

In conclusion the authors thank Drs. D. A. MacInnes, T. Shedlovsky and A. S. Brown of the Rockefeller Institute for Medical Research for their coöperation in calibrating the instruments used in this research and for their helpful advice in the problems encountered in producing suitable silver-silver chloride electrodes.

Summary

1. The electromotive force of the cell Tl (solid), TlCl(m), AgCl, Ag has been determined by combining measurements on the cells Tl(dilute amalgam), TlCl(m), AgCl, Ag, and Tl(solid), Tl₂SO₄(0.03 M) Tl(dilute amalgam), for temperatures from 0 to 50° employing thalious chloride of molalities from 0.0005 to 0.01 *m*.

2. The logarithms of the activity coefficients of thalious chloride when plotted against the square root of the molality exhibit an *experimental slope* which is somewhat *greater* than the predictions of the Debye-Hückel limiting law in regions of high dilution, although our results indicate that the *limiting slope* is 0.506 at 25° in agreement with the theory. This finding is in contradiction to conclusions drawn by Davies and others based upon determinations by the solubility method at higher concentrations, who report an apparent limiting slope equal to 0.38.

3. The experimental results follow the predictions of the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory when the parameter "*a*" is assigned a value of 0.93 Ångström. This "*a*" value, however, is smaller than the distance of closest approach (3.3 Å.) deduced from crystal structure measurements, and is of doubtful physical significance.

4. The results may be more satisfactorily explained on the basis of incomplete dissociation. The failure of the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory to account for the data when "*a*" is assigned a value of the same order of magnitude as the distance of closest approach of the ions deduced from crystal structure measurements shows that the theory makes no pretense of accounting for incomplete dissociation, a point concerning which there has been some difference of opinion.

5. The values of the partial molal heats of dilution of thalious chloride computed by the aid of the Gibbs-Helmholtz equation have been tabulated.

For the cell Tl(solid), TlCl(m), AgCl, Ag, at twenty-five degrees

$$\begin{array}{ll} E^\circ = 0.55833 & - \Delta F^\circ = 12,877 \text{ calories} \\ dE^\circ/dT = 6.646 \times 10^{-4} & - \Delta H^\circ = 8,307 \text{ calories} \end{array}$$

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Ternary Systems of Urea and Acids. I. Urea, Nitric Acid and Water. II. Urea, Sulfuric Acid and Water. III. Urea, Oxalic Acid and Water

BY LAWRENCE H. DALMAN

Introduction

A study of the literature shows that the salts of urea have received little systematic treatment although the nitrate and oxalate, because of their slight solubility, were utilized as tests for urea almost a century ago. Regnault¹ crystallized these salts and from their analyses derived the formulas now generally assigned to them although the investigations of Marchand² appear to indicate that the salts contain water of crystallization. More recently DuToit³ employed phase rule methods to determine the constitution of the salts formed in aqueous solutions of urea with each of

five common acids. In the absence of experimental data, however, his findings cannot be regarded as conclusive.

It seemed desirable therefore to make a systematic study of the solubility relations of urea with the various acids and to determine the constitution and limits of stability of the existing salts. In the present investigation a phase rule study was made of the three ternary systems consisting of urea, water and each of the following: nitric, sulfuric and oxalic acids. Further work on urea-acid systems is now in progress.

Experimental Part

Materials.—The urea and oxalic acid were Mallinckrodt "Analytical Reagent." Analyses of this urea by the stand-

(1) Regnault, *J. prakt. Chem.*, **16**, 286 (1839).

(2) Marchand, *ibid.*, [I] **34**, 248 (1845); **35**, 481 (1845).

(3) DuToit, *Verlag. Wetenschappen*, **22**, 573 (1913).

ard urease method showed an average urea content of 99.6%. Two recrystallizations from water gave no appreciable improvement of this figure. The hydrated oxalic acid averaged 99.89% of its theoretical value by titration with alkali.

The nitric and sulfuric acids were Baker and Adamson concentrated c. p. quality. Before standardization the nitric acid was diluted and aerated. Sulfuric acid ranging up to 100% was obtained by mixing fuming sulfuric with the regular concentrated acid.

Procedure.—Solubilities were measured by analysis of solutions obtained by agitation of the three components in glass-stoppered tubes in an electrically controlled thermostat for at least twelve hours. This was found to be sufficient time for the systems to reach equilibrium. Temperature variations were within $\pm 0.02^\circ$. Samples of the clear saturated solution were taken up in a pipet (warmed when necessary) and weighed in stoppered 125-cc. Erlenmeyer flasks. To prevent ingress of solid material the end of the pipet was protected by a piece of cotton cloth held securely by means of thread.

The acid content of the sample was determined by direct titration with standard alkali using phenolphthalein as indicator. Urea was determined as ammonia by the standard urease method as outlined by Fox and Gelhard⁴ and used for the measurement of the solubility of urea by Pinck and Kelly.⁵ Preliminary experiments showed that this method is equally applicable to the measurement of urea-acid mixtures providing the acid is carefully neutralized before the urea analysis is made.

The routine analysis of urea is as follows. A few cc. of saturated solution was pipetted into a 125-cc. Erlenmeyer flask, diluted when necessary, and an aliquot taken so that the sample always contained approximately 0.1 g. of urea. The acid was neutralized in the presence of methyl red and the sample diluted to 40 cc. Ten cc. of the urease solution was then added and the flask set in water at 50° . After fifteen minutes the contents were cooled to room temperature and a slight excess of 0.1 *N* hydrochloric acid added. The sample was next aerated for fifteen minutes to remove carbon dioxide and finally the excess acid was titrated with 0.1 *N* sodium hydroxide and the quantity of urea calculated from the actual amount of acid used to neutralize the converted ammonia.

Referring to the precision of the urease method for the determination of urea, Fox and Geldard reported that duplicate analyses agreed within $\pm 0.1\%$. This accuracy was confirmed in general in the present investigation although the values for the solubility of urea reported here at 10, 25 and 40° show considerable variation from the results of Pinck and Kelly. As a check on the urease method the solubility of urea was also determined at 25° by evaporation. The average of four analyses gave a value of 54.54% as compared to 54.5% by means of urease. Moreover, the figures reported here at 25 and 40° are in good agreement with those of Shnidman and Sunier,⁶ whose measurements were made by the synthetic method of Alexejew. It appears therefore that the urease method is valid and that the disparity of Pinck and Kelly's data

can probably be attributed to the fact that the solutions failed to reach equilibrium in the time allotted.

The data thus obtained from the analyses of the saturated solutions, and the compositions of the original complexes have been expressed in weight per cent. and assembled in Tables I–III. In the last column are indicated the saturating solid phases which have been abbreviated as follows: Ur for urea; Ur·N for $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$; Ur_2S for $[\text{CO}(\text{NH}_2)_2]_2 \cdot \text{H}_2\text{SO}_4$; Ur·S for $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$; Ur_2O for $[\text{CO}(\text{NH}_2)_2]_2 \cdot \text{H}_2\text{C}_2\text{O}_4$; Ur·O for $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ and Ox for $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The identification of the various solid phases has been established by means of the extrapolated tie lines and confirmed, in the case of the double salts, by the results of direct analyses as shown in Table IV.

I. Urea, Nitric Acid and Water

This system was studied at 10, 25 and 40° ; experimental data are given in Table I. At each of these temperatures the isotherm consists of two curves which correspond to the same two solid phases, namely, urea and urea nitrate $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$. Although the tie lines of the 10 and 25° isotherms are not shown in Fig. 1, they extrapo-

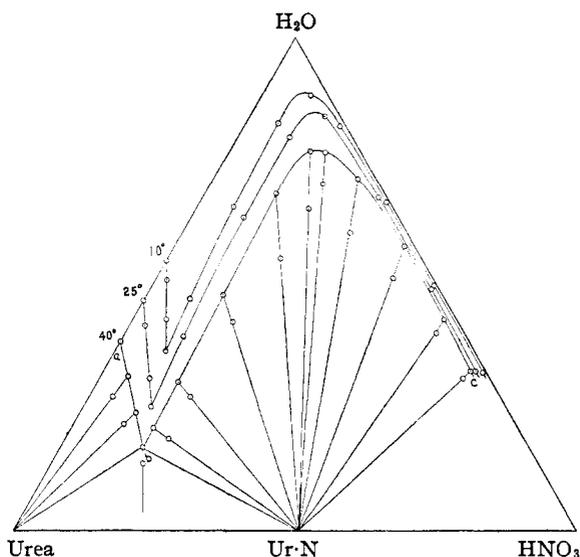


Fig. 1.—10, 25 and 40° isotherms.

late to the same solid phases as those of the 40° isotherm which is given in complete detail. The compositions of the various isothermally invariant points shown in the tables are the average of two independent analyses.

DuToit reported that urea nitrate decomposes in nitric acid exceeding 74%. No evidence of decomposition was noted at the concentrations studied although the analyses have not been carried beyond the range of the concentrated nitric acid. The slight extensions of the curves

(4) Fox and Geldard, *Ind. Eng. Chem.*, **15**, 743 (1923).

(5) Pinck and Kelly, *THIS JOURNAL*, **47**, 2170 (1925).

(6) Shnidman and Sunier, *J. Phys. Chem.*, **36**, 1232 (1932).

TABLE I
UREA-NITRIC ACID-WATER

| Original complex Wt., % Urea | complex Wt., % HNO ₃ | Satd. soln. | | Solid phase |
|------------------------------------|---------------------------------------|----------------|----------------------------|-------------|
| | | Wt., % Urea | Wt., % HNO ₃ | |
| 10° | | | | |
| .. | .. | 46.0 | 0.0 | Ur |
| 52.0 | 2.0 | 48.1 | 2.2 | Ur |
| 56.0 | 6.0 | 52.5 | 6.5 | Ur |
| 57.5 | 10.5 | 54.7 | 9.0 | Ur + Ur-N |
| 44.9 | 10.0 | 44.7 | 8.1 | Ur-N |
| 30.0 | 10.0 | 28.4 | 6.8 | Ur-N |
| 15.0 | 10.0 | 11.7 | 5.8 | Ur-N |
| 10.0 | 15.0 | 3.2 | 8.5 | Ur-N |
| 5.0 | 20.0 | 1.1 | 17.0 | Ur-N |
| 5.0 | 35.0 | 0.5 | 33.0 | Ur-N |
| 5.0 | 50.0 | 0.4 | 50.0 | Ur-N |
| 5.0 | 66.0 | 0.4 | 67.2 | Ur-N |
| 25° | | | | |
| .. | .. | 54.5 | 0.0 | Ur |
| 60.0 | 3.0 | 56.8 | 3.2 | Ur |
| 64.0 | 9.0 | 61.6 | 9.7 | Ur |
| 64.5 | 14.0 | 63.1 | 12.1 | Ur + Ur-N |
| 50.0 | 15.0 | 50.0 | 11.2 | Ur-N |
| 30.0 | 15.0 | 27.1 | 9.4 | Ur-N |
| 16.4 | 15.3 | 11.1 | 9.1 | Ur-N |
| 10.0 | 20.0 | 2.4 | 13.5 | Ur-N |
| 5.0 | 32.8 | 1.3 | 31.2 | Ur-N |
| 5.0 | 50.0 | 1.4 | 49.9 | Ur-N |
| 5.0 | 65.0 | 1.7 | 66.1 | Ur-N |
| 40° | | | | |
| .. | .. | 62.3 | 0.0 | Ur |
| 70.0 | 5.0 | 64.9 | 5.8 | Ur |
| 70.0 | 10.0 | 67.0 | 11.0 | Ur |
| 71.0 | 16.0 | 68.3 | 14.7 | Ur + Ur-N |
| 64.0 | 17.0 | 64.7 | 14.7 | Ur-N |
| 55.0 | 18.0 | 55.6 | 14.3 | Ur-N |
| 40.0 | 18.0 | 38.9 | 13.9 | Ur-N |
| 25.0 | 20.0 | 19.5 | 12.5 | Ur-N |
| 15.0 | 20.0 | 8.9 | 14.3 | Ur-N |
| 10.0 | 20.0 | 6.2 | 16.9 | Ur-N |
| 10.0 | 30.0 | 3.1 | 25.5 | Ur-N |
| 7.0 | 42.0 | 1.8 | 40.8 | Ur-N |
| 5.0 | 55.0 | 2.1 | 55.1 | Ur-N |
| 5.0 | 35.0 | 2.4 | 65.3 | Ur-N |

beyond the final points are therefore intended merely to show that the curves are incomplete.

II. Urea, Sulfuric Acid and Water

In Table II are recorded data of the solubility measurements made at 10 and 25°. The isotherms which have been plotted together in Fig. 2 are of great similarity, thus indicating that the same solid phases exist at both of these temperatures. It is evident from the extrapolation of the tie lines of the complete 25° isotherm that the solid phases are urea and two double salts, [CO(NH₂)₂]₂·H₂SO₄ and CO(NH₂)₂·H₂SO₄.

TABLE II
UREA-SULFURIC ACID-WATER

| Original complex Wt., % Urea | complex Wt., % H ₂ SO ₄ | Satd. soln. | | Solid phase |
|------------------------------------|---|----------------|--|--------------------------|
| | | Wt., % Urea | Wt., % H ₂ SO ₄ | |
| 10° | | | | |
| .. | .. | 46.0 | 0.0 | Ur |
| 50.0 | 1.0 | 47.0 | 1.0 | Ur |
| 52.0 | 3.0 | 48.6 | 3.2 | Ur |
| 55.0 | 5.0 | 51.1 | 5.4 | Ur |
| 58.0 | 10.8 | 54.2 | 11.9 | Ur |
| 60.0 | 17.0 | 57.2 | 18.0 | Ur |
| 63.0 | 23.0 | 60.4 | 24.6 | Ur |
| 63.5 | 28.5 | 62.2 | 28.2 | Ur + Ur ₂ S |
| 56.0 | 31.6 | 56.0 | 30.1 | Ur ₂ S |
| 50.0 | 35.0 | 48.7 | 32.7 | Ur ₂ S |
| 43.0 | 38.4 | 40.4 | 37.2 | Ur ₂ S |
| 40.0 | 45.0 | 36.8 | 44.9 | Ur ₂ S |
| 40.0 | 49.8 | 37.9 | 50.2 | Ur ₂ S |
| 40.0 | 53.0 | 38.7 | 51.6 | Ur ₂ S + Ur-S |
| 35.0 | 55.0 | 34.2 | 52.4 | Ur-S |
| 30.0 | 54.5 | 28.9 | 53.6 | Ur-S |
| 25.0 | 57.0 | 22.0 | 56.0 | Ur-S |
| 19.0 | 61.0 | 15.7 | 60.4 | Ur-S |
| 15.0 | 68.0 | 12.6 | 68.4 | Ur-S |
| 18.0 | 72.0 | 15.9 | 72.9 | Ur-S |
| 22.0 | 73.0 | 19.7 | 74.0 | Ur-S |
| 26.0 | 73.6 | 24.7 | 74.6 | Ur-S |
| 25° | | | | |
| .. | .. | 54.5 | 0.0 | Ur |
| 60.0 | 5.0 | 57.6 | 5.4 | Ur |
| 61.7 | 8.9 | 59.2 | 9.6 | Ur |
| 62.1 | 14.7 | 60.9 | 15.0 | Ur |
| 65.0 | 18.0 | 62.4 | 19.3 | Ur |
| 69.0 | 22.0 | 64.5 | 24.9 | Ur |
| 67.5 | 30.5 | 65.8 | 29.3 | Ur + Ur ₂ S |
| 60.0 | 32.0 | 60.6 | 31.0 | Ur ₂ S |
| 54.0 | 34.0 | 54.1 | 33.2 | Ur ₂ S |
| 50.0 | 37.0 | 49.2 | 35.7 | Ur ₂ S |
| 46.0 | 40.0 | 44.1 | 39.0 | Ur ₂ S |
| 42.0 | 46.0 | 40.3 | 46.4 | Ur ₂ S |
| 42.5 | 49.5 | 40.7 | 50.2 | Ur ₂ S |
| 43.5 | 53.5 | 42.2 | 52.7 | Ur ₂ S + Ur-S |
| 39.0 | 54.0 | 39.4 | 53.2 | Ur-S |
| 33.0 | 56.0 | 31.8 | 55.0 | Ur-S |
| 27.0 | 59.0 | 25.0 | 57.9 | Ur-S |
| 22.0 | 62.5 | 19.8 | 62.4 | Ur-S |
| 22.0 | 68.0 | 19.3 | 68.9 | Ur-S |
| 27.0 | 70.0 | 24.3 | 72.1 | Ur-S |
| 28.0 | 71.4 | 26.5 | 72.9 | Ur-S |

III. Urea, Oxalic Acid and Water

The solubility data obtained in the study of this system at 10, 25 and 40° are assembled in Table III. While the solubility measurements for the hydrated oxalic acid are in good agreement with the figures recorded in Seidell's tables⁷ at 25 and 40°, the value reported here at 10° is 5.41%, that in Seidell 5.731%.

(7) Seidell, "Solubilities," Van Nostrand Co., New York, 1919 p. 468.

The isotherm at 10° consists of three sectors which as will be seen from Fig. 3 correspond to the three solid phases, urea, the double salt $[\text{CO}(\text{NH}_2)_2]_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ and oxalic acid $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. At 25 and 40° the isotherms contain a new sector lm shown in Fig. 4 which as will be explained later first appears in the system at 21.22°. Its length at 25°, however, is too small to permit of accurate portrayal and so this isotherm has been omitted. The single tie line which emanates from this new curve extrapolates to a point on the base line approximating the composition $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$. The proof of this composition is based on the analysis of the solid phase.

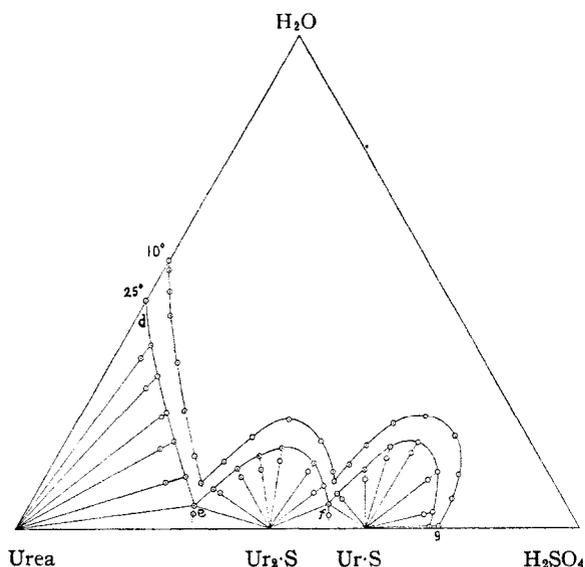


Fig. 2.—10 and 25° isotherms.

The Quintuple Point.—Referring to the isotherms shown in Figs. 3 and 4, it will be seen that the curve lm for the mono-urea oxalate originates at the isothermally invariant point j when the system already contains vapor, liquid solution and two solid phases. The entrance of the fifth phase results in an invariant system with no degrees of freedom. This quintuple point was determined at 21.22° by the usual method of noting the point of constant temperature on a cooling curve obtained when a properly chosen complex was stirred in a Beckmann freezing point tube. The composition of the liquid phase at the quintuple point is $\text{CO}(\text{NH}_2)_2$, 1.26%; $\text{H}_2\text{C}_2\text{O}_4$, 9.40%; H_2O , 89.34%.

The Anhydrous Double Salts.—Inspection of the accompanying isotherms shows that the tie lines extending from the solubility curves of the

TABLE III
UREA-OXALIC ACID-WATER

| Original Wt., % Urea | complex Wt., % $\text{H}_2\text{C}_2\text{O}_4$ | Satd. soln. Wt., % Urea | Wt., % $\text{H}_2\text{C}_2\text{O}_4$ | Solid phase |
|----------------------------|---|-------------------------------|--|--|
| 10° | | | | |
| | | 46.0 | 0.0 | Ur |
| 50.0 | 5.0 | 46.2 | .2 | Ur + Ur_2O |
| 45.0 | 5.0 | 43.3 | .2 | Ur_2O |
| 35.0 | 5.0 | 32.2 | .2 | Ur_3O |
| 20.0 | 5.0 | 15.6 | .2 | Ur_2O |
| 10.0 | 5.0 | 4.6 | .4 | Ur_2O |
| 5.0 | 5.0 | 1.2 | 2.3 | Ur_2O |
| 5.0 | 15.0 | .9 | 5.7 | Ur_2O + Ox |
| .. | .. | 0.0 | 5.4 | Ox |
| 25° | | | | |
| | | 54.5 | 0.0 | Ur |
| 58.0 | 3.0 | 54.6 | 0.3 | Ur + Ur_2O |
| 50.0 | 10.0 | 47.9 | .3 | Ur_2O |
| 40.0 | 10.0 | 35.0 | .3 | Ur_2O |
| 30.0 | 5.0 | 26.9 | .6 | Ur_2O |
| 20.0 | 10.0 | 9.4 | .9 | Ur_3O |
| 10.0 | 10.7 | 1.9 | 5.0 | Ur_2O |
| 13.0 | 19.0 | 1.5 | 10.3 | Ur_2O + $\text{Ur}\cdot\text{O}$ |
| 5.0 | 22.0 | 1.4 | 11.0 | $\text{Ur}\cdot\text{O}$ + Ox |
| .. | .. | 0.0 | 10.2 | Ox |
| 40° | | | | |
| .. | .. | 62.3 | 0.0 | Ur |
| 68.0 | 5.0 | 62.4 | .5 | Ur + Ur_2O |
| 60.0 | 5.0 | 60.5 | .5 | Ur_2O |
| 55.0 | 5.0 | 55.0 | .5 | Ur_2O |
| 50.0 | 5.0 | 49.2 | .5 | Ur_2O |
| 35.0 | 5.0 | 32.4 | .6 | Ur_2O |
| 20.0 | 5.0 | 16.1 | .9 | Ur_2O |
| 10.0 | 5.0 | 6.6 | 2.2 | Ur_2O |
| 10.0 | 10.0 | 3.9 | 5.8 | Ur_2O |
| 10.0 | 15.0 | 3.1 | 11.2 | Ur_2O |
| 12.0 | 23.0 | 2.8 | 14.7 | Ur_2O + $\text{Ur}\cdot\text{O}$ |
| 10.0 | 25.0 | 2.5 | 16.9 | $\text{Ur}\cdot\text{O}$ |
| 5.0 | 27.0 | 2.2 | 19.3 | $\text{Ur}\cdot\text{O}$ + Ox |
| 1.0 | 25.0 | 1.2 | 18.7 | Ox |
| .. | .. | 0.0 | 17.8 | Ox |

various double salts converge generally toward points on the base line, thus indicating that the double salts are anhydrous. In order to verify the compositions denoted by the extrapolated tie lines, the individual salts were grown by slow evaporation of water at room temperature from solutions in which these salts were the stable phases, and then subjected to analysis.

The identification of the mono-urea oxalate varied somewhat from the above procedure due to the fact of its incongruent solubility. In order to ensure the crystallization of this salt, a solution represented by a point on the curve lm, near to l, was allowed to evaporate slowly in an oven maintained at 40°. The evaporation was inter-

rupted before the loss of water carried the total composition outside of the area in which this salt is the stable phase.

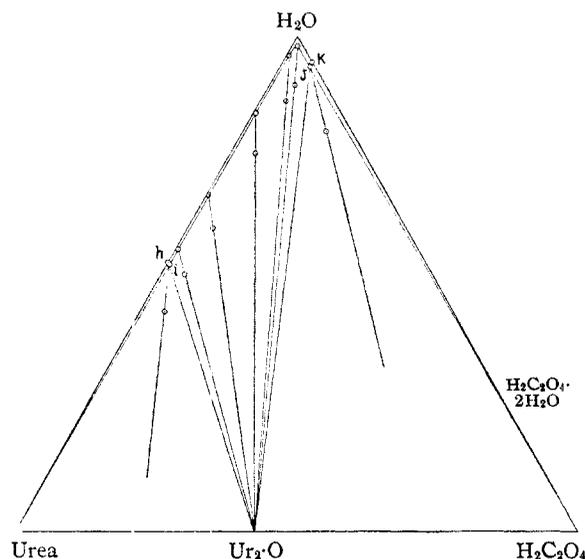


Fig. 3.—10° isotherm.

About 5–10 g. of crystals was obtained of each salt; after being thoroughly centrifuged they were analyzed. The results of the analyses of the five double salts which are given in the table below prove beyond question that they are anhydrous.

TABLE IV

| | Calculated, % | | | Found, % | | |
|--------------------|---------------|-------|------------------|----------|------|------------------|
| | Urea | Acid | H ₂ O | Urea | Acid | H ₂ O |
| Ur·N | 48.79 | 51.21 | 0.00 | 48.6 | 50.7 | 0.7 |
| Ur ₂ ·S | 55.05 | 44.95 | .00 | 54.3 | 44.3 | 1.3 |
| Ur·S | 37.97 | 62.03 | .00 | 37.4 | 60.9 | 1.7 |
| Ur ₂ ·O | 57.12 | 42.88 | .00 | 56.9 | 42.7 | 0.5 |
| Ur·O | 39.98 | 60.02 | .00 | 39.7 | 59.6 | .7 |

The formulas of the urea salts thus established agree with those reported in the literature—mono-urea oxalate, however, has not been reported previously.

Discussion of Results

A comparison of the isotherms of the three ternary systems shows that the solubility of urea is generally increased upon the addition of acid to the point where salt formation occurs. While the nitrate and oxalates are stable salts of low solubility, the sulfates are deliquescent and dissolve freely. The solubility of urea nitrate decreases rapidly with increase of nitric acid in the system and reaches a minimum when the total nitric acid concentration is about 50%. The solubility of

the di-urea oxalate, in contrast, becomes progressively smaller with increase of urea.

As the isotherm approaches the base line with rising temperatures, the solutions of the urea sulfates become more and more viscous. This condition accounts for the rather high percentage of water found in the analyses of these salts, since it was quite impossible to free them satisfactorily from the sirupy mother liquor. Moreover, the salts, particularly the mono-urea-sulfate, are deliquescent. A rough determination of the melting points of the two urea sulfates showed that they are both near 70°.

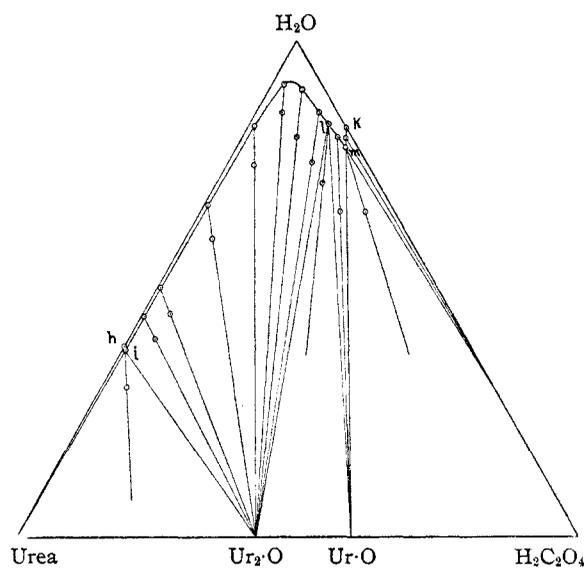


Fig. 4.—40° Isotherm.

The author wishes to express his thanks to Dr. Arthur E. Hill of New York University for his interest in this work and for offering the facilities of the Nichols Laboratory, where a part of this work was done.

Summary

1. The solubility relationships in the systems urea–nitric acid–water and urea–oxalic acid–water have been studied at 10, 25 and 40°; the system urea–sulfuric acid–water has been studied at 10 and 25°.
2. The following salts have been found to exist: CO(NH₂)₂·HNO₃, [CO(NH₂)₂]₂·H₂SO₄, CO(NH₂)₂·H₂SO₄, [CO(NH₂)₂]₂·H₂C₂O₄ and CO(NH₂)₂·H₂C₂O₄.
3. The mono-urea oxalate has been found to be stable only above 21.22°.