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A STUDY OF SATURATED SOLUTIONS

of

POTASSIUM NITRATE AND SILVER NITRATE

By

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A. U. B.

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I N T R O D U C T I O N

This is my first experience in doing such kind of work, and I have come to the conclusion that one should not attempt to do research work unless he is free from the rush of ringing bells and the obligations of ordinary routine duties of class work. One should work in an atmosphere of absolute freedom from any external disturbances and should feel that he has solid twelve hours at his disposal for the investigation of the problem he has at hand.

The problem of "Saturated Salt Solution" has alluring attractions for anybody who is inclined to theoretical pursuits. It can, by no means, be exhaustively studied in one year; it is a problem that may easily be extended over a couple of years. I hope some member of the future generation will carry on the torch.

Before attempting to give a detailed account of my work, I should like to express my deep gratitude to the personnel of the Chemistry Department for giving me this opportunity to pursue advanced study. In particular, I thank

Prof. W. A. West for putting his private laboratory at my disposal, for his many helpful and constructive suggestions, for his continual coaching and for his design of a special pipette, described elsewhere, without which the work would have been impossible or at least greatly impaired.

The present research has ^{as} an aim the investigation of the solubility relationships of potassium nitrate and silver nitrate when found simultaneously in the same saturated solution; to find out whether the two salts form a double salt or not and if they do what is the molecular quantity of each constituent in this double salt.

I. PREPARATION OF PURE REAGENTS AND STANDARD SOLUTIONS.

Pure salts and standard solutions to be used in this work were prepared as follows:

1. Preparation of pure potassium nitrate:

The solubility of potassium nitrate is known to be 247 grams per 100cc of boiling water. About 400 grams of crude salt were put in 300cc of water and boiled. The salt dissolved completely. The solution was then filtered while hot to remove impurities. The clear filtrate was cooled to room temperature when a very large amount of the salt crystallized out. The crystals were separated from the saturated solution by suction, dried between sheets of filter paper and placed in an electric oven set at 105°C to completely dry. There was no need to repeat the process since the original salt was fairly pure.

2. Preparation of 2 liters of $\frac{1}{10}$ N potassium thiocyanate: Potassium thiocyanate is a deliquescent salt, therefore a standard solution can not be prepared directly by weighing a definite quantity. Standardization is done in a round about method. An approximately $\frac{1}{10}$ N solution is made by dissolving 10 grams of the salt in a liter water and this solution is standardized against standard silver nitrate solution using ferric alum as an indicator. So I first prepared my standard silver nitrate solution.

An approximately $\frac{1}{10}$ N solution of silver nitrate is made by dissolving 17 grams in 1 liter of water. To standardize this I followed Volhard's method, namely a definite volume of the silver nitrate solution is added to a definite weight of potassium bromide. A large portion of this silver nitrate solution goes to react with the potassium bromide, and a small excess is left over; this excess of silver nitrate is determined by titrating with potassium thiocyanate. Similarly another 25cc of silver nitrate solution is titrated with potassium thiocyanate from these data the normality of the silver nitrate solution is calcu-

lated and consequently that of potassium thiocyanate. A list of data and the method for calculation follows:

Solution pipetted: 25cc silver nitrate (approx. $\frac{1}{10}$ N)

Solution in burette: Potassium thiocyanate (approx. $\frac{1}{10}$ N)

	<u>1st. trial</u>	<u>2nd trial</u>	<u>3d trial</u>
2d. reading	22.2	44.4	22.15
1t. reading	<u>0.0</u>	<u>22.3</u>	<u>0.00</u>
cc used	22.2	22.1	22.15

therefore average volume of KCNS used is 22.15 cc. Also of this silver nitrate solution 25cc were added to 0.2757 grams of potassium bromide and the excess ~~titrated~~ silver nitrate titrated with 1.7cc of potassium thiocyanate.

Calculation:

$25\text{ccAgNO}_3 : 22.15\text{ccKCNS} = X\text{cc excess AgNO}_3 : 1.72\text{ccKCNS}$

Therefore: $\text{Excess AgNO}_3 = \frac{25}{22.15} \times 1.72 = 1.92\text{cc}$

Total AgNO_3 : 25cc

Excess AgNO_3 : 1.92cc

AgNO_3 reacted with 0.2757g
KBr: 23.08cc

$V(\text{AgNO}_3 \text{ in cc}) \times N(\text{of AgNO}_3) = \text{Mg.eg. (of AgNO}_3) =$
 $= \text{Mg.eg. (of KBr)}$

$23.08 \times N = \frac{0.2757 \times 1000}{119.02}$

$$\text{Therefore Normality of AgNO}_3 = \frac{0.2757 \times 1000}{119.02 \times 23.08} = .1004$$

3. Having thus determined the normality of silver nitrate we proceed to calculate that of potassium thiocyanate:

<u>AgNO₃</u>		<u>KCNS</u>	
v	n	v	n
25	.1004	22.15	x

$$X = \frac{25 \times .1004}{22.15} = .1133 \text{ N}$$

Therefore our standered potassium thiocyanate to be used in all our subsequent analytical work is $\frac{1}{10}$ N with a factor of 1.133.

As a check against this normality, a 90% American silver dime was weighed and dissolved in nitric acid. After boiling, the solution was diluted to 100cc in a volumetric flask and 25cc of this solution were titrated with ~~one~~ potassium thiocyanate solution. The results obtained and the calculations made are as follows:

Solution pipetted: 25cc silver nitrate

Solution in burette: Potassium thiocyanate, .1133N

2nd reading	28cc
1st reading	<u>0</u>
cc used	28cc

Weight of silver dime: .3800 g

Percent of silver in coin: 90%

Calculation:

$$\begin{aligned} .3800\text{g coin} &= 380 \text{ Mg coin} = 380 \times .90 = 342\text{MgAg} \\ &= \frac{342 \text{ Mg.eg. Ag}}{107.88} = \frac{342 \text{ Mg.eg. of KCNS}}{107.88} \end{aligned}$$

$$\begin{aligned} V(\text{of KCNS in cc}) \times N(\text{of KCNS}) &= \text{Mg.eg. (of KCNS)} \\ 28 \qquad \qquad \times N \qquad \qquad &= \frac{342}{107.88} \end{aligned}$$

$$N = \frac{342}{107.88 \times 28} = .1132$$

4. Preparation of the ferric alum indicator solution: 5 grams of iron alum are dissolved in 50cc of water and 50cc of concentrated nitric acid are added to the solution; the solution is next boiled vigorously to expel oxides of nitrogen.

II. Description of the Apparatus used in this research.

1. A description of the outfit used in this research is quite appropriate. The constant temperature bath consists of a cylindrical Pyrex glass jar which permits full visibility of all immersed objects. This glass jar measures 30 cms. in height and 30 cms. in diameter and fits an iron base. Joined to the iron base is the control box which contains a relay, condenser and resistors.

Fig. 1. The glass jar is filled with water to about 10 cms. from the top. In this water is immersed the following units.

a. Two electrical heaters attached to 2 clamps tightened firmly to the rim of the jar. Fig. 2 and Fig. 3. The heater stamped at a lower wattage rating is used with the intermittent and the one with the higher wattage is connected to the receptacle marked continuous.

b. Thermostat. The thermostat is a simple form of the vapor type. Fig. 4. To fill the thermostat requires a little bit of experience before one can do it successfully. The tube is inclined about 45 degrees. With the dropper, add as much mercury as the tube will hold; then put the thumb over the opening and invert the tube several times



Fig. 1

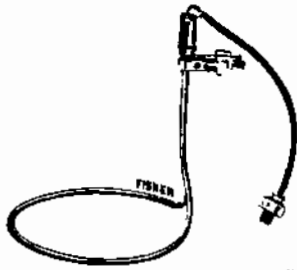


Fig. 2

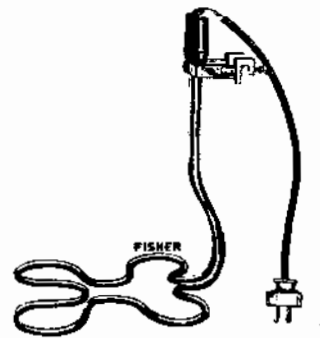


Fig. 3

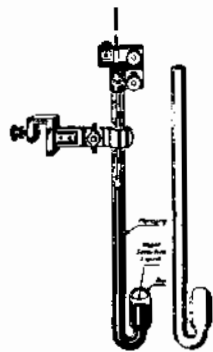


Fig. 4

to bring the mercury into the bulb. Refill the tube and repeat the operation until the bulb is completely filled and the mercury reaches within about 5mm from the top of the long tube.

Add a little bit of the sensitive liquid in this remaining part of the tube and leave a little air space above it so a small air bubble will be carried into the bulb with the liquid. Place the thumb over the end of the tube and invert it to allow the sensitive liquid to rise into the bulb. Pour the excess mercury carefully out of the long tube. Place the cap and contact rod assembly and clamp to the rim of the glass jar.

As soon as the cord from the control box is inserted into the socket and the switches of both continuous and intermittent heaters turned on, the signal light goes on. As the temperature of the bath rises, the vapor changes in pressure and as the pressure increases the mercury rises in the vertical tube.

To adjust the bath for a definite temperature, keep the heaters on until the thermometer has almost reached the point desired. The switch for the continuous heater is then turned off and the contact rod is lowered to the surface of the mercury. As this contact is made, the relay opens, cutting off

the intermittent heater. This is indicated by the signal light going off. As the temperature just cools down the reverse process takes place. The signal light continuously goes off and on showing the maintenance of a constant temperature.

For temperatures not higher than 70°C, water is a convenient bath medium and as sensitive liquids to put in the thermostat, the following liquids are suitable:

<u>Liquid</u>	<u>Approximate Sensitive Range.</u>
Ether	26-37°C
Acetone	48-60°C
Chloroform	53-65°C
Carbon tetrachloride	69-81°C
Water	92-104°C

Intermediate ranges can be obtained by blending liquids of ranges lower and higher than the desired range. Care should be taken not to surpass these limits otherwise the vapor pressure of the enclosed liquid may push the mercury out of the tube.

c. Stirrer. Adequate stirring is essential to attain uniformity of temperature throughout the bath. To achieve this a stirrer is immersed in the bath medium and operated by means of a motor clamped to a vertical rod. ^{Fig. 5.} Adequate agitation is thus given all parts of the bath.

d. At thermometer. A short thermometer calibrated

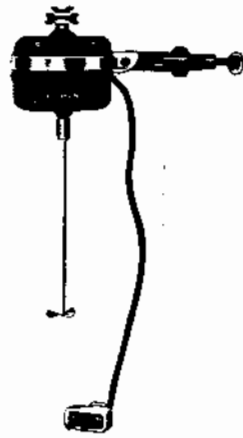


Fig. 5

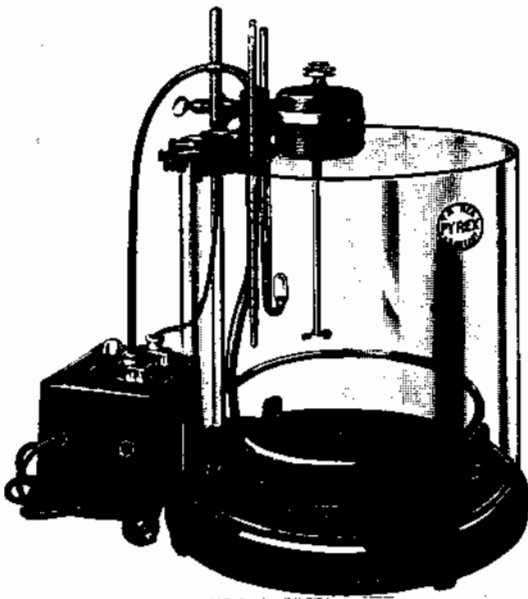


Fig 6



Fig. 7

against a standard one is clamped to the rim of the glass jar and read by means of a magnifying glass. Each division on the thermometer scale represents 0.2° .

c. A flask containing a solution of salt mixture, a short glass rod stirrer and covered with a cap made of copper foil to prevent any water from going into it while the stirrer is turning, is suspended in the bath. Both the top of the thermometer and the level of the solution in the flask should be below the surface of the water in the glass jar. Fig. 6 shows the complete outfit assembled, and Fig. 7 shows the same assemblage without the flask and with one heater only.

2. Another indispensable piece of apparatus used in this work is a pipette of a special design intended to suck a certain portion of the solution after it has reached equilibrium at a certain temperature. Fig. 8.

It is not longer than 20 cms. so that it can easily be hung by means of a platinum wire from the pan of the balance and weighed. Moreover at its widest part it is not more than 3 cms. wide, so that it can easily enter into a wide mouth Erlenmeyer flask to suck the saturated solution.

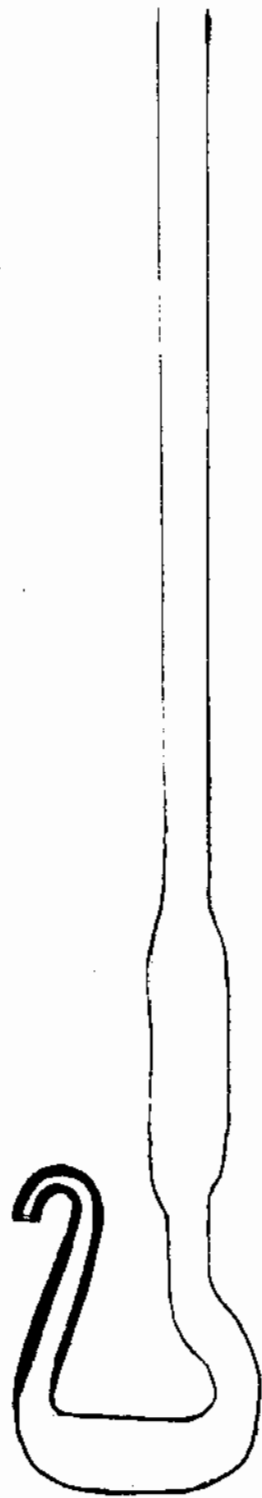


Fig 8

The tip of the pipette is slanting downward to prevent the escape of the solution. The lower portion is made of thick walled glass 1mm in diameter to prevent evaporation and the vertical upper portion is 5 or 6 mm. in diameter to facilitate washing out the content of the pipette with water. The horizontal bulb is made large enough to hold 1 or 2cc of the saturated solution. The technique of the use of the pipette will be described elsewhere.

Finally to make the list complete, other important pieces of apparatus, necessary in the investigation of our problem, and which are so familiar to the reader that they need no further description other than naming them are the following

- a. An analytic balance
- b. A standard pipette and burette
- c. An electric oven and an electric heater.

3. Before proceeding to a detailed description of the manipulative processes followed in this research, I should like to say a few words about the theory and technique of thermometer calibration.

Precise temperature measurement demands many requirements: First, the thermometer tube must be of uniform bore. Second, glass continues to shrink very slowly over many years. The shrinkage is very small indeed, and does not make appreciable

difference in the length of the tube, but it does make a difference in the volume of the bulb. As time goes on the bulb shrinks to a smaller volume and therefore we get a higher reading. But the relative readings on the stem remain the same. As a result of this shrinkage it is essential to determine the upward ~~shift~~ of the zero point, i.e., check the zero point of a given thermometer against a standard one.

Third, glass not only shrinks, but when heated and cooled, it does not come back immediately to its former condition. For instance, if the zero point of a thermometer that has been standing in the laboratory for years is determined; and if this same thermometer is first heated and cooled and then its zero point determined, the former and the latter determinations may not agree. Because Manufacturers first heat the thermometer, then cool it and afterwards determine the zero point, similar procedure must be followed in the laboratory, to compensate for the fact that it has been standing at room temperature for a long time.

Lastly, if a thermometer is immersed in a hot liquid whose vapor pressure is appreciable at higher temperature, mercury may distill off and

and when cooled may condense in the upper parts of the tube. Therefore it is wise to examine a thermometer with a magnifying glass to find out if any droplets of mercury have adhered to the side of the tube.

The calibration was done according to the following manner:

Ice and water exposed to air were put together, stirred well to bring the mixture to equilibrium. The bulb of a standard thermometer of range $0^{\circ} - 100^{\circ}\text{C}$, was immersed in this equilibrium mixture. If more than the bulb is immersed in the liquid, the thermometer may not register the correct temperature, for ice is lighter than water and floats on the surface.

A second thermometer to be calibrated of range $0^{\circ} - 55^{\circ}\text{C}$ was first immersed in water at 50°C and then allowed to cool to room temperature. The reason why the same precaution with regard to heating and cooling was not taken with the standard thermometer is because it had already been used the day before and that precaution had been taken care of.

By means of a rubber band the standard and the ordinary thermometers were fastened together in such a manner that their bulbs came near each

other and were immersed in the equilibrium mixture of ice and water. Both standard and ordinary thermometer read 0°C . Following a similar procedure I obtained the following results:

<u>Reading of standard Thermometer.</u>	<u>Reading of ordinary Thermometer.</u>
0°	0°
14°	14.2
29°	29.12
42°	42.1
58°	58.28
73°	73.2

In taking the above readings the following precautions were observed:

The two thermometers are fastened together by a rubber band to keep them as close as possible.

The thermometers were immersed in water up to the point where the mercury thread rises; in other words, all the mercury was immersed in water to avoid the error of emergent stem.

While taking a temperature reading it is advisable to stir the water with the thermometers to avoid any difference of temperature in different parts of the liquid.

Water serves as a good medium for checking, up to 70° - 75° , after that evaporation takes place so fast, that a liquid of higher boiling point should be used.

According to the certificate accompanying the

standard thermometer, some correction must be applied to its reading. The certificate says when the standard thermometer reads 25° actually the temperature is 0.1 of a degree lower than what it is, so that the exact temperature corresponding to the standard thermometer reading of 25° is 25.1° . Similarly when it reads 50° , the correct temperature is 50.1° . At 0° and 75° , the reading of the standard thermometer is exact without any correction. The following table gives the corrected standard thermometer readings and the corresponding readings of the ordinary thermometer which is to be used in the solubility determinations:

<u>Readings of the standard thermometer.</u>	<u>Corrected readings of the standard thermometer.</u>	<u>Readings of the ordinary thermometer.</u>
0	0	0
14	14.1	14.2
29	29.1	29.12
42	42.1	42.1
58	58.1	58.28
73	73.0	73.2

Interpolating for temperatures between 0 and 75° we obtain the following table:

<u>Reading of the ordinary thermometer</u>	<u>Corrected thermometer.</u>
0	0
5	5.0
10	9.9
15	14.9
20	19.9

Reading of the ordinary
thermometer (cont.)

Corrected ther-
mometer (cont.)

25
30
35
40
45
50
55
60
65
70
75

25
30
35
40
45
49.9
54.8
59.8
64.8
69.8
74.8

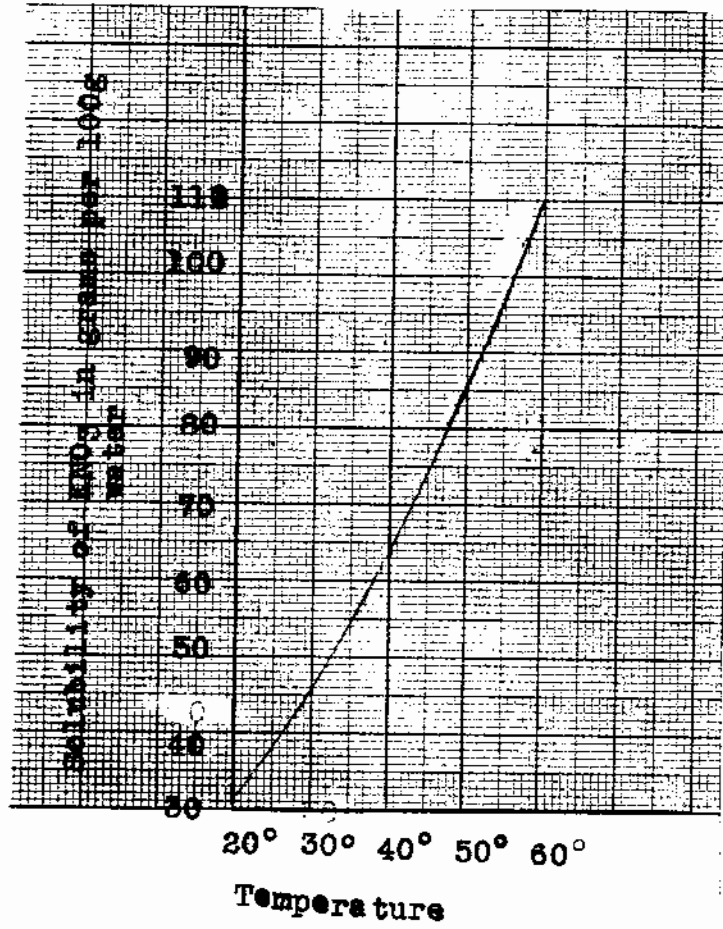
III. How to find the solubility of potassium nitrate and silver nitrate.

For the sake of simplicity I started my work with potassium nitrate alone and made several determinations of its solubility at various temperatures. The results are given in the table following on the next page.

The results of determinations number 1, 4 and 5 are not satisfactory, and the error in all three is in the same direction. Evidently the determination was made before the solution reached equilibrium. Moreover, the last two determinations are especially important because the solution in number 8 was brought to saturation by heating it from a lower temperature to 60.3° , where as the solution of number 9 was brought to saturation by saturating it at a higher temperature and cooling it to 60.3° . Both determinations gave consistent results which agree with the interpolated value. The interpolation of the solubilities at these different temperatures is made from the accompanying graph.

Having thus obtained consistent results and become acquainted with the technique, I proceeded

Determination No.	Observed Temperature	Corrected Temperature	Weight of Solution	Weight of dry salt	Weight of Water	Grams of salt per 100g. of Water	Results interpolated from graph
1	22.6	22.5	1.1046	.2626	.8420	31.2	35.2
2	36.0	36	1.1538	.4124	.7414	55.6	56.5
3	45.2	45.2	1.0840	.4611	.6229	74.0	73.9
4	59.2	59	1.5986	.8105	.7881	103	106
5	44.9	44.9	1.4097	.5867	.8230	71.2	73.3
6	36.2	36.2	1.3793	.4975	.8818	56.4	57.0
7	28.6	28.6	1.4600	.4444	1.0156	43.8	44.5
8	60.3	60.1	1.4759	.7730	.7029	110	110
9	60.3	60.1	1.3430	.7066	.6364	111	110



to the actual problem, namely the determination of the solubility of potassium nitrate and silver nitrate when found together, meanwhile postponing the explanation of the method used and calculations made in finding the results given in the preceding table. These will be sufficiently explained in connection with the actual case.

In general, to determine solubility there are 2 methods, the synthetic and the analytic. The synthetic method consists in taking a definite weight of the solvent and adding to it gradually known quantities of the solute until no more of it dissolves at a certain fixed temperature. In the analytic method we start with an already saturated solution and find out how much solute it contains. In this work the analytic method was followed.

The method used in our work has not been uniform throughout. As the work progressed difficulties arose, and therefore certain modifications of the method at some points were imperative, in order to meet these difficulties. I shall try to point out such changes in method as they came along.

1. Preparation of a saturated solution at a fixed temperature in a constant-temperature bath.

To serve as a guide in preparing a saturated solution of the two salts to start with, I looked up in the Handbook of Physics and Chemistry, the solubility of silver nitrate and potassium nitrate separately. The solubility both in grams per 100g of water and in moles per 100 grams of water is given in the following table:

: Tempera- : tube.	: KNO ₃ per 100 grs. of Water :		: AgNO ₃ per 100 grs. of Water :	
	Grams	Moles	Grams	Moles
: 0°	: 13.3	: .132	: 122	: .72
: 10°	: 20.9	: .207	: 170	: 1
: 20°	: 31.6	: .313	: 222	: 1.30
: 30°	: 45.8	: .453	: 300	: 1.76
: 40°	: 63.9	: .632	: 376	: 2.21
: 50°	: 85.5	: .846	: 455	: 2.68
: 60°	: 110	: 1.09	: 525	: 3.09
: 70°	: 138	:	:	:
: 80°	: 169	:	: 669	:

Mol. wt. of AgNO₃ = 169.888

" " " KNO₃ = 101.104

Into a 200cc wide mouth Erlenmeyer flask or still better a wide mouth bottle of about the same size , 75cc of water is put. To this water 1 mole of each salt namely 170 grams of silver nitrate and 101 grams of Potassium nitrate is added. This solution is to be used for a solubility determination at room temperature (16.7°). Obviously enough of these two salts will dissolve to saturate the solution and leave behind plenty of undissolved solid of each kind.

The flask is covered with a cap, immersed in the bath medium and clamped as near the thermometer as possible to such a depth that the surface of the solution in the flask remains lower than the surface of the water in the glass jar.

For solubility determinations at room temperature obviously there is no need to use the electric heaters and the thermostat. The solution with plenty of solid at the bottom is allowed to stand in the bath medium overnight to come to equilibrium. The next day the stirrer is operated to maintain constant temperature and the solution is stirred occasionally with a glass rod to establish equilibrium between the liquid and the solid phases.

On the other hand if the solubility determination is to be made at some other temperature besides

room temperature, exactly the same procedure is followed, except that naturally use is made of the heaters and the thermostat. Ample time must be given to the solution to come to equilibrium, 7 or 8 hours may be necessary.

Having made a solubility determination of a solution which has stood in contact with its solid phase for a long time, one way of deciding whether that solution had actually come to equilibrium or not is to heat the solution to a temperature higher than the first one, more or less saturate it at this higher temperature and then cool it from the high temperature to the first one and maintain the solution at this temperature in contact with the solid phase for a fairly long time with constant stirring and make a second determination at the same temperature. The two determinations will agree if in both conditions the solution had actually reached equilibrium. In other words, in one case we make a saturated solution from a dilute one by heating it while it is in contact with the solid phase, and in the second case we obtain a saturated solution by cooling a solution saturated at a higher temperature.

Having made sure that the solution has reached saturation we proceed to suck a sample of it for analysis.

2. Sucking a sample of saturated solution.

The pipette while empty is weighed together with the platinum wire with which it will be hung from the pan of the balance. It is put in the electric oven set at a temperature a few degrees higher than the temperature of the equilibrium solution. This is done in order to prevent the cooling of the solution when the pipette is inserted in it.

The end of the pipette is closed with the finger and inserted in the equilibrium solution with the curved portion under the surface of the liquid. The air inside is cooled and as a result the solution is pushed in through the capillary end. Previously, however, another method was used, namely after the pipette was introduced into the solution with the external end closed with the finger, sufficient time was allowed for the air in the pipette to acquire the same temperature as the solution. This was indicated by the ceasing of air bubbles to come out from the tip of the pipette. The finger was removed, and by capillary action the solution was sucked in.

As soon as the lower horizontal bulb is full of the solution, the pipette is quickly removed and plunged into ice cold water, this is specially important if the temperature of the solution is not very high. While plunging the pipette in ice cold water, care should be taken to keep the tip of the pipette above the surface of the water. This process cools the pipette and helps to suck in, t

solution left in the capillary portion of the pipette. Otherwise, as soon as the pipette is taken out of the solution, crystallization may take place, and if some of the water goes off the tip, the concentration would change. By this means and by having the end of the tip facing downward, this difficulty is avoided.

The pipette is inclined the proper amount and thoroughly and carefully washed on the outside with a jet of water, taking care not to allow any water coming near the tip of the pipette, otherwise it would be sucked in, and dilute the solution. After the washing, the main part of the pipette is dried with a towel and the tip and vicinity with a filter paper. It is left to stand in the air for a few minutes to get thoroughly dry. Next it is hung by means of the platinum wire from the pan and weighed.

3. Proper way of emptying the pipette.

The content of the pipette is emptied into a clean weighed beaker by blowing carefully into the pipette driving out as much of the solution as possible. Distilled water is introduced from a wash bottle into the pipette and again the latter is emptied by gentle blowing. This is repeated several times and finally the pipette is washed on the outside by directing a stream of water against it.

4. Method of evaporating a saturated solution to dryness.

The beaker containing both the solution and washings is placed on the electric heater under the hood and evaporated. Although the electric heater was adjusted to deliver the minimum amount of heat, in order to prevent rapid heating or boiling and thus cause spattering, yet in spite of this, we found out that towards the end there was spattering. To still minimize this effect, a piece of thin copper wire in the form of a circular loop was put between the heater and the beaker to introduce a thin layer of air between the two and prevent direct contact. While the evaporation is going on an inverted porcelain dish supported on 2 tripods is placed over the beaker to prevent any solid material from falling into it.

When all traces of visible water disappear, the beaker containing the dry residue is put in the drying oven set at a temperature of 110° to dry completely and kept there at least over night. It is then removed and left in a desiccator for several hours to cool and finally it is weighed.

The difference between the weight of the beaker containing the dry solute and that of the empty beaker gives the weight of the solute. Likewise, the dif-

ference between the weight of the pipette containing the solution and that of the pipette when empty gives the weight of the solution. Subtracting the weight of the solute from the weight of the solution, we obtain the weight of the solvent water,

e.g.,
Weight of pipette + platinum wire = 13.5480 g.
" + solution = 11.2464 g.
" of pipette + " " = 11.2464 g.
Hence, weight of solution = 2.3016 g.

Weight of beaker + solute = 48.3598 g.
" " " = 46.9690 g.
Hence, weight of solute = 1.3908 g.

The weight of the solute, namely, 1.3908 g., is made up of the weight of 2 solids, potassium nitrate and silver nitrate. To find the weight due to each one, we proceed as follows:

5. Determination of the silver nitrate content.

We add to the dry residue in the beaker a few cc of water to dissolve it. The solution is poured into a 100cc volumetric flask, the beaker is rinsed several times, and washings added to the flask; enough water is added to make the volume 100cc. 25cc of this solution is pipetted and titrated with our standard potassium thiocyanate solution in order to determine the silver nitrate.

6. Determination of the potassium nitrate content.

To another 25cc solution, HCl is added to precipitate the silver ions as silver chloride. This precipitate is filtered off, or rather decanted, washed thoroughly and filtrate and washings received in a weighed beaker. In precipitating the silver ions, in order to effect a separation from potassium nitrate, an important difficulty is met with. Some of the silver chloride remains in the colloidal state and therefore passes into the filtrate along with the potassium chloride. One suggestion to meet this difficulty is to add a small amount of very dilute nitric acid (.04N) to the solution to help coagulate colloidal silver chloride. But this was of no avail. Silver chloride has an appreciably more solubility at higher temperature than at room temperature and therefore though heating renders the solution clearer, on cooling, the filtrate will deposit some of its dissolved silver chloride, thereby increasing the weight of the potassium chloride, which will be obtained on evaporating the filtrate to dryness. The best way is to precipitate the silver ions and allow the beaker to stand over night in which time the colloidal particles will settle.

To the clear filtrate more HCl is added to completely convert all the potassium nitrate to potassium

chloride. As usual the filtrate is evaporated on the electric heater, dried in the oven, cooled in the desiccator and weighed to find the quantity of KCl. From the results of the volumetric titration and from the weight of potassium chloride obtained, the weight of silver nitrate and potassium nitrate are calculated respectively. The sum of these 2 weights must agree with the original weight of the solute, namely, in this case 1.3908 grams, obtained by direct evaporation of the taken solution. The following examples are illustrative of the methods of calculation.

7. Examples of methods of calculation.

Weight of solution taken	= 2.3016 g.
" " solute contained in this solution	= 1.3908 g.
Volume in which above solute dissolved	= 100cc
Volume of solution pipetted	= 25cc
Solution in burette: KCNS	= .1 N, 1.33
2nd reading: 31.8	
1st reading: <u>20.0</u>	
cc used	11.8

$$11.8 \times 1.133 = \text{Mg. eg. of KCNS} = \text{Mg. eg. of AgNO}_3$$

Hence, $11.8 \times 1.133 \times 169.888 = \text{Mg. of AgNO}_3 \text{ contained in 25cc}$

Therefore, $\frac{11.8 \times 1.133 \times 169.888}{1000} \times \frac{100}{25} = \overset{9085}{\text{grams of AgNO}_3 \text{ found in 100cc of above solution.}}$

As to the weight of potassium nitrate:

Volume of solution pipetted = 25cc

Weight of KCl found in this
volume = .0916 g

$$\text{Hence, } .0916 \times \frac{\text{KNO}_3}{\text{KCl}} \times \frac{100}{25} = .0916 \times \frac{101.104 \times 4}{74.553} = .4969 \text{ gr. c}$$

KNO₃ found in
100cc

Sum of the weights of 2 salts = .9085 + .4969 = 1.4054g

Weight of the water in the sample = 2.3016 - 1.3908 =
=.9108g

Grams of AgNO₃ per 100g of H₂O = $\frac{.9085 \times 100}{.9108} = 99.75$

Grams of KNO₃ per 100g of H₂O = $\frac{.4969 \times 100}{.9108} = 54.56$

Or to put these results in the form of a table, we obtain the table on next page.

8. Modified method of analysis.

This method of procedure, however, was soon abandoned for 2 reasons. In the first place it was observed that on heating the equilibrium solution of the 2 salts to dryness, part of the silver nitrate underwent decomposition into silver oxide. Second, it is rather a long method. To obviate these 2 difficulties a modified method was followed.

The modification consists in the following: After sucking a sample of the equilibrium solution and weighing it, rather than evaporate it and find the weight of the solid mixture of the two salts and then dissolve in 100cc of water, I say rather than do this, dilute the weighed sample of the equilibrium solution directly to a definite

Observed Temperature	Corrected Temperature	Weight of Solution	Weight of dry mixture of Salts	Weight of Water	Weight of Silver Nitrate	Weight of Potassium Nitrate	Sum of Salts	Grams of Silver Nitrate per 100g water	Grams of Potassium Nitrate per 100g water
16.7°	16.6°	2.3016	1.3908	.9108	.9085	.4969	1.4059	99.75	54.56

volume in a volumetric flask, without determining the weight of the solid mixture of salts first, and then continue as before. It is true we lose a valuable check but we gain time and obviate a possible source of error.

With this new procedure, the only change in the method of calculation would be in finding the weight of the water in the removed sample of equilibrium solution. The weight of the water would be equal to the weight of the sample solution minus the sum of the weights of the two salts. In the first method the weight of the water was equal to the weight of the solution minus the weight of the dry mixture after evaporation.

IV. Results of solubility determinations using a solution saturated with respect to both salts.

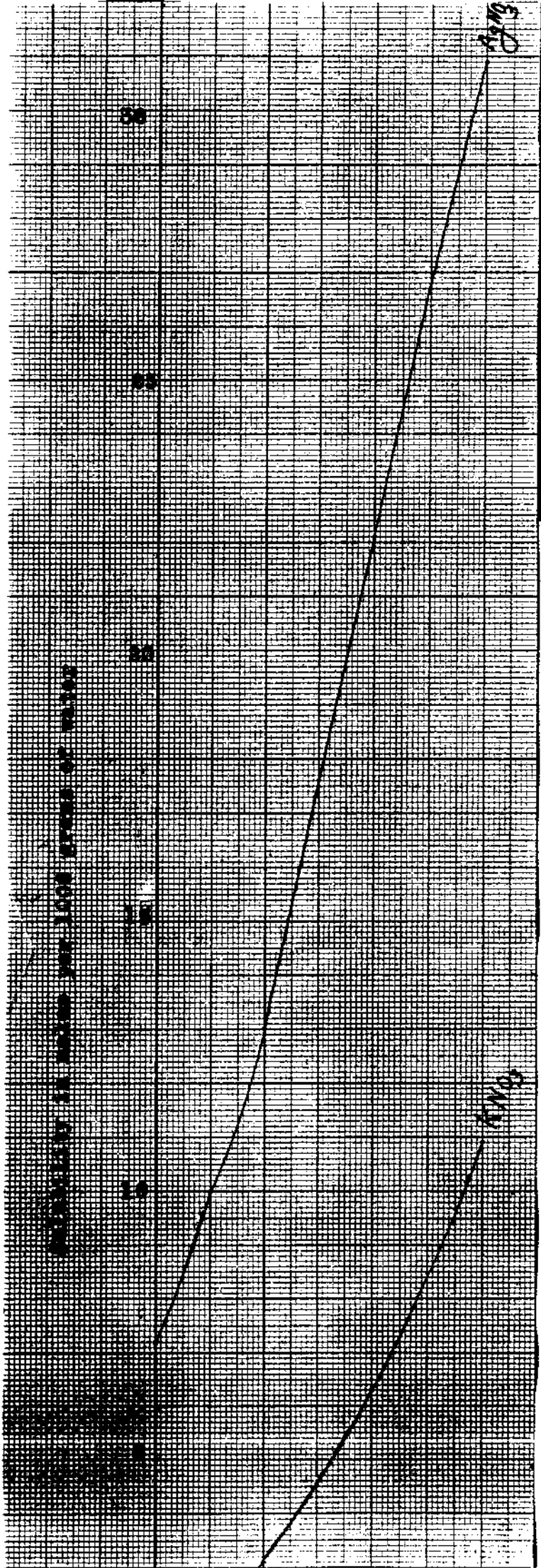
1. Following this new method of procedure I made three solubility determinations at 18° , 28.8° and 36.2° . The solution used in making the determination at the highest temperature contained 345 grams of silver nitrate and 126 grams of potassium nitrate in 75cc water, i.e. it contained 27.07 moles of silver nitrate and 16.61 moles of potassium nitrate per 1000 grs. water. The results are tabulated on the next page and represented on the graph following page 36.

In addition, the data taken from the Handbook of Physics and Chemistry concerning the solubility of silver nitrate and potassium nitrate, separately, given on page 18, ^{are} ~~is~~ plotted and from the graphs of the solubility of silver nitrate and potassium nitrate, we interpolate for the solubilities of these 2 salts at the above mentioned three temperatures. These results, for the sake of comparison, are given in the above mentioned table.

By studying this table, we observe this important fact that the presence of the two salts together in the same saturated solution increases the mutual solubility of each salt.

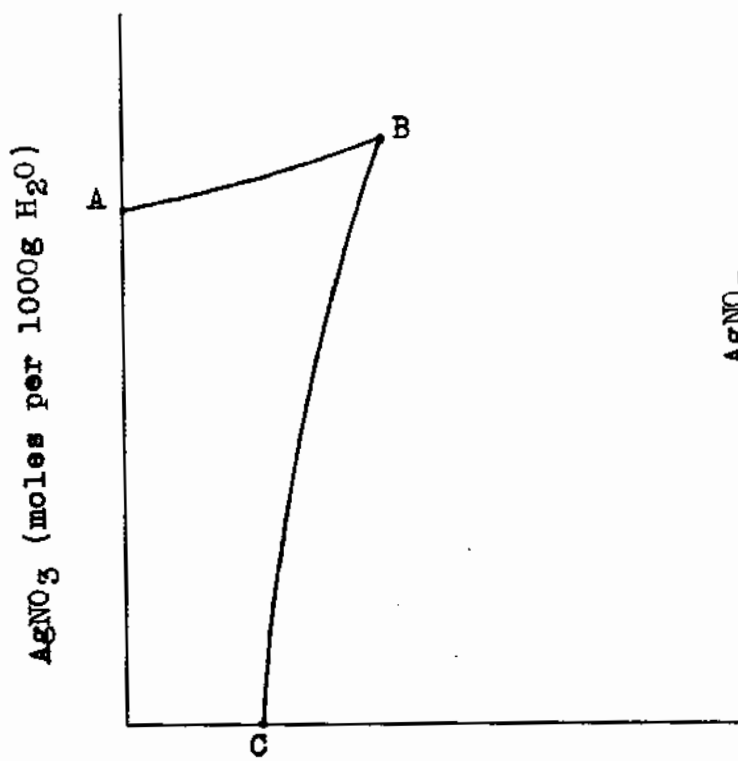
Having established this fact, our next attempt is to find the effect of progressively increasing amount of potassium nitrate on the solubility of silver nitrate at

Determination No.	1	2	3
Observed Temperature	18	28.8	36.2
Corrected Temperature	17.9	28.8	36.2
Weight of Solution.	2.5700	2.0158	1.8824
Weight of Silver Nitrate.	1.6815	1.3127	1.2496
Weight of Potassium Nitrate.	.2821	.3016	.3157
Weight of Water	.6064	.4015	.3171
Grams of Silver Nitrate per 100gms. Water.	277.29	326.95	394.07
Moles of Silver Nitrate per 1000g Water.	16.32	19.24	23.20
Value interpolated from graph for moles of silver Nitrate per 1000g Water.	12.3	16.8	20.4
Grams of Potassium Nitrate per 100g. Water.	46.52	75.12	99.56
Moles of Potassium Nitrate per 1000g. Water.	4.60	7.43	9.85
Value interpolated from graph for moles of Potassium Nitrate per 1000g. Water.	2.95	4.32	5.59



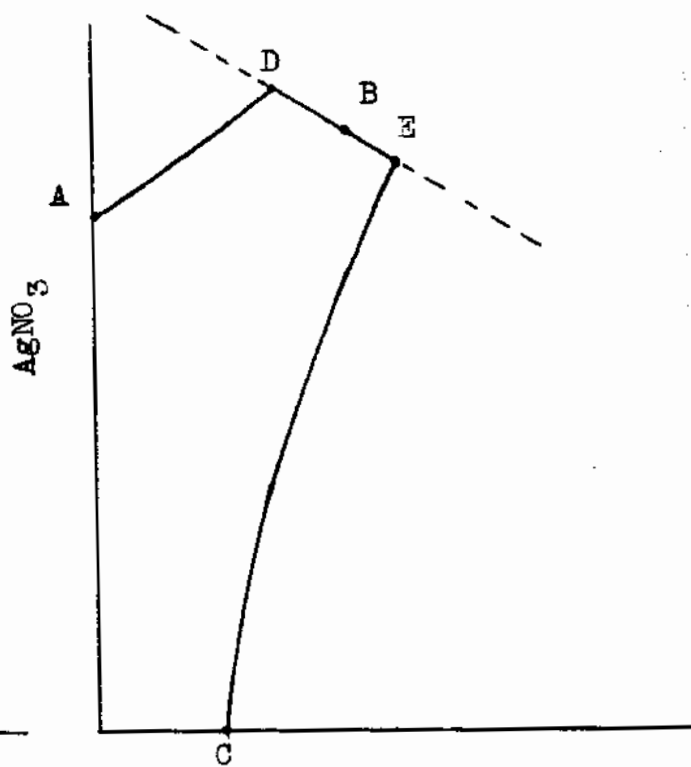
the three above mentioned temperatures. Room temperature, however, being a fluctuating one depending upon the season, it was impossible to reproduce another determination at exactly 18° . Times had changed and so the room temperature determination was in the vicinity of 20 and 21° .

2. Taking as an example the data so far obtained relating to the isothermal at 31.2° , for convenience sake when reduced to a smaller scale and plotted, the general shape of the resulting curve will be represented by one of the following 2 possibilities:



KNO_3 (moles per 1000g H_2O)

Graph No. 1



KNO_3

Graph No. 2

In graph No. 1, the area included between the 2 curves and the 2 axes represents an unsaturated solution of potassium nitrate and silver nitrate, i.e. it stands for the existence of one single phase. Above the curve AB solid silver nitrate alone exists and similarly to the right of the curve BC solid potassium nitrate alone exists. Any point on the curve AB except points A or B, and any point on the curve BC except points B or C represents solid and liquid phases in equilibrium. Point B is a triple one where solid silver nitrate, solid potassium nitrate and their saturated solution coexist.

In graph 2, again the area bounded by the three curves and 2 axes stands for an unsaturated solution. Above AD solid silver nitrate alone exists and to the right of CE solid potassium nitrate alone exists and above DE the double salt in the solid state alone exists. Moreover curve AD stands for solid silver nitrate in equilibrium with a saturated solution, curve CE stands for solid potassium nitrate in equilibrium with a saturated solution and curve DE stands for solid double salt in equilibrium with a saturated solution. Points D and E are triple points. D represents the co-existence of solid silver nitrate, solid compound salt and solution i.e. three phases and E represents the co-existence of solid potassium nitrate, solid double salt and solution.

For the curve DE, adding more potassium nitrate, for instance, will result in decreased solubility of silver nitrate, and the point B will shift down the line;

unlike the case represented in graph No. 1 where the point B remains fixed, no matter how much solid excess of either salt is added. To find out which one of the 2 graphs represents the true state of affair in our problem, we need further data and we direct our attention now to the accumulation of more data confining ourselves to the region between A and B.

V. Determination of the solubility for a solution saturated in silver nitrate and unsaturated in potassium nitrate.

Our next drive is to determine the solubility for a solution saturated only with respect to silver nitrate and unsaturated with respect to potassium nitrate and to observe the effect of uniformly and progressively increasing concentration of potassium nitrate on the solubility of silver nitrate.

1. Procedure.

To an exactly 100cc of distilled water placed in a wide mouth 250cc bottle 448 grams (2.64 moles) of silver nitrate are added. This quantity of salt is enough to saturate the solution and leave behind an excess, this is true, at least, for the lowest 2 temperatures out of the three we are investigating. To the above saturated solution .2 moles (20.22 grams) of potassium nitrate are added, put in the constant temperature bath, allowing enough time to come to equilibrium at room temperature (20.1°). A sample is removed by means of the pipette and the amount of silver nitrate in the sample is determined volumetrically as usual. The determination of the potassium nitrate, however, is no more done in accordance with the usual method, but is determined from the known concentration of the potassium nitrate solution. Thus, the weight of silver nitrate is subtracted from the weight of

the solution, the difference represents the weight of potassium nitrate solution. We want to know how many grams of this solution are due to solid potassium nitrate and how many to water. This we can find out from our knowledge of the concentration of potassium nitrate. We have been using 100 grams water in which we placed .2 moles or $.2 \times 101.1 = 20.22$ grams of potassium nitrate. Therefore the factor for potassium nitrate in the potassium nitrate solution is $\frac{20.22}{100+20.22} = \frac{20.22}{120.22}$

This factor is multiplied by the known weight of the potassium nitrate solution mentioned above. The product equals the weight of the solid potassium nitrate in the sample.

2. Illustrative examples of calculation.

The following example illustrates the method:

Weight of sample taken at $20.1^{\circ} = 2.7252$

" " silver nitrate in the
sample = 1.8740

Therefore, weight of potassium
nitrate solution = 0.8512

But for a solution containing 20.2 grams potassium nitrate per 100 grams of water, the factor is $\frac{20.2}{120.2}$

Hence, weight of potassium nitrate in 0.8512 grams of solution = $.8512 \times \frac{20.2}{120.2} = .1432$ g.

Sum of the weights of the 2 salts = $1.8740 + .1432 =$
 $= 2.0172$ g.

Weight of the water in the sample =
= 2.7252 - 2.0172 = 0.7080 g.

Grams of AgNO_3 per 10^0 g H_2O = $\frac{1.8740}{.7080} \times 100 = 264.69\text{g}$

Grams of KNO_3 per 10^0 g H_2O = $\frac{.1432 \times 100}{.7080} = 20.0\text{g}$

The last answer checks up nicely with the known concentration of potassium nitrate.

Before proceeding further .7080 grams of water and .1432 grams of potassium nitrate are added to the bottle to make allowance for the quantities removed in determining the silver nitrate, thus restoring the solution to a concentration of .2 moles potassium nitrate per 10^0 grams of water. This allowance is made at the end of each determination before proceeding to a new one by adding the calculated quantities of potassium nitrate and water.

Similarly, another .2 moles of potassium nitrate is added, solution brought to equilibrium at room temperature (21.6), at 28.8° and at 36.2°, following the same procedure, in each case silver nitrate is determined and potassium nitrate calculated. The factor of potassium nitrate for this concentration is $\frac{40.4}{140.4}$.

Again another .2 moles of potassium nitrate is added, making in all a total concentration of .6 moles of potassium nitrate per $100\text{g H}_2\text{O}$. This quantity of potassium nitrate with reference to room temperature would make a saturated solution and since our investigation is concerned with a solution which is unsaturated with

respect to potassium nitrate, we therefore omit the room temperature determination and confine our work to 2 determinations, one at 28.8° and one at 36.2° .

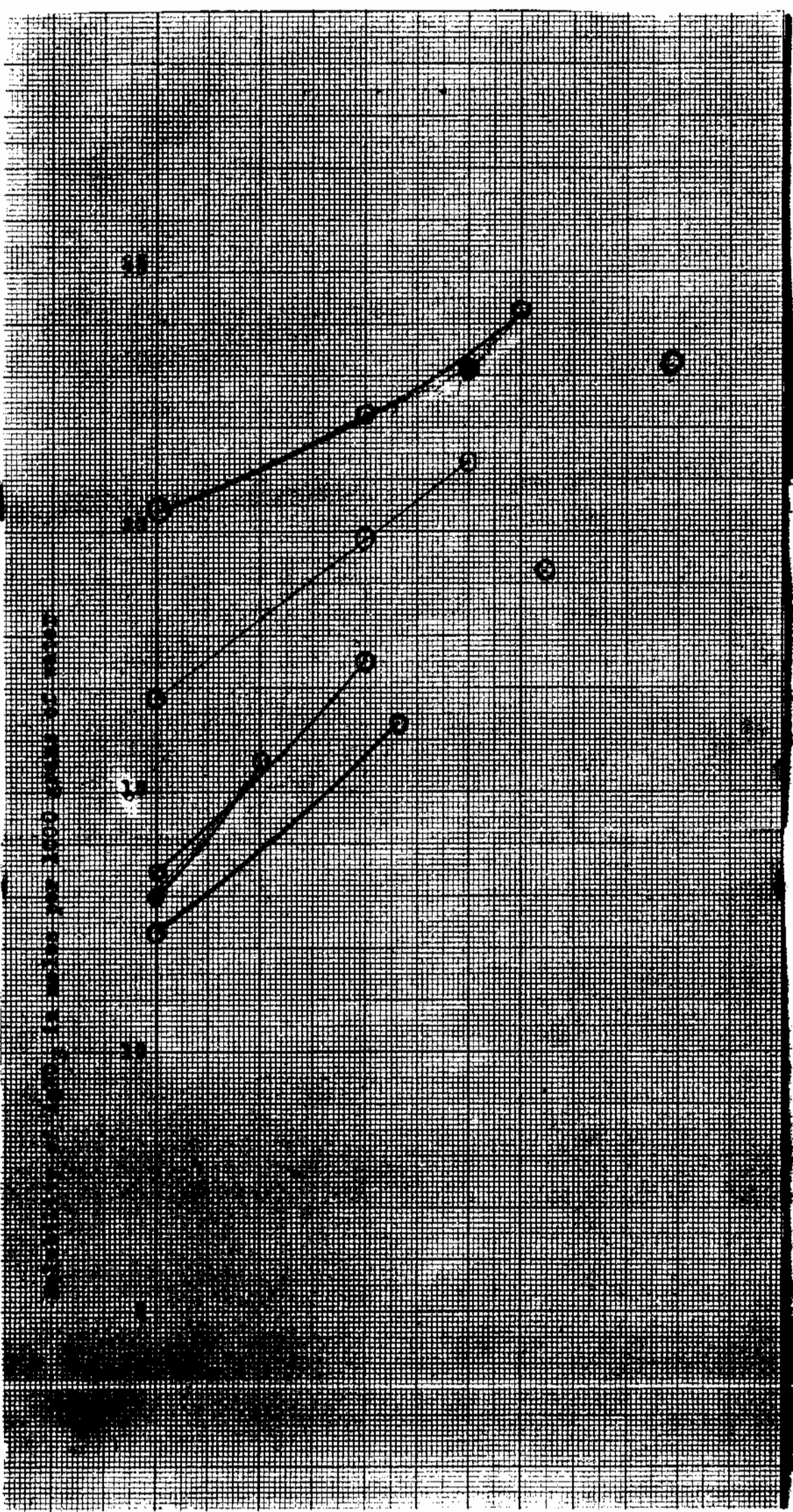
Finally .1 mole of potassium nitrate is added making a solution containing .7 moles of the salt in 100 grams of water. A determination at 36.3° only is made. The factor for potassium nitrate in this concentration is naturally $\frac{70.7}{170.7}$.

This makes in all 7 determinations, the results of which are given in the table on the next page.

3. Tabulation and graphing of results.

Again we notice a successive increase in the solubility of silver nitrate because of the presence of potassium nitrate, and at the same temperature, the solubility of silver nitrate increases as the concentration of potassium nitrate increases, e.g., at 28.8° when 4 moles of potassium nitrate per 1000 gr. of water are present, the solubility of silver nitrate is 18.84 moles per 1000 grams of water and when 6 moles of the salt are present at the same temperature the solubility of silver nitrate rises to 21.36 moles per 1000 gr. of water. The data represented in the above mentioned table are plotted on the following graph. The blue color stands for an isothermal at 17.9° , the red for 28.8° and the green for 36.2° .

Determination		No.	Observed	Temperature Corrected	Temperature	Weight of Solution	Weight of Silver Nitrate	Weight of Potassium Nitrate	Weight of Water	Grams of Silver Nitrate per 100g water.	Moles of Silver Nitrate per 1000g Water	Value interpolated from graph for moles of Silver Nitrate per 1000g. Water.	Grams of Potassium Nitrate per 100g Water	Moles of Potassium Nitrate per 1000g Water.	Value interpolated from graph for moles of Potassium Nitrate per 1000g. Water.
1			20.1	20		2.7252	1.8740	.1432	.7080	264.69	15.58	13.0	20	2	3.13
2			21.6	21.5		2.0853	1.4182	.1921	.4750	298.57	17.57	13.47	40.44	4	3.37
3			28.8	28.8		2.6428	1.8655	.2238	.5535	337.04	19.84	16.8	40.43	4	4.35
4			36.2	36.2		2.4049	1.7531	.1877	.4641	377.74	22.24	20.4	40.44	4	5.5
5			28.8	28.8		1.9772	1.3705	.2291	.3776	363.00	21.36	16.8	60.67	6	4.35
6			36.2	36.2		2.8744	2.0403	.3149	.5192	392.97	23.13	20.40	60.65	6	5.5
7			36.2	36.2		2.8613	2.0226	.3476	.4911	411.85	24.24	20.40	70.78	7	5.5



If time permitted, it would be most enlightening to start from the other end by reversing the process, namely, by adding gradually increasing amounts of silver nitrate to a solution saturated with respect to potassium nitrate.

CONCLUSION:-

Now coming back to our research problem as stated on page 1, namely, the investigation of the solubility relationships of potassium nitrate and silver nitrate when found together in the same saturated solution, and finding out whether a double salt is formed or not, and if such a salt is formed what is its molecular structure; in other words stated graphically, whether graph No. 1 or graph No. 2 ^{shown on page 30} represents the true state of affairs, from the preliminary data thus far obtained we can draw no definite conclusions.

In as much as the solubility of both compounds is increased when found in presence of each other, it is evident that such a double salt of a higher solubility than either constituent is formed.

Moreover, as to its molecular structure the excess -which is the compound salt- left over in the three determinations given in the table following page 29 is as follows: the ratio in moles of silver nitrate to potassium nitrate in determination No. 1 is 10.75 to 12.02, in No. 2 it is 7.83 to 9.19 and in No. 3 it is 1.91 to 3.47 respectively. From these results no conclusion can be drawn. In all three cases, however, the compound has more potassium nitrate than silver nitrate.