Heat of dilution measurements for four aminobutyric acids will be reported soon.

## Summary

Intermediate heats of dilution of aqueous solutions of α- and β-alanine have been measured over the concentration range from 1.3 to 0.001*m* at 25°. By extrapolation to zero concentration, relative apparent molal heat contents have been evaluated and relative partial molal heat contents have been calculated.

PITTSBURGH, PENNSYLVANIA
RECEIVED DECEMBER 21, 1945

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[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

# Thermal Data. XIX. The Heat Capacity, Entropy and Free Energy of Urea

BY ROBERT A. RUEHRWEIN AND HUGH M. HUFFMAN[1]

Urea is of considerable interest as an organic compound and also because of the important role it plays in physiological processes. Lewis and Burrows[2] studied the equilibrium between urea, carbon dioxide, ammonia and water and calculated the free energy change in the reaction

$$CO_2(g) + 2NH_3(g) = CO(NH_2)_2(S) + H_2O(g)$$

A comparison of third law and equilibrium free energy data is of value in helping to settle the question of randomness in the crystal lattice of urea due to hydrogen bonding. Urea has also been reported[3] to undergo higher order transitions in the temperature ranges −6 to 5° and 25 to 37°.

In this paper we have reported the results of our investigation of the heat capacity of urea over the temperature range 19 to 320° K.

## Experimental

**Apparatus.**—The measurements were made in an aneroid adiabatic calorimeter, the details of which have been published[4] so that only a brief description need be given here. The calorimeter was made of copper. Temperature measurements were made with a platinum resistance thermometer of laboratory designation H-8. All electrical measurements were made with a "White" double potentiometer in conjunction with a sensitive galvanometer and calibrated resistors. Time was measured with an electric stop clock. The energy measurements were made in terms of the international joule and converted to conventional calories by dividing by 4.1833. The precision of the measurements was approximately ±0.1%.

**Material.**—J. T. Baker C. P. urea was dissolved in redistilled water at 60° and then allowed to crystallize in a cold room at about 0°. The crystals were filtered from the mother liquor and dried to constant weight in phosphorus pentoxide vacuum.

The material was lightly compressed into the calorimeter in layers, about 2-mm. thick, separated by thin copper disks which were in thermal contact with the walls of the calorimeter and the reëntrant thermometer well. The cover was then soldered in place, helium admitted to the gas space through a small tube in the cover, which was finally closed with a drop of soft solder.

TABLE I

MOLAL HEAT CAPACITY OF UREA

Mol. weight = 60.058; 0°C. = 273.16° K.

| *T*, °K. | Δ*T* | $C_p$, cal./degree | *T*, °K. | Δ*T* | $C_p$, cal./degree |
|---|---|---|---|---|---|
| 19.45 | 0.994 | 1.139 | 152.43 | 11.180 | 13.031 |
| 20.53 | 1.166 | 1.286 | 163.35 | 10.676 | 13.715 |
| 22.09 | 1.947 | 1.529 | 173.81 | 10.254 | 14.372 |
| 25.25 | 4.384 | 2.026 | 183.87 | 9.868 | 15.007 |
| 29.56 | 4.232 | 2.719 | 193.57 | 9.536 | 15.615 |
| 33.36 | 3.371 | 3.324 | 202.95 | 9.238 | 16.204 |
| 36.82 | 3.551 | 3.858 | 210.50 | 5.753 | 16.698 |
| 40.68 | 4.160 | 4.414 | 217.75 | 8.743 | 17.130 |
| 44.57 | 3.626 | 4.950 | 226.38 | 8.527 | 17.648 |
| 48.52 | 4.281 | 5.477 | 234.81 | 8.324 | 18.165 |
| 52.59 | 3.857 | 5.956 | 243.04 | 8.134 | 18.682 |
| 55.97 | 2.705 | 6.348 | 248.97 | 2.074 | 19.082 |
| 56.72 | 4.390 | 6.429 | 251.04 | 2.062 | 19.209 |
| 59.42 | 4.205 | 6.722 | 251.09 | 7.954 | 19.197 |
| 63.48 | 3.904 | 7.141 | 266.44 | 7.615 | 20.197 |
| 67.27 | 3.677 | 7.492 | 268.66 | 3.904 | 20.357 |
| 72.21 | 6.196 | 7.905 | 272.54 | 3.858 | 20.640 |
| 78.18 | 5.757 | 8.386 | 274.00 | 7.460 | 20.712 |
| 83.77 | 5.415 | 8.829 | 276.39 | 3.822 | 20.854 |
| 87.92 | 6.226 | 9.105 | 281.42 | 7.329 | 21.161 |
| 89.06 | 5.157 | 9.192 | 282.06 | 7.528 | 21.220 |
| 93.02 | 4.991 | 9.471 | 288.72 | 7.202 | 21.619 |
| 99.34 | 7.637 | 9.825 | 289.52 | 7.382 | 21.706 |
| 106.79 | 7.259 | 10.273 | 296.83 | 7.247 | 22.172 |
| 113.89 | 6.945 | 10.698 | 304.02 | 7.115 | 22.648 |
| 121.31 | 7.904 | 11.148 | 311.07 | 6.985 | 23.089 |
| 130.10 | 9.940 | 11.669 | 318.01 | 6.877 | 23.544 |
| 140.95 | 11.765 | 12.342 | | | |

## Results

In Table I we have listed the experimentally determined specific heats over the temperature range 19 to 320° K. Values at integral temperatures, taken from a smooth curve through all of the data, are given in Table II. An excess absorption of energy, above the regular curve, was observed in the temperature range 255 to 265° K. Since this temperature was considerably below that reported by Sokolov[3] for the second order transition, we suspected that it was probably due to some other cause. A calculation showed that the energy absorption was in the temperature range where a saturated aqueous solution of urea would be expected to melt. Hence the presence of

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[1] Present address: Bureau of Mines, Bartlesville, Okla.

[2] G. N. Lewis and G. H. Burrows, THIS JOURNAL, **34**, 1515 (1912).

[3] V. A. Sokolov, *C. A.*, **34**, 5733[5] (1940).

[4] Ruehrwein and Huffman, THIS JOURNAL, **65**, 1620 (1943).

TABLE II

MOLAL HEAT CAPACITY OF UREA AT INTEGRAL TEMPERATURES

Mol. weight = 60.058; 0°C. = 273.16° K.

| $T$, °K. | $C_p$, cal./degree | $T$, °K. | $C_p$, cal./degree |
|---|---|---|---|
| 20 | 1.21 | 140 | 12.28 |
| 25 | 1.99 | 150 | 12.88 |
| 30 | 2.79 | 160 | 13.51 |
| 35 | 3.58 | 170 | 14.13 |
| 40 | 4.32 | 180 | 14.76 |
| 45 | 5.02 | 190 | 15.39 |
| 50 | 5.65 | 200 | 16.02 |
| 55 | 6.24 | 210 | 16.64 |
| 60 | 6.79 | 220 | 17.26 |
| 65 | 7.28 | 230 | 17.87 |
| 70 | 7.73 | 240 | 18.49 |
| 75 | 8.14 | 250 | 19.14 |
| 80 | 8.54 | 260 | 19.79 |
| 85 | 8.91 | 270 | 20.44 |
| 90 | 9.25 | 280 | 21.09 |
| 95 | 9.57 | 290 | 21.72 |
| 100 | 9.87 | 298.16 | 22.26 |
| 110 | 10.46 | 300 | 22.38 |
| 120 | 11.07 | 310 | 23.02 |
| 130 | 11.67 | 320 | 23.77 |

water was suspected. The calorimeter was opened and evacuated for a considerable period of time without any significant change in mass. A rough calculation was made of the amount of water present and this amount was added to the calorimeter.

Additional measurements over the same temperature range now showed that the excess energy absorption was approximately doubled. Our conclusion was that water had been present in the original sample. We estimated the amount of water to be 0.052 g. and the data were corrected for this amount on the assumption that it behaved as pure water. This assumption may tend to decrease slightly the accuracy of our measurements.

## Discussion

The experimental data have been utilized to calculate the entropy of urea at 298.16° K. The results of this calculation are summarized in Table III.

TABLE III

THE MOLAL ENTROPY OF UREA, CAL. DEGREE$^{-1}$

Mol. weight = 60.058; 0°C. = 273.16° K.

| | | P, H & B |
|---|---|---|
| $S_{20°}$ (Debye, 4 ° freedom = 154.1) | = 0.434 | |
| $\Delta S_{20-90°}$ (graphical) | = 7.299 | |
| $[S_{90°}$ | = 7.733] | 7.93 |
| $\Delta S_{90-298.16}$ (graphical) | = 17.263 | 17.25 |
| $S_{298.16}$ | = 25.00 ± 0.05 | 25.2 |

Parks, Huffman and Barmore[5] measured the heat capacity of urea over the temperature range 90 to 298° K. and calculated the entropy at 298.1° K. This calculation involved an empirical extrapolation over the temperature range 0 to 90° K. The constants in the empirical extrapolation formula they used were derived from data on compounds that were considerably different in composition from urea. For this reason we have thought it of interest to compare their data with that of this research and have included it in Table III. The extrapolated entropy of Parks, Huffman and Barmore[5] at 90° K. is about 0.2 entropy unit higher than determined in this investigation.

The heat of combustion of urea was determined by Huffman.[6] The value reported corrected, for an error in the heat of combustion of benzoic acid[7] which was used as the calorimetric standard, becomes $-\Delta H_{(298.16°\text{K})}$ = 151,053 calories/mole. This datum has been used in conjunction with the entropy reported here to calculate the free energy of formation of urea at 298.16° K. The data are summarized in Table IV. In making this calculation, we have used the values[8a] 1.361, 31.211, 49.003 and 45.767 calories per degree for the molal entropies of graphitic carbon, hydrogen, oxygen and nitrogen, respectively, and the values[8b] 68,317 and 94,052 calories for the molal heats of formation of liquid water and gaseous carbon dioxide, respectively.

Lewis and Burrows[2] studied the equilibrium in the reaction

$$CO_2(g) + 2NH_3(g) = H_2O(g) + CO(NH_2)_2(\text{solid})$$

From their data they calculated for this reaction

TABLE IV

THE MOLAL FREE ENERGY OF FORMATION OF UREA AT 298.16° K.

| | |
|---|---|
| Heat of comb., $\Delta H°$, kcal. | −151.053 |
| $\Delta H_f°$, kcal. | − 79.634 |
| $\Delta S_f°$, cal./degree | −109.056 |
| $\Delta F_f°$, kcal. | − 47.118 |

TABLE V

SYNTHESIS OF UREA MOLAL FREE ENERGY FROM THERMAL DATA AT 298.16°

(1) $N_2(g) + CO_2(g) + 2H_2O(l) = {}^3/_2O_2 + CO(NH_2)_2$; $\Delta H$ = 151,053 cal.[a]

(2) $2NH_3(g) = N_2(g) + 3H_2(g)$; $\Delta H$ = 21,860 cal.[b]

(3) $2H_2(g) + O_2(g) = 2H_2O(l)$; $\Delta H$ = 136,635 cal.[c]

(4) $H_2(g) + {}^1/_2O_2(g) = H_2O(g)$; $\Delta H$ = −57,798 cal.[c]

(5) $\Sigma = CO_2(g) + 2NH_3(g) = H_2O(g) + CO(NH_2)_2(s)$; $\Delta H$ = −21,520 cal.

$\Delta S$(react. 5) = 24.996 + 45.106 − 2(46.034) − (51.061);

$\Delta S = -73.027$[8b,6] cal./degree

$-T\,\Delta S = 21{,}774$

$\Delta F = 254$

[a] Reference 7. [b] Reference 6. [c] Reference 8a.

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(5) G. S. Parks, H. M. Huffman and M. Barmore, THIS JOURNAL, **55**, 2733 (1933).

(6) H. M. Huffman, *ibid.*, **62**, 1009 (1940).

(7) R. S. Jessup, *Bur. Standards J. Research*, **29**, 247 (1942).

(8) American Petroleum Institute Research project 44 at the National Bureau of Standards. Selected values of the properties of hydrocarbons: (a) Table $0_t$; July 31, 1944, (b) Table $0_n$; May 31, 1945.

at 25°, $\Delta F = 288$ calories. Using the equation $\Delta F = \Delta H - T\Delta S$ and the best available data we find $\Delta F = 254$ calories. The calculation and the sources of the data used are summarized in Table IV. It is interesting to note that there are available two values for the heat of formation of ammonia one of which was obtained from thermal data and the other from equilibrium measurements. Stephenson and McMahon[9] have recently recalculated the available equilibrium data. From equilibrium data they find for the formation of ammonia at 25° $\Delta H = -10{,}930$ and from thermal data $\Delta H = -11{,}040$. If the latter datum is used we find for the reaction given above $\Delta F = 474$ calories.

The agreement of the free energy calculated from the best thermal data with that calculated from the equilibrium data of Lewis and Burrows[2] indicate that there is no randomness in the structure of urea which persists to extremely low temperatures.

The measurements were extended to 48° in hopes that we would obtain evidence of the second order transitions reported by Sokolov.[3] No anomalies in the specific heat curve were observed over the entire range with the exception of that previously discussed which we believe has been accounted for in a satisfactory manner.

## Summary

The heat capacity of urea has been measured over the temperature range 19 to 320° K.

The molal entropy and free energy of formation at 298.16° K. have been calculated.

Excellent agreement between third law values and equilibrium values was demonstrated for a synthesis of urea.

BARTLESVILLE, OKLA.

RECEIVED MAY 6, 1946

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[9] Stephenson and McMahon, THIS JOURNAL, **61**, 407 (1939).

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[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

# Catalytic Hydrogenolysis of Nitrate Esters

BY LESTER P. KUHN

The hydrolysis of nitrate esters to the corresponding alcohols is usually accompanied by undesirable oxidation reactions wherein the alcohols are converted to aldehydes and other products.[1] Hence denitration is usually effected by reducing agents such as tin and hydrochloric acid,[1] zinc and iron in acetic acid,[2] and ammonium polysulfide.[3] These methods leave much to be desired when dealing with certain sugar nitrates in that it is difficult to separate the free sugar from the inorganic salts in good yield. Also other groups may be attacked by the rather vigorous conditions employed.

The present work shows that nitrate groups may be smoothly reduced by catalytic hydrogenolysis, a method which has not been previously reported.

To determine the most effective catalyst a series of experiments was made using amyl nitrate and hydrogen at 1500 p.s.i. The results are given in Table I.

Because of the high temperature required with the copper–chromium catalyst much decomposition ensues. The nickel and platinum catalysts are also unsatisfactory because they reduce the nitrogen to ammonia to which the unreacted nitrate groups are sensitive and side reactions occur. If the reaction is stopped when the pressure change is equivalent to two moles of gas per mole of nitrate, both ammonia and nitrate are present, indicating that it is impossible to halt the reaction at the elementary nitrogen stage. If acid is added to neutralize the ammonia that is formed, no reaction takes place.

TABLE I

HYDROGENOLYSIS OF AMYL NITRATE

| Catalyst | T, °C. | Time, hr. | Form of nitrogen in product | Pressure change in moles of gas/mole of nitrate |
|---|---|---|---|---|
| Copper–chromium | 160–180 | 3 | ....... | ... |
| Raney nickel | 60–70 | 1 | Ammonia | 3.5–4 |
| Platinum | 60–70 | 1 | Ammonia | 3.5–4 |
| Palladium on calcium carbonate | 25 | 0.25 | $N_2$ | 2 |

In contrast to these catalysts, the palladium on calcium carbonate is highly satisfactory. The reaction appears to proceed according to the equation

$$2RONO + 5H_2 \longrightarrow 2ROH + N_2 + 4H_2O$$

Actually, two and one-half moles of hydrogen are consumed per mole of nitrate, but since one-half mole of nitrogen is formed the net pressure change is two moles of gas per nitrate. The equation is in harmony with the observed pressure change and the facts that the solution after hydrogenolysis is neutral and gives negative tests for nitrate, nitrite, and hydroxylamine.

Palladium on charcoal is a more active catalyst than palladium on calcium carbonate. In the presence of the former at 1,500 pounds pressure of hydrogen the nitrate is reduced to ammonia.

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[1] Sidgwick, "Organic Chemistry of Nitrogen," new edition revised by Taylor and Baker, Oxford University Press, 1942, p. 8.

[2] DeWar and Fort, *J. Chem. Soc.*, 495 (1944).

[3] Bock, Simmerl and Johnston, *J. prakt. Chem.*, **158**, 8–20 (1941).