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Low-Temperature Heat Capacity of Urea

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The heat capacity of urea was measured with an adiabatic calorimeter in the temperature range 15–310 K. The data were extrapolated to 0 K by a model function to derive some standard thermodynamic functions including the enthalpy increments $\Delta_0^T H$, the entropy increments $\Delta_0^T S$, and the Giauque function $(= \Delta_0^T S - \Delta_0^T H/T)$. A simple model for the reproduction of the experimental heat capacities of urea, based on the Debye and Einstein functions, is described. The Debye characteristic temperature determined in this way was compared with those calculated from properties other than the heat capacity. Any positive evidence of a suggested phase transition in urea around 190 K was not observed in the present heat capacity measurements. Possible existence of a phase with a Gibbs energy lower than that realized in the present investigation is discussed briefly.

KEY WORDS: Debye temperature; heat capacity; thermodynamic functions; urea.

1. INTRODUCTION

The heat capacity and phase behavior of urea, $(NH_2)_2CO$, are the subjects of the investigation reported in this paper. Urea crystallizes into a tetragonal lattice, $P\bar{4}2_1m$, with two molecules per unit cell [1]. It is well-known that urea and its derivatives can be considered as model compounds of more complicated materials such as polypeptides. From this standpoint, their thermodynamic properties in both aqueous and nonaqueous solutions are currently studied. Moreover, crystalline urea is

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known to be useful as one of the optical materials which exhibit nonlinear properties. Owing to its slightly hygroscopic nature, however, the crystal is subjected to some constraints in the actual use. Synthesis of some urea derivatives which improve the situation is highly desirable.

The heat capacity C_p of urea has been measured by Ruehrwein and Huffman [2] and Sasaki and Yokotake [3], in the temperature range 19–310 K, using adiabatic calorimetry. Moreover, differential scanning calorimetry has been used to determine C_p in the range 260–510 K [4, 5]. In these investigations [2–5], no transition was detected except that for the melting at about 406 K [4]. However, after the low-temperature investigations [2, 3], there have been a few reports of a phase transition in urea below room temperature [6, 7]. In particular, Lebioda et al. [6] have reported an anomaly in the data for the *c*-axis lattice parameter. Using x-ray analysis at temperatures in the range 93–293 K, they found a local maximum in the *c* parameter at about 190 K. They interpreted this anomaly as being a result of a phase transition. In view of these reports [6, 7], we found it desirable to reinvestigate the heat capacity of urea. We shall, however, report data which do not corroborate the existence of a phase transition.

2. EXPERIMENTAL

The heat capacity was measured at temperatures in the range 15–310 K with an adiabatic calorimeter which has been described in detail elsewhere [8]. The inaccuracy in C_p was estimated as 1% at 20 K and 0.3% at 300 K. The amount of sample was 3.0798 g (= 0.051282 mol), after buoyancy correction using a density of urea of $1.3\ \mathrm{g \cdot cm^{-3}}$. In order to improve heat transfer in the sample cell, a small amount of helium gas was introduced.

The starting material, Fluka BioChemika MicroSelect, >99.5%, was recrystallized four times from ethyl acetate (Fluka; >99.5%; H_2O, <0.005%) and then dried in vacuum for 3 days at 60°C. The purity was better than 99.92% as determined from the analysis of the fractional melting curve obtained by differential scanning calorimetry (Perkin–Elmer, DSC-II).

The measurements of heat capacity were carried out by a discontinuous heating mode. The temperature rise due to a single energizing was about 0.7 K below 80 K and the step was increased progressively to 2 K as the temperature was raised. After each step, the temperature drift in the sample cell was measured during a period of 10 min. Since we were especially interested in the thermal behavior of urea around 190 K, this temperature range was investigated in three runs. The thermal histories of the sample for the three runs were as follows: (I) cooled from room temperature to 80 K (directly followed by the heat capacity measurements); (II) cooled from room temperature to 15 K, heated up to 85 K during measurements, and annealed at 85 K for 10 h; and (III) cooled from room temperature to 150 K, then heated to about 190 K, where the sample was annealed and the temperature drift versus time was recorded. In all runs, the cooling rate was about $1\ \mathrm{K \cdot min^{-1}}$.

3. RESULTS AND DISCUSSION

The values of molar heat capacity of urea are given in Table I and are presented in Fig. 1 together with those reported previously [2, 3]. The present data agree to within 0.5% with those of Ruehrwein and Huffman [2], although being in general slightly lower than those of Ref. 2. Our data and those of Sasaki and Yokotake [3] agree to within ±3%. In view of the good agreement between our data and those of Ruehrwein and Huffman [2], the data of Sasaki and Yokotake [3] are considered to be subject to large errors. In fact, they reported an estimated error of 5%.

From the experimental data shown in Fig. 1, it can be seen that the heat capacities exhibit no anomaly which can be associated with the previously reported phase transition [6, 7]. The data were further examined after division by temperature. In general, it is easier to detect a phase transition in a plot of C_p/T vs T than in the C_p curve itself, because the strong temperature dependence of the normal vibrational capacity is tempered by division with T. Slow evolution and absorption of heat by the sample are also a sensitive indicator of first-order phase transitions and glass transitions. Therefore, the temperature drift rate was examined as a function of temperature. Neither C_p/T nor the temperature drift rate showed any anomalous behavior indicative of a phase transition or a glass transition in the temperature range 15–310 K.

The experimental heat capacity data were used to calculate some standard thermodynamic functions including the enthalpy increments $\Delta_0^T H$, the entropy increments $\Delta_0^T S$, and the Giauque function Φ $(= \Delta_0^T S - \Delta_0^T H/T)$. The results are summarized in Table I. In the calculations, a model function, which has been fitted to the experimental heat capacities, was used to extrapolate the data down to 0 K.

The Debye and Einstein models for the isochoric heat capacity C_v were used to reproduce the experimental heat capacity data. A combination of these two models together with a term to account for the difference $C_p - C_v$ was fitted to the experimental data.

Each urea molecule has 24 degrees of freedom in total. These are divided into the following molecular motions: 18 intramolecular vibrations, 3 rotations, and 3 vibrations associated with the motions of the whole molecule. We have used Einstein oscillators to describe C_v associated with the intramolecular vibrations. The Einstein temperatures were calculated using experimental data for the wavenumbers of the intramolecular vibrations. Measured IR and Raman data and assignments of the intramolecular modes of solid urea are reported by many authors and are somewhat

Table I. Thermodynamic Functions of Urea: Heat Capacity C_p, Enthalpy Increment $\Delta_0^T H$, Entropy Increment $\Delta_0^T S$, and Giauque Function Φ $(=\Delta_0^T S-\Delta_0^T H/T)$ $(R=8.31451\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}})$

T (K)	C_p/R	$\Delta_0^T H/R$ (K)	$\Delta_0^T S/R$	Φ/R
10	0.08367	0.2088	0.02783	0.006950
20	0.6082	3.234	0.2169	0.05520
30	1.396	13.20	0.6103	0.1702
40	2.165	31.07	1.119	0.3422
50	2.836	56.17	1.676	0.5529
60	3.403	87.45	2.245	0.7875
70	3.879	123.9	2.806	1.036
80	4.285	164.8	3.351	1.292
90	4.640	209.5	3.877	1.550
100	4.962	257.5	4.383	1.808
110	5.264	308.6	4.870	2.064
120	5.560	362.7	5.341	2.318
130	5.856	419.8	5.797	2.568
140	6.156	479.9	6.242	2.815
150	6.462	543.0	6.677	3.058
160	6.771	609.1	7.104	3.297
170	7.084	678.4	7.524	3.534
180	7.398	750.8	7.938	3.767
190	7.714	826.4	8.346	3.997
200	8.032	905.1	8.750	4.225
210	8.353	987.0	9.150	4.450
220	8.674	1072	9.546	4.672
230	8.996	1160	9.938	4.893
240	9.314	1252	10.33	5.111
250	9.630	1347	10.71	5.328
260	9.944	1445	11.10	5.542
270	10.26	1546	11.48	5.755
273.15	10.36	1578	11.60	5.822
280	10.58	1650	11.86	5.966
290	10.90	1757	12.24	6.176
298.15	11.16	1847	12.54	6.346
300	11.22	1868	12.61	6.384
310	11.52	1982	12.98	6.591

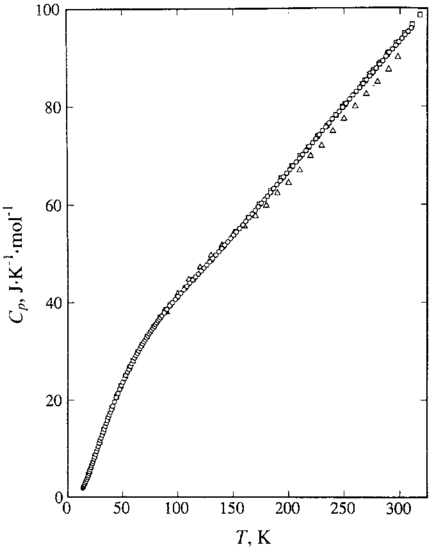

Fig. 1. Variation of the molar heat capacity C_p of urea as a function of temperature T. (○) Present work; (□) Ruehrwein and Huffman [2]; (△) Sasaki and Yokotake [3].

different. Our calculations were based on the following assignments [9, 10]: $\nu_{\mathrm{NH,stretch}} = 3400$ (4), $\nu_{\mathrm{HNH,bend}} = 1650$ (2), $\nu_{\mathrm{HNH,wag}} = 785$ (2), $\nu_{\mathrm{HNH,rock}} = 1150$ (2), $\nu_{\mathrm{HNH,twist}} = 556$ (2) $\nu_{\mathrm{NCN,bend}} = 558$ (1), $\nu_{\mathrm{NCN,rock}} = 570$ (1), $\nu_{\mathrm{CO,\,out\,of\,plane}} = 717$ (1), $\nu_{\mathrm{CO,stretch}} = 1600$ (1), $\nu_{\mathrm{CN,stretch}} = 1000$ (1), and $\nu_{\mathrm{CN,\,stretch}} = 1460$ (1), where the degeneracy is given in parentheses and the unit of the wavenumbers is cm^{-1}. The heat capacity due to the rotational and vibrational motions of the whole molecule was calculated, respectively, using one Einstein oscillator and one Debye oscillator, each having a degeneracy of 3. The Einstein and Debye temperatures, Θ_{E} and Θ_{D}, associated with these oscillators were left as adjustable parameters in the fitting procedure. In addition to these two adjustable parameters, we fitted a constant A which was defined by the expression: $C_p - C_v = AC_p^2T$. Consequently, the constant A accounted for the difference between the isobaric and the isochoric heat capacities.

Using our experimental data in the range 15–200 K in the fitting procedure, the model described above could reproduce the measured heat capacity data to within $\pm 1.5\%$, except for $T < 20$ K. The values of the fitted parameters were $\Theta_{\mathrm{D}} = 135.0$ K, $\Theta_{\mathrm{E}} = 228.6$ K, and $A = 7.7 \times 10^{-6}\ \mathrm{mol \cdot J^{-1}}$. The Einstein characteristic temperature $\Theta_{\mathrm{E}} = 228.6$ K corresponds to a wavenumber of $160\ \mathrm{cm}^{-1}$. In a Raman investigation [11], it has been found that urea exhibits Raman scattering at 134 and 177 cm^{-1}. Consequently, the derived value of Θ_E is not unrealistic. If we used the heat capacity data in the whole range of 15–310 K in the fitting procedure, then the fit deteriorated significantly; the fitted Θ_D did not, however, change significantly. Thus the model described above is considered to be too simple to account for the heat capacity values at temperatures above 200 K. A more elaborate model, using two Einstein oscillators each of degeneracy 1.5 instead of only one of degeneracy 3, was tried. However, the fit improved only slightly. The same try with the Debye oscillator (two of degeneracy 1.5) yielded a similar result. In summary, our simple model for the heat capacity of urea works quite well for temperatures below 200 K.

Ruehrwein and Huffman [2] calculated a Θ_D using only their low-temperature heat capacity data. They assumed that the data could be described using one Debye oscillator of degeneracy 4. With this model they obtained $\Theta_D = 154.1$ K. If their approach is applied to our experimental data in the temperature range 15–100 K, then we can obtain $\Theta_D = 155.5$ K, confirming their calculation. However, the standard deviation for this fit was about seven times larger than that for our model described above.

One of the parameters obtained in our model was Θ_D. It is sometimes useful to obtain a rough estimate of Θ_D without doing time-consuming heat capacity measurements. To explore the extent to which that can be done, the present value of Θ_D was compared with those of some expressions given in the literature.

There are several ways of estimating the Debye temperature using experimental data for various physical properties. The most direct way is to use an equation which was derived originally for a simple monatomic crystal. This standard solid-state equation is given by

$$\Theta_D = \frac{hv_{\text{ave}}}{k_B}\left[\frac{6\pi^2 N}{V}\right]^{1/3} \tag{1}$$

where v_{ave} is the average sound velocity, N is the number of primitive cells in volume V, and the other symbols have their usual meaning. Unfortunately, however, no simple way exists to calculate the average sound velocity in a tetragonal lattice such as that of urea. In order to use Eq. (1), we simply assumed that the average sound velocity in the tetragonal lattice of urea could be approximated by the formula for an elastically isotropic cubic lattice. That is, the longitudinal sound velocity v_l and the transverse sound velocity v_t are given by the expressions

$$v_l = \left[\frac{c_{11}}{\rho}\right]^{1/2} \tag{2}$$

and

$$v_t = \left[\frac{c_{11} - c_{12}}{2\rho}\right]^{1/2} \tag{3}$$

where c_{11} and c_{12} are the elastic constants, and ρ is the density. The comon way to calculate the average velocity v_{ave} from v_t of the two transverse modes and v_l of the longitudinal mode is given by the following expression:

$$v_{ave} = \left[\frac{2}{v_t^3} + \frac{1}{v_l^3}\right]^{-1/3} 3^{1/3} \tag{4}$$

Using experimental data for the elastic constants [12], we obtained $v_{ave} = 2400\ m \cdot s^{-1}$. By associating the quantity V/N in Eq. (1) with the volume per molecule (75 Å^3 [13]), Eq. (1) yields $\Theta_D = 169$ K, compared to our fitted value of 135 K. If the unit cell volume is used instead of the volume per molecule, then the calculated value becomes $\Theta_D = 134$ K. In such an association of V/N, the vibrating unit would be that of the unit cell. That is, each vibrating unit would consist of two urea molecules. However, there is no evidence for the assumption that the molecules would be bound in pairs in the crystalline lattice of urea. The substantial difference between Θ_D determined from the heat capacity data and the one calculated using Eq. (1) is probably due to an inappropriate estimate of v_{ave}. In addition, we must consider the fact that the value of Θ_D derived from the heat capacity data changes to some extent with temperature.

Another way of estimating Θ_D is to use the Lindemann melting formula [14]. Here Θ_D is given by the expression

$$\Theta_D = \frac{C}{V_{mol}^{1/3}} \left[\frac{T_m}{M}\right]^{1/2} \tag{5}$$

where T_m is the melting point (K), V_{mol} the molar volume ($cm^3 \cdot mol^{-1}$), M the molar mass ($g \cdot mol^{-1}$), and C a constant. In the literature, however, different values can be found for the constant C: $C = 200$ [14], $C = 134$ [15], and $C = 78$ [16], in units of $K^{1/2} \cdot cm \cdot g^{1/2} \cdot mol^{-5/6}$. [The last value, $C = 78$, is our estimate of C from a form of the Lindemann melting formula slightly different from that given in Eq. (5).] The largest value for C (200 [14]) gives the best agreement with the value for Θ_D determined from the heat capacity data (135 K). Using $C = 200$ in Eq. (5), we obtained $\Theta_D = 146$ K.

The most sophisticated way in which we estimated Θ_D was to utilize data for volume as a function of temperature. The Grüneisen formula [16] provides a relation between the volume V and the internal energy per unit volume U,

$$\frac{V(T)-V(0)}{V(0)}=\kappa\gamma U(T) \tag{6}$$

where κ is the isothermal compressibility, γ the Grüneisen constant, and $V(0)$ the volume at 0 K. In order to derive Eq. (6) one uses the assumption that the vibrational frequency of the lattice modes is a function of volume. (In particular, $\Delta\nu/\nu=-\gamma\,\Delta V/V$.) In general, the various lattice modes exhibit different values of γ. Consequently, one cannot simply add together U associated with widely different lattice modes such as intra- and intermolecular vibrational modes. We assumed that only the part of the internal energy associated with the intermolecular vibrations should be included in the calculation of $U(T)$ in Eq. (6). This can be justified by the fact that the thermal expansion of urea is due mainly to changes in the intermolecular distances [17]. Consequently, Eq. (6) could be a good approximation for the relation between the volume and the internal energy arising from the intermolecular vibrations.

The data for unit cell volume, given by Swaminathan et al. [1], in the range 12–173 K were used in the fitting procedure of Eq. (6). We calculated $U(T)$ using a single Debye oscillator (degeneracy 3), with Θ_D as an adjustable parameter. In addition to Θ_D, the volume at 0 K and a constant ($=\kappa\gamma$) were used as adjustable parameters. The following data for the fitted parameters were obtained: $\Theta_D = 160.3$ K, $V(0) = 145.06$ Å^3 (volume of the unit cell at 0 K), and $\kappa\gamma = 1.69 \times 10^{-9}$ Pa^{-1}. By a comparison with a calculated value of $\kappa\gamma$ using common magnitudes for $\kappa(=10^{-10}$ Pa$^{-1})$ and γ $(=2)$, we find that our value is slightly larger than that expected. Most probably, the model we used for U is not satisfactory. A larger U, including perhaps that due to the rotational intermolecular modes, would decrease the value of $\kappa\gamma$. Addition of U arising from the rotational modes to that from the vibrational modes was tried in the fitting procedure of Eq. (6). An Einstein oscillator (degeneracy 3) with Θ_E as an additional parameter was used for the calculation of the internal energy due to the rotational modes. This fit, however, yielded unrealistic values of both Θ_D and Θ_E. Possibly this is because the rotational and the vibrational modes exhibit significantly different values of γ.

During the fitting procedure of Eq. (6), we found that the standard deviation of the fit did not depend strongly on Θ_D. Consequently, even small errors in the volume data can result in a substantial error in the fitted Θ_D. That is, the described approach using the Grüneisen formula to estimate Θ_D requires very accurate volume data as a function of temperature. Moreover, in order to estimate Θ_D from the Grüneisen formula [Eq. (6)], the best association of U in Eq. (6) appears to be the internal energy arising from the intermolecular vibrational modes only.

In summary, using only a set of data of one substance, it is premature to make a definite conclusion about the various ways of estimating Θ_D. However, in the case of urea, none of the ways described provided a very good estimate of Θ_D. We found that the best agreement with Θ_D determined from the heat capacity data was obtained using the Lindemann melting formula [14], though we are left, even in this case, with the uncertainty in the value of the constant C, whose physical meaning is not entirely obvious.

4. CONCLUDING REMARKS

It is clear that the present sample of urea, like that of the other investigators [1–3, 13, 17–19], did not undergo a phase transition. However, this does not exclude the possibility that another phase, with a Gibbs energy lower than that of the phase concerned in the present investigation, exists at low temperatures. It might be that the formation of this hypothetical phase is difficult and can be accomplished only under special conditions. Lebioda et al. [6] proposed that a substantial amount of lattice defects is required for nucleation of the phase. Moreover, investigations of urea at high pressures have revealed some crystalline modifications which are stable at elevated pressures [20–22]. In particular, Bridgman [20] has investigated the P–T phase diagram in the temperature range 273–430 K and at pressures up to about 0.8 GPa. At room temperature and a pressure of about 0.5 GPa, he detected a phase transition for which the phase line exhibited a positive dT/dP. These data for the P–T coordinates of the phase line can be extrapolated to atmospheric pressure. The phase line is expected to intersect atmospheric pressure at about 90 K. This is far from 190 K, where the reported anomaly in the c-axis lattice parameter occurred [6]. However, in view of these reports [6, 20], a low-temperature high-pressure study of the discussed phase line of urea would certainly be interesting. In such an investigation, it should be possible to establish whether the described high-pressure phase of urea could be obtained also at atmospheric pressure and low temperatures by overcoming a kinetic hindrance due to possible slow kinetics of transformation.

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