SEPARATION OF
ALKALI COMPOUNDS BY AMMONIA

THESIS FOR THE DEGREE OF M. S.

Howard W. Eck

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Alkalies
Title

SEPARATION OF ALKALI COMPOUNDS
BY AMMONIA

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Howard W. Eck
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D T Ewing

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-INTRODUCTION-

It had been observed some years ago that when strong ammonium hydroxide was added to a saturated solution of potassium sulfate, a white precipitate was formed, but when the strong ammonium hydroxide was added to sodium sulfate, no precipitate was formed; and it was thought that possibly a qualitative separation might be possible.

A search of the literature revealed that in several instances this problem has been touched upon, but no one has ever used ammonia or ammonium hydroxide as a means of separating sodium from potassium compounds.

In a series of articles entitled "Liquid Ammonia as a Solvent" published in the Journal of Chemical Education by W. Conrad Fernelius, Ohio State Univ., Warren C. Johnson, Univ. of Chicago, Vol. V, 665-6, (June 1928), we find some information bearing on this problem, under sub-title of "Solubility Relationships of Liquid Ammonia." The authors state that "Ammonia differs from water in its inability to dissolve the sulfates, sulfites, the alkaline carbonates, phosphates, and oxalates, the hydroxides of the alkaline earth metals. The thiocyanates appear to be most soluble in liquid ammonia."

Similarly an article in Chemical Abstracts, 17-2998, "Ammonia and Carbonates of the Potassium Group" from the Ber. 56 B., 1454-5, (1923) we find the following:

"When the anhydrous, neutral carbonate of K, Rb, or Cs is added to an aqueous solution of NH_3, of any concentration at a temperature below 20°C, rise of temperature being prevented by external cooling, at saturation two layers form, the upper containing within 1% of all the NH_3 and the lower within 1% of all the carbonate. Water of neither layer is at the disposal of the other layer. If to this system a little $Cu(AcO)_2$ is added, all the Cu, except traces, dissolves in the lower layer. If the carbonate layer is not completely saturated, addition of Cu salt causes the layers to coalesce, but upon further addition of carbonate to saturation, separation of the layers again takes place, practically all the Cu being in the lower layer. Copper can thus be removed from NH_3 solution by shaking with solid K_2CO_3 to saturation."

One of the questions involved here is whether the precipitation of the alkali salts in NH_3 solutions is just due to a difference in solubility in ammonia and water solutions, or does some change take place in chemical composition or structure of the compound. We have a short reference on this point found in C.A. 16:2076 which states that "Complex salts are not formed in dilute solutions with salts of alkaline and alkaline earth metals, because of the presence of H_2O. Crystalline salts of some of these are known to exist in NH_3."

In studying the ammonia solutions it has been found that ammonia, up to a concentration of .4 N is dissolved as NH_4OH and above that as NH_3. The results which show the solubility of substances in ammonia are based on a certain percent of NH_3 in solution. Some work has been done on "Solubility of NH_4 salts in ammonia" as a method for the distinguishing and separation of mono-and polybasic acids in C.A. 20:534. In an article by E. Weitz; Z. Elektrochem. 31, 546(1925), he states that "Salts of mono-basic acids increase the aqueous solubility of NH_3 (they diminish the partial pressure of NH_3) while those of poly-basic acids decrease the solubility (by increasing the partial pressure of the NH_3). The influence of NH_3 on the aqueous solubility of NH_4 salts makes possible the distinguishing of poly-basic acids and the separation of mono- and polybasic acids, and can be made a criterion between mono- and polybasicity."

Some work directly bearing on the problem was found in C.A. 18:3256, namely, "Separating Alkali Metal Salts from Aqueous Ammonia", by C. E. Dolbear; U.S. 1,505,078 Aug. 12, in which he found that "Mixtures of alkali metal salts are treated with aqueous NH_3 solution to effect fractional separation; for example, NaCl and KCl may be dissolved from mixed Searles Lake salts (containing also Na_2SO_4, Na_2CO_3, and borax)."

Something of interest along this line where ammonium oxalate is used as a reagent for distinguishing between potassium and sodium salts was discovered by L. Meyerfeld. In C.A. 20:1189 and Z. Anal. Chem. 67, 150-1 (1925), he stated that "$Na_2C_2O_4$ is much less soluble in water than is $K_2C_2O_4$. The former salt precipitates when a salt solution of $(NH_4)_2C_2O_4$ is mixed with a saturated solution of NaCl."

A method in common use for the precipitation of Li by the use of NH_4OH and Na_2HPO_4 is found in "Qualitative Analysis for the Rare Elements" by Noyes and Bray. They state the following: "Filtrate containing Li salts, $HClO_4$ and C_2H_5OH is boiled with HNO_3. Then add C_2H_5OH and make strongly ammonical with NH_4OH; and add Na_2HPO_4. A precipitate of Li_3PO_4 results." You see in this separation of Li_3PO_4 we depend on its relative insolubility in strong ammonia solution.

Of course as stated before this difference in solubility of sodium and potassium sulfate in water and aqueous ammonia was noted, although no definite solubility curves were run to determine just what was the solubility in the varying concentrations of ammonia. It might also be possible that other sodium or potassium compounds would exhibit like behavior in these tests, or in fact we might expect a difference in solubility of all the compounds in the alkaline and alkaline earth families.

If no chemical change took place in the aqueous ammonia solution, we might then presuppose that if a difference in solubility was noted, and if this difference was of sufficient magnitude, an effective qualitative separation of the compounds might be possible.

-APPARATUS AND MATERIALS-

A tank of anhydrous ammonia gas was obtained and an apparatus for precipitation of the salts was devised. The ammonia was liberated from the tank in the form of a gas and the solution became warm from the bumping of the liquid. A large jar of water surrounding the precipitation tube aided in preventing a large increase in temperature.

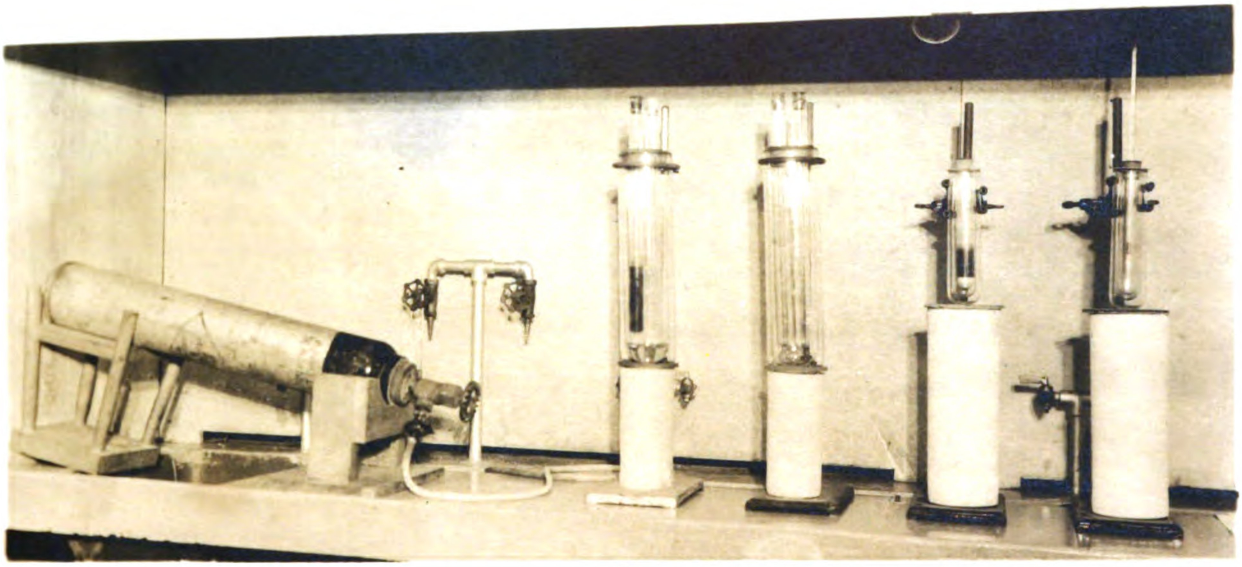
In the top of the tube was placed a two hole rubber stopper with a long glass tube going to within a short distance of the bottom, and a short tube which let the excess gas escape from the ignition tube, that was used for these experiments. The rubber tubing from the ammonia tank was fastened to the curved end of the long tube and the ammonia gas was allowed to bubble through the solution, while the excess gas escaped through the short tube at the top. A long piece of rubber tubing was attached to this and the excess gas was allowed to escape into the hood.

A more economical way would be to pass the ammonia gas from the tube through a large trap bottle and into a jar containing water. This would give an ammonia solution which might be used for other purposes. The trap bottle is necessary because the pressure of the gas is not constant and will suck the ammonia solution back into the tube.

The flow of NH_3 from the tank must be started to prevent the solution in the ignition tube from being pulled into the rubber hose upon opening the valve in the ammonia tank. This ammonia contains a small amount of water and could be dried by means of metallic sodium, but such refinement is not necessary here because we only need a saturated ammonia solution. However, if the solubility of the substance in liquid ammonia was wanted, this drying step would be of utmost importance. As the substances which we are most interested in, in this experiment, are insoluble in liquid ammonia, this piece of work will deal entirely with aqueous ammonia solutions of lower concentrations, which do not call for special pressure apparatus.

The apparatus pictured in this thesis consists of dewar tubes, into which a two hole stopper was placed, and the ignition tubes inserted in these. The dewar tubes contained solutions which tend to lower the temperature of the solution during the precipitation process with ammonia gas. In some cases small quantities of liquid ammonia were placed in the dewar tubes. The solution in the dewar tube might be precooled water, liquid ammonia, solid carbon dioxide in alcohol, liquid air, or any other solution which would lower the temperature to the desired level. In liquid ammonia where the solubilities are determined at the boiling point of the liquid ammonia, it is advisable to have the outer container filled with the liquid NH_3, so that a constant temperature may be maintained. If temperaturesbelow the boiling point of ammonia are desired, solid carbon dioxide in alcohol would be very good, or if extremely low temperatures that would solidify ammonia are desired, liquid air can be used in the dewar tubes.

It will be remembered that the ammonia should be let



LIQUID AMMONIA PRECIPITATION APPARATUS

in, in the form of a gas, with the first apparatus previously described. However, where the dewar tubes are used, the liquid ammonia may be added, and when the excess gas volatilizes, the concentration of the ammonia can be determined at the desired temperature, usually 25° C.

The materials used in this work consisted mainly of the purified salts of the alkaline and alkaline earth elements. In the preliminary experiments all the available sodium and potassium salts were used along with the chlorides of the alkaline earths, magnesium, and ammonium. The sulfates of the Li, NH_4, and Mg; and the nitrates of

NH_4, alkaline earths, and magnesium; and the carbonates of Li, and NH_4 were used in addition to the sodium and potassium salts. The sodium sulfate and the potassium sulfate used in the solubility experiment were purified by recrystallization from water three times. They were dried in the centrifuge. Coarse crystals of from one to three mm. in diameter were used.

-PROCEDURE-

Test tubes which held about 15 cc were filled to within 3 cm. of the top. Rubber stoppers were then placed in the ends of the tubes, and fastened over these a thin wide rubber band or tubing to hold the stoppers in and keep the water out. These were then wired to a revolving wheel and placed in a thermostat for a few hours. The rate of rotation was about 40 revolutions per minute. The process was stopped and the test tubes were brought to the top, stoppers removed, and the contents removed in two portions by filtering pipettes.

These pipettes were provided with tips connected by means of rubber tubes. Cotton was placed in these tips and the tips removed after the pipettes were filled. The contents were weighed and then evaporated in small porcelain dishes, covered with watch glasses, on a steam bath. The residue was cautiously heated over a bunsen flame, very low at first and increasing to full intensity in one hour. The residue was kept covered during heating to constant weight, which was usually attained very shortly.

In order to determine the strength of the NH_3 solution a pipette was inserted into it, and the NH_3 passed directly into a standard acid solution. To determine the amount of salt dissolved in the NH_3 solution, one must either obtain a separate portion or evaporate the neutralized solution, and then volatalize the ammonium salts.

A 10 cc pipette was constructed by putting two 5 cc pipettes together and then calibrating it so that it would deliver two 5 cc portions. The first portion was evaporated to dryness and the weight of dissolved salt in 5 cc of solution obtained, and from this the solubility was determined in grams per 1000 cc. The other five cc was delivered into a flask containing a standard acid, and the excess acid titrated, and from this the concentration of the ammonia calculated. The solubility of the salt was then expressed in grams per 100 cc, and the concentration as a certain percent NH_3 solution.

Strong ammonium hydroxide solution, approximately 28% NH_3, was placed in contact with solid K_2SO_4 and shaken for a period to saturate the solution. Ten cc of this solution was then drawn off and evaporated in a weighed crucible. The residue represented the solubility of K_2SO_4 in 28% NH_3.

After solubility curves were determined on K_2SO_4 and Na_2SO_4 in varying concentrations of NH_3, it was then necessary to determine how the other substances behaved in ammonia solutions. What was wanted in these qualitative tests was a comparison between the solubility of the salt in water and its solubility in ammonia solutions. Lower concentrations did not provide sufficient precipitate for comparison with the K_2SO_4 precipitate, so that only strong NH_3 solutions and NH_3 gas were used as precipitating agents. The former was added to a saturated solution of the salt at 25° C, and as stated before, a precipitate was obtained with K_2SO_4. Now many of the salts did not precipitate as the resulting concentration of the ammonia was not sufficient to cause precipitation; but upon the addition of NH_3 gas to the saturated solution of their salt, a copious precipitate was obtained. Of course the concentration of the resulting NH_3 solution depended on the salt being used for the experiment, but was approximately 32% NH_3 at 25° C.

Ten cc of the saturated solution of the salt was used in every case, and the temperature maintained at 25° C, so that any precipitate formed was due to a change in solubility of the salt, and not due to a change in solubility with temperature. Since the volume of the solution increased upon the addition of NH_3, the amount of precipitate was used as a basis of comparison.

The steps in the precipitation process were then as follows: first, preparation of the saturated solution of the salt in water, noting its solubility at 25° C; second, treatment of 10 cc of this solution with strong ammonium hydroxide, 28% NH_3, observing the amount of precipitation; third, treatment of another ten cc with NH_3 gas, noting the amount of the precipitate; fourth, comparison of this precipitate with the one produced with K_2SO_4.

-RESULTS-

We have noted previously a difference in the behavior of K_2SO_4, when treated with strong ammonium hydroxide, in contrast to the behavior of Na_2SO_4, when similarly treated. Now from this we might presuppose that K_2SO_4 was insoluble in strong NH_3 solutions, and that Na_2SO_4 was soluble in these solutions. This would be then a fine scheme for the separation of potassium from sodium compounds, by first converting them to sulfates, and then precipitating with NH_3; and only the K_2SO_4 would precipitate in the strong ammonium hydroxide. However by passing NH_3 gas into the saturated solutions of the salts, we also got a precipitate with Na_2SO_4. In other words increasing the concentration of the NH_3 decreased the solubility of the Na_2SO_4 to the extent that it also precipitated like the K_2SO_4, and the amount in each case was approximately the same. But we found that K_2SO_4 was much less soluble in water than Na_2SO4, and considering the same amount of precipitate in each case with NH_3 gas, the relative solubility showed the K_2SO_4 to be also much more insoluble in NH_3 than the Na_2SO_4.

As was expected, we found that practically all of the salts exhibited a difference in solubility in water and in strong NH_3 solutions. Also in some cases the solubility of the salt was greater in saturated ammonia solutions than in water, but in most cases the addition of the NH_3 gas decreased the solubility of the salt. No general rule could be stated but in most cases potassium salts seemed to be more insoluble in saturated NH_3 solutions than the corresponding sodium salts. However, as will be seen by looking at the table, there were many notable exceptions where the opposite was true. Specific cases where the potassium salt was more insoluble in water than the corresponding sodium salt may be seen in the table, but the same salts in saturated NH_3 solutions exhibited a reversal in that the sodium salt was more insoluble in this solution than the corresponding potassium salt.

Since qualitative tests depend on the bulk of the precipitate formed, the number 20 found in the table under solubility in 32% NH_3, would mean twice as much precipitate formed in this case as with the K_2SO_4, which is represented by 10 in the table. A precipitate with the rating of 2 would be only one fifth as much as the K_2SO_4, and so on through the table.

Solubilities in water are expressed in grams per 100 cc. In some cases only a symbol is used because information on its solubility is unavailable, since presumably its solubility has not been determined as yet. The symbol s represents soluble, sl. s. slightly soluble, and v.s. very soluble. This solubility for each salt is the first number in each table.

The second term in the table expresses the solubility of the salt when 28% NH_3 is added to it. The symbol L represents light precipitation, M medium precipitation, and H heavy precipitation. Where no symbol was used in this space no precipitate was obtained, and this was true in most cases.

The third number represents the amount of precipitate obtained in the 32% NH_3 solution, taking the K_2SO_4 precipitate equal to 10.

Table of Solubilities and Relative Precipitations of Salts

	K	Na	Li	NH_4	Ca	Ba	Sr	Mg
F	92 0	4 2						
Cl	34 40	36 2	79 0	37 0	75 M 35	36 o	53 0	55 M 85
Br	65 20	48 0						
I	144	179 1						
ClO_3	7 8	101 0						
BrO_3	7 10	35						
IO_3	8 M 15	9 H 85						
SO_4	11 M 10	25 10	25 L 30	75 50				30 H 45

	K	Na	Li	NH_4	Ca	Ba	Sr	Mg
HSO_4	51 H 90	50 50						
SO_3		27 30						
HSO_3	s. M 60	sl.s. 30						
S	s. H 60	16 1						
NO_3	32 15	88 0		192 0	43 L 1	9 0	71 L 0	65 H 95
NO_2	75 50	46 8						
PO_4	193 # 0	11 H 95						
HPO_4	v.s. H 95	7 M 85						
H_2PO_4	25 M 60	85 H 100						
CO_3	53 4	22 M 45	1.3 10	100 0				
HCO_3	25 8	10 45						
SiO_3	s. 0	s. H 100						

	K	Na	Li	NH_4	Ca	Ba	Sr	Mg
CrO_4	62 L 80	47 0						
Cr_2O_7	12 60	64 M 95						
CN	72 25	s. 30						
CNS	69 0	v.s. 0						
$K_3Fe(CN)_6$	33 10							
$K_4Fe(CN)_6$	28 H 50							
C_2O_4	33 H 40	4 M 15						
HC_2O_4	2.2 10	1.7 2						
$H_3(C_2O_4)_2$	1.8 .5	s. 5						
$C_4H_4O_6$	50 80							
$NaKC_4H_4O_6$	26 100							
$HC_4H_4O_6$	.5 0							

	K	Na	Li	NH_4	Ca	Ba	Sr	Mg
$C_2H_3O_2$	256 0	124 0						
$C_6H_5O_7$	167 70	91 70						
AsO_2	s. 30							
$HAsO_3$		v.s. 95						
BO_2		s. 5						
MnO_4	6 H 50							

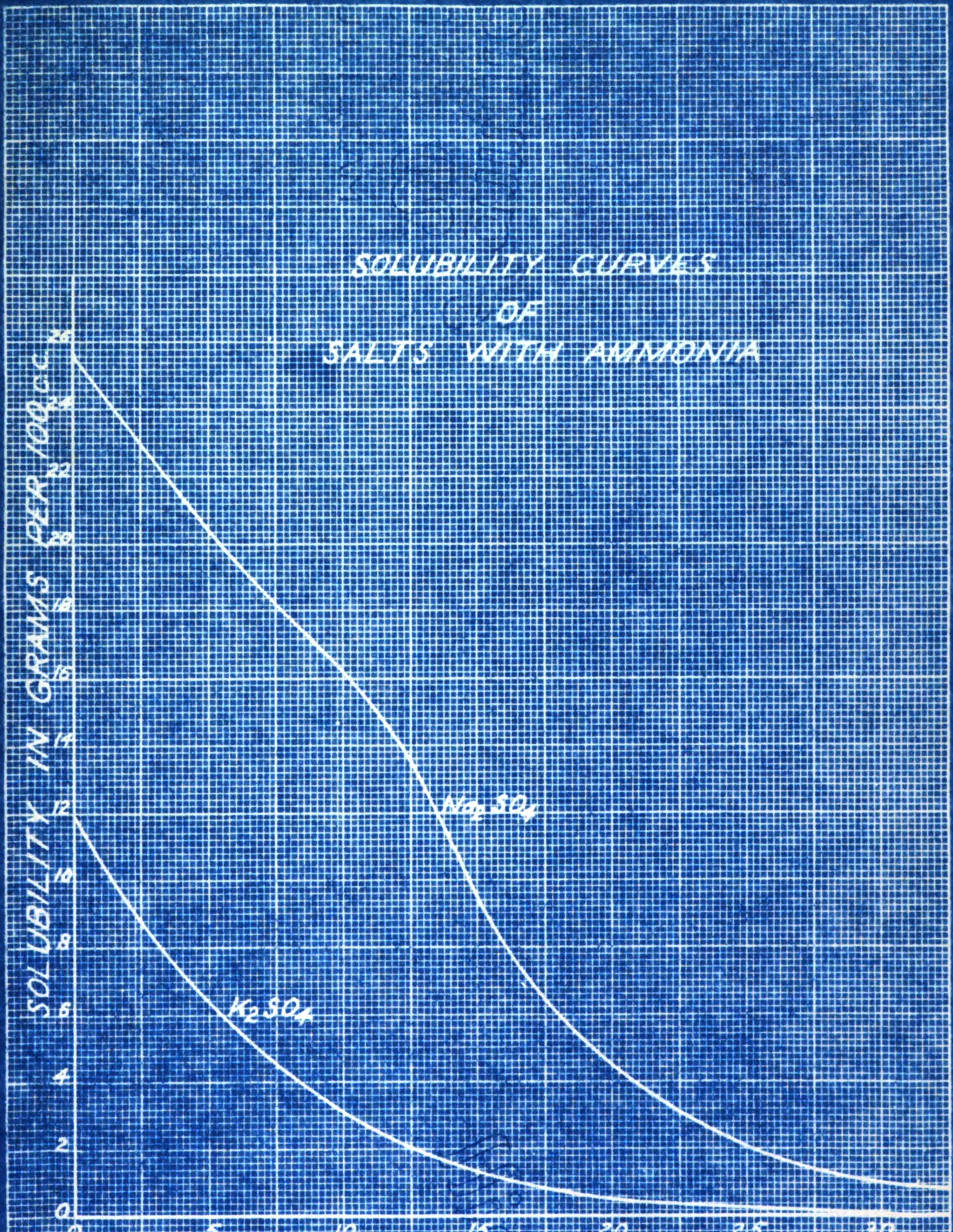
In the precipitation experiments with strong ammonium hydroxide and NH_3 gas, we discovered how the salts behaved in these solutions in comparison with aqueous solutions. The relative amount of precipitation was the criteria of separation in each pair of the sodium and potassium salts. After observing the amount of precipitate formed for qualitative tests, it was also of interest to determine just how much of the salt was still left in solution after complete precipitation.

Since the sulfates are very common and easily produced in solution, it was thought advisable to run solubility curves on the sodium and potassium sulfates as a basis for comparison. We wanted to determine the solubility of these salts in different concentrations of ammonia, and plot on a graph the solubility of the salt in grams per 100 cc of solution against the percent ammonia in the solution.

The following table shows the results of the solubility experiments, and the accompanying graph illustrates clearly the decreasing solubility of the salts with increasing ammonia concentrations.

Table of Solubilities in Varying Ammonia Concentrations

% NH_3	Solubility of K_2SO_4	Solubility of Na_2SO_4
0	11.660g.	25.662g.
5.6	5.660"	20.020"
8.4	3.873"	17.225"
11.2	2.654"	15.547"
14	1.577"	11.407"
16.8	.947"	6.987"
19.6	.601"	4.555"
22.4	.389"	3.006"
25.2	.240"	1.885"
28	.145"	1.227"
32.5	.025"	.886"



SOLUBILITY CURVES
OF
SALTS WITH AMMONIA

-DISCUSSION-

Perhaps the most interesting aspects of this work relate to the distinguishing features which tend to show the behavior of the different salts during the ammonia precipitation process. If we look at the Table of Solubilities and Relative Precipitations of the Salts, we observe many interesting features among the salts. The important points of separation will now be pointed out.

Na_2F_2 is much more insoluble in water than K_2F_2, and we observe that the same condition holds in 32% NH_3, namely, the Na_2F_2 precipitates while the K_2F_2 remains in solution.

The chlorides offer an interesting example of the behavior with NH_3. The KCl precipitates freely, the NaCl very slightly, LiCl and NH_4Cl remain in solution, $CaCl_2$ precipitates freely, while $BaCl_2$ and $SrCl_2$ show no precipitate; and $MgCl_2$ almost completely precipitates, which undoubtedly is due to the formation of magnesium hydroxide. From this we can see that large amounts of KCl can be precipitated in solutions containing NaCl, LiCl, or NH_4Cl, simply by passing NH_3 gas into the saturated solution of these salts. Also $CaCl_2$ can be separated from $BaCl_2$ and $SrCl_2$ in a like manner, the $CaCl_2$ even precipitating in a saturated solution treated with 28% NH_3.

KBr is more soluble in water than NaBr, yet when NH_3 gas is added, solubility is reversed, and KBr precipitates. This would tend to show that the potassium salts seem to be more insoluble in the 32% NH_3 solution than the corresponding sodium salts.

However, the iodates tend to show quite the opposite behavior. The $NaIO_3$ is a little more soluble in water than KIO_3, but in 32% NH_3 the $NaIO_3$ precipitates almost completely, while the KIO_3 shows only slightly above normal precipitation.

Since tha Ca, Ba, Sr, sulfates are almost completely insoluble in water, we neglected them because they are also insoluble in NH_3. In the 32% NH_3 we find precipitates in all the remaining cases. The Li_2SO_4 is more insoluble than the Na_2SO_4 in 32% NH_3 and they have the same solubility in water. The $(NH_4)_2SO_4$ seems to be the only one of the ammonium salts that precipitated.

The bisulfates are interesting when treated with 28% NH_3, since they have approximately the same solubility in water. The $KHSO_4$ shows a heavy precipitate, while the $NaHSO_4$ shows no precipitate.

We expected that all the nitrates would be soluble in 32% NH_3, but even here the KNO_3 is difficultly soluble to the extent that it precipitates. Again the $Mg(OH)_2$ is formed as an insoluble precipitate from the $Mg(NO_3)_2$.

The normal phosphates are very interesting. The K_3PO_4 is very much more soluble in water than Na_3PO_4. K_3PO_4 is a deliquescent substance, and when treated with 28% NH_3, or when NH_3 gas is passed into the saturated solution of the salt, a two phase system is produced, which on long standing does not break down, as long as the NH_3 content is maintained. The upper phase contains most of the ammonia, while the lower phase contains most of the potassium phosphate. Now if we take Na_3PO_4 which isn't so soluble in water as the K_3PO_4, and treat the saturated solution with 28% NH_3, or with NH_3 gas, we get almost complete precipitation.

Li_2CO_3 is sparingly soluble in water and is very insoluble in the 32% NH_3.

Na_2SiO_3 precipitates completely with NH_3 or with 28% NH_3 solution, while K_2SiO_3 shows no tendency to precipitate.

K_2CrO_4 is more soluble in water than Na_2CrO_4, but K_2CrO_4 precipitates heavily when NH_3 is added, while Na_2CrO_4 shows no evidence of precipitation. When dichromates are used, both the Na and K salts precipitated from their saturated solutions.

Both of the cyanides precipitate while the thio-cyanates appear to be the most soluble substances in NH_3. Although the $K_4Fe(CN)_6$ is less soluble in water than $K_3Fe(CN)_6$, the former precipitates much more heavily with NH_3 than the later, even giving a heavy precipitate of $K_4Fe(CN)_6$ when treated with 28% NH_3 solution.

The acetates offer an example where neither the Na or K salts precipitate, but unlike the thio-cyanates, do not increase their solubility in NH_3 solution.

The precipitate of $KMnO_4$ which is formed in the precipitation process with NH_3 changes on standing to MnO_2.

In every case we might take each salt and run its solubility in concentrations of ammonia from 0% to 100%, and after getting all this data, plot curves which show the behavior of the salts when NH_3 is added. In most cases, we have pointed out the decreasing solubility with increasing ammonia content, and as the sulfates are used in this work, reference to the graph illustrates this point.

K_2SO_4 is an anhydrous salt and the solubility curve is smooth, decreasing with increases in NH_3 content.

Na_2SO_4 in crystalline form exists as a decahydrate and as a heptahydrate, and also there is an anhydrous form. Now the undissolved salt is always in equilibrium with the dissolved salt, and if anhydrous Na_2SO_4 is the solid phase, then Na_2SO_4 in solution exists in equilibrium with this. If we start with $Na_2SO_4(H_2O)_{10}$ and add NH_3 removing the amount of water available to the salt, we might expect to pass through $Na_2SO_4(H_2O)_7$, and finally in strong ammonia solutions, only the Na_2SO_4 anhydrous would exist. Now in water, $Na_2SO_4(H_2O)_{10}$ is soluble to the extent of about 26 grams per 100 cc, while $Na_2SO_4(H_2O)_7$ is about 44 grams per 100 cc soluble, while anhydrous Na_2SO_4 is even more soluble. However, when NH_3 is added, the solubility of the salt decreases, and if the curve's deflection is extrapolated to the zero line, the approximate location of the $Na_2SO_4(H_2O)_7$ and anhydrous Na_2SO_4

could be located. The curve of the Na_2SO_4 thus differs from K_2SO_4 because of the possible hydrates formed.

-SUMMARY-

This work is unique in that it opens an entirely new field for speculation and investigation in inorganic chemistry. Here we have a precipitating agent, namely ammonia gas, which does not depend on common ion action, or formation of a new compound such as complex ammonia salts. The observed precipitation is due solely to a change in solubility from water to strong aqueous ammonia solutions.

Of course, when the solubility of the salt decreases in the solution, precipitation takes place. If the solubility remains the same, or is actually increased upon the addition of ammonia, no precipitation of the salt is observed. Thiocyanates seemed to increase their solubility in aqueous ammonia, acetates remained the same, while most of the other salts of the alkaline metals showed a tendency to decrease in solubility and precipitate. Each salt seemed to exhibit a definite solubility in aqueous ammonia, usually different from that in water, and this could not be predicted. Usually the potassium salt was more insoluble than the sodium salt, yet in some cases, the opposite was true. This followed generally the solubility order in water, the potassium salt being slightly more insoluble than the corresponding sodium salt.

Since the ammonia used does not enter into chemical union with the salts, it may be used over in industrial applications of this method of precipitation. For example, saturated salt brines containing chlorides, bromides, nitrates, or chlorates may be treated with ammonia gas, and the resulting precipitates, largely potassium salts, separated from the bulk of the brine. The ammonia gas could be volatilized by heating the brine and used again to treat a new sample. Precipitates rich in potassium salts could then be further treated. Any magnesium salts would in this process produce the insoluble hydroxide, which could be filtered off from the water soluble potassium salts.

Analytical schemes, where large samples are available, in which only a flame test for potassium or sodium salts is used, could further improve the tests by using some of the things presented in this work. The residue in the form of sulfates, containing sodium and potassium salts, after the volatilization of ammonium salts, could be dissolved in a small amount of water, such as 5 cc, to make a saturated solution, and then treated with strong ammonium hydroxide. The presence of a white precipitate would indicate the presence of potassium in the final residue.

It is unnecesary to elucidate further on this scheme of precipitation, since numerous applications would present themselves in pursuance of this research.