Additivity of Thermodynamic Properties of Organic Compounds in the Crystalline State. 3. Heat Capacities and Related Properties of Urea Phenyl Derivatives

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Heat capacities of 1,1-diphenylurea, 1,3-diphenylurea, and 1,1-dimethyl-3-phenylurea in the range (5 to 300) K were measured with an adiabatic calorimeter. Related thermodynamic functions were obtained. These functions were proved to conform to additivity principles. Taking into account the parameters developed earlier for alkylureas, the additive parameters of the phenyl group for calculation of the heat capacity, entropy, and thermal enthalpy of organic compounds in the crystalline state were derived.

Introduction

In two previous papers[1,2] we showed that the heat capacities and related properties of organic substances (alkanes, alkenes, alkanols, and alkanones) in crystalline state could be predicted by the additive method with a reasonable accuracy (about 5%). However, no way has been found to use the information about the phase transitions that is often available in the absence of any heat capacity data. After the previous publications,[1,2] we measured the heat capacities and obtained the related thermodynamic functions for three phenyl urea derivatives: 1,1-diphenylurea (**11**), 1,3-diphenylurea (**13**), and 1,1-dimethyl-3-phenylurea (**113**), that allowed us to derive the additive parameters of the phenyl group for calculations of thermodynamic properties in the crystalline state. Another aim of this work was to check if the knowledge of the values of the temperatures and enthalpies of the solid-to-solid transitions could improve the prediction of the entropies and thermal enthalpies for crystals of organic compounds.

Experimental Section

Substance **13** was synthesized by heating of aniline hydrochloride with urea in water according to ref 3. The product was treated with water at $T = 373$ K to remove any impurity of phenylurea, crystallized from ethyl acetate, and sublimed in a vacuum at $T = 428$ K. **11** and **113** were synthesized at the Mendeleev University of Chemical Technology (Moscow) and sublimed twice in a vacuum. The identity of the substances was proved by NMR spectroscopy. The amount of CO_2 in the products of combustion (99.93% of theoretical value) was used as an indirect characteristic of purity for **13**. **13** was found to be not hygroscopic. However, the samples were kept in a desiccator over P_2O_5. The density of **13** measured in a pycnometer with isooctane as a pycnometric liquid is 1239 $kg{\cdot}m^{-3}$ at $T = 293$ K, in accordance with literature data.[4]

Heat capacities in the temperature range (5 to 300) K were measured in an adiabatic calorimeter TAU-1 produced by VNIIFTRI (Moscow) and described in detail.[5] The temperature scale adopted was ITS-90. The uncertainty of heat capacity measurements was about 2% at $T = 5$ K, decreased at higher temperatures, and did not exceed 0.4% at $T > 40$ K. The reliability of the device was proved by periodical measurements of the heat capacity of benzoic acid (K-1 reference sample). Samples of **11** (0.496 89 g), **13** (0.374 48 g), and **113** (0.861 56 g) were loaded in stainless steel containers sealed by indium rings. Total heat capacities of containers with samples were measured in separate experiments under adiabatic conditions maintained with an electronic device. Temperature increments were 0.2 K near 5 K and up to 5 K near 300 K. Those increments can be roughly estimated by the differences between the mean temperatures of successive experiments (Tables 1−3). The total heat capacity of a container with a sample was calculated in each experiment as the relation of a heat input to a temperature increment corrected for a temperature drift slope in a conventional manner. The heat capacities of the samples were obtained after subtraction of heat capacities of containers measured in separate series and were not less than 50% of the total heat capacities of the samples with containers in the whole temperature range.

The enthalpy of the solid-phase transition shown by **11** was measured in two experiments that covered the temperature range of the transition after subtraction of the heat spent for heating of crystal I to the transition temperature and crystal II above T_{tr} (Table 4).

Results and Discussion

Among the studied substances, only **11** showed a solid-to-solid transition in the range (5 to 300) K (Figure 1). The transition occurred at $T = 287 \pm 0.5$ K (peak temperature) and had a very small enthalpy $\Delta_{tr}H_m = 19 \pm 4$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$. We cannot explain its nature without crystallographic and spectroscopic studies that were not subjects of the present work. It is evident from the value of $\Delta_{tr}H_m$ that the transition was not caused by formation of plastic crystals.

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10.1021/je0155150 CCC: $22.00

Table 1. Experimental Heat Capacity of 1,1-Diphenylurea

T	C_s	T	C_s	T	C_s
K	$J\cdot K^{-1}\cdot mol^{-1}$	K	$J\cdot K^{-1}\cdot mol^{-1}$	K	$J\cdot K^{-1}\cdot mol^{-1}$
		Series 1			
5.25	0.502	19.44	17.33	51.45	63.34
5.55	0.599	20.23	18.59	53.84	65.66
5.89	0.723	21.10	20.16	56.07	67.88
6.27	0.860	22.17	22.00	58.18	69.78
6.69	1.030	23.26	23.86	60.18	71.71
7.07	1.223	24.27	25.54	62.15	73.60
7.48	1.503	25.36	27.38	64.89	75.66
7.92	1.807	26.52	29.39	67.23	77.61
8.39	2.151	27.60	31.21	69.45	79.37
8.87	2.546	28.61	32.89	72.63	81.58
9.38	3.011	29.70	34.75	76.61	84.60
9.90	3.601	30.95	36.90	80.35	87.50
10.38	4.070	32.43	39.18	83.89	89.99
10.87	4.646	34.06	41.82	87.27	92.56
11.44	5.286	35.55	44.06	90.51	94.88
12.02	6.037	36.93	46.05	93.63	97.21
12.62	6.871	38.22	47.97	97.02	99.41
13.23	7.662	39.45	49.65	100.66	101.92
13.92	8.648	40.60	50.99	104.19	104.18
14.66	9.717	41.71	52.60	107.60	106.59
15.35	10.72	42.76	53.78	110.93	109.00
16.03	11.80	43.80	55.01	114.17	111.12
16.74	12.91	45.03	56.45	117.50	113.43
17.38	13.91	46.53	58.12	120.94	115.71
18.04	14.87	48.05	59.79	124.29	117.94
18.71	16.03	49.51	61.36		
		Series 2			
120.77	115.33	178.27	156.83	236.47	203.52
124.32	117.74	182.80	160.11	241.70	207.49
128.37	120.41	187.26	163.63	247.32	211.99
132.90	123.46	191.67	167.07	252.91	216.54
137.31	126.44	196.48	170.80	258.45	220.66
141.63	129.65	201.67	175.09	263.95	225.28
145.86	132.57	206.81	179.19	269.42	229.69
150.01	135.64	211.87	183.50	275.52	234.29
154.54	138.80	216.89	187.21	282.24	243.10
159.46	142.40	221.85	191.70	288.99	242.10
164.28	145.99	226.77	195.52	295.52	248.40
169.02	149.55	231.64	199.11	301.97	255.06
173.68	153.21				
		Series 3			
273.32	232.84	282.44	241.36	287.03	256.19
276.20	235.15	283.89	242.48	288.57	242.50
279.08	238.09	285.33	243.89	290.00	243.46
281.00	239.95				

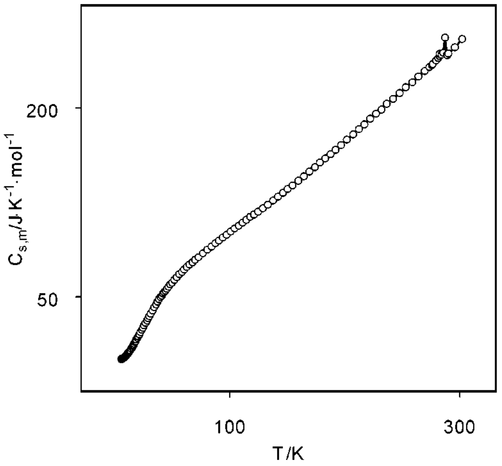

Figure 1. Temperature dependence of the heat capacity of crystalline 1,1-diphenylurea.

Table 2. Experimental Heat Capacity of 1,3-Diphenylurea

T	C_s	T	C_s	T	C_s
K	$J\cdot K^{-1}\cdot mol^{-1}$	K	$J\cdot K^{-1}\cdot mol^{-1}$	K	$J\cdot K^{-1}\cdot mol^{-1}$
		Series 1			
6.62	1.456	12.57	8.176	20.44	20.15
7.01	1.729	13.15	9.081	20.89	20.86
7.39	2.000	13.69	9.881	21.32	21.51
7.73	2.335	14.19	10.60	21.87	22.28
8.04	2.603	14.72	11.43	22.52	23.32
8.39	2.957	15.27	12.20	23.14	24.37
8.77	3.246	15.78	12.98	23.73	25.26
9.12	3.641	16.27	13.75	24.37	26.28
9.45	4.084	16.73	14.44	25.12	27.38
9.86	4.501	17.27	15.27	25.89	28.70
10.36	5.039	17.86	16.18	26.83	30.09
10.82	5.727	18.43	17.04	27.93	31.80
11.24	6.283	18.97	17.86	28.95	33.36
11.63	6.810	19.48	18.64	29.91	35.04
12.05	7.403	19.97	19.42		
		Series 2			
31.87	37.84	50.19	60.81	85.13	90.19
32.82	39.35	52.13	62.68	87.85	92.52
33.89	40.97	54.59	65.10	90.48	94.40
35.07	42.61	56.91	67.41	93.04	96.07
36.29	44.39	59.08	69.42	95.51	97.99
37.56	46.17	61.52	71.55	98.57	100.05
38.76	47.80	64.20	73.81	102.19	102.54
39.89	49.28	66.74	76.00	105.68	104.96
41.22	50.76	69.15	78.00	109.08	107.17
42.72	52.55	72.51	80.47	112.38	109.50
44.28	54.43	76.27	83.51	115.60	111.65
45.88	56.19	79.36	85.99	118.75	113.71
47.39	57.87	82.31	88.18	121.83	115.80
48.82	59.47				
		Series 3			
124.87	118.00	148.77	134.38	178.56	156.01
128.16	119.87	152.39	136.68	182.76	158.88
131.75	122.28	156.65	139.66	186.91	162.06
135.27	124.75	161.17	142.95	191.02	165.08
138.73	127.10	165.61	146.24	195.08	168.55
142.13	129.49	169.99	149.33	199.11	171.54
145.48	132.01	174.31	152.50		
		Series 4			
203.87	174.95	240.87	204.20	276.06	231.94
209.32	179.52	246.00	207.89	280.99	235.70
214.70	183.45	251.08	212.18	285.91	238.92
220.04	187.84	256.12	215.91	290.82	242.77
225.32	191.80	261.14	220.18	295.67	246.67
230.55	195.75	266.14	224.15	300.48	250.20
235.74	199.86	271.11	227.84		

The smoothed values of heat capacities and the related thermodynamic functions of the studied compounds are given in Tables 5−7. The heat capacities were extrapolated below $T = 5$ K as cubic functions of temperature. The probable error of such an extrapolation was comparable with the experimental uncertainty of heat capacity measurements, 2% near $T = 5$ K, and did not affect the thermodynamic functions at higher temperatures. Formation of stable crystals of the studied compounds and zero residual entropy at $T = 0$ K are confirmed by the absence of any glasslike transitions and corresponding anomalies on the heat capacity curves.

In our previous study,[2] the thermodynamic functions of alkylureas were approximated as sums of an according function of urea and increments corresponding to substitution of N−H by N−CH_3 (P_i) or of C−H by C−CH_3 (P_j), and to the appearance of each new C−C−C chain (P_k), C−C−N chain (P_l), and N−C−N chain (P_m). Two new parameters are necessary for the compounds studied in this work. The first (P_{Ph}) corresponds to substitution of N−H by N−phenyl. The second ($P_{Ph,Ph}$) corresponds to the appearance of a

Table 3. Experimental Heat Capacity of 1,1-Dimethyl-3-phenylurea

T	C_s	T	C_s	T	C_s
K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
		Series 1			
5.30	0.333	18.43	9.806	49.96	51.54
5.80	0.437	19.53	11.18	53.26	55.27
6.23	0.529	20.76	12.71	56.88	59.38
6.69	0.670	21.97	14.32	60.18	62.98
7.18	0.816	23.23	15.98	63.64	66.59
7.70	1.006	24.54	17.73	67.27	70.25
8.33	1.241	25.85	19.58	70.67	73.41
8.95	1.524	27.17	21.48	74.18	76.85
9.49	1.796	28.38	23.07	77.82	80.16
10.06	2.128	29.62	24.94	81.61	83.26
10.65	2.480	30.95	26.81	85.55	86.61
11.18	2.852	32.41	28.76	89.30	89.67
11.72	3.209	34.05	31.07	92.89	92.51
12.28	3.611	35.71	33.30	96.66	95.39
12.79	4.048	37.36	35.56	100.60	98.43
13.32	4.519	39.02	37.82	104.40	101.17
13.96	5.080	40.56	40.01	108.40	104.03
14.65	5.680	42.16	41.88	112.57	106.89
15.37	6.429	44.24	44.60	116.61	109.71
16.25	7.325	47.02	47.98	120.54	112.32
17.33	8.530				
		Series 2			
118.76	110.86	177.73	147.35	244.29	187.15
122.94	113.56	182.62	150.15	249.23	190.05
127.48	116.51	187.77	153.23	254.12	193.25
131.89	119.31	192.83	156.31	259.51	196.60
136.20	122.06	197.81	159.09	265.52	200.57
140.80	125.04	202.71	162.06	271.42	204.55
145.68	128.21	207.88	165.00	277.23	208.20
150.45	130.83	213.30	168.39	282.97	211.70
155.11	133.78	218.64	171.58	288.62	215.21
159.69	136.64	223.91	174.84	294.20	218.47
164.18	139.20	229.11	178.15	299.71	221.87
168.59	141.84	234.23	181.18	305.15	225.20
173.11	144.63	239.29	184.22		

Table 4. Measurements of the Enthalpy of the Solid Phase Transition for 1,1-Diphenylurea (Mass of the Sample 0.496 89 g)[a]

T_1	T_2	Q	Q_{cal}	H_1	H_2	$\Delta_{tr}H$	$\Delta_{tr}H_m$
K	K	J	J	J	J	J	$J \cdot mol^{-1}$
272.44	292.04	42.567	31.563	8.103	2.864	0.037	16
272.53	292.84	44.150	32.720	8.054	3.324	0.052	22

[a] T_1 is the initial temperature of the experiment, T_2 is the final temperature of the experiment, Q is the energy supplied, Q_{cal} is the energy expended for heating the calorimeter cell from T_1 to T_2, H_1 is the energy necessary for heating the sample in the crystal II state from T_1 to T_{tr} = 287 K, H_2 is the energy necessary for heating the sample in the crystal I state from T_{tr} to T_2, and $\Delta_{tr}H$ is the enthalpy of the transition cr,II to cr,I.

new phenyl–N–phenyl chain, for example, during introduction of the second phenyl group to phenylurea, leading to formation of 1,1-diphenylurea. A property of alkylphenylurea P_{APU} can be calculated as a sum of the corresponding property of urea P_{urea} and additive increments P_{index} multiplied by their occurrences n_{index}:

$$P_{APU} = P_{urea} + \sum n_{index} P_{index}$$

where index enumerates the above-mentioned types of contributions to the property. For example, 1-methyl-3,3-diphenylurea can be built from urea in the following way:

$$\mathrm{NH_2{-}CO{-}NH_2} \rightarrow \mathrm{phenyl{-}NH{-}CO{-}NH_2} \rightarrow \mathrm{phenyl_2N{-}CO{-}NH_2} \rightarrow \mathrm{phenyl_2N{-}CO{-}NH{-}CH_3}$$

Its thermodynamic property can be approximated, in accordance with this scheme, by a sum

$$P = P_{urea} + P_{Ph} + (P_{Ph} + P_{Ph,Ph}) + P_i = P_{urea} + 2P_{Ph} + P_{Ph,Ph} + P_i$$

This result does not depend on the sequence of substitutions leading from urea to the final product. A matrix of coefficients n for the studied compounds is given in Table 8.

We checked additivity relations for the thermodynamic functions of phenylureas in two ways. In the first way, we used the parameters P_i to P_m derived in our previous work,[2] and calculated the P_{Ph} and $P_{Ph,Ph}$ parameters by the least-squares method after subtraction of properties of urea and values of appropriate P_i to P_m increments[2] from the properties of **11**, **13**, and **113** at each temperature (Tables 5–7). We took into account the data for all crystalline phases of compounds showing solid-phase transitions (Tables 13–16 of the preceding paper[2]).

The values of the parameters obtained are given in Table 9, and square-averaged deviations of the calculated values of the thermodynamic properties of **11**, **13**, and **113** from the experimental ones are given in Table 10. The deviations, except for those at the lowest temperatures, do not exceed 5% for the heat capacities and are even much less for other thermodynamic functions. Using the parameters obtained, we calculated the thermodynamic functions for phenylurea not involved in evaluation of the additive

Table 5. Thermodynamic Functions (in $J \cdot K^{-1} \cdot mol^{-1}$) of 1,1-Diphenylurea

T/K	C_p	S	H/T	$-G/T$	T/K	C_p	S	H/T	$-G/T$	T/K	C_p	S	H/T	$-G/T$
							Crystal II							
0	0	0	0	0	70	79.63	67.09	39.99	27.10	190	165.81	182.19	91.88	90.31
5	0.437	0.146	0.109	0.036	80	87.30	78.23	45.43	32.80	200	173.80	190.90	95.78	95.12
10	3.68	1.194	0.900	0.294	90	94.57	88.93	50.49	38.44	210	181.85	199.58	99.69	99.89
15	10.21	3.852	2.857	0.995	100	101.49	99.26	55.25	44.01	220	189.98	208.22	103.61	104.62
20	18.26	7.860	5.675	2.185	110	108.22	109.25	59.76	49.49	230	198.07	216.85	107.54	109.31
25	26.79	12.85	9.045	3.806	120	114.94	118.95	64.07	54.88	240	206.13	225.45	111.48	113.97
30	35.25	18.49	12.71	5.777	130	121.65	128.41	68.24	60.17	250	214.14	234.02	115.43	118.60
35	43.20	24.53	16.51	8.020	140	128.49	137.68	72.30	65.38	260	222.11	242.58	119.38	123.20
40	50.29	30.77	20.30	10.47	150	135.52	146.78	76.28	70.50	270	230.00	251.11	123.33	127.78
45	56.50	37.06	23.98	13.08	160	142.78	155.76	80.21	75.55	280	237.95	259.62	127.28	132.34
50	61.97	43.30	27.51	15.79	170	150.26	164.64	84.11	80.53	287	243.52	265.56	130.04	135.52
60	71.37	55.46	34.06	21.39	180	157.95	173.44	88.00	85.45					
							Crystal I							
287	240.24	265.63	130.11	135.52	298.15	251.14	274.99	134.43	140.56	300	252.95	276.55	135.16	141.39
290	243.18	268.14	131.27	136.87										

Table 6. Thermodynamic Functions (in J·K^{-1}·mol^{-1}) of 1,3-Diphenylurea

T/K	C_p	S	H/T	$-G/T$	T/K	C_p	S	H/T	$-G/T$	T/K	C_p	S	H/T	$-G/T$
							Crystal							
0	0	0	0	0	80	86.38	78.88	45.04	33.84	200	172.07	190.96	95.21	95.75
5	0.653	0.218	0.163	0.055	90	93.91	89.49	50.06	39.43	210	179.80	199.54	99.05	100.49
10	4.655	1.655	1.230	0.425	100	101.12	99.76	54.80	44.95	220	187.61	208.08	102.90	105.18
15	11.83	4.846	3.534	1.312	110	107.87	109.72	59.32	50.39	230	195.48	216.60	106.75	109.84
20	19.45	9.298	6.555	2.744	120	114.39	119.38	63.64	55.74	240	203.38	225.08	110.61	114.47
25	27.25	14.47	9.907	4.562	130	121.15	128.80	67.80	61.00	250	211.28	233.55	114.48	119.06
30	35.12	20.14	13.46	6.680	140	128.05	138.03	71.86	66.17	260	219.17	241.99	118.36	123.63
35	42.55	26.11	17.09	9.026	150	135.07	147.11	75.84	71.27	270	227.00	250.40	122.24	128.17
40	49.29	32.24	20.70	11.54	160	142.22	156.05	79.76	76.29	280	234.74	258.80	126.12	132.68
45	55.29	38.40	24.22	14.19	170	149.50	164.89	83.65	81.24	290	242.35	267.17	129.99	137.18
50	60.67	44.51	27.60	16.91	180	156.91	173.64	87.51	86.13	298.15	248.42	273.97	133.15	140.82
60	70.10	56.43	33.91	22.51	190	164.44	182.33	91.36	90.96	300	249.78	275.51	133.86	141.65
70	78.50	67.87	39.69	28.18										

Table 7. Thermodynamic Functions (in J·K^{-1}·mol^{-1}) of 1,1-Dimethyl-3-phenylurea

T/K	C_p	S	H/T	$-G/T$	T/K	C_p	S	H/T	$-G/T$	T/K	C_p	S	H/T	$-G/T$
							Crystal							
0	0	0	0	0	80	81.93	62.52	38.22	24.30	200	160.45	170.35	89.40	80.95
5	0.275	0.092	0.069	0.023	90	90.28	72.65	43.54	29.11	210	166.43	178.32	92.93	85.40
10	2.090	0.721	0.539	0.182	100	97.99	82.57	48.61	33.96	220	172.46	186.20	96.40	89.80
15	6.024	2.247	1.658	0.589	110	105.06	92.25	53.42	38.82	230	178.54	194.00	99.84	94.16
20	11.76	4.734	3.439	1.295	120	111.73	101.67	58.01	43.67	240	184.69	201.73	103.25	98.48
25	18.41	8.059	5.756	2.303	130	118.22	110.88	62.39	48.49	250	190.88	209.40	106.63	102.77
30	25.41	12.03	8.447	3.586	140	124.52	119.87	66.60	53.27	260	197.13	217.00	109.99	107.01
35	32.37	16.47	11.37	5.105	150	130.65	128.67	70.67	58.00	270	203.40	224.56	113.33	111.23
40	39.10	21.24	14.42	6.821	160	136.69	137.29	74.61	62.69	280	209.69	232.07	116.66	115.41
45	45.52	26.22	17.52	8.698	170	142.65	145.76	78.43	67.33	290	215.95	239.54	119.98	119.56
50	51.59	31.33	20.63	10.71	180	148.58	154.08	82.17	71.91	298.15	221.03	245.60	122.67	122.92
60	62.77	41.74	26.74	15.01	190	154.50	162.27	85.82	76.46	300	222.18	246.97	123.28	123.68
70	72.82	52.19	32.61	19.57										

Table 8. Matrix of the Occurrences of All Kinds of Substitutions and Interactions in the Studied Phenylureas

code	compound	n_i	n_j	n_k	n_l	n_m	n_{Ph}	$n_{Ph,Ph}$
	phenylurea	0	0	0	0	0	1	0
11	1,1-diphenylurea	0	0	0	0	0	2	1
13	1,3-diphenylurea	0	0	0	0	0	2	0
113	1,1-dimethyl-3-phenylurea	2	0	0	0	1	1	0

parameters. Experimental thermodynamic properties of phenylurea were reported for $T = (100, 200, \text{and } 300)$ K.[6] As shown in Table 11, the deviations of the additive predictions from the experimental values are within 5% of the latter.

In the second way, we used the whole set of alkylureas and alkylphenylureas for evaluation of the phenyl group increments and re-evaluation of the parameters for alkylureas. The alternative parameter set obtained in this way is very similar to the first one. The temperature dependence of the parameters for C−N−C interaction[2] shows jumps caused by the phase transitions of tetraalkylureas. These jumps were smoothed by 1−2 J·K^{-1}·mol^{-1} when the second way of evaluation was applied. Approximation of the properties of **11**, **13**, and **113** by the new parameters is a bit better, but the prediction for phenylurea is, in general, of the same quality as that of the prediction in the first way. The square-averaged deviations of the calculated properties from the experimental values are given in Table 12.

Many alkylurea derivatives show phase transitions in the crystalline state. The additive parameters proposed in the previous paper[2] and this paper do not allow us to take into account a knowledge of the characteristics of phase transitions during prediction of the entropies and thermal enthalpies for new compounds. That may be done in the following manner. Enthalpies and entropies of phase

Table 9. Additive Parameters (*C*, *S*, *H*, and *G* in J·K^{-1}·mol^{-1}) for Calculations of Thermodynamic Functions (Heat Capacity, C_p, Entropy, *S*, Enthalpy Function, $(H - H(0))/T$, and Gibbs Energy Function, $(G - H(0))/T$, Respectively) of Phenylureas

T/K	C_{Ph}	$C_{Ph,Ph}$	S_{Ph}	$S_{Ph,Ph}$	H_{Ph}	$H_{Ph,Ph}$	G_{Ph}	$G_{Ph,Ph}$
10	1.8	−0.5	0.7	−0.3	0.5	−0.2	0.2	−0.1
15	4.2	−0.6	1.8	−0.5	1.3	−0.4	0.5	−0.2
20	6.5	0.1	3.4	−0.7	2.4	−0.4	1.0	−0.3
25	8.8	1.0	5.0	−0.5	3.4	−0.2	1.7	−0.4
30	11.0	1.7	6.9	−0.3	4.5	0.1	2.4	−0.4
35	13.1	2.1	8.7	0.1	5.6	0.4	3.1	−0.3
40	15.0	2.4	10.6	0.3	6.6	0.6	4.0	−0.3
45	16.6	2.4	12.4	0.6	7.7	0.8	4.8	−0.2
50	18.1	2.3	14.3	0.9	8.6	0.9	5.6	−0.1
60	20.7	1.9	17.8	1.2	10.4	1.1	7.4	0.1
70	23.1	1.4	21.2	1.5	12.1	1.2	9.1	0.3
80	25.5	1.0	24.4	1.6	13.6	1.2	10.8	0.5
90	27.9	0.6	27.5	1.8	15.1	1.1	12.5	0.6
100	30.2	0.2	30.6	1.8	16.4	1.1	14.2	0.7
110	32.2	0.1	33.6	1.8	17.8	1.0	15.8	0.8
120	34.2	0.3	36.4	1.9	19.1	0.9	17.4	0.9
130	36.3	0.2	39.3	1.8	20.3	0.8	19.0	1.0
140	38.5	0.1	42.1	1.8	21.5	0.8	20.5	1.0
150	40.7	0.1	44.8	1.9	22.7	0.8	22.1	1.0
160	42.8	0.5	47.5	1.8	23.9	0.8	23.6	1.1
170	45.0	1.0	50.1	2.0	25.1	0.8	25.0	1.2
180	47.3	1.6	52.8	2.0	26.2	0.8	26.5	1.2
190	49.7	2.1	55.4	2.2	27.4	0.9	27.9	1.3
200	52.2	2.6	57.9	2.4	28.6	1.0	29.4	1.3
210	54.4	3.5	60.5	2.5	29.7	1.1	30.8	1.3
220	56.6	4.5	63.1	2.7	30.9	1.3	32.2	1.4
230	58.9	5.5	65.7	2.9	32.0	1.5	33.6	1.5
240	61.2	6.3	68.2	3.2	33.1	1.9	35.1	1.4
250	63.5	7.1	70.7	3.5	34.3	2.0	36.5	1.5
260	65.7	7.8	73.3	3.8	35.5	2.2	37.8	1.6
270	68.0	8.5	75.8	4.1	36.6	2.4	39.2	1.7
280	76.4	−3.2	79.2	2.6	38.6	1.1	40.7	1.5
290	79.3	−6.3	82.2	2.0	40.1	0.6	42.1	1.4
298.15	81.4	−4.7	84.4	1.9	41.3	0.3	43.1	1.6
300	81.8	−4.3	85.1	1.5	41.6	0.1	43.5	1.4

Table 10. Square-Averaged Deviations of the Calculated Properties of the Three Studied Alkylphenylureas from the Experimental Ones

T	C_p	S	$(H - H(0))/T$	$-(G - H(0))/T$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
10	0.6	0.2	0.1	0.1
15	1.3	0.6	0.4	0.2
20	1.7	1.0	0.7	0.4
25	1.8	1.5	0.9	0.5
30	2.0	1.8	1.0	0.7
35	1.9	2.1	1.2	0.9
40	1.8	2.3	1.3	1.1
45	1.5	2.5	1.3	1.2
50	1.3	2.7	1.3	1.4
60	0.8	2.8	1.3	1.6
70	0.3	3.0	1.1	1.8
80	0.1	2.9	1.0	2.0
90	0.1	3.0	0.9	2.0
100	0.2	3.0	0.9	2.1
110	0.3	2.9	0.7	2.2
120	0.4	3.0	0.6	2.2
130	0.4	2.9	0.5	2.3
140	0.5	2.8	0.5	2.3
150	0.5	2.8	0.4	2.3
160	0.0	2.7	0.4	2.4
170	0.3	2.9	0.5	2.4
180	0.8	2.9	0.4	2.5
190	0.9	3.0	0.4	2.5
200	1.1	3.1	0.6	2.5
210	1.9	3.2	0.7	2.5
220	2.8	3.4	0.7	2.5
230	3.8	3.5	0.9	2.6
240	4.6	3.7	1.3	2.5
250	5.5	3.9	1.4	2.5
260	6.3	4.1	1.6	2.6
270	7.2	4.3	1.7	2.7
280	8.2	2.3	0.1	2.4
290	9.2	1.3	0.9	2.3
298.15	9.6	1.1	1.3	2.4
300	9.6	0.6	1.6	2.1

Table 11. Experimental and Predicted Values of Thermodynamic Properties (in $J \cdot K^{-1} \cdot mol^{-1}$) of Phenylurea

	C_p		S		H/T		$-G/T$	
T/K	exp	calc	exp	calc	exp	calc	exp	calc
100	70.15	71.2	62.57	66.9	36.49	37.7	26.08	29.2
200	117.7	119.1	125.6	130.6	65.05	66.3	60.55	64.4
298.15	171.8	174.5	182.5	188.7	91.20	92.9	91.30	95.8
300	173.1	175.4	183.6	189.9	91.70	93.4	91.90	96.5

transitions are subtracted from the corresponding thermodynamic properties of alkylureas (or the corresponding thermodynamic functions are obtained by integrating C_p and C_p/T, respectively, ignoring the contributions of the phase transitions). Then additive parameters are developed for such "jumpless" thermodynamic functions. The "jumpless" thermodynamic functions for a new compound can be calculated using "jumpless" additive parameters. To predict the values for the true thermodynamic functions, the known (measured) values of the enthalpies and entropies of the phase transition have to be added to the "jumpless" values.

We calculated the "jumpless" additive parameters for alkyl- and phenylureas. However, the average error of approximation of the "jumpless" thermodynamic properties (Table 13) does not substantially differ from the one of the approximation of the true values affected by the phase transitions (Table 12). That is why we concluded the proposed way to take into account the known characteristics of the solid-phase transitions was not effective. Such a conclusion is consistent with a worse additivity of heat capacities among other thermodynamic properties, despite the absence of large jumps of the heat capacities during

Table 12. Square-Averaged Deviations of the Properties of the Alkylureas and Alkylphenylureas Calculated by the Second Way from the Experimental Values

T	C_p	S	$(H - H(0))/T$	$-(G - H(0))/T$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
10	0.4	0.2	0.1	0.04
15	0.9	0.4	0.3	0.1
20	1.2	0.7	0.5	0.2
25	1.3	1.0	0.6	0.3
30	1.4	1.2	0.8	0.5
35	1.3	1.4	0.8	0.6
40	1.2	1.6	0.9	0.7
45	1.1	1.7	0.9	0.8
50	1.1	1.8	0.9	0.9
60	1.2	1.9	0.9	1.1
70	1.4	2.0	0.9	1.2
80	1.5	2.1	0.9	1.3
90	1.6	2.1	0.9	1.4
100	1.6	2.2	0.9	1.4
110	1.7	2.2	0.9	1.5
120	1.7	2.3	0.9	1.5
130	1.8	2.3	1.0	1.6
140	2.0	2.3	1.0	1.6
150	2.1	2.4	1.0	1.7
160	2.3	2.5	1.1	1.7
170	3.2	2.6	1.1	1.8
180	3.7	2.7	1.2	1.8
190	4.1	2.8	1.2	1.8
200	4.7	2.5	2.2	1.9
210	5.7	2.6	2.2	1.8
220	6.7	2.7	2.1	1.8
230	7.8	2.8	2.1	1.8
240	9.1	3.1	1.7	1.6
250	10.3	3.3	1.9	1.7
260	11.3	3.5	2.1	1.7
270	12.8	3.6	2.2	1.7
280	7.0	3.4	2.1	1.7
290	6.9	2.4	1.2	1.6
298.15	7.6	5.2	4.1	1.8
300	7.9	4.9	4.0	1.6

Table 13. Square-Averaged Deviations of the Calculated "Jumpless" Properties of the Alkylureas and Alkylphenylureas from the Experimental Values

T	C_p	S	$(H - H(0))/T$	$-(G - H(0))/T$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
10	0.4	0.2	0.1	0.04
15	0.9	0.4	0.3	0.1
20	1.2	0.7	0.5	0.2
25	1.3	1.0	0.6	0.3
30	1.4	1.2	0.8	0.5
35	1.3	1.4	0.8	0.6
40	1.2	1.6	0.9	0.7
45	1.1	1.7	0.9	0.8
50	1.1	1.8	0.9	0.9
60	1.2	1.9	0.9	1.1
70	1.4	2.0	0.9	1.2
80	1.5	2.1	0.9	1.3
90	1.6	2.1	0.9	1.4
100	1.6	2.2	0.9	1.4
110	1.7	2.2	0.9	1.5
120	1.7	2.3	0.9	1.5
130	1.8	2.3	1.0	1.6
140	2.0	2.3	1.0	1.6
150	2.1	2.4	1.0	1.7
160	2.3	2.5	1.1	1.7
170	3.2	2.5	1.1	1.7
180	3.7	2.6	1.2	1.8
190	4.1	2.7	1.3	1.8
200	4.7	2.8	1.4	1.8
210	5.7	3.0	1.5	1.9
220	6.7	3.1	1.7	1.9
230	7.8	3.4	1.8	2.0
240	9.1	3.5	2.1	1.7
250	10.3	3.9	2.4	1.7
260	11.3	4.2	2.7	1.8
270	12.8	4.6	3.0	1.9
280	7.0	4.0	2.6	1.8
290	6.9	4.1	2.7	1.8
298.15	7.6	4.4	2.8	1.9
300	7.9	4.3	2.8	1.8

the solid-to-solid transitions (See figures in our previous publication[2]).

Conclusion

The additive parameters for prediction of the heat capacities and the related properties of phenylureas were developed. The expected accuracy of the prediction is 5%. The parameters developed earlier for alkylureas are transferable to alkylphenylureas without essential loss of accuracy.

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Received for review September 5, 2001. Accepted December 5, 2001.

JE0155150