[Contribution from the Ammonia Department of E. I. du Pont de Nemours & Company]

The Solubility of Urea in Water. The Heat of Fusion of Urea

By F. W. Miller, Jr., and H. R. Dittmar

In a recent communication[1] dealing with the solubility of urea in water between 20 and 70°, Shnidman and Sunier discuss the ideality of urea–water solutions. Although their data give a straight line when plotted on a log *N* *vs.* 1/*T* basis, calculation of the melting point of urea from the curve gives a value of 142° instead of 132.7°, the correct melting point. This leads these investigators to the conclusion that the curve must deviate from a straight line as the solution becomes more concentrated in urea; that urea–water solutions are non-ideal.

The solubility curve of urea in water from 70° to the melting point of urea is, therefore, of interest in showing how and where the slope of the log *N* *vs.* 1/*T* curve digresses from that of an ideal solution. Jänecke[2] in a comprehensive study of the system ammonia–carbon dioxide–water, gives the solubility of urea in water from −11.5 to 120°. These data include only three determinations above 70° and from their apparent irregularity seem insufficient to give a reliable continuation of the above curve.

The results reported here include thirteen solubility determinations between 70 and 130°. The points found form a reasonably smooth curve which terminates at the true melting point of urea.

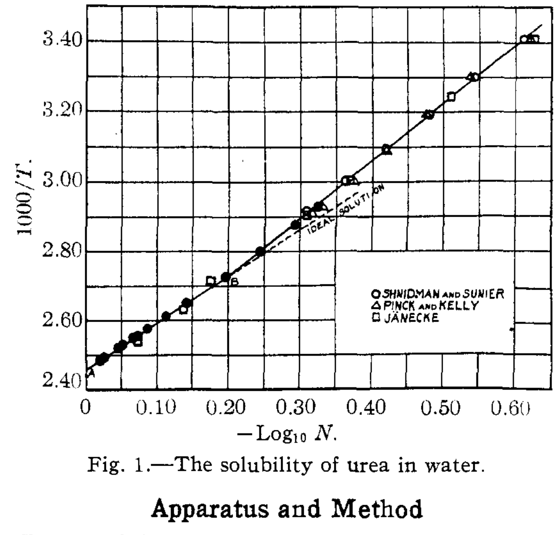

Fig. 1.—The solubility of urea in water.

Apparatus and Method

Because of the ease and rapidity with which urea hydrolyzes above 100°, a method was required which would give relatively rapid measurements. Consequently, the synthetic method was employed. The apparatus consisted of an air-jacketed Pyrex tube (approximately 2.5 by 20 cm.) which was provided with an ordinary hand-operated glass-loop stirrer.

In making a determination 25 g. to 50 g. of urea (Mallinckrodt c. p. grade, m. p. 132.6°) was weighed in the tube. A Lunge weighing pipet was used to introduce a definite quantity of water. The apparatus was heated in a paraffin bath until the solute dissolved. The well stirred solution was cooled rapidly until crystallization began. The temperature was then increased at the rate of one degree per minute or less with vigorous stirring until only a few crystals remained. The temperature at this point was recorded as the solution temperature. Results could be duplicated to within 0.2°. Precautions were taken to minimize losses of water and to prevent the condensation of water in the upper parts of the solubility tube. In order to reduce the influence of the hydrolytic products formed at the higher temperatures, not more than three determinations were made with one charge of urea. Below 100°, however, several measurements could be obtained by adding additional amounts of water to the solution.

A partial immersion thermometer graduated in tenths of a degree was used. This was calibrated against a standard thermometer.

Results.—The results are shown in Table I and plotted in Fig. 1. The data of Shnidman and Sunier,[1] Jänecke[2] and Pinck and Kelly[3] are included for comparison.

Discussion of Results

From Fig. 1 it can be seen that the log *N* *vs.* 1/*T* curve for urea fulfils the requirements for an ideal solution until the mole fraction of urea becomes less than approximately 0.6. For solutions more dilute in urea than this, the deviations from the law become appreciable. This seems to be in agreement with the calculations of Shnidman and Sunier,[1] using the data of Perman and Lovett, to

Table I

Solubility of Urea in Water

Mole fraction, N	Solution temp., °C.	Mole fraction N	Solution temp., °C.
1.0000	132.6	0.8190	115.3
0.9591	128.8	.7702	109.9
.9450	127.5	.7217	104.4
.9004	123.2	.6343	93.8
.8891	121.9	.5680	84.4
.8578	118.7	.5095	75.3
.8456	118.3	.4741	68.5

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

(2) Jänecke, *Z. Elektrochem.*, **36**, 647 (1930).

(3) Pinck and Kelly, This Journal, **47**, 2170 (1925).

show that the deviations from the ideal solution decrease with increasing concentrations of urea.

The slope of the curve for that portion of it which may be represented by a straight line (AB), is -757.58, with the intercept at 0.002464 on the $1/T$ axis. This corresponds to a heat of fusion[4] of 3470 (approx.) and a melting point of 132.7°.

The values obtained by Shnidman and Sunier in the neighborhood of 70° are appreciably higher than those obtained here. While it is true that the tendency of our method would be in the direction of low results, despite precautions taken against loss of water, the values obtained are in good agreement with those of Pinck and Kelly.[3] Furthermore, it is clear that the curve of Shnidman and Sunier cannot continue as a straight line if it is to terminate in the melting point of urea. There must be a change in slope and curvature. From the fact that Shnidman and Sunier agree well with Pinck and Kelly up to 50° (except for the 20° point) and from the nature of the curve obtained in this work, it is probable that in the neighborhood of 70° the values of Shnidman and Sunier are high and those obtained here somewhat low. The true curve should probably show a gradual transition from the one curve to the other in this region as indicated in Fig. 1.

Summary

1. The solubility of urea in water between 70° and the melting point of urea (132.7°) has been determined by the synthetic method.

2. The results when plotted on a log N *vs.* $1/T$ basis show that the urea–water solutions appear ideal when the mole fraction of urea is greater than approximately 0.6.

3. The heat of fusion of urea is calculated to be 3470 cal./mole.

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[4] For perfect solutions the differential heat of solution is equivalent to the heat of fusion; Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 229.

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, AT THE UNIVERSITY OF CALIFORNIA]

The Heat Capacities of Magnesium, Zinc, Lead, Manganese and Iron Carbonates at Low Temperatures[1]

BY C. TRAVIS ANDERSON[2]

This report on the carbonates of magnesium, zinc, lead, manganese and iron supplements earlier publications[3] relative to the carbonates of the first periodic group and the alkaline earth group.

The method, apparatus and accuracy have been described previously.[4]

Materials.—In Table I are shown the materials used. All the samples were crushed and screened to -14 $+35$ mesh. Carbon tetrachloride was used in determining the densities of the carbonates by the precise method described in a previous paper.[3b]

The Specific Heats.—The experimental results obtained for the magnesium, zinc, lead, manganese and iron carbonates are shown in Tables II, III, IV, V and VI, respectively. The data, given in gram calories (15°) per gram formula weight, have been corrected for the impurities as previously indicated. The calculations were made on the basis of Mg, 24.32; Zn, 65.37; Pb, 207.20; Mn, 54.93; Fe, 55.84; C, 12.00; and O, 16.00.

No previous low temperature measurements have been made on any of these carbonates. The results obtained in this investigation on the heat capacities of magnesite, smithsonite and cerussite are shown graphically in Fig. 1. Figure 2 gives the graphic representations of the heat capacities of rhodochrosite and siderite.

Calculation of Entropies.—The conventional method was used in calculating the entropies. The experimental heat capacity curves coincided at low temperatures with Debye functions having the following parameters (Θ): for magnesite, 354; smithsonite, 243; cerussite, 90; rhodochrosite, 223; and siderite 179. Combinations of Debye and Einstein functions were made to fit

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[3] (a) Anderson, THIS JOURNAL, **55**, 3621 (1933); (b) **56**, 340 (1934).

[4] Anderson, *ibid.*, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).