# DOUBLE SALT STUDY IN THE SYSTEMS AMMONIUM NITRATE-UREA, AND AMMONIUM NITRATE—UREA—WATER

BY

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# Double Salt Study in the Systems,
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# Ammonium Nitrate-Urea-Water.

## l. Introduction.

Ammonium nitrate would make a practicable fertilizer, if a double salt or a mixed salt containing ammonium nitrate could be formed that was non-hygroscopic. If a double salt could be formed with urea it would make a very concentrated fertilizer, due to the high percentage of available nitrogen. No references could be found in literature to such a salt or to the systems, ammonium nitrate-urea and ammonium nitrate-urea-water. However some preliminary work has been done in this laboratory by Tavenner in 1921, and Jones and Rhodes in 1922, on the system ammonium nitrate-urea-water. This system was studied first, and out of it grew the study of the second system, ammonium nitrate-urea. The more complete study was made of the second system, ammonium nitrate-urea. The object of the study was about the same in both systems, to see if a double salt ammonium nitrate-urea is formed under normal conditions. In the system ammonium nitrate-urea, to study the phenomenon of the low melting point of the two salts when mixed together. In the system ammonium nitrate-urea-water, to measure the solubility of the two salts in the presence of each other at different concentrations in a saturated solution.

## ll. Experimental methods.

### (1) The System Ammonium-Nitrate-Urea.

Each of the two salts were re-crystallized from solution several times, and were as pure as could readily be obtained in this way. The two systems were worked out on

the following principle.

If a double salt is formed in the mixture there will be two definite compositions of the solution at a given temperature. They will remain constant in equilibrium with the variable solid phase as the composition of the system is altered. One of these will exist when both ammonium nitrate and the double salt are present as solids, and the other when urea and the double salt are present as solids. When the compositions are plotted, there will be three corves if a double salt is formed, one curve each of ammonium nitrate and urea, and between these should be a curve on which the double salt is formed. If no double salt is formed there will be but two curves, and at the point of intersection both ammonium nitrate and urea will exist in solid phases, or in the case of the freezing curve the intersection will be a eutectic.

(a) Preliminary experiments.

A mixture of ammonium nitrate and urea when heated to about 50° C. yields a clear liquid, and on cooling this yields cubical crystals at the eutectic point. A preliminary study was made of this system in order to be absolutely sure no moisture was in the crystals to give a solution. The following molar proportions of ammonium nitrate and urea; 9;1, 75;25,6;4,4;6,25;75, were carefully weighed out and put in Y tubes, care being taken not to mix them, ammonium nitrate on one side, and urea on the other. The ammonium nitrate side

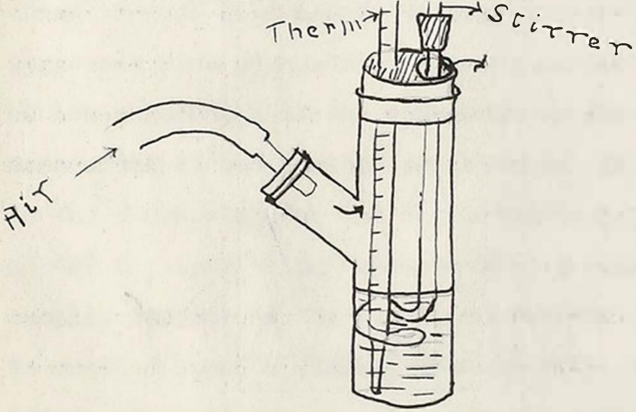
was placed in an oil bath, heated to about 170° C., the urea side was placed in a water bath, heated to about 80°C. A vacuum pump was applied, and heat maintained fairly constant for 2½ hours. At the end of this time the tubes were sealed off under a vaccum. Having been heated to these temperatures for such a period of time, it could be reasonably assumed that no moisture was present in the crystals. The two salts were mixed, reheated in a water bath, and in each case a solution was obtained between 45° C. and 100° C. In tubes 6;4, 4;6, and 75;25, all the crystals went into solution. The freezing points of the excess compound and the eutectics of these three samples were determined by reading the temperature of the bath. As no account for super-cooling of the salts could be taken, this method was inaccurate, and was discarded as a means for a complete study of the system.

### (b) The Final Experiments.

The analysis of the system ammonium nitrate-urea partly was carried out in a drying box, which consisted of a large tight wooden box, one side being fitted with a glass, at the top, a large removable glass pane, thru which the operations on the inside could be observed, and which served as an admittance to the box. Two holes were madein the side, and fitted with rubber sleeve protectors to which rubber gloves had been glued. The box was lined inside and out with oil cloth, making it air tight. In this box was placed large quantities of calcium chloride, a balance, and a large quantity of the two compounds to be used, having been previously dried

in a desiccator.

The salts were weighed out in the box, put in a freezing tube having a thermometer, stirrer, and two rubber stoppers. On the stirrer was placed a small stopper that fitted into a hole in the big stopper. The arm of the tube was closed with a one-hole rubber stopper, carrying a small glass tube on which was fastened a small rubber tube with a pinch cock. A diagram is given below.



Before leaving the box, the compounds were stoppered in the tube so that no air could get in. The tube was removed from the box, and the air that had bubbled thru concentrated $H_2SO_4$ was passed thru the arm of the tube and out thru the hole around the stirrer. This prevented moist air from getting into the tube while the freezing point was being made. The mixture was heated in a Crisco bath until all the crystals were in solution, care being taken not to raise the temperature any higher than was necessary. Though in most cases it was necessary to carry the temperature about 15 or 20 degrees above the freezing point to get a complete saturation with ease. It seemed to go from a solid to a liquid

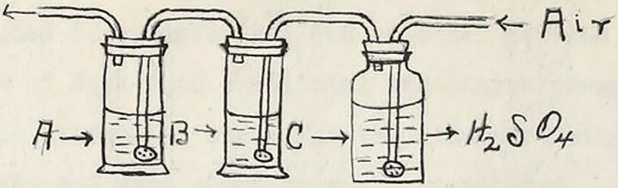
phase very slowly. The results given in ~~the~~ Table I. were taken as the first solid phase came out of solution, cooling taking place in the air.

## (2) The System Ammonium-Nitrate-Urea-Water.

The study of the system, ammonium nitrate-urea-water, was about the same as that carried out by Tavenner in this laboratory. Various proportions of the two compounds were prepared in aqueous solution. Determinations of the percentage of the compounds in the solution were made after it had reached equilibrium. The samples were kept in the thermostat for six days, the temperature being kept at 40° C., care being taken to have a solid phase in each sample. Samples of the liquid phase were drawn off at 40° C. in small Erlenmyer flasks, then weighed and diluted to a liter for analysis. The character of the crystals was enough identification of the solid phase. No account of the moisture was taken, tho the samples were kept as free from it as possible. The percentage of ammonium nitrate and urea in liquid phase was accomplished for each compound by an ammonia determination. One compound was decomposed at a time, without the other being affected.

### (a) Ammonia in Ammonium Nitrate.

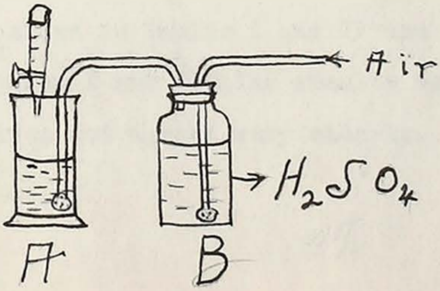
For the determination of ammonia in ammonium nitrate an apparatus like the following was used.



A 10 C.C. portion from the liter solution was added to the cylinder B, together with a little distilled water, and enough solid potassium carbonate to saturate the solution. A measured quantity of a standard HCl solution was added to the cylinder A. Suction was applied for 40 minutes and a vigorous stream of air was drawn thru. The ammonia produced by the potassium carbonate was carried into the acid, the excess of acid was titrated against a standard base, methyl red being used as an indicator. A little caprylic alcohol was added to B to prevent foaming as the air was being drawn thru. Potassium carbonate does not decompose urea at room temperature.

### (b) Ammonia in Urea.

For the determination of ammonia in urea an apparatus like the following was used.



A 10 C.C. portion of the liter solution under investigation was added to cylinder A., and an equal portion of aqueous extract of Jack Bean containing the enzyme urease was added. This was allowed to stand for ten minutes. Methyl red and caprylic alcohol were added in small quantities, standard acid was run in from a burette, keeping the solution as near neutral as possible, because the enzyme is ineffective in an acid or strong basic solution. A gentle stream of air was passed thru the reacting solution to keep it well stirred. After it had run for 30 minutes, an excess acid was added, and the solution allowed to stand. The excess acid was titrated with a standard base after ten minutes. Ammonium nitrate is not affected by the enzyme urease.

The aqueous solution of the Jack Bean containing the enzyme urease was prepared by removing the outer covering of the bean, crushing the kernal in a mortar, and putting one crushed kernal in about 75 C.C. of water, warmed to about 40°. This was stirred frequently for 20 minutes, and filtered until clear. It was found best not to powder the bean, for it then passed thru the filter paper.

## III Experimental Data.

The data are shown in Tables I and II and are expressed graphically in Figures I and II. The results as given were checked among themselves and agreed very closely.

Very rough determinations of the melting points were made of potassium nitrate-urea and sodium nitrate-urea in approximately 50-50 molar proportions. The melting point of the former was about 107°, and 67° for the latter. This might prove to be an interesting point for further investigation.

## Table I

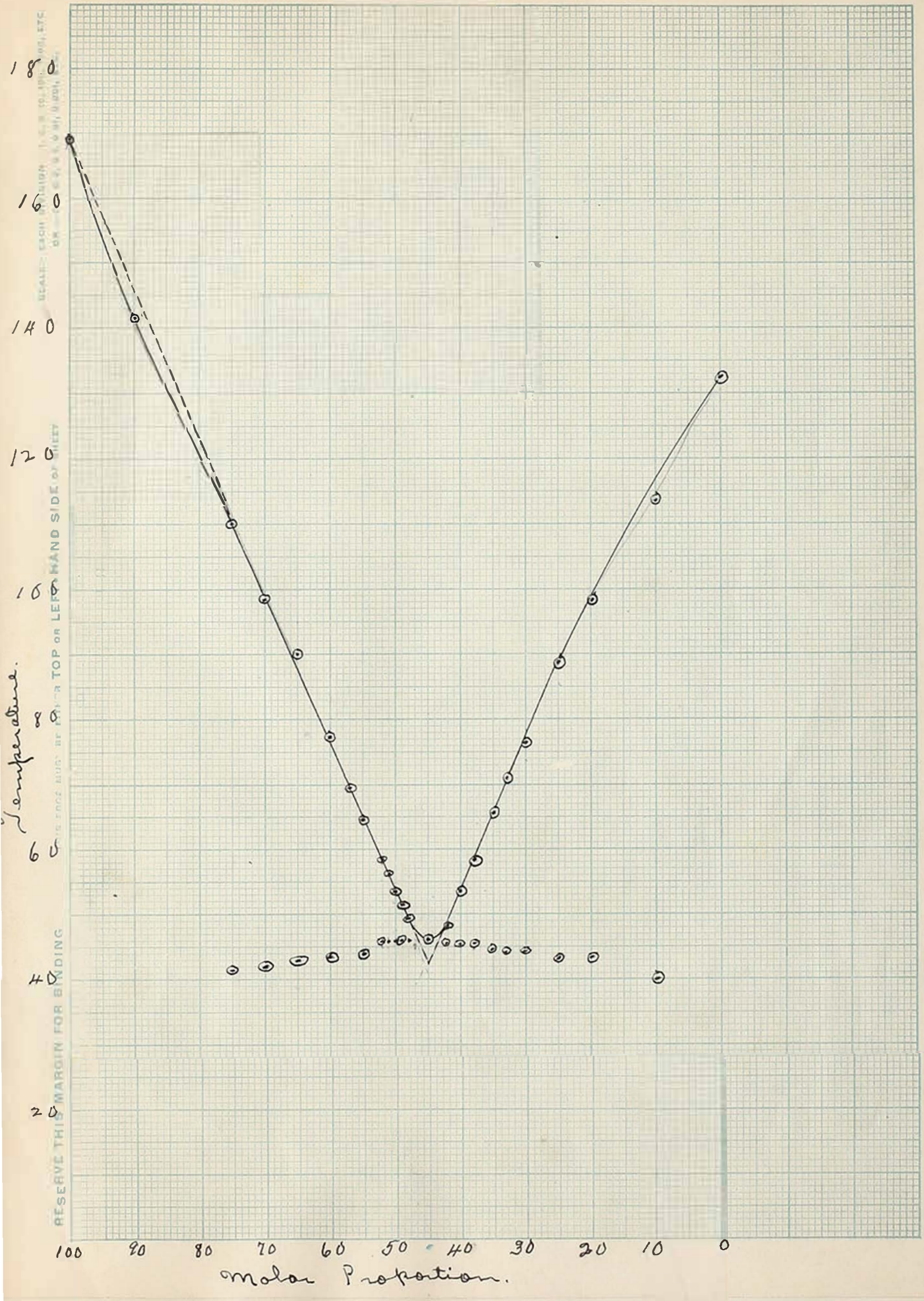
Freezing points of Ammonium Nitrate-Urea.

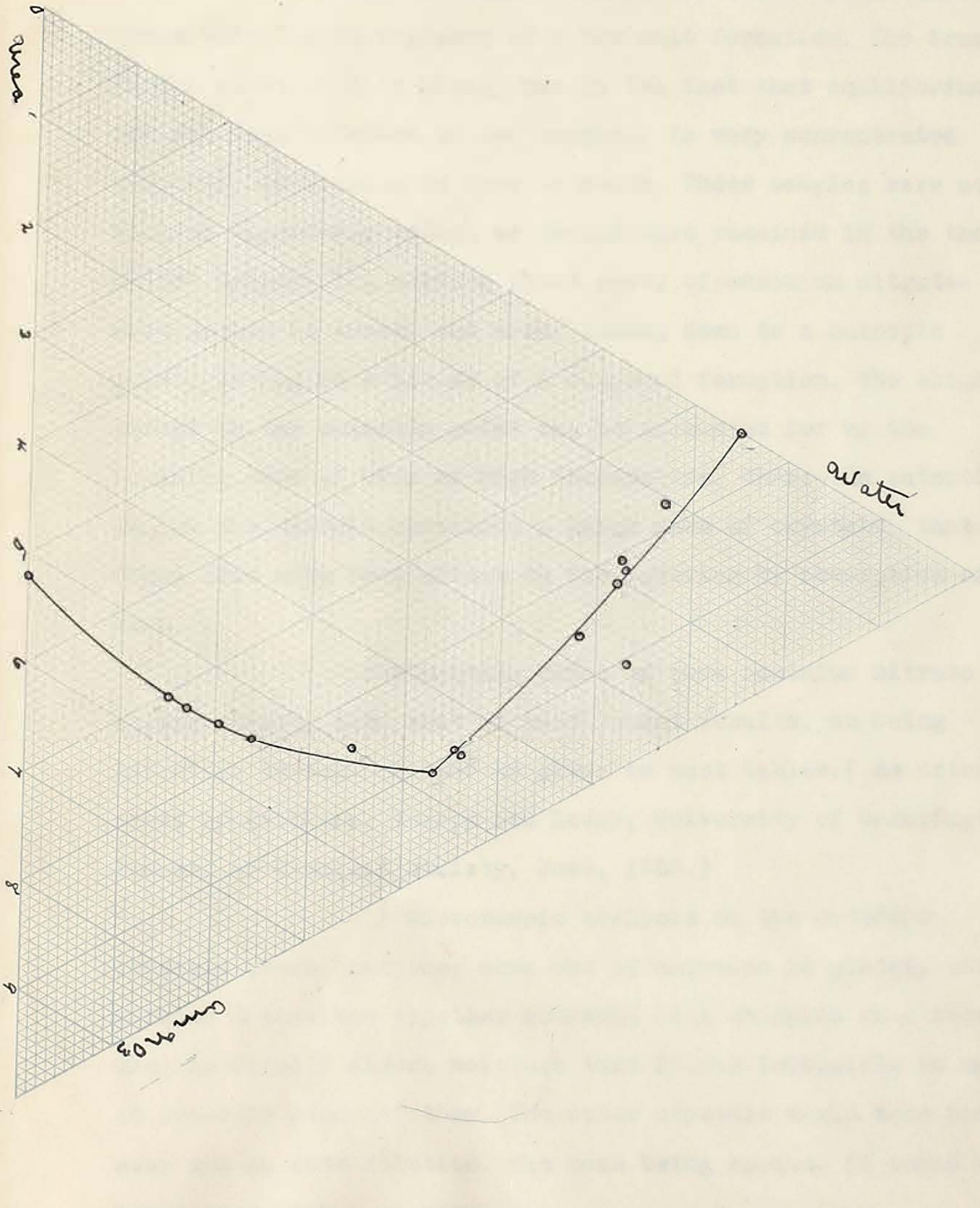
| Mol. Prop. $AmNO_3$-Urea | Freezing Points Excess Compound. | | Eutectic. |
|---|---|---|---|
| Ammonium Nitrate in excess. | | | |
| 100-0 | 169.6 | (Journal of the Chemical Soc.) | |
| 90-10 | 141.5 | | |
| 75-25 | 110.0 | | 41.5 |
| 70-30 | 98.1 | | 41.7 |
| 65-35 | 90.0 | | 42.8 |
| 60-40 | 77.1 | | 43.2 |
| 57-43 | 69.6 | | -- - |
| 55-45 | 64.5 | | 44.0 |
| 52-48 | 58.0 | | -- - |
| 51-49 | 56.0 | | 46.0 |
| 50-50 | 53.5 | | 46.0 |
| 49-51 | 51.5 | | 46.0 |
| 48-52 | 49.3 | | 46.1 |
| 45-55 | 00.0 | | 46.0 |
| | | | |
| Urea in Excess. | | | |
| 42058 | 48.2 | | 45.2 |
| 40-60 | 53.7 | | 45.8 |
| 35-65 | 65.8 | | 44.9 |
| 38-62 | 58.5 | | 45.3 |
| 33-57 | 71.0 | | 44.3 |
| 30-70 | 76.4 | | 44.2 |
| 25-75 | 89.0 | | 43.3 |
| 20-80 | 98.0 | | 43.3 |
| 10-90 | 113.0 | | 40.0 |
| 0-100 | 132.6 | (Hand Book) | -- - |

## Table II

### The System Ammonium Nitrate-Urea-Water.

| Experimental | | | | Solution | | | Solid Ph |
|---|---|---|---|---|---|---|---|
| Approx. No.Br. in Sample. | | | | % | % | % | |
| No. | $AmNO_3$ | Urea | $H_2O$ | $AmNO_3$ | Urea | $H_2O$ | |
| 1. | 14.0 | 2.0 | 4.0 | 67.0 | 10.5 | 22.3 | $AmNO_3$ |
| 2. | 12.5 | 3.0 | 2.5 | 62.5 | 18.1 | 19.4 | " |
| 3. | 12.5 | 4.5 | 2.0 | 63.3 | 27.4 | 9.3 | " |
| 4. | 18.0 | 5.0 | 4.0 | 63.1 | 18.9 | 18.0 | " |
| 5. | 19.0 | 6.0 | 4.0 | 62.1 | 20.6 | 17.3 | " |
| 6. | 20.0 | 10.0 | 3.5 | 58.4 | 27.4 | 14.2 | " |
| 7. | 2.0 | 10.0 | 3.0 | 15.2 | 55.5 | 29.3 | Urea |
| 8. | 3.0 | 11.0 | 4.0 | 17.0 | 55.3 | 27.7 | " |
| 9. | 4.0 | 11.0 | 4.0 | 20.6 | 55.0 | 24.4 | " |
| 10. | 5.0 | 16.0 | 4.0 | 23.9 | 54.6 | 21.5 | " |
| 11. | 7.0 | 10.0 | 1.0 | 34.7 | 49.8 | 15.5 | " |
| 12. | 10.0 | 10.0 | 0.5 | 45.5 | 44.4 | 10.1 | Both |
| 13. | 10.0 | 10.0 | 0.5 | 46.1 | 44.0 | 9.9 | " |
| 14. | 25.0 | 25.0 | 0.0 | 43.1 | 47.7 | 9.2 | " |
| From Solubility Tables. | | | | | | | |
| 15. | -- - | -- - | - - | 75.0 | -- - | 25.0 | |
| 16. | -- - | -- - | - - | -- - | 52.0 | 48.0 | |


180
160
140
120
100
80
60
40
20
Temperature.
100
90
80
70
60
50
40
30
20
10
0
Molar Proportion.


Urea
0
1
2
3
4
5
6
7
8
9
Water

## IV. Discussion.

The ammonium nitrate-urea-water system curve shows very little evidence of a new salt formation. The break in the curve is most likely due to the fact that equilibrium had not been attained in the samples. In very concentrated solution equilibrium is hard to reach. These samples were not stirred vigorously enough or should have remained in the thermostat longer. The melting point curve of ammonium nitrate-urea system is smooth and even, coming down to a eutectic point, giving no evidence of a compound formation. The slight change in the eutectic point can be accounted for by the breaking down of urea at high temperature. Where the eutectic is low the mixture contained a large mass of crystals, that might also have some effect on the lowering by absorption of heat.

The melting point of pure ammonium nitrate agrees closely with that of most recent results, as being 169.6° C. instead of 156° as given in most tables.( As determined by Millican, Joseph and Lowry, University of Cambridge, Journal of Chemical Society, June, 1922.)

A microscopic analysis of the eutectic crystals shows that they come out of solution in plates, and arrange themselves together somewhat like shingles on a roof. They so readily absorb moisture that it was impossible to make an accurate study of them. The outer crystals would soon break away and go into solution. The mass being opaque, it could not be studied with a microscope.

In making up samples to a liter for analysis in the system ammonium nitrate-urea-water, it was noticed that the eutectic crystals went into solution slower than either of the two salts, evidently due to the compactness of the mixture.

The eutectic crystals of ammonium nitrate-urea would make excellent drying material for desiccators. In order to get the best yield of eutectic crystals, a 45-55 ~~mean~~ molar proportion of ammonium nitrate and urea should be taken.

V. Summary.

(1) A study has been made of the system ammonium nitrate-urea-water at 40°C , and of the system ammonium nitrate urea.

(2) From the study of these systems no evidence was found of a compound formation.

(3) A mixture of ammonium nitrate and urea gives a phenomenal melting point lowering, being 46° C. in a 45-55 molar proportion.