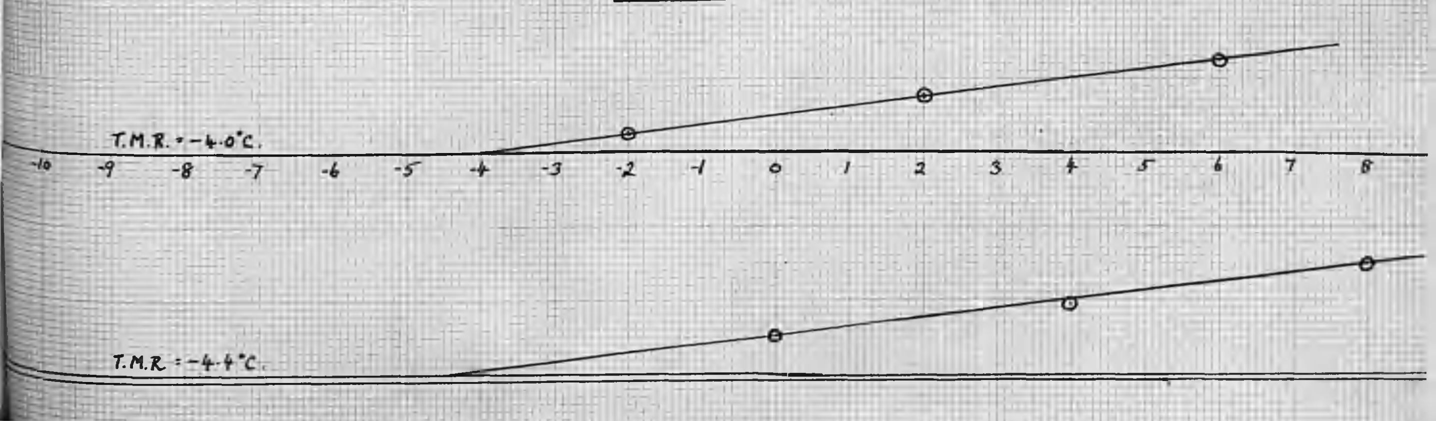
$\frac{N}{4}$ H.COOH.



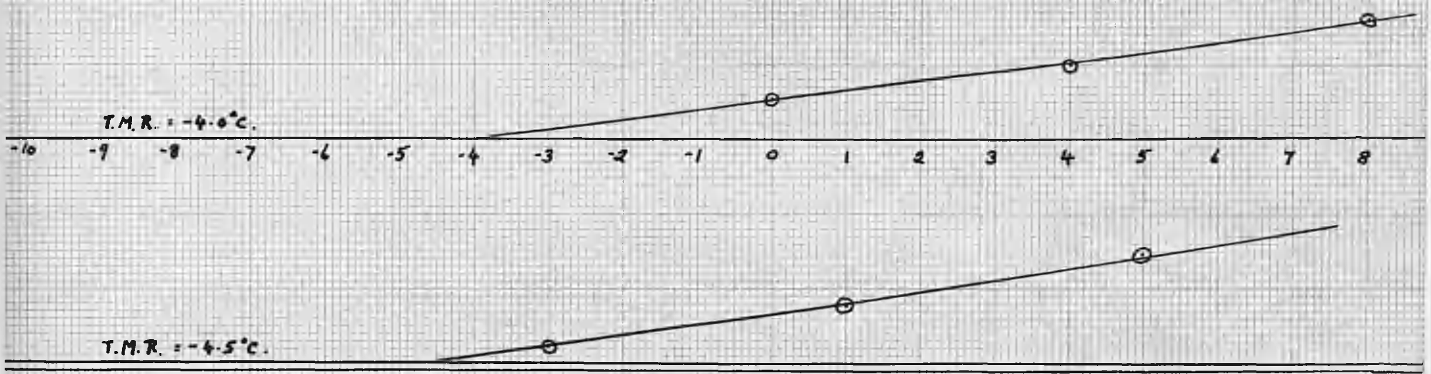
$\frac{N}{2}$ H.COONa.



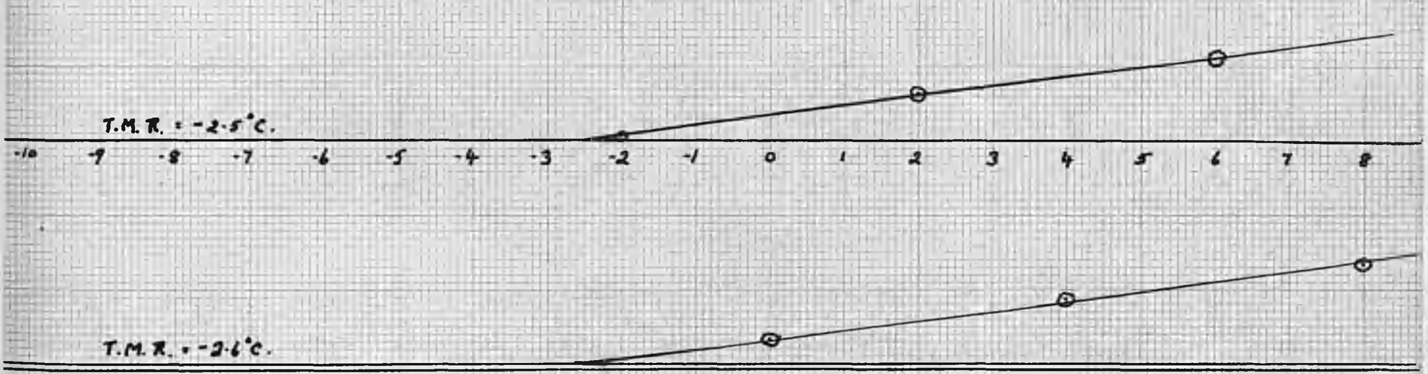
$\frac{N}{4}$ H.COONa.



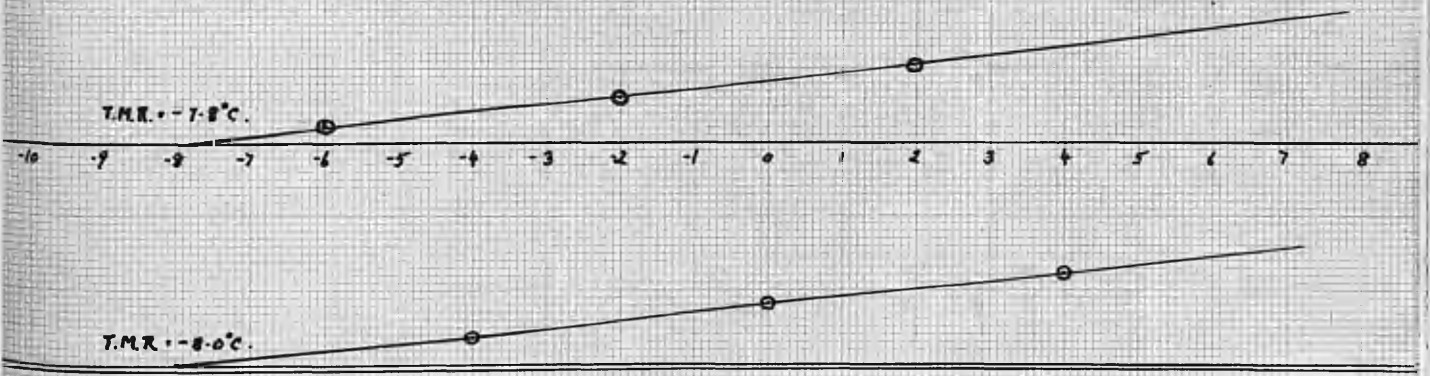
$\frac{N}{2}$ CH_3COOH



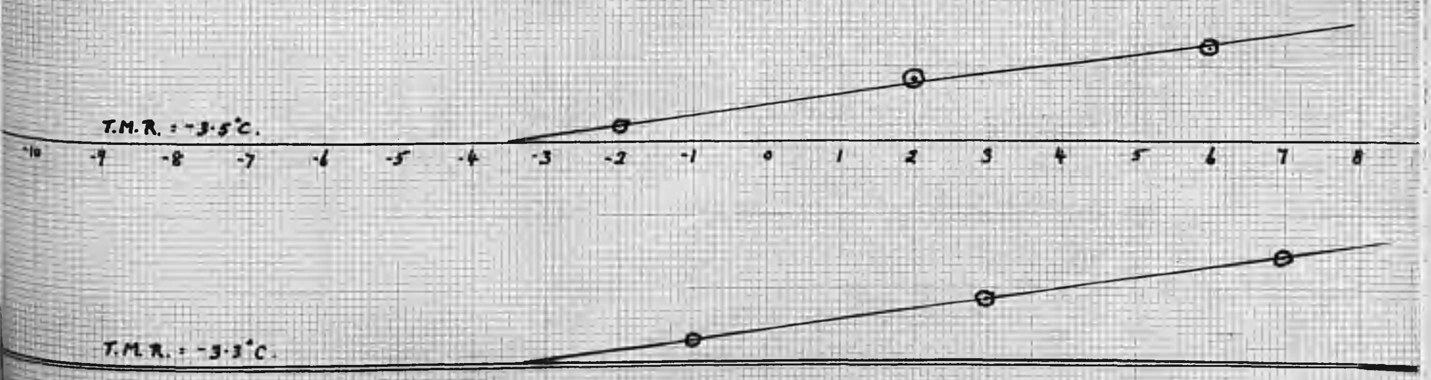
$\frac{N}{4}$ CH_3COOH.



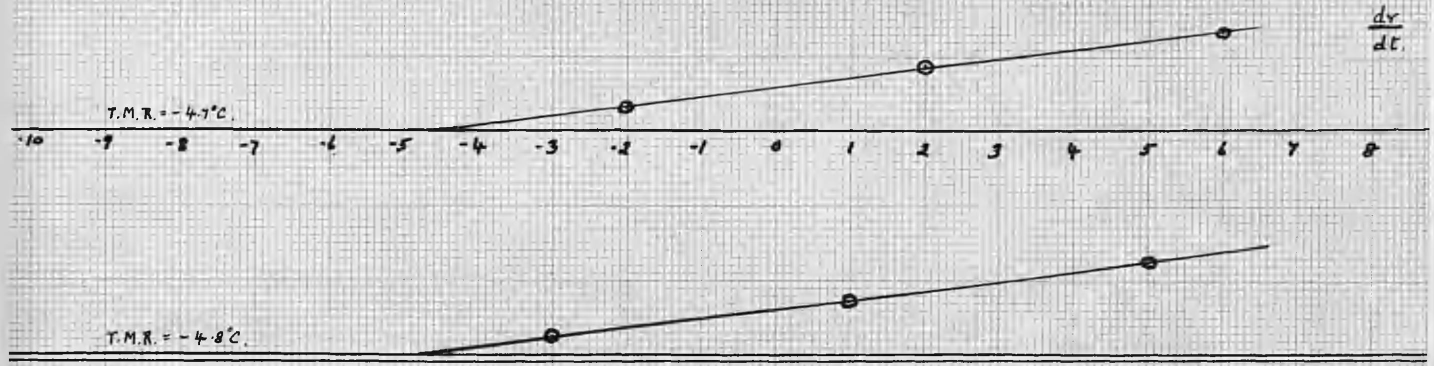
$\frac{N}{2}$ CH_3COONa.



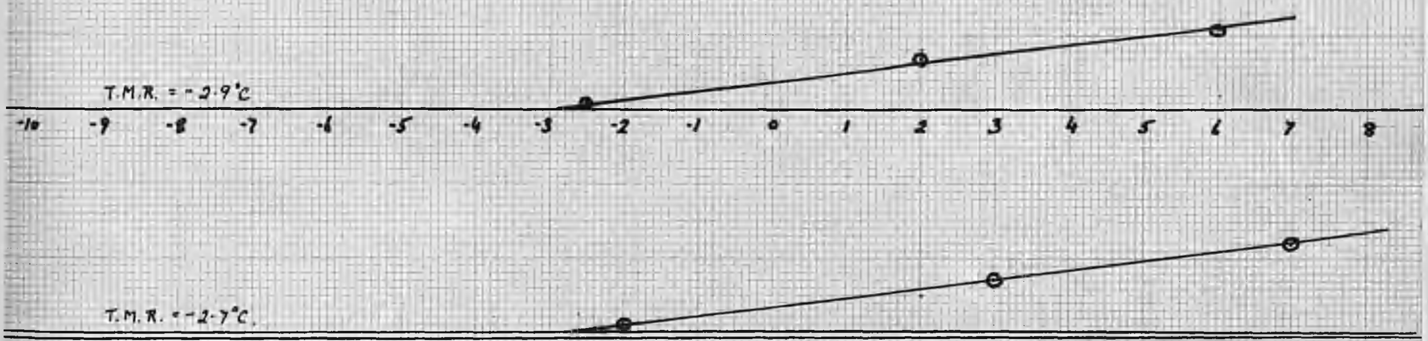
$\frac{N}{4}$ CH_3COONa



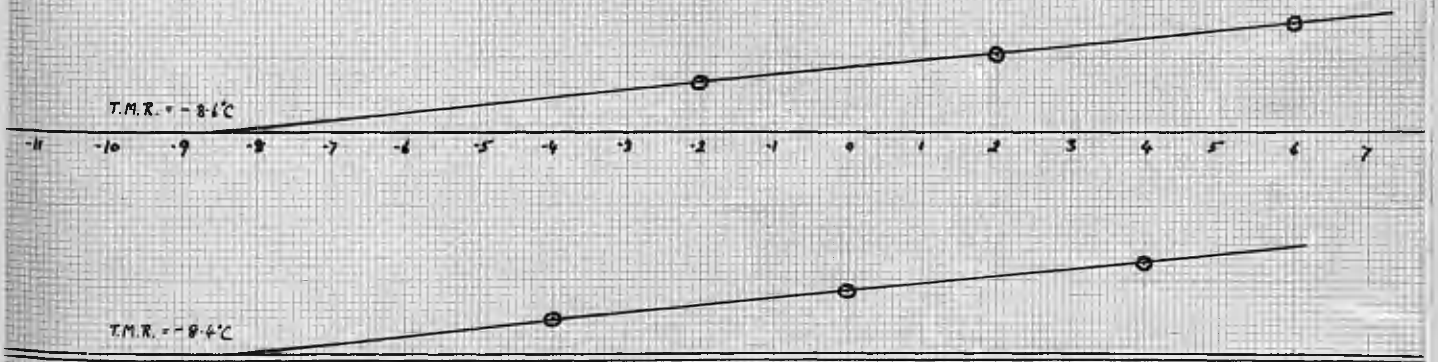
$\frac{N}{2}\,C_2H_5COOH$.



$\frac{N}{4}\,C_2H_5COOH$



$\frac{N}{2}\,C_2H_5COONa$.



$\frac{N}{4}\,C_2H_5COONa$.