[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

EQUILIBRIUM IN THE SYSTEM: UREA, METHYL ALCOHOL

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While investigating in this Laboratory the rate of crystallization from supersaturated solutions, Dr. John D. Jenkins observed that when a supersaturated solution of urea in methyl alcohol at 0° is violently agitated, a solid phase separates that is quite different in crystal form from that of ordinary urea. Further investigation showed that at a given temperature this form of urea was much less soluble in methyl alcohol than the ordinary form and that the crystals probably contained one molecule of alcohol of solvation to each molecule of urea. The solvated crystals changed to the non-solvated urea at a temperature a few degrees below that of the room.

The following investigation was undertaken to determine accurately (1) the composition of this solvated form of urea, (2) its transition temperature and (3) the solubilities of both forms in methyl alcohol.

Experimental Part

Materials.—The methyl alcohol was purified by drying an acetone-free preparation over lime, refluxing and distilling. The product used boiled at 64.1° (744.3 mm.).

The urea was recrystallized from pure methyl alcohol.

Temperature Control.—An ordinary thermostat was used for temperatures down to 0°. Below that temperature freezing mixtures suggested by Guthrie[1] were used, with the following salts: potassium chloride, ammonium chloride, sodium nitrate, ammonium sulfate, sodium chloride, sodium bromide, giving temperature ranges from —9.85° to —24.90°. In each case the salt used was stirred vigorously with ice and water in a well insulated container, giving a bath that was constant to ±0.05° for a length of time sufficient to permit the solubility determinations to be made.

The determination at —78° was made in a bath of carbon dioxide, snow and ether.

Method.—Saturated solutions of urea in methyl alcohol with an excess of the solid phase were placed in test-tubes 5 cm. × 25 cm., which were allowed to come to constant temperature in the bath while being vigorously stirred. Samples of the liquid phase were taken by the method described by Walton and Judd.[2] The weighed sample was analyzed by evaporating the alcohol under reduced pressure at room temperature and weighing the residue. The accuracy of this method was tested by dissolving known weights (0.2–0.5 g.) of pure urea in methyl alcohol and evaporating the alcohol. In six such determinations the average weight of the residue was within 0.3 mg. of the weight of the sample taken, showing conclusively the reliability of this method of analysis.

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[1] Guthrie, *Phil. Mag.*, **49**, 269 (1875).

[2] Walton and Judd, THIS JOURNAL, **33**, 1036 (1911).

Composition of the Solvated Crystals.—The crystals were prepared by vigorously stirring a saturated solution of urea in methyl alcohol at 0°; the excess of alcohol was then decanted and small amounts of the solid phase were placed in weighing bottles in a vacuum desiccator at 0°. In the bottom of the desiccator approximately 100 cc. of a saturated solution of urea in methyl alcohol was placed and 5 cc. of water then added to this solution. After 24 hours the crystals (packed in ice to prevent loss of the combined alcohol) had lost practically all of the free alcohol and the weighing bottles were removed, stoppered and weighed, which gave the weight of the solvated crystals. The crystals were then allowed to stand at room temperature to remove the alcohol of solvation, weighed and the alcohol of solvation was calculated. The results are shown in Table I.

TABLE I

COMPOSITION OF SOLVATED UREA CRYSTALS

Solid phase, g.	0.1710	0.3646	0.2592	0.1956	0.1544	0.2677	0.1968	0.1444	0.2603	0.1654	0.1505	0.1160	0.0709	0.1282	0.0764	0.1083	0.1040	0.1028
Combined CH_3OH, g.	.0964	.2116	.1300	.1047	.0938	.1616	.1048	.0700	.1494	.0970	.0838	.0682	.0408	.0760	.0426	.0690	.0626	.0524
CH_3OH: $CO(NH_2)_2$, mols.	1.06	1.09	.965	1.01	1.14	1.15	.998	.907	1.07	1.10	1.04	1.10	1.08	1.07	1.17	1.09	1.13	.966

It is evident from these results that the formula for the solvated form of urea is $CO(NH_2)_2.CH_3OH$.

Solubility Data.—The data for the solubilities of the two forms of urea expressed in grams of non-solvated urea per 100 g. of methyl alcohol at various temperatures are given in Table II and shown graphically in Fig. 1. Curve A represents the solubility of the metastable non-solvated form, while Curve B shows the solubility of the solvated form.

TABLE II

SOLUBILITY OF UREA IN METHYL ALCOHOL

1. Temp., °C.		18.79	18.14	16.63	15.23	8.03	7.33	0.25	−9.85	−15.20	−17.00	−17.15	−17.45	−17.60	−18.10	−20.20	−20.55	−21.30	−24.90	−78.00
2. G. of $CO(NH_2)_2$ per 100 g. of CH_3OH	Non-solvated	...	21.16	...	19.73	...	16.70	14.24	11.64	10.92	...	...	...	...	...	...	...	...	...	...
3.	Solvated	20.27	19.56	17.72	16.47	11.30	10.98	7.71	4.88	3.93	3.63	3.57	3.76	3.45	3.48	3.25	3.16	3.17	2.89	0.32

In a number of instances, in analyzing solutions to determine the solubility, the solvated crystals remained in the solvated state even at room temperatures. This case is analogous to that of certain hydrated salts, notably sodium sulfate decahydrate, $Na_2SO_4.10H_2O$, which may be kept as such for a considerable length of time even when it is in a metastable condition.

It appears from the solubility curves that the ordinary or non-solvated form of urea becomes metastable at temperatures below the transition point, 19.20° and, as would be expected the unstable phase is the more soluble.

Determination of the Transition Point.—The solubility curves show that the transition point of urea into urea-monomethanol $CO(NH_2)_2 \cdot CH_3OH$, is approximately 19.2°. To check this point, some solvated crystals were placed in a dilatometer and the temperature was allowed to rise gradually. With different samples the transition points observed were: 19.16°; 17.29°; 17.58°; 17.78°; 17.95° and 19.44°. This lack of agreement may be attributed to the slow rate of change of the crystals and the very considerable heat change involved.

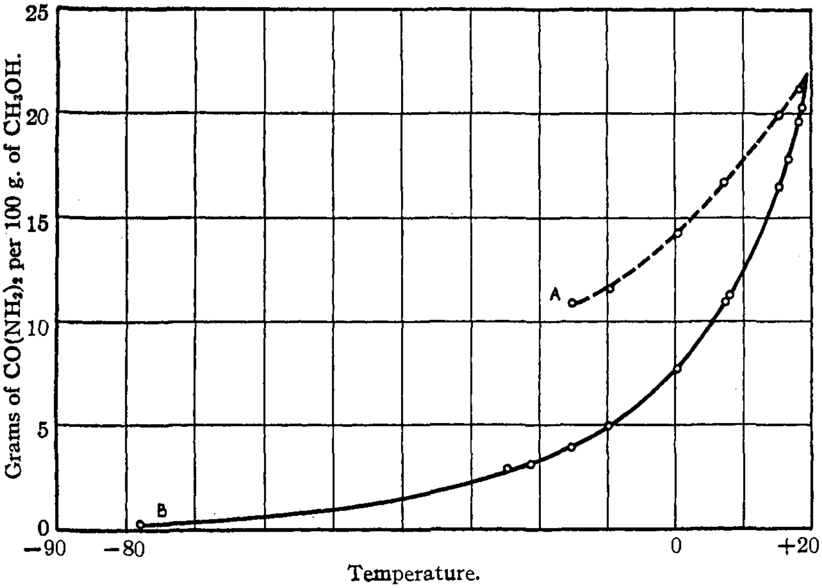

Fig. 1.

The dilatometric method being unsatisfactory, a method depending on thermal change was tried. Approximately 15 g. of solvated urea at a temperature of approximately 10°, together with a small amount of alcohol, was placed in a large test-tube and the mixture stirred rapidly. A thermometer was placed in the tube and the tube and crystals were allowed to come to room temperature slowly. The temperature was taken every minute over a period of 15 minutes. When the results were plotted against time, a very considerable break in the curve was shown at 19.25°. This figure for the transition point is in agreement with the value (19.20°) obtained from the solubility curves.

Speyers[3] and Timofeiew[4] have determined solubilities of urea in methyl

[3] Speyers, *Am. J. Sci.*, **4**, 14, 294 (1902).

[4] Timofeiew, *Dissertation*, Kharkhov, 1894.

alcohol as shown in Table I. This work checks closely with that of Timofeiew in so far as the data are comparable, whereas the results of Speyers differ considerably.

Summary

1. The composition of an alcoholated form of urea has been established and found to be $CO(NH_2)_2.CH_3OH$.
2. A study of its solubility together with that of non-solvated urea has been made.
3. The transition point of these two forms of urea was found to be +19.25°.

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IODINE AS AN EMULSIFYING AGENT

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To illustrate the Nernst distribution law some ether was shaken with water to which had been added iodine and potassium iodide.[1] An emulsion formed and slowly creamed. The cream, which was very viscous, lasted for several days. Since the cream rose it represented an emulsion of ether in water or, to be exact, of wet ether in ethereal water.

No emulsion could be prepared from ether and water alone so it was evident that the emulsifying agent was iodine, potassium iodide or potassium tri-iodide. We failed to secure an emulsion on shaking ether with a freshly prepared aqueous solution of potassium iodide, yet an old solution enabled us to make a very poor emulsion. Probably a very little iodine was released by the action of light or by the action of the carbon dioxide and oxygen of the air. This led us to try iodine alone as the emulsifying agent for the system ether-in-water. Good emulsions were obtained, improving as the concentration of iodine in the wet ether was increased up to 1%.

In attempting to prepare emulsions of 75% by volume, we found very little value in a 0.05% solution of iodine in wet ether. A very unstable 50% emulsion was, however, prepared with this concentration of iodine. At a 0.1% concentration of iodine a fair 75% emulsion was made while a 1.0% iodine solution showed the maximum emulsifying power in this system.

That potassium tri-iodide could not be held responsible for emulsification was shown by trying to emulsify ether in an aqueous solution of iodine and potassium iodide containing an excess of the iodide. This gave us a much poorer emulsion than a similar solution containing a good deal less

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[1] W. H. Chapin in this Laboratory.