Additivity of Thermodynamic Properties of Organic Compounds in Crystalline State. 2. Heat Capacities and Enthalpies of Phase Transition of Alkyl Derivatives of Urea in Crystalline State

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The heat capacities and enthalpies of phase transitions for urea and 13 alkyl derivatives of urea [methyl-, 1,1-dimethyl-, 1,3-dimethyl-, ethyl-, (1-methylethyl)-, tetramethyl-, 1,1-diethyl-, 1,3-diethyl-, butyl-, (1,1-dimethylethyl)-, 1,3-bis(1,1-dimethylethyl)-, tetraethyl-, octyl-, and (1-methylpropyl)urea] in the temperature range from 5 to 320 K have been measured by adiabatic calorimetry. The thermodynamic functions of these compounds were obtained from smoothed heat capacity values. The results were used to show that an additive scheme for the calculation of the thermodynamic properties of crystals of alkyl derivatives of urea, without taking into consideration the phase distinctions in crystals, gives reasonable accuracy.

Introduction

In the previous article (*1*) we established a method for making additive calculations of the thermodynamic properties of crystals, C_s, $S°(T)$, $[G°(T) - H°(0)]/T$, and $[H°(T) - H°(0)]/T$, with a reasonable accuracy at temperatures lower than the first solid-to-solid transition temperature. The method was applied to alkanes, alkenes, alkanols, and alkanones (*1*) at $T < 298.15$ K. For many of these compounds phase transitions occur at relatively low temperatures; hence, there are few compounds available for testing additivity relations in the crystal state.

It is important to test the applicability of additive calculations for the thermodynamic properties of crystalline organic compounds at temperatures up to 300 K. However, it was not possible to make the comparison because of the absence of thermodynamic data on a representative series of crystals of organic compounds at $T \geq 250$ K in publications and reference books at our disposal. Hence, we have measured the heat capacities in the range from 5 to 320 K for a number of alkyl derivatives of urea having a regularly changing structure: urea (**I**), methylurea (**II**), 1,1-dimethylurea (**III**), 1,3-dimethylurea (**IV**), ethylurea (**V**), isopropylurea (**VI**), tetramethylurea (**VII**), 1,1-diethylurea (**VIII**), 1,3-diethylurea (**IX**), *n*-butylurea (**X**), *tert*-butylurea (**XI**), 1,3-di-*tert*-butylurea (**XII**), tetraethylurea (**XIII**), and *n*-octylurea (**XIV**). These compounds, excluding tetramethylurea and tetraethylurea, form stable crystals from 5 to 320 K. The above compounds have relatively few solid-to-solid transitions, and they do not exhibit a plastic crystal state in the temperature range studied. Hence, their thermodynamic properties allow the investigation of additivity rules for heat capacities and entropies of crystals over a wide temperature range. Additionally, alkyl derivatives of urea have many practical uses (*2*).

Experimental Procedure

Sources, preparation and purification methods, and final purity of most of the compounds **I**–**XIV** were described earlier (*3*). Samples of 1,3-dimethylurea (**IV**), 1,3-diethylurea (**IX**), tetraethylurea (**XIII**), and *n*-octylurea (**XIV**), not described in ref 3, were synthesized in our laboratory from nitrourea, phosgene, and mono- and dialkylamines according to well-known methods (*2, 4, 5*). Crystalline compounds were purified by repeated crystallization from ethanol solution followed by sublimation in a vacuum ($P = 300$ Pa; $T \leq 350$ K). Liquid tetraethylurea (**XIII**) was distilled in a helium flow at $T = 330$ K. The structure of prepared compounds was checked by NMR spectroscopy.

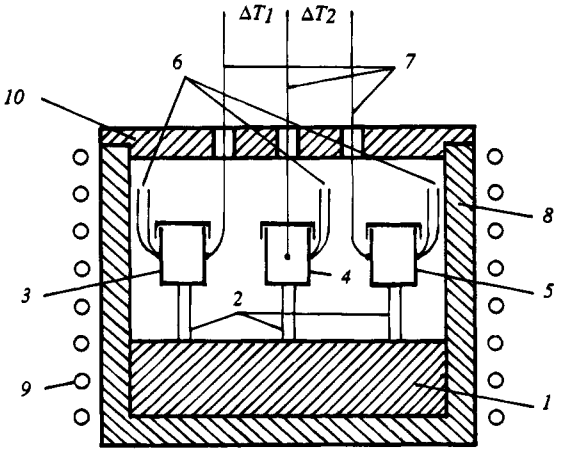

Figure 1. Scheme of the measurement unit of the triple heat bridge calorimeter: 1, copper block; 2, copel rods; 3, pan with examined sample; 4, empty pan; 5, pan with reference sample (copper bar); 6, copper-to-constantan thermocouples for temperature measurements; 7, copper thermocouple wires; 8, copper sleeve; 9, nichrome wire heater; 10, thermoisolation material.

Purity of tetraethylurea (**XIII**) was determined with a gas–liquid chromatograph Chrom 5 using a column filled with 15% polyethylene glycol 20000 on Polysorb W. The content of **XIII** in the sample is 99.9 mol %. Purity of **IV**, **IX**, and **XIV** was estimated from gravimetric analyses of products of combustion in a calorimetric bomb according to the procedure of Rossini (*6*). The relation of the experimental mass of CO_2 to the theoretical one was 0.9978 for **IV**, 0.9986 for **IX**, and 0.9994 for **XIV**.

The low-temperature heat capacity of the compounds **I**–**XIV** at temperatures 5 to 300 K was measured in a vacuum adiabatic calorimeter TAU-1, fabricated by VINIIFTRI (National Scientific and Research Institute for Physical-technical and Radio-technical Measurements) in Moscow. The probable error of the heat capacity values is considered to be ±0.4% at temperatures from 40 to 320 K; this error is increased at $T < 40$ K, and it is $\pm 0.02 C_p$ at helium temperatures. The samples were loaded into a stainless-steel container (volume of 0.6 or 1.1 cm^3, respectively), which were filled with helium gas to provide heat

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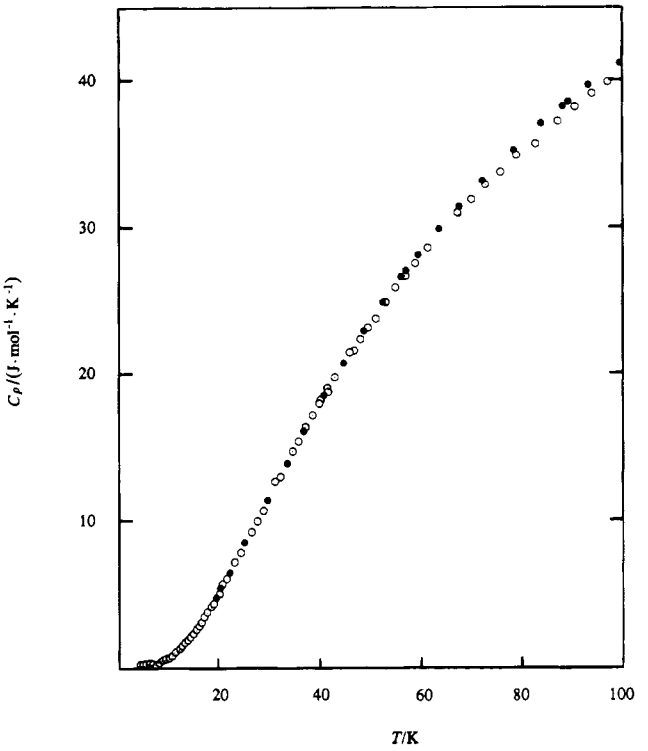


Figure 2. Temperature dependence of the heat capacity of urea (**I**): ○, this work (Table 18); ●, ref 7.

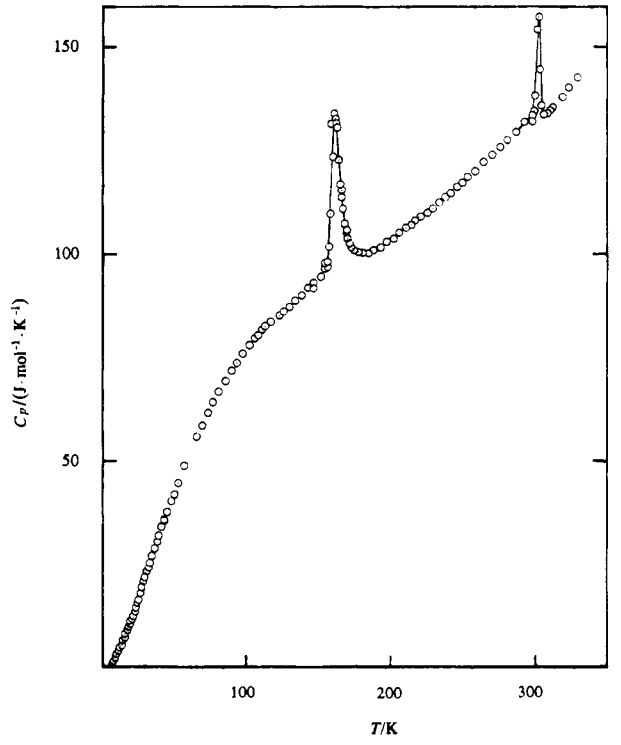


Figure 3. Temperature dependence of the heat capacity of 1,3-dimethylurea (**IV**).

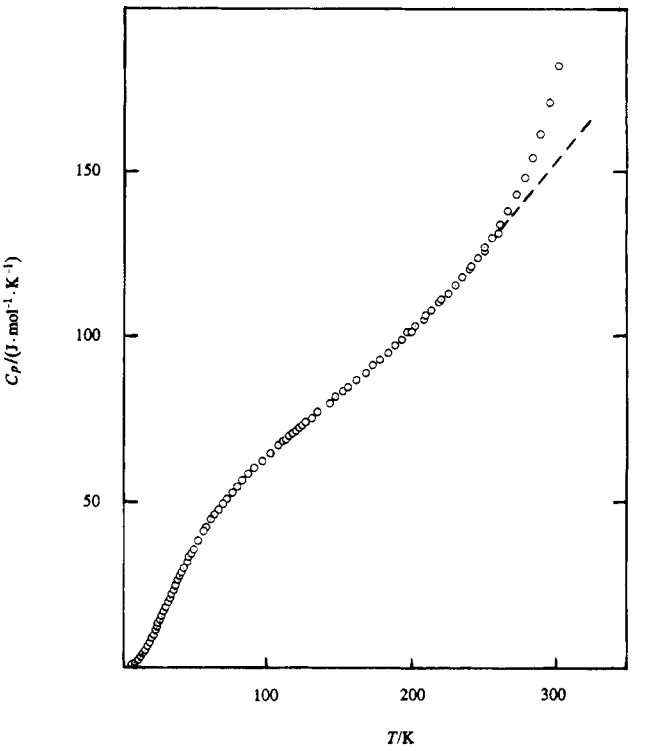


Figure 4. Temperature dependence of the heat capacity of ethylurea (**V**): ○, experimental points (Table 18); – –, extrapolating curve for $T > 250$ K.

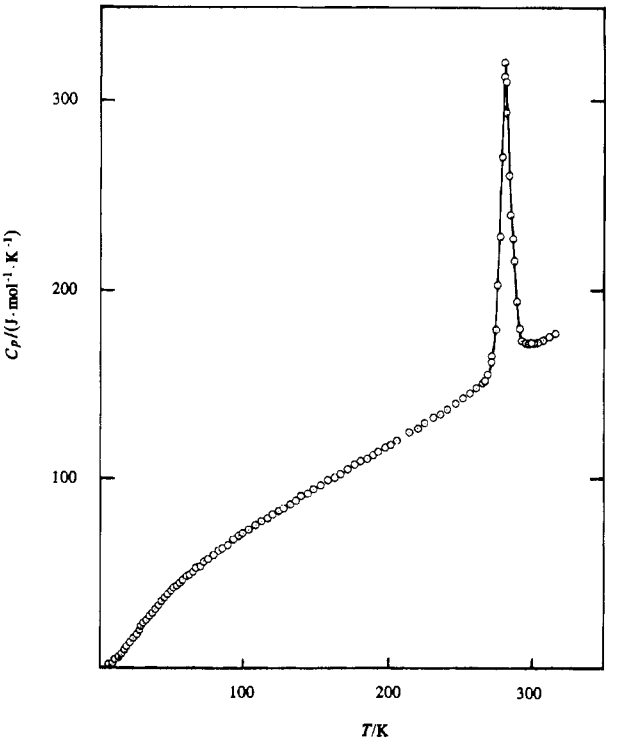


Figure 5. Temperature dependence of the heat capacity of (1-methylethyl)urea (**VI**).

exchange. The container seal was made by an indium gasket. The containers were inserted into the calorimetric sleeves and provided with Manganin heaters. The sleeve was suspended by three nylon cords within the adiabatic shield. The relative temperature between the adiabatic shield and the calorimetric sleeve was determined by a four-junction differential thermocouple [(0.999Cu + 0.001Fe)-to-Chromel]. The emf of the thermocouple, after preliminary amplification by a microvoltnanoampermeter, went to the terminals of a regulation device, which assured automatic adiabatic shield control with proportional, integral, and differential action. The measurement of absolute temperature was made with capsule-type (iron + rhodium) resistance thermometers ($R_0 = 45.32$ and 101.83 Ω). These thermometers were installed on the inner surface of the adiabatic shield. The thermometers were fabricated and calibrated by VINIIFTRI. The reliability of the calorimetric apparatus was confirmed by measuring the heat capacities of standard benzoic acid K-1 and high-

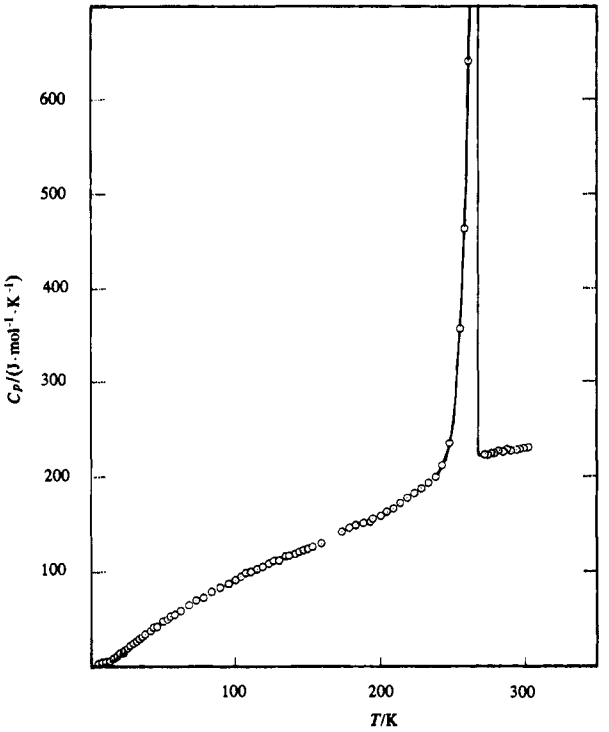


Figure 6. Temperature dependence of the heat capacity of tetramethylurea (**VII**).

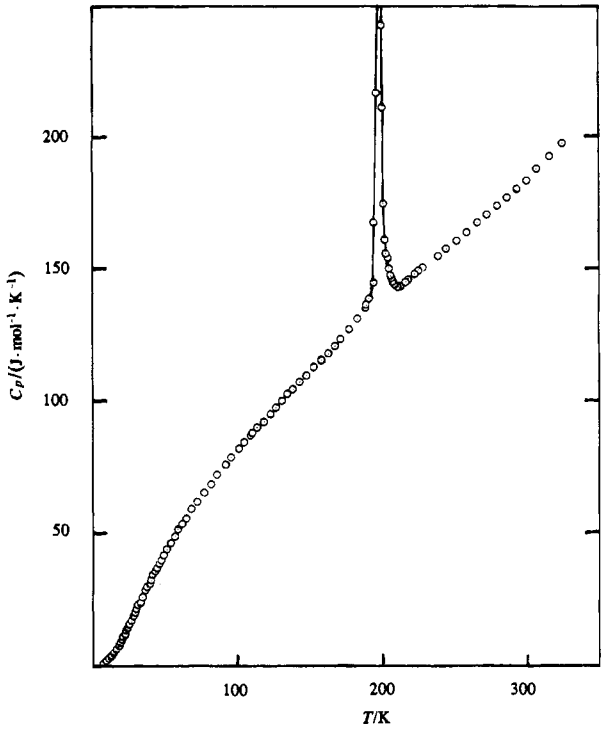


Figure 7. Temperature dependence of the heat capacity of 1,1-diethylurea (**VIII**).

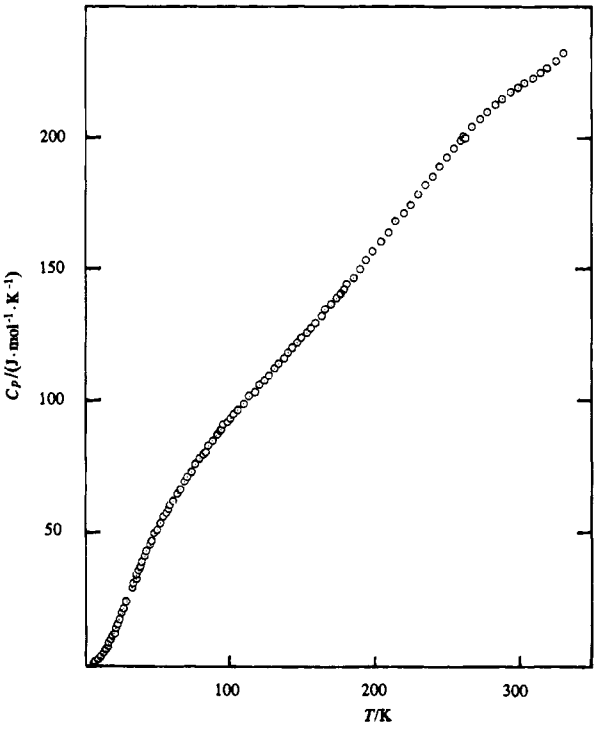


Figure 8. Temperature dependence of the heat capacity of 1,3-diethylurea (**IX**).

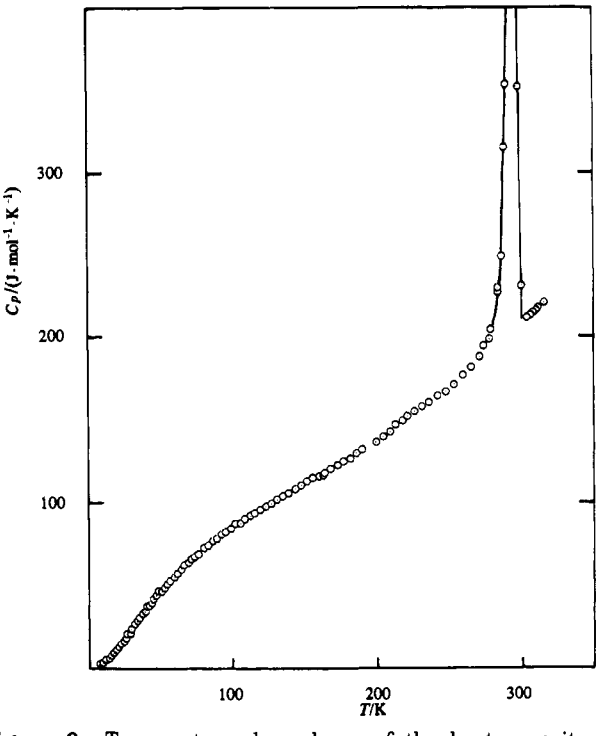


Figure 9. Temperature dependence of the heat capacity of butylurea (**X**).

purity copper. Measurements made for the reference compounds showed an agreement with the best literature heat capacity data within above-mentioned uncertainties.

Heat capacities for some compounds at $T > 300$ K and enthalpies of solid-to-solid transition and of fusion for 1,3-diethylurea were measured by the triple heat bridge method. The basic part of the device (Figure 1) is a cylindrical copper block (1). Three copel (a kind of constantan) rods (2) with length of 15 mm and diameter of 3 mm are attached to this block by diffusion welding, so that they are installed symmetrically about the axis of rotation of the block. Three copper pans of similar mass and geometry (3–5) with volume of 1 cm^3 supplied with covers are welded to the rods. The copper block is fitted closely into a massive copper sleeve (8) supplied with a nichrome heater (9) coiled on its outward surface. To avoid oxidation, the measurement unit is heated in an argon atmosphere at the pressure of 4 kPa. One pan (3) is filled with the sample under study, the next one (4) is filled with a reference substance of well-known heat capacity (copper of 99.95% purity or benzoic acid K-1), and the last one (5) is empty.

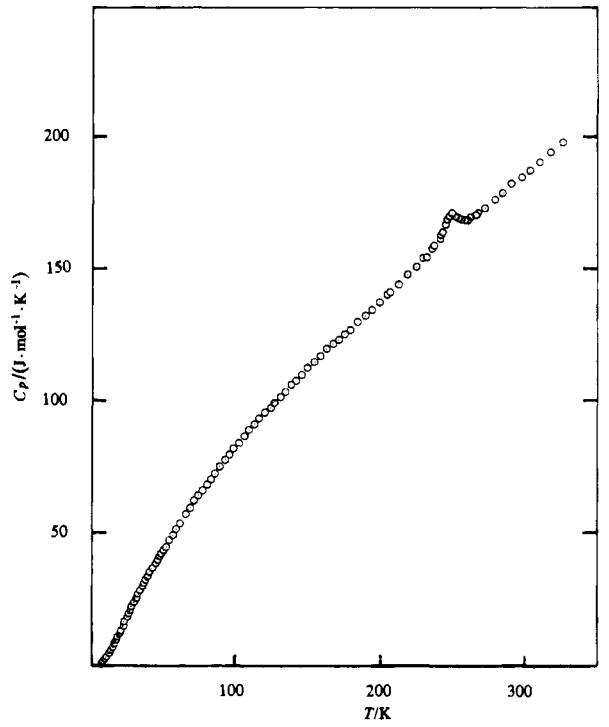


Figure 10. Temperature dependence of the heat capacity of (1,1-dimethylethyl)urea (**XI**).

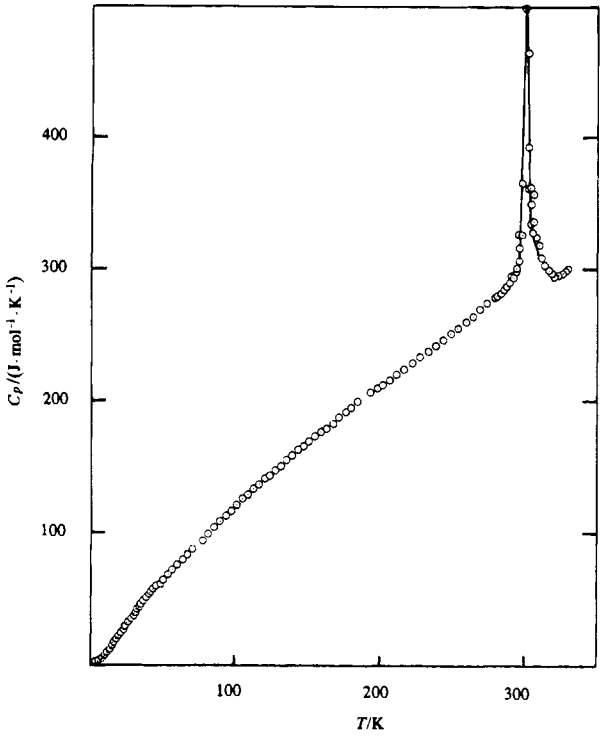


Figure 11. Temperature dependence of the heat capacity of 1,3-di-*tert*-butylurea (**XII**).

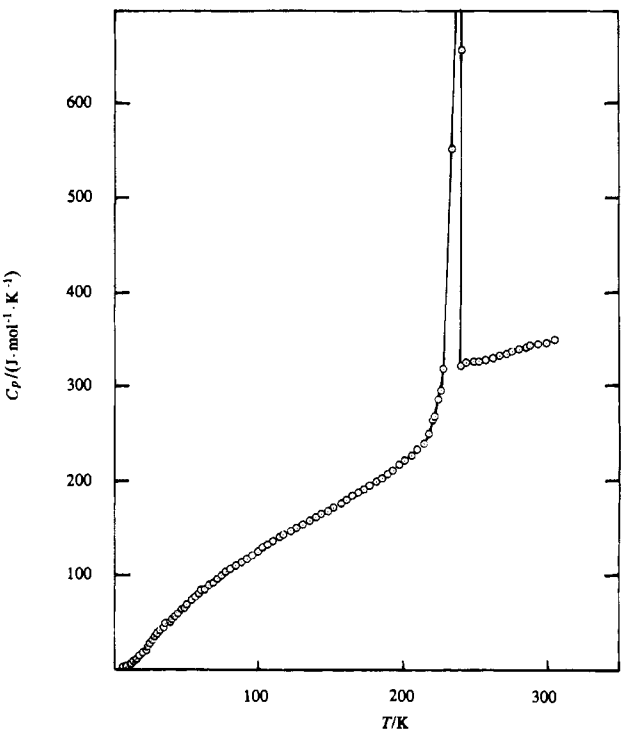


Figure 12. Temperature dependence of the heat capacity of tetraethylurea (**XIII**), crystal and liquid.

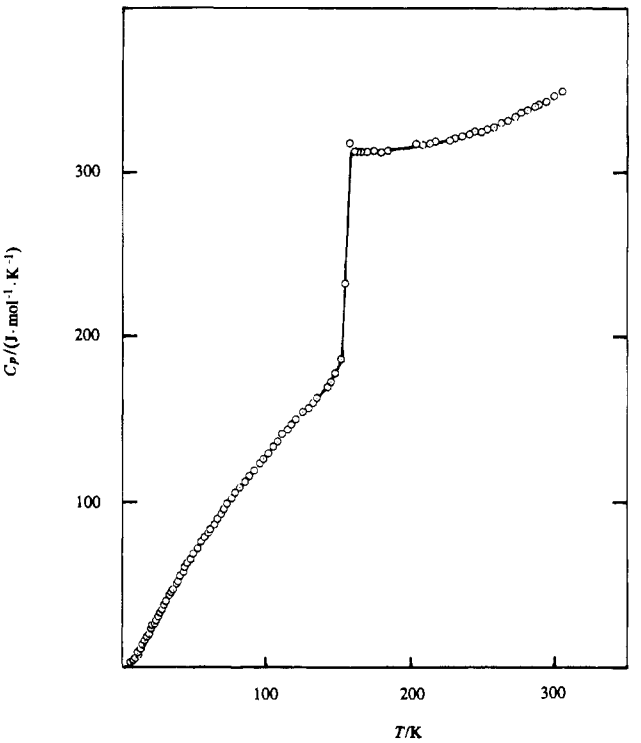


Figure 13. Temperature dependence of the heat capacity of tetraethylurea (**XIII**), glass and liquid.

The copper pans, the copel rods, and the copper block form three differential thermocouples, which are connected to a digital voltmeter via copper wires soldered to the pans. Heat exchange between the block and the pans during heating or cooling of the block is realized mostly through the copel rods. These processes are accompanied by the appearance of a temperature difference ΔT_1 between void pan 5 and pan 3 and a temperature difference ΔT_2 between void pan 5 and pan 4, measured by the differential thermocouples. The copper-to-constantan thermocouple (6), calibrated with a platinum resistance thermometer, is used for temperature measurements of the pan with the sample under study.

An electronic regulator allows heating of the measurement block with a constant rate of 1−7 K·min^{-1}. The relation between ΔT_1 and ΔT_2 during heating with a constant low rate allows the calculation of the specific heat capacity of the sample from

$$C_x = C_{Cu}(m_{Cu}/m_x)(\Delta T_1/\Delta T_2) \quad (1)$$

where C_{Cu} is the specific heat capacity of copper and m_{Cu}

Table 1. Smoothed Experimental Heat Capacity C_s of Condensed Alkylureas

compound	C_s/(J·K^{-1}·mol^{-1}) at T = 0.0 K	5.0 K	10.0 K	15.0 K	20.0 K	25.0 K	30.0 K	35.0 K	40.0 K	45.0 K
urea	0.0	0.0746	0.640	2.333	5.051	8.268	11.67	14.94	18.00	20.85
methylurea	0.0	0.1215	0.969	3.062	6.160	10.00	14.22	18.48	22.86	27.18
ethylurea	0.0	0.2290	1.748	4.632	8.561	13.17	18.19	23.26	28.06	32.49
1,1-dimethylurea	0.0	0.0800	0.734	2.684	6.110	10.49	15.57	21.02	26.42	31.58
1,3-dimethylurea	0.0	0.3565	2.516	6.284	10.83	15.88	21.30	26.79	32.14	37.23
(1-methylethyl)urea	0.0	0.3011	2.190	6.060	11.22	16.52	22.05	27.44	32.35	36.71
butylurea	0.0	0.3203	2.430	6.340	11.35	16.98	23.01	29.14	35.10	40.78
(1-methylpropyl)urea	0.0	0.7287	4.576	10.31	16.77	22.95	29.03	34.80	40.05	44.81
(1,1-dimethylethyl)urea	0.0	0.3666	2.736	7.190	12.61	18.39	24.19	29.69	34.77	39.51
1,1-diethylurea	0.0	0.1856	1.463	4.465	9.040	14.73	20.62	26.51	32.19	37.60
1,3-diethylurea	0.0	0.2852	2.294	6.741	12.65	19.22	26.06	33.23	39.93	45.82
tetramethylurea	0.0	0.1961	1.841	5.850	11.57	17.82	24.12	30.18	35.94	41.43
octylurea	0.0	0.3529	2.672	7.372	13.92	21.35	29.58	37.90	46.19	54.28
1,3-di-*tert*-butylurea	0.0	0.9997	6.139	13.81	22.30	30.67	38.54	45.79	52.47	58.71
tetraethylurea	0.0	0.3278	3.530	10.35	18.87	27.78	36.76	45.43	53.64	61.36

compound	C_s/(J·K^{-1}·mol^{-1}) at T = 50.0 K	60.0 K	70.0 K	80.0 K	90.0 K	100.0 K	110.0 K	120.0 K	130.0 K	140.0 K
urea	23.48	28.13	32.06	35.39	38.29	41.00	43.66	46.29	48.90	51.48
methylurea	31.21	38.20	44.47	49.83	54.55	58.67	62.30	65.65	68.63	71.41
ethylurea	36.51	43.59	49.69	55.04	59.75	63.93	67.84	71.69	75.43	79.09
1,1-dimethylurea	36.43	45.32	53.27	60.21	66.13	71.35	76.25	80.57	84.54	88.22
1,3-dimethylurea	42.06	50.92	58.82	65.78	71.76	76.79	80.95	84.37	87.48	90.70
(1-methylethyl)urea	40.64	47.72	54.32	60.53	66.22	71.53	76.57	81.34	86.03	90.65
butylurea	46.11	55.82	64.43	72.10	78.92	85.06	90.90	96.17	101.3	106.5
(1-methylpropyl)urea	49.21	57.41	65.23	72.67	79.61	86.04	92.45	98.77	104.8	110.5
(1,1-dimethylethyl)urea	44.01	52.59	60.79	68.55	75.80	82.66	89.39	95.67	101.6	107.3
1,1-diethylurea	42.69	52.01	60.33	67.89	74.90	81.54	87.93	93.86	99.63	105.3
1,3-diethylurea	51.29	61.74	70.95	78.96	86.64	93.60	99.44	105.6	111.9	118.2
tetramethylurea	46.70	56.77	66.33	75.38	83.82	91.66	99.00	105.9	112.5	118.2
octylurea	62.10	76.67	89.69	101.2	111.3	120.5	129.0	136.9	144.4	151.5
1,3-di-*tert*-butylurea	64.62	75.89	86.91	97.97	109.1	120.2	130.7	140.5	150.2	159.6
tetraethylurea	68.65	82.17	94.49	105.7	116.0	125.8	135.4	144.3	152.9	161.4

compound	C_s/(J·K^{-1}·mol^{-1}) at T = 150.0 K	160.0 K	170.0 K	180.0 K	190.0 K	200.0 K	210.0 K	220.0 K	230.0 K	240.0 K
urea	54.05	56.62	59.19	61.76	64.34	66.93	69.54	72.16	74.80	77.46
methylurea	74.11	76.69	79.18	81.64	84.10	86.55	89.02	91.51	94.06	96.66
ethylurea	82.72	86.36	90.05	93.84	97.77	101.9	106.2	110.8	115.7	121.0
1,1-dimethylurea	91.67	94.94	98.05	101.1	104.0	106.8	109.6	112.4	115.2	117.9
1,3-dimethylurea	94.35	97.80*	96.04	98.47	100.9	103.3	105.8	108.6	111.4	114.4
(1-methylethyl)urea	95.22	99.75	104.3	108.8	113.3	117.8	122.4	127.0	131.7	136.6
butylurea	111.5	116.4	121.2	126.4	131.9	138.1	144.7	151.5	157.8	163.6
(1-methylpropyl)urea	115.9	121.0	126.0	130.9	135.6	140.3	145.1	149.9	154.8	159.9
(1,1-dimethylethyl)urea	112.8	118.1	123.2	128.2	133.2	138.2	143.3	148.7	154.4	159.7*
1,1-diethylurea	111.0	116.7	122.6	128.9	135.1*	137.6	142.3	147.2	151.8	156.3
1,3-diethylurea	124.5	130.8	137.2	143.8	150.5	157.4	164.4	171.6	178.8	185.9
tetramethylurea	124.4	132.1	140.3	147.5	153.0	158.9	168.1	178.1	188.0	198.0
octylurea	158.3	165.1	171.8	178.6	185.5	192.6	199.8	207.3	215.1	223.2
1,3-di-*tert*-butylurea	168.8	177.7	186.4	195.0	203.4	211.6	219.8	228.0	236.2	244.5
tetraethylurea	169.9	178.6	187.7	197.4	208.1	219.7	231.5	243.3	255.1*	323.0

compound	C_s/(J·K^{-1}·mol^{-1}) at T = 250.0 K	260.0 K	270.0 K	280.0 K	290.0 K	298.15 K	300.0 K	310.0 K	320.0 K	330.0 K
urea	80.13	82.82	85.51	88.22	90.92	93.13	93.63	96.33	99.02	101.7
methylurea	99.28	102.0	104.7	107.7	111.4	114.7	115.5	119.6	123.9	128.5
ethylurea	126.6	131.5		142.0		151.5				
1,1-dimethylurea	120.7	123.5	126.3	129.1	131.9	134.3	134.9	137.5	140.1	142.6
1,3-dimethylurea	117.4	120.6	123.9	127.2	130.6	133.3	133.9	133.8	138.3	142.8
(1-methylethyl)urea	141.5	146.4	151.3	156.2*	167.2	170.3	171.0	174.9		
butylurea	169.5	175.4	181.2	187.1	192.9*	207.9	209.4	217.1	224.8	
(1-methylpropyl)urea	165.2	170.6	176.1	181.7	187.3	191.8	192.8	198.1	203.0	
(1,1-dimethylethyl)urea	163.0	167.8	172.6	177.4	181.8	185.5	186.3	191.0	195.8	
1,1-diethylurea	160.7	165.2	169.9	174.6	179.4	183.3	184.2	189.2	194.0	198.8
1,3-diethylurea	192.9	199.4	205.5	210.9	215.7	219.0	219.8	223.3	227.0	230.8
tetramethylurea	208.0	217.9	227.9*	225.3	227.7	229.6	230.0	232.4	235.0	237.8
octylurea	231.6	240.5	249.8	259.5	269.9	278.7	280.8	292.5	304.9	
1,3-di-*tert*-butylurea	253.0	261.8	270.9	279.6	288.4	295.6	297.3	282.6	291.9	301.1
tetraethylurea	325.9	329.4	333.4	337.7	342.2	345.7	346.5	350.8	354.8	358.8

and m_x are the masses of the copper standard and of the sample, respectively. Values of enthalpies of transition are determined by integrating the function $C_p = f(T)$ in the temperature range of transition. Uncertainty in temperature measurements is ±0.05 K. Samples are weighted with an accuracy of $\pm 1 \times 10^{-5}$ g and are placed usually into a steel container, the heat capacity of which is determined separately and is subtracted from C_x (*1*). The uncertainty

Table 2. Entropy S° of Condensed Alkylureas Based on Experimental Measurements of the Heat Capacity

	$S°/(J·K^{-1}·mol^{-1})$ at T =									
compound	0.0 K	5.0 K	10.0 K	15.0 K	20.0 K	25.0 K	30.0 K	35.0 K	40.0 K	45.0 K
urea	0.0	0.0249	0.203	0.743	1.766	3.237	5.041	7.088	9.285	11.57
methylurea	0.0	0.0405	0.323	1.074	2.361	4.135	6.327	8.845	11.60	14.54
ethylurea	0.0	0.0763	0.604	1.823	3.665	6.061	8.903	12.09	15.51	19.08
1,1-dimethylurea	0.0	0.0267	0.223	0.837	2.046	3.866	6.219	9.027	12.19	15.60
1,3-dimethylurea	0.0	0.1188	0.911	2.608	5.027	7.976	11.35	15.04	18.97	23.05
(1-methylethyl)urea	0.0	0.1004	0.776	2.345	4.765	7.833	11.33	15.14	19.13	23.20
butylurea	0.0	0.1068	0.841	2.524	5.005	8.134	11.76	15.77	20.05	24.51
(1-methylpropyl)urea	0.0	0.2432	1.776	4.691	8.528	12.94	17.66	22.58	27.57	32.57
(1,1-dimethylethyl)urea	0.0	0.1222	0.958	2.867	5.662	9.092	12.96	17.11	21.41	25.78
1,1-diethylurea	0.0	0.0619	0.493	1.596	3.485	6.105	9.307	12.93	16.84	20.95
1,3-diethylurea	0.0	0.0951	0.760	2.467	5.189	8.174	12.81	17.37	22.26	27.30
tetramethylurea	0.0	0.0654	0.570	2.001	4.447	7.694	11.50	15.68	20.09	24.64
octylurea	0.0	0.1176	0.918	2.839	5.805	9.697	14.31	19.50	25.10	31.01
1,3-di-*tert*-butylurea	0.0	0.3345	2.388	6.293	11.41	17.29	23.59	30.08	36.64	43.18
tetraethylurea	0.0	0.1093	1.078	3.706	7.823	12.99	18.85	25.17	31.78	38.54

	$S°/(J·K^{-1}·mol^{-1})$ at T =									
compound	50.0 K	60.0 K	70.0 K	80.0 K	90.0 K	100.0 K	110.0 K	120.0 K	130.0 K	140.0 K
urea	13.91	18.61	23.25	27.75	32.09	36.27	40.30	44.21	48.02	51.74
methylurea	17.61	23.93	30.29	36.59	42.74	48.71	54.48	60.05	65.42	70.61
ethylurea	22.71	30.01	37.20	44.19	50.95	57.47	63.74	69.81	75.70	81.42
1,1-dimethylurea	19.18	26.63	34.22	41.80	49.24	56.48	63.51	70.34	76.95	83.35
1,3-dimethylurea	27.23	35.70	44.15	52.47	60.57	68.40	75.92	83.12	89.99	96.59
(1-methylethyl)urea	27.27	35.32	43.18	50.84	58.30	65.56	72.61	79.48	86.18	92.72
butylurea	29.09	38.37	47.64	56.75	65.65	74.28	82.67	90.80	98.70	106.4
(1-methylpropyl)urea	37.52	47.22	56.66	65.87	74.83	83.55	92.05	100.4	108.5	116.5
(1,1-dimethylethyl)urea	30.18	38.97	47.69	56.32	64.82	73.16	81.36	89.41	97.31	105.0
1,1-diethylurea	25.18	33.80	42.45	51.01	59.42	67.66	75.73	83.64	91.38	98.97
1,3-diethylurea	32.41	42.71	52.95	62.95	72.69	82.19	91.38	100.3	109.0	117.5
tetramethylurea	29.28	38.69	48.17	57.62	66.99	76.24	85.32	94.23	103.0	111.5
octylurea	37.14	49.77	62.59	75.33	87.84	100.1	111.9	123.5	134.8	145.7
1,3-di-*tert*-butylurea	49.68	62.46	74.99	87.31	99.50	111.6	123.5	135.3	147.0	158.4
tetraethylurea	45.39	59.12	72.73	86.09	99.14	111.9	124.3	136.5	148.4	160.0

	$S°/(J·K^{-1}·mol^{-1})$ at T =									
compound	150.0 K	160.0 K	170.0 K	180.0 K	190.0 K	200.0 K	210.0 K	220.0 K	230.0 K	240.0 K
urea	55.38	58.95	62.46	65.91	69.32	72.69	76.02	79.31	82.58	85.82
methylurea	75.63	80.50	85.22	89.81	94.29	98.67	103.0	107.2	111.3	115.3
ethylurea	87.00	92.46	97.81	103.1	108.2	113.4	118.4	123.5	128.5	133.5
1,1-dimethylurea	89.55	95.57	101.4	107.1	112.7	118.1	123.3	128.5	133.6	138.5
1,3-dimethylurea	103.0	109.2*	116.9	122.5	127.9	133.1	138.2	143.2	148.1	152.9
(1-methylethyl)urea	99.13	105.4	111.6	117.7	123.7	129.6	135.5	141.3	147.0	152.7
butylurea	113.9	121.3	128.5	135.5	142.5	149.4	156.3	163.2	170.1	176.9
(1-methylpropyl)urea	124.3	131.9	139.4	146.8	154.0	161.0	168.0	174.9	181.6	188.3
(1,1-dimethylethyl)urea	112.6	120.1	127.4	134.6	141.7	148.6	155.5	162.3	169.0	175.7*
1,1-diethylurea	106.4	113.8	121.0	128.2	135.3*	152.9	159.7	166.5	173.1	179.7
1,3-diethylurea	125.9	134.1	142.2	150.3	158.2	166.1	174.0	181.8	189.6	197.3
tetramethylurea	119.9	128.1	136.4	144.6	152.8	160.7	168.7	176.8	184.9	193.1
octylurea	156.4	166.8	177.1	187.1	196.9	206.6	216.2	225.6	235.0	244.4
1,3-di-*tert*-butylurea	169.8	180.9	192.0	202.9	213.6	224.3	234.8	245.2	255.5	265.8
tetraethylurea	171.4	182.7	193.8	204.8	215.7	226.7	237.7	248.7	259.8*	341.5

	$S°/(J·K^{-1}·mol^{-1})$ at T =									
compound	250.0 K	260.0 K	270.0 K	280.0 K	290.0 K	298.15 K	300.0 K	310.0 K	320.0 K	330.0 K
urea	89.03	92.23	95.41	98.56	101.7	104.3	104.8	107.9	111.1	114.1
methylurea	119.3	123.3	127.2	131.0	134.9	138.0	138.7	142.6	146.4	150.3
ethylurea	138.6	143.6		153.8		163.0				
1,1-dimethylurea	143.4	148.2	152.9	157.5	162.1	165.8	166.6	171.1	175.5	179.9
1,3-dimethylurea	157.6	162.3	166.9	171.5	176.0	179.6	180.5	185.0	189.4	193.7
(1-methylethyl)urea	158.4	164.1	169.7	175.3*	186.1	190.8	191.8	197.5		
butylurea	183.8	190.5	197.2	203.9	210.6*	229.9	231.2	238.2	245.2	
(1-methylpropyl)urea	195.0	201.6	208.1	214.6	221.1	226.3	227.5	233.9	240.3	
(1,1-dimethylethyl)urea	182.7	189.2	195.6	202.0	208.3	213.4	214.5	220.7	226.8	
1,1-diethylurea	186.1	192.5	198.8	205.1	211.3	216.3	217.5	223.6	229.7	235.7
1,3-diethylurea	205.1	212.8	220.4	228.0	235.5	241.5	242.8	250.1	257.2	264.3
tetramethylurea	201.4	209.7	218.2*	276.1	284.0	290.3	291.8	299.3	306.8	314.0
octylurea	253.6	262.9	272.1	281.4	290.7	298.3	300.0	309.4	318.9	
1,3-di-*tert*-butylurea	275.9	286.0	296.1	306.1	316.0	324.1	326.0	341.5	350.6	359.8
tetraethylurea	354.7	367.6	380.1	392.3	404.2	413.8	415.9	427.3	438.5	449.5

of the heat capacity measurements obtained using the reference compounds (copper, benzoic acid, corundum) did not exceed 1.5–2%.

Experimental heat capacity data for alkylureas measured by vacuum adiabatic calorimetry, excluding those of methylurea published in ref 15, are given in Table 18.

Table 3. Gibbs Energy Function $[G°(T) - H°(0)]/T$ of Condensed Alkylureas Based on Experimental Measurements of the Heat Capacity

	$\{[G°(T) - H°(0)]/T\}/(J·K^{-1}·mol^{-1})$ at T =									
compound	0.0 K	5.0 K	10.0 K	15.0 K	20.0 K	25.0 K	30.0 K	35.0 K	40.0 K	45.0 K
urea	0.0	0.0062	0.050	0.178	0.437	0.843	1.388	2.054	2.819	3.664
methylurea	0.0	0.0101	0.081	0.272	0.622	1.140	1.816	2.638	3.583	4.636
ethylurea	0.0	0.0191	0.153	0.488	1.039	1.796	2.738	3.843	5.086	6.441
1,1-dimethylurea	0.0	0.0067	0.054	0.198	0.496	0.978	1.649	2.497	3.508	4.660
1,3-dimethylurea	0.0	0.0297	0.234	0.719	1.482	2.478	3.670	5.027	6.523	8.132
(1-methylethyl)urea	0.0	0.0251	0.199	0.626	1.343	2.326	3.530	4.914	6.440	8.076
butylurea	0.0	0.0267	0.213	0.678	1.434	2.452	3.695	5.129	6.724	8.452
(1-methylpropyl)urea	0.0	0.0608	0.470	1.360	2.656	4.265	6.101	8.102	10.22	12.43
(1,1-dimethylethyl)urea	0.0	0.0306	0.243	0.770	1.629	2.770	4.141	5.695	7.389	9.189
1,1-diethylurea	0.0	0.0155	0.124	0.409	0.925	1.688	2.684	3.885	5.257	6.771
1,3-diethylurea	0.0	0.0238	0.190	0.633	1.414	2.509	3.879	5.474	7.265	9.208
tetramethylurea	0.0	0.0163	0.137	0.491	1.154	2.126	3.365	4.822	6.453	8.220
octylurea	0.0	0.0294	0.233	0.751	1.620	2.837	4.353	6.141	8.157	10.37
1,3-di-*tert*-butylurea	0.0	0.0837	0.636	1.830	3.564	5.713	8.164	10.83	13.65	16.56
tetraethylurea	0.0	0.0273	0.249	0.916	2.102	3.748	5.768	8.084	10.63	13.35

	$\{[G°(T) - H°(0)]/T\}/(J·K^{-1}·mol^{-1})$ at T =									
compound	50.0 K	60.0 K	70.0 K	80.0 K	90.0 K	100.0 K	110.0 K	120.0 K	130.0 K	140.0 K
urea	4.571	6.519	8.579	10.70	12.83	14.97	17.09	19.19	21.26	23.30
methylurea	5.779	8.276	10.97	13.78	16.66	19.56	22.48	25.38	28.25	31.09
ethylurea	7.886	10.97	14.20	17.52	20.86	24.20	27.51	30.78	34.01	37.19
1,1-dimethylurea	5.932	8.757	11.85	15.12	18.50	21.94	25.40	28.86	32.31	35.73
1,3-dimethylurea	9.832	13.44	17.22	21.11	25.05	28.99	32.92	36.81	40.63	44.40
(1-methylethyl)urea	9.792	13.38	17.08	20.82	24.57	28.31	32.02	35.69	39.32	42.90
butylurea	10.29	14.19	18.31	22.55	26.84	31.16	35.46	39.74	43.97	48.16
(1-methylpropyl)urea	14.69	19.31	23.97	28.64	33.27	37.87	42.41	46.89	51.32	55.69
(1,1-dimethylethyl)urea	11.07	14.99	19.04	23.16	27.32	31.49	35.65	39.79	43.92	48.01
1,1-diethylurea	8.400	11.91	15.66	19.54	23.51	27.51	31.53	35.54	39.54	43.52
1,3-diethylurea	11.27	15.66	20.25	24.97	29.73	34.50	39.26	43.98	48.64	53.26
tetramethylurea	10.09	14.07	18.27	22.60	27.01	31.47	35.96	40.44	44.92	49.37
octylurea	12.73	17.85	23.32	29.03	34.87	40.78	46.71	52.63	58.52	64.36
1,3-di-*tert*-butylurea	19.55	25.64	31.80	37.97	44.13	50.27	56.39	62.48	68.53	74.54
tetraethylurea	16.22	22.22	28.47	34.84	41.26	47.69	54.09	60.45	66.76	73.00

	$\{[G°(T) - H°(0)]/T\}/(J·K^{-1}·mol^{-1})$ at T =									
compound	150.0 K	160.0 K	170.0 K	180.0 K	190.0 K	200.0 K	210.0 K	220.0 K	230.0 K	240.0 K
urea	25.32	27.31	29.28	31.22	33.13	35.03	36.90	38.75	40.59	42.40
methylurea	33.90	36.66	39.38	42.05	44.68	47.27	49.82	52.33	54.81	57.24
ethylurea	40.33	43.42	46.46	49.46	52.42	55.34	58.22	61.07	63.89	66.69
1,1-dimethylurea	39.11	42.45	45.75	49.00	52.21	55.36	58.48	61.54	64.56	67.54
1,3-dimethylurea	48.09	51.72*	55.37	58.94	62.43	65.83	69.16	72.41	75.60	78.72
(1-methylethyl)urea	46.43	49.92	53.37	56.78	60.14	63.47	66.76	70.01	73.24	76.43
butylurea	52.29	56.38	60.40	64.38	68.31	72.20	76.03	79.85	83.62	87.37
(1-methylpropyl)urea	60.01	64.26	68.47	72.61	76.71	80.75	84.74	88.68	92.57	96.43
(1,1-dimethylethyl)urea	52.06	56.08	60.06	64.00	67.91	71.77	75.59	79.38	83.13	86.84*
1,1-diethylurea	47.46	51.38	55.26	59.12	62.94*	66.88	71.14	75.31	79.43	83.46
1,3-diethylurea	57.82	62.33	66.80	71.21	75.58	79.91	84.20	88.46	92.69	96.89
tetramethylurea	53.79	58.18	62.54	66.87	71.18	75.46	79.71	83.94	88.15	92.35
octylurea	70.14	75.86	81.51	87.10	92.62	98.08	103.5	108.8	114.1	119.3
1,3-di-*tert*-butylurea	80.51	86.44	92.32	98.16	104.0	109.7	115.4	121.1	126.7	132.3
tetraethylurea	79.19	85.30	91.36	97.35	103.3	109.2	115.0	120.9	126.7*	132.5

	$\{[G°(T) - H°(0)]/T\}/(J·K^{-1}\ mol^{-1})$ at T =									
compound	250.0 K	260.0 K	270.0 K	280.0 K	290.0 K	298.15 K	300.0 K	310.0 K	320.0 K	330.0 K
urea	44.21	45.99	47.76	49.52	51.27	52.68	53.00	54.72	56.43	58.14
methylurea	59.65	62.02	64.36	66.67	68.96	70.80	71.22	73.46	75.68	77.88
ethylurea	69.47	72.22		77.69		82.60				
1,1-dimethylurea	70.48	73.38	76.23	79.05	81.84	84.09	84.59	87.31	90.00	92.66
1,3-dimethylurea	81.78	84.78	87.74	90.65	93.51	95.82	96.34	99.13	101.9	104.6
(1-methylethyl)urea	79.59	82.73	85.85	88.94*	92.18	94.81	95.41	98.61		
butylurea	91.09	94.79	98.46	102.1	104.7*	108.9	109.6	113.6	117.6	
(1-methylpropyl)urea	100.2	104.0	107.7	111.4	115.1	118.1	118.7	122.4	125.9	
(1,1-dimethylethyl)urea	90.53	94.20	97.84	101.4	105.0	107.9	108.6	112.1	115.6	
1,1-diethylurea	87.44	91.36	95.23	99.04	102.8	105.8	106.5	110.2	113.8	117.4
1,3-diethylurea	101.1	105.2	109.3	113.4	117.5	120.8	121.6	125.6	129.6	133.6
tetramethylurea	96.55	100.7	104.9*	110.8	116.6	121.3	122.4	127.9	133.4	138.8
octylurea	124.5	129.7	134.8	139.8	144.9	149.0	149.9	154.9	159.9	
1,3-di-*tert*-butylurea	137.8	143.3	148.8	154.2	159.6	164.0	165.0	170.5	176.0	181.5
tetraethylurea	141.2	149.6	157.9	166.1	174.1	180.5	182.0	189.7	197.3	204.8

Temperature dependencies of the heat capacity for alkylureas are shown in Figures 2–13. There are compounds possessing phase transitions in the temperature range 5–320 K and also three following compounds. The heat capacity of urea from our measurements in the range 5–100 K is compared with literature data (7) in Figure 2.

Table 4. Reduced Enthalpy $[H°(T) - H°(0)]/T$ of Condensed Alkylureas Based on Experimental Measurements of the Heat Capacity

	$\{[H°(T) - H°(0)]/T\}/(J·K^{-1}\ mol^{-1})$ at T =									
compound	0.0 K	5.0 K	10.0 K	15.0 K	20.0 K	25.0 K	30.0 K	35.0 K	40.0 K	45.0 K
urea	0.0	0.0186	0.1526	0.5645	1.329	2.393	3.652	5.034	6.466	7.908
methylurea	0.0	0.0304	0.242	0.800	1.740	2.996	4.500	6.200	8.025	9.911
ethylurea	0.0	0.0572	0.451	1.333	2.625	4.280	6.167	8.257	10.43	12.64
1,1-dimethylurea	0.0	0.0200	0.169	0.639	1.550	2.888	4.567	6.543	8.675	10.93
1,3-dimethylurea	0.0	0.0891	0.676	1.887	3.545	5.520	7.667	10.03	12.45	14.93
(1-methylethyl)urea	0.0	0.0753	0.577	1.720	3.420	5.520	7.800	10.23	12.70	15.13
butylurea	0.0	0.0801	0.629	1.847	3.570	5.680	8.067	10.63	13.33	16.07
(1-methylpropyl)urea	0.0	0.1822	1.306	3.333	5.850	8.680	11.57	14.49	17.35	20.13
(1,1-dimethylethyl)urea	0.0	0.0917	0.715	2.100	4.035	6.320	8.833	11.40	14.02	16.60
1,1-diethylurea	0.0	0.0464	0.369	1.187	2.560	4.400	6.633	9.057	11.58	14.18
1,3-diethylurea	0.0	0.0713	0.570	1.833	3.775	6.204	8.933	11.89	14.99	18.09
tetramethylurea	0.0	0.0490	0.433	1.507	3.290	5.560	8.133	10.86	13.63	16.42
octylurea	0.0	0.0882	0.686	2.087	4.185	6.880	9.967	13.37	16.95	20.64
1,3-di-*tert*-butylurea	0.0	0.2499	1.752	4.460	7.850	11.60	15.43	19.26	23.00	26.62
tetraethylurea	0.0	0.0819	0.829	2.793	5.700	9.240	13.07	17.09	21.15	25.20

	$\{[H°(T) - H°(0)]/T\}/(J·K^{-1}·mol^{-1})$ at T =									
compound	50.0 K	60.0 K	70.0 K	80.0 K	90.0 K	100.0 K	110.0 K	120.0 K	130.0 K	140.0 K
urea	9.335	12.09	14.67	17.06	19.26	21.30	23.21	25.02	26.76	28.43
methylurea	11.84	13.65	19.33	22.82	26.09	29.14	32.00	34.67	37.17	39.52
ethylurea	14.82	19.05	23.00	26.67	30.10	33.27	36.24	39.03	41.69	44.23
1,1-dimethylurea	13.26	17.87	22.37	26.67	30.74	34.54	38.12	41.47	44.64	47.62
1,3-dimethylurea	17.40	22.27	26.93	31.36	35.52	39.41	43.00	46.32	49.36	52.19
(1-methylethyl)urea	17.48	21.93	26.10	30.02	33.73	37.25	40.59	43.79	46.86	49.83
butylurea	18.80	24.18	29.33	34.20	38.80	43.12	47.20	51.07	54.73	58.24
(1-methylpropyl)urea	22.82	27.92	32.69	37.22	41.56	45.69	49.65	53.48	57.19	60.80
(1,1-dimethylethyl)urea	19.12	23.98	28.66	33.16	37.50	41.68	45.71	49.62	53.39	57.04
1,1-diethylurea	16.78	21.88	26.80	31.46	35.91	40.14	44.20	48.09	51.84	55.45
1,3-diethylurea	21.14	27.05	32.70	37.99	42.97	47.68	52.12	56.32	60.35	64.25
tetramethylurea	19.18	24.62	29.90	35.03	39.99	44.76	49.36	53.79	58.05	62.15
octylurea	24.40	31.92	39.26	46.30	52.97	59.27	65.23	70.88	76.25	81.36
1,3-di-*tert*-butylurea	30.12	36.82	43.19	49.35	55.37	61.30	67.14	72.85	78.46	83.86
tetraethylurea	29.18	36.90	44.26	51.25	57.88	64.18	70.23	76.03	81.62	87.00

	$\{[H°(T) - H°(0)]/T\}/(J·K^{-1}·mol^{-1})$ at T =									
compound	150.0 K	160.0 K	170.0 K	180.0 K	190.0 K	200.0 K	210.0 K	220.0 K	230.0 K	240.0 K
urea	30.06	31.64	33.18	34.70	36.19	37.66	39.12	40.56	41.99	43.41
methylurea	41.73	43.84	45.84	47.76	49.61	51.40	53.14	54.82	56.48	58.08
ethylurea	46.67	49.04	51.35	53.60	55.84	58.00	60.19	62.41	64.61	66.83
1,1-dimethylurea	50.44	53.13	55.68	58.11	60.47	62.70	64.86	66.95	69.00	71.00
1,3-dimethylurea	54.88	57.45*	61.53	63.56	65.42	67.25	69.05	70.77	72.48	74.17
(1-methylethyl)urea	52.70	55.50	58.24	60.89	63.53	66.15	68.71	71.27	73.78	76.29
butylurea	61.63	64.88	68.06	71.17	74.21	77.25	80.29	83.36	86.48	89.58
(1-methylpropyl)urea	64.29	67.69	70.94	74.17	77.26	80.30	83.29	86.18	89.09	91.92
(1,1-dimethylethyl)urea	60.58	64.00	67.35	70.56	73.74	76.85	79.90	82.91	85.87	88.83*
1,1-diethylurea	58.97	62.40	65.76	69.11	72.42*	86.00	88.57	91.14	93.70	96.21
1,3-diethylurea	68.07	71.75	75.41	79.06	82.63	86.20	89.76	93.32	96.87	100.5
tetramethylurea	66.09	69.94	73.88	77.78	81.58	85.30	89.00	92.82	96.74	100.8
octylurea	86.27	91.00	95.53	99.94	104.3	108.5	112.7	116.8	120.9	125.0
1,3-di-*tert*-butylurea	89.27	94.50	99.65	104.7	109.7	114.6	119.4	124.1	128.8	133.5
tetraethylurea	92.27	97.38	102.4	107.4	112.4	117.5	122.7	127.9	133.1*	209.0

	$\{[H°(T) - H°(0)]/T\}/(J·K^{-1}·mol^{-1})$ at T =									
compound	250.0 K	260.0 K	270.0 K	280.0 K	290.0 K	298.15 K	300.0 K	310.0 K	320.0 K	330.0 K
urea	44.83	46.24	47.64	49.04	50.44	51.58	51.84	53.23	54.62	56.00
methylurea	59.68	61.27	62.81	64.36	65.93	67.21	67.50	69.13	70.75	72.45
ethylurea	69.12	71.54		76.07		80.50				
1,1-dimethylurea	72.92	74.81	76.67	78.50	80.28	81.74	82.03	83.81	85.50	87.21
1,3-dimethylurea	75.84	77.50	79.15	80.82	82.45	83.82	84.13	85.90	87.50	89.09
(1-methylethyl)urea	78.80	81.31	83.81	86.32*	93.90	95.96	96.40	98.87		
butylurea	92.64	95.73	98.78	101.8	104.9*	121.0	121.6	124.5	127.6	
(1-methylpropyl)urea	94.72	97.54	100.4	103.2	106.0	108.3	108.8	111.6	114.3	
(1,1-dimethylethyl)urea	92.20	95.00	97.78	100.5	103.3	105.5	106.0	108.6	111.3	
1,1-diethylurea	98.68	101.2	103.6	106.1	108.5	110.5	111.0	113.4	115.8	118.3
1,3-diethylurea	104.0	107.5	111.1	114.5	117.9	120.6	121.3	124.5	127.6	130.7
tetramethylurea	104.8	109.0	113.2*	165.3	167.3	169.0	169.4	171.4	173.3	175.2
octylurea	129.1	133.2	137.4	141.6	145.8	149.3	150.1	154.5	159.0	
1,3-di-*tert*-butylurea	138.1	142.7	147.3	151.8	156.4	160.1	160.9	171.0	174.6	178.3
tetraethylurea	213.6	218.0	222.1	226.2	230.1	233.2	233.9	237.6	241.2	244.8

Ethylurea has an unusual rise of C_s at $T >$ 250 K, probably caused by a phase transition at $T >$ 300 K. Its heat capacity was extrapolated for $T >$ 250 K, as is shown in Figure 4. 1,3-Diethylurea (Figure 8) has a little anomaly in heat capacity.

Table 5. Phase Transitions of Alkylureas in Condensed State[a]

code	compound	transition type[b]	T/K	$\Delta_{tr}H$/(kJ·mol^{-1})	$\Delta_{tr}S$/(J·K^{-1}·mol^{-1})	refs
I	urea	cr → l	406.1	14.0	34.5	9–11, 13, 14
II	methylurea	cr → l	375	14.3	38.1	15
III	1,1-dimethylurea	cr → l	455	29.8	65.5	10, 11
IV	1,3-dimethylurea	crIII → crII	161.3	0.318	1.97	this work
		crII → crI	301.2	0.077	0.26	this work
		crI → l	379.5	13.0	34.2	9–12
V	ethylurea	cr → l	366	14.1	38.5	9, 10
VI	(1-methylethyl)urea	crIII → crII	280.8	1.41	5.02	this work
		crII → crI	375.5	2.31	6.15	10
		crI → l	429	17.5	40.8	9, 10
VII	tetramethylurea	cr → l	270.48	13.45	49.73	this work
			272.0	14.10	51.84	11
			270.48	13.45	49.73	accepted
VIII	1,1-diethylurea	crII → crI	197.32	2.07	10.51	this work
		crI → l	343	16.8	49.0	9, 10, 16
IX	1,3-diethylurea	crII → crI	339.4	1.87	5.51	10
			340.8	1.66	4.87	this work[c]
		crI → l	385.0	13.14	34.13	9
			383.4	12.46	32.50	10
			386.5	12.74	32.96	this work[c]
X	butylurea	crIII → crII	294.1	4.05	13.77	this work
			313.1	7.02	22.4	10
			294.1	4.05	13.77	accepted
		crII → crI	345.0	0.86	2.5	9, 10
		crI → l	368	14.0	38.0	9, 10
XI	(1,1-dimethylethyl)urea	crII → crI	249.0	0.102	0.41	this work
		crI → l	449.8	33.1	73.4	10
XII	1,3-di-*tert*-butylurea	crII → crI	301.7	1.904	6.31	this work
XIII	tetraethylurea	cr → l	239.7	16.90	70.50	this work

[a] The thermodynamic characteristics of phase transition occurring at $T > 320$ K are given to show that these transitions do not influence selection of thermodynamic data for additive calculations at $T \leq 320$ K. They are averaged by our and literature measurements after critical review. The information on the other phase transitions includes literature values, values obtained in the experimental part of this work, and, if necessary, values accepted for use in this work. [b] cr, crystal; l, liquid. [c] Measured by the triple heat bridge method.

Experimental heat capacities were smoothed by polynomials using the least-squares method. The temperature range of experimental measurements was divided by several intervals for each compound, and each interval had its own polynomial. Errors of smoothing were always less than experimental uncertainties. Thermodynamic functions of the substances, obtained from the smoothed heat capacities values, are given in Tables 1–4. The phase transition properties of the alkylureas in the condensed state are given in Table 5.

Only the low-temperature heat capacities for urea in the temperature range 19.5–318 K had been published earlier by Ruehrwein and Huffman (*7*). We measured the heat capacity of urea from 5 to 100 K and found satisfactory agreement with those values. The difference between our results and those in ref 7 did not exceed 1.0%. Hence, the values of the thermodynamic properties of crystalline urea, given in Tables 1–4, were obtained by a joint treatment of our results at the temperatures from 5 to 100 K as well as the data (*7*) for the interval 19.5–318 K.

Additive Calculations of Thermodynamic Properties of Crystalline Urea Alkyl Derivatives

For the additive calculations of the thermodynamic properties of crystalline alkylureas, we used the data for crystals that are stable in the temperature range from 0 K to T_{trs} (Tables 1–4). The upper temperature limit is marked with an asterisk for those substances that undergo solid-to-solid transitions at $T < 298.15$ K (Tables 1–4).

Prediction methods based on constants related to the effective atoms or effective bonds for alkylurea derivatives could not be applied in this work. Parameters corresponding to effective atoms CO–$(N)_2$, N–$(CO)(H)_2$, N–(C)(C)(H), and N–$(CO)(C)_2$ could not be evaluated from systems of equations for compounds **I**–**XIV** because the number of linearly independent equations in such a system is less than the number of variables. A similar conclusion holds for systems of equations based on effective bond classification within the set of compounds **I**–**XIV**.

Table 6. Matrix of Coefficients n_i, n_j, n_l, n_m, and n_k for Alkylureas II–XIV

code	compound	n_i	n_j	n_l	n_m	n_k
II	methylurea	1	0	0	0	0
III	1,1-dimethylurea	2	0	0	1	0
IV	1,3-dimethylurea	2	0	0	0	0
V	ethylurea	1	1	1	0	0
VI	(1-methylethyl)urea	1	2	2	0	1
VII	tetramethylurea	4	0	0	2	0
VIII	1,1-diethylurea	2	2	2	1	0
IX	1,3-diethylurea	2	2	2	0	0
X	butylurea	1	3	1	0	2
XI	(1,1-dimethylethyl)urea	1	3	3	0	3
XII	1,3-di-*tert*-butylurea	2	6	6	0	6
XIII	tetraethylurea	4	4	4	2	0
XIV	octylurea	1	7	1	0	6

It was shown previously (*3*) that a substitution incremental scheme is applicable to calculate the enthalpies of formation of alkylurea derivatives in the crystalline state. Urea is used as a reference compound for the alkyl derivatives, which are obtained by incremental substitution of CH_3 groups for H. The value of a thermodynamic property P for an alkylurea derivative is represented by the sum

$$P(\text{alkylurea}) = P(\text{urea}) + n_i\Delta P(CH_3)_N + n_j\Delta P(CH_3)_C + n_l\Delta P(CCN) + n_m\Delta P(CNC) + n_k\Delta P(CCC) \quad (2)$$

where $\Delta P(CH_3)_N = P_i$ is the fraction of thermodynamic property corresponding to substitution of a CH_3 group for H in urea; $\Delta P(CH_3)_C = P_j$ is the fraction of thermodynamic property corresponding to substitution of a CH_3 group for an H atom in the alkyl substitute; $\Delta P(CCN) = P_l$, $\Delta P(CNC) = P_m$, and $\Delta P(CCC) = P_k$ are fractions of thermodynamic

Table 7. Additive Constants for Calculation of Heat Capacity C_s of Crystalline Alkylureas

	J·K^{-1}·mol^{-1}				
T/K	C_i	C_j	C_l	C_m	C_k
5	0.11	−0.05	0.08	−0.16	0.08
10	0.69	−0.11	0.45	−0.82	0.29
15	1.5	0.1	0.8	−1.5	0.4
20	2.3	0.5	1.2	−1.8	0.4
25	3.2	1.0	1.3	−2.2	0.2
30	4.3	1.8	1.2	−2.7	0.0
35	5.4	2.7	0.9	−3.6	−0.3
40	6.7	3.6	0.6	−4.5	−0.6
45	7.8	4.4	0.1	−5.2	−0.9
50	8.9	5.2	−0.3	−5.8	−1.1
60	11.0	6.6	−1.0	−6.9	−1.3
70	13.0	7.7	−1.6	−7.8	−1.3
80	14.8	8.5	−1.8	−8.4	−1.1
90	16.5	9.0	−1.8	−9.0	−0.7
100	17.8	9.4	−1.7	−9.1	−0.4
110	18.6	9.7	−1.4	−8.5	0.0
120	19.3	10.1	−1.1	−7.9	0.3
130	19.9	10.4	−0.7	−7.4	0.5
140	20.5	10.9	−0.3	−7.2	0.6
150	21.1	11.3	0.1	−7.0	0.7
160	21.8	11.6	0.4	−6.4	0.8
170	23.9	11.8	0.4	−7.8	1.0
180	24.6	12.4	0.7	−7.5	0.8
190	25.0	13.5	1.0	−7.0	0.2
200	25.2	14.8	1.4	−6.1	−0.7
210	26.1	15.8	1.5	−5.3	−1.2
220	27.2	16.7	1.5	−4.6	−1.5
230	28.3	17.6	1.5	−4.0	−1.9
240	22.9	23.7	3.8	(10.5)	−7.6
250	23.1	25.3	4.1	(13.0)	−8.6
260	23.4	26.8	4.3	(15.5)	−9.4
270	23.8	28.6	4.6	(17.6)	−10.6
280	23.9	29.3	4.4	(−6.9)	−10.1
290	20.5	35.4	6.6	(0.0)	−15.9
298.15	21.6	34.6	6.0	(−2.0)	−14.0

Table 8. Additive Constants for Calculation of Entropy $S°(T)$ of Crystalline Alkylureas

	J·K^{-1}·mol^{-1}				
T/K	S_i	S_j	S_l	S_m	S_k
5	0.04	−0.02	0.03	−0.05	0.03
10	0.26	−0.08	0.19	−0.34	0.15
15	0.7	−0.1	0.4	−0.8	0.3
20	1.2	0.0	0.7	−1.3	0.4
25	1.8	0.1	1.0	−1.5	0.5
30	2.5	0.4	1.3	−2.1	0.5
35	3.3	0.7	1.4	−2.6	0.5
40	4.1	1.1	1.5	−3.2	0.4
45	4.9	1.6	1.6	−3.7	0.3
50	5.8	2.1	1.6	−4.3	0.2
60	7.6	3.2	1.4	−5.5	0.0
70	9.5	4.3	1.2	−6.6	−0.2
80	11.3	5.4	1.0	−7.7	−0.4
90	13.2	6.4	0.8	−8.7	−0.5
100	15.0	7.4	0.6	−9.7	−0.5
110	16.7	8.3	0.5	−10.5	−0.5
120	18.4	9.2	0.4	−11.2	−0.5
130	19.9	10.0	0.3	−11.8	−0.5
140	21.4	10.8	0.2	−12.4	−0.5
150	22.9	11.5	0.2	−12.9	−0.4
160	24.2	12.3	0.3	−13.3	−0.4
170	24.9	13.1	0.4	−12.5	−0.3
180	26.3	13.8	0.5	−13.0	−0.3
190	27.6	14.5	0.5	−13.4	−0.2
200	28.3	15.7	0.8	−12.5	−0.7
210	29.6	16.4	0.8	−12.8	−0.8
220	30.9	17.2	0.9	−13.0	−0.8
230	32.1	18.0	1.0	−13.2	−0.9
240	31.4	20.2	1.7	(−9.4)	−2.5
250	32.3	21.2	1.8	(−8.9)	−2.9
260	33.3	22.2	2.0	(−8.4)	−3.1
270	34.5	24.0	2.3	(−8.4)	−4.6
280	35.0	24.3	2.4	(−11.1)	−4.0
290	33.2	29.6	4.3	(−6.0)	−9.2
298.15	33.7	28.7	4.2	(−5.9)	−7.5

Table 9. Additive Constants for Calculation of Gibbs Energy Function $-[G°(T) - H°(0)]/T$ of Crystalline Alkylureas

	J·K^{-1}·mol^{-1}				
T/K	G_i	G_j	G_l	G_m	G_k
5	0.01	0.00	0.01	−0.01	0.01
10	0.07	−0.03	0.05	−0.09	0.04
15	0.2	−0.1	0.1	−0.2	0.1
20	0.4	−0.1	0.3	−0.4	0.2
25	0.6	0.0	0.4	−0.7	0.2
30	0.9	0.0	0.5	−0.9	0.3
35	1.2	0.1	0.6	−1.1	0.3
40	1.5	0.2	0.7	−1.3	0.3
45	1.8	0.3	0.8	−1.6	0.3
50	2.2	0.5	0.9	−1.8	0.3
60	2.9	0.8	1.0	−2.3	0.3
70	3.7	1.3	1.1	−2.8	0.2
80	4.6	1.7	1.1	−3.4	0.2
90	5.4	2.2	1.0	−3.9	0.1
100	6.3	2.7	1.0	−4.5	0.0
110	7.2	3.1	1.0	−5.0	0.0
120	8.0	3.6	0.9	−5.5	−0.1
130	8.9	4.1	0.9	−5.9	−0.1
140	9.7	4.5	0.8	−6.4	−0.1
150	10.5	5.0	0.8	−6.8	−0.1
160	11.4	5.4	0.8	−7.2	−0.2
170	11.4	5.9	0.9	−6.4	−0.2
180	12.2	6.3	0.9	−6.7	−0.2
190	13.0	6.8	0.9	−7.1	−0.2
200	13.3	7.5	1.0	−6.5	−0.6
210	14.1	7.9	1.0	−6.8	−0.6
220	14.8	8.3	1.0	−7.0	−0.6
230	15.5	8.7	1.0	−7.3	−0.6
240	15.5	9.7	1.2	(−6.1)	−1.2
250	16.3	10.4	1.3	(−6.5)	−1.6
260	16.8	10.5	1.3	(−6.3)	−1.3
270	17.6	11.3	1.3	(−6.7)	−1.7
280	18.1	11.4	1.3	(−6.6)	−1.4
290	17.7	13.4	2.1	(−4.8)	−3.3
298.15	18.1	13.1	2.0	(−4.8)	−2.6

Table 10. Additive Constants for Calculation of Reduced Enthalpy $[H°(T) - H°(0)]/T$ of Crystalline Alkylureas

	J·K^{-1}·mol^{-1}				
T/K	H_i	H_j	H_l	H_m	H_k
5	0.03	−0.01	0.02	−0.04	0.02
10	0.19	−0.06	0.14	−0.25	0.11
15	0.5	0.0	0.3	−0.6	0.2
20	0.8	0.0	0.5	−0.8	0.2
25	1.2	0.2	0.6	−1.1	0.2
30	1.6	0.4	0.7	−1.3	0.2
35	2.1	0.6	0.8	−1.5	0.2
40	2.6	0.9	0.8	−1.9	0.1
45	3.1	1.3	0.7	−2.2	0.0
50	3.6	1.6	0.7	−2.5	−0.1
60	4.5	2.4	0.5	−2.8	−0.3
70	5.7	3.1	0.2	−3.8	−0.4
80	6.7	3.7	0.0	−4.3	−0.5
90	7.7	4.2	−0.2	−4.8	−0.6
100	8.7	4.7	−0.4	−5.2	−0.6
110	9.5	5.2	−0.5	−5.5	−0.5
120	10.3	5.6	−0.6	−5.8	−0.5
130	11.0	5.9	−0.6	−5.9	−0.4
140	11.7	6.3	−0.6	−6.0	−0.3
150	12.3	6.6	−0.5	−6.1	−0.3
160	12.9	6.9	−0.5	−6.1	−0.2
170	13.5	7.2	−0.4	−6.2	−0.1
180	14.1	7.5	−0.4	−6.3	−0.1
190	14.6	7.7	−0.3	−6.3	−0.0
200	15.0	8.2	−0.2	−6.0	−0.2
210	15.5	8.5	−0.1	−6.0	−0.2
220	16.0	8.9	0.0	−5.9	−0.3
230	16.5	9.2	0.0	−5.9	−0.3
240	15.9	10.5	0.5	(−3.3)	−1.3
250	16.2	11.1	0.6	(−2.7)	−1.7
260	16.5	11.7	0.7	(−2.1)	−1.9
270	16.9	12.7	0.9	(−1.8)	−2.8
280	16.9	12.9	1.0	(−4.4)	−2.5
290	15.5	16.0	2.2	(−1.1)	−5.8
298.15	15.6	15.6	2.2	(−1.1)	−4.9

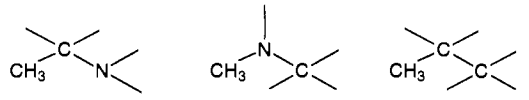
Table 11. Experimental and Calculated by Incremental Additive Method with (in Square Brackets) and without (in Parentheses) Taking into Consideration Phase Changes Values of the Thermodynamic Functions for Some Crystalline Alkylureas at Different Temperatures

	J·K⁻¹·mol⁻¹											
	$C_s(T)$			$S°(T)$			$-[G°(T) - G°(0)]/T$			$[H°(T) - H°(0)]/T$		
compound	100 K	200 K	298.15 K	100 K	200 K	298.15 K	100 K	200 K	298.15 K	100 K	200 K	298.15 K
ethylurea	63.93	101.90	152.00	57.47	113.40	163.00	24.20	55.34	82.60	33.27	58.00	80.50
	[66.5]	[108.4]		[59.3]	[117.5]		[24.9]	[56.9]		[34.3]	[60.7]	
	(66.5)	(106.1)	(151.8)	(59.3)	(118.2)	(170.9)	(24.9)	(57.3)	(85.5)	(34.3)	(60.9)	(85.4)
1,1-diethylurea	81.54	137.60	183.30	67.66	152.90	216.30	27.51	66.88	105.80	40.14	86.00	110.51
	(82.9)	(143.9)	(192.9)	(72.6)	(150.1)	(219.3)	(30.4)	(70.9)	(106.5)	(42.1)	(79.2)	(112.9)
tert-butylurea	82.66	138.20	185.50	73.16	148.60	213.40	31.49	71.77	107.90	41.68	76.85	105.45
	[80.9]	[138.7]		[73.7]	[148.3]		[32.4]	[72.2]		[41.3]	[76.1]	
	(80.9)	(138.7)	(192.2)	(73.7)	(148.3)	(213.8)	(32.4)	(72.2)	(108.1)	(41.3)	(76.1)	(105.6)
1,3-diethylurea	93.60	157.40	219.00	82.19	166.10	241.50	34.50	79.91	120.80	47.68	86.20	120.64
	[92.0]	[149.8]		[82.3]	[162.3]		[34.9]	[78.7]		[47.4]	[83.7]	
	(92.0)	(145.3)	(210.5)	(82.3)	(163.6)	(237.6)	(34.9)	(79.5)	(118.3)	(47.4)	(84.1)	(119.2)

Table 12. Average Percentage Deviation Values of Calculated Thermodynamic Functions of Crystalline Alkylureas from Experimentally Derived Values

T/K	C	S	G	H
5	19.1	19.1	18.9	19.1
10	18.3	19.7	19.8	19.6
15	13.2	16.5	18.3	15.8
20	9.6	13.5	15.8	12.6
25	6.7	11.3	13.7	10.1
30	4.8	9.3	12.0	8.1
35	3.4	7.8	10.6	6.6
40	2.4	6.6	9.4	5.4
45	1.9	5.7	8.4	4.4
50	1.8	5.0	7.5	3.6
60	2.0	3.9	6.2	3.9
70	2.1	3.2	5.3	2.1
80	2.0	2.7	4.6	2.0
90	1.9	2.4	4.0	1.9
100	1.8	2.1	3.6	1.9
110	1.7	2.0	3.2	1.9
120	1.7	1.9	3.0	1.8
130	1.7	1.9	2.7	1.8
140	1.7	1.8	2.5	1.7
150	1.7	1.8	2.4	1.7
160	1.8	1.8	2.2	1.7
170	1.9	1.7	1.9	1.8
180	2.2	1.7	1.9	1.7
190	2.4	1.7	1.8	1.7
200	2.9	1.3	1.1	1.6
210	3.4	1.3	1.2	1.6
220	3.8	1.4	1.2	1.6
230	4.2	1.4	1.2	1.7
240	4.3	1.5	1.2	1.9
250	4.9	1.8	1.0	2.3
260	5.1	1.9	1.3	2.4
270	5.5	1.6	1.0	2.2
280	2.7	1.9	1.5	2.3
290	0.1	0.1	0.0	0.0
298.15	0.5	1.1	0.9	1.2

property, taking into consideration the interaction of each new substituting group with polyvalent atoms of the molecule skeleton in 1,3-positions



and n_i, n_j, n_k, n_l, and n_m are the numbers of the appropriate substituting groups and their interactions.

The sequence of the H → CH_3 substitutions to create the necessary alkylurea derivative is not important for obtaining the calculation formula (eq 2). Let us give some examples of expressions for calculation of the thermodynamic properties of urea alkyl derivatives by group contributions.

Table 13. Additive Constants for Calculation of Heat Capacity C_s of Crystalline Alkylureas Ignoring Phase Changes

	J·K⁻¹·mol⁻¹				
T/K	C_i	C_j	C_l	C_m	C_k
5	0.11	−0.05	0.08	−0.16	0.08
10	0.69	−0.11	0.45	−0.82	0.29
15	1.5	0.1	0.9	−1.5	0.4
20	2.3	0.5	1.2	−1.8	0.4
25	3.2	1.0	1.3	−2.2	0.2
30	4.3	1.8	1.2	−2.7	0.0
35	5.4	2.7	0.9	−3.6	−0.3
40	6.7	3.6	0.6	−4.5	−0.6
45	7.8	4.4	0.1	−5.2	−0.9
50	8.9	5.2	−0.3	−5.8	−1.1
60	11.0	6.6	−1.0	−6.9	−1.3
70	13.0	7.7	−1.6	−7.8	−1.3
80	14.8	8.5	−1.8	−8.4	−1.1
90	16.5	9.0	−1.8	−9.0	−0.7
100	17.8	9.4	−1.7	−9.1	−0.4
110	18.6	9.7	−1.4	−8.5	0.0
120	19.3	10.1	−1.1	−7.9	0.3
130	19.9	10.4	−0.7	−7.4	0.5
140	20.5	10.9	−0.3	−7.2	0.6
150	21.1	11.3	0.1	−7.0	0.7
160	21.8	11.6	0.4	−6.4	0.8
170	21.3	12.2	0.9	−3.7	0.9
180	21.7	12.9	1.3	−2.7	0.7
190	21.9	13.9	1.7	−1.9	0.1
200	22.2	15.0	1.9	−1.4	−0.4
210	22.8	15.9	2.1	−0.1	−0.7
220	23.5	16.7	2.2	1.0	−1.0
230	24.3	17.6	2.2	2.1	−1.2
240	25.1	18.3	2.2	(2.9)	−1.2
250	26.1	19.1	2.0	(3.6)	−1.4
260	27.0	19.8	1.8	(4.3)	−1.2
270	27.7	20.3	1.7	(5.6)	−0.8
280	23.6	27.6	3.7	(−14.9)	−8.0
290	24.0	29.3	3.7	(−16.4)	−8.8
298.15	24.6	31.1	3.0	(−17.6)	−9.3
300	24.7	31.3	2.9	(−17.6)	−9.2
310	23.9	36.3	−0.4	(−16.7)	−12.8
320	23.1	34.4	−1.5	(−11.0)	−8.4

Example 1, 1,1-Diethylurea. The sequence of substitution of H by CH_3 at transition from urea to 1,1-diethylurea can be presented by the following scheme:

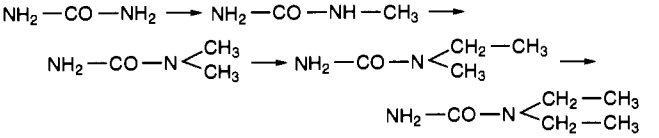


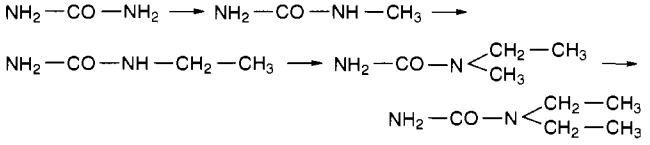
Table 14. Additive Constants for Calculation of Entropy $S°(T)$ of Crystalline Alkylureas Ignoring Phase Changes

	J·K⁻¹·mol⁻¹				
T/K	S_i	S_j	S_l	S_m	S_k
5	0.04	−0.02	0.03	−0.05	0.03
10	0.26	−0.08	0.19	−0.34	0.15
15	0.7	−0.1	0.4	−0.8	0.3
20	1.2	0.0	0.7	−1.3	0.4
25	1.8	0.1	1.0	−1.5	0.5
30	2.5	0.4	1.3	−2.1	0.5
35	3.3	0.7	1.4	−2.6	0.5
40	4.1	1.1	1.5	−3.2	0.4
45	4.9	1.6	1.6	−3.7	0.3
50	5.8	2.1	1.6	−4.3	0.2
60	7.6	3.2	1.4	−5.5	0.0
70	9.5	4.3	1.2	−6.6	−0.2
80	11.3	5.4	1.0	−7.7	−0.4
90	13.2	6.4	0.8	−8.7	−0.5
100	15.0	7.4	0.6	−9.7	−0.5
110	16.7	8.3	0.5	−10.5	−0.5
120	18.4	9.2	0.4	−11.2	−0.5
130	19.9	10.0	0.3	−11.8	−0.5
140	21.4	10.8	0.2	−12.4	−0.5
150	22.9	11.5	0.2	−12.9	−0.4
160	24.2	12.3	0.3	−13.3	−0.4
170	26.0	13.0	0.2	−14.3	−0.3
180	27.2	13.7	0.3	−14.5	−0.2
190	28.4	14.4	0.3	−14.6	−0.2
200	29.1	15.7	0.7	−13.6	−0.9
210	30.2	16.5	0.8	−13.6	−0.9
220	31.3	17.2	0.9	−13.6	−1.0
230	32.3	18.0	0.9	−13.5	−1.0
240	33.1	19.1	1.2	(−12.8)	−1.4
250	34.2	19.8	1.3	(−12.7)	−1.5
260	35.2	20.5	1.3	(−12.5)	−1.4
270	36.6	21.7	1.5	(−13.2)	−2.1
280	36.6	23.1	1.8	(−15.3)	−2.7
290	37.7	25.1	2.2	(−17.7)	−4.3
298.15	38.4	26.6	1.7	(−18.2)	−4.6
300	38.9	27.5	1.8	(−19.9)	−5.6
310	39.8	27.7	2.6	(−20.4)	−5.0
320	40.4	29.3	2.8	(−21.3)	−5.9

The following expression for calculation of a thermodynamic property P corresponds to this sequence:

$$P[NH_2CON(C_2H_5)_2] = P(NH_2CONH_2) + \Delta P(CH_3)_N + [\Delta P(CH_3)_N + \Delta P(CNC)] + [\Delta P(CH_3)C + \Delta P(CCN)] + [\Delta P(CH_3)_C + \Delta P(CCN)] = P(\text{urea}) + 2\Delta P(CH_3)_N + 2\Delta P(CH_3)_C + \Delta P(CNC) + 2\Delta P(CCN) = P(\text{urea}) + 2P_i + 2P_j + P_m + 2P_l$$

This equation does not depend on the sequence of substitutions. For example, using an alternate scheme we obtain the same expression:



$P[NH_2—CO—N(C_2H_5)_2] = P(NH_2CONH_2) + \Delta P(CH_3)_N + [\Delta P(CH_3)_C + \Delta P(CCN)] + [\Delta P(CH_3)_N + \Delta P(CNC)] + [\Delta P(CH_3)_C + \Delta P(CCN)] = P(\text{urea}) + 2\Delta P(CH_3)_N + 2\Delta P(CH_3)_C + \Delta P(CNC) + 2\Delta P(CCN) = P(\text{urea}) + 2P_i + 2P_j + P_m + 2P_l$

Example 2. 1,3-Diethylurea. Any sequence of substitutions of H by CH_3 can be selected for transition from urea to 1,3-diethylurea, as in the previous example:

NH_2-CO-NH_2 →
NH_2-CO-NH-CH_3 → NH_2-CO-NH-CH_2-CH_3 →
CH_3-NH-CO-NH-CH_2-CH_3 →
CH_3-CH_2-NH-CO-NH-CH_2-CH_3

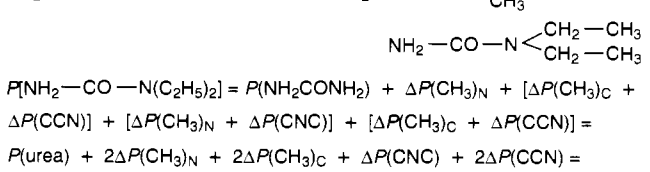
So, the following expression holds for 1,3-diethylurea:

$$P(C_2H_5NHCONHC_2H_5) = P(NH_2CONH_2) + \Delta P(CH_3)_N + [\Delta P(CH_3)_C + \Delta P(CCN)] + \Delta P(CH_3)_N + [\Delta P(CH_3)_C + \Delta P(CCN)] = P(\text{urea}) + 2\Delta P(CH_3)_N + 2\Delta P(CH_3)_C + 2\Delta P(CCN) = P(\text{urea}) + 2P_i + 2P_j + 2P_l$$

Table 15. Additive Constants for Calculation of Gibbs Energy Function $-[G°(T) - H°(0)]T$ of Crystalline Alkylureas Ignoring Phase Changes

	J·K⁻¹·mol⁻¹				
T/K	G_i	G_j	G_l	G_m	G_k
5	0.01	0.00	0.01	−0.01	0.01
10	0.07	−0.03	0.05	−0.09	0.04
15	0.2	−0.1	0.1	−0.2	0.1
20	0.4	−0.1	0.3	−0.4	0.2
25	0.6	0.0	0.4	−0.7	0.2
30	0.9	0.0	0.5	−0.9	0.3
35	1.2	0.1	0.6	−1.1	0.3
40	1.5	0.2	0.7	−1.3	0.3
45	1.8	0.3	0.8	−1.6	0.3
50	2.2	0.5	0.9	−1.8	0.3
60	2.9	0.8	1.0	−2.3	0.3
70	3.7	1.3	1.1	−2.8	0.2
80	4.6	1.7	1.1	−3.4	0.2
90	5.4	2.2	1.0	−3.9	0.1
100	6.3	2.7	1.0	−4.5	0.0
110	7.2	3.1	1.0	−5.0	0.0
120	8.0	3.6	0.9	−5.5	−0.1
130	8.9	4.1	0.9	−5.9	−0.1
140	9.7	4.5	0.8	−6.4	−0.1
150	10.5	5.0	0.8	−6.8	−0.1
160	11.4	5.4	0.8	−7.2	−0.2
170	12.2	5.8	0.7	−7.6	−0.2
180	13.0	6.2	0.7	−8.0	−0.2
190	13.8	6.6	0.7	−8.3	−0.2
200	14.5	7.1	0.7	−8.6	−0.2
210	15.2	7.5	0.7	−8.9	−0.2
220	15.9	7.9	0.7	−9.1	−0.3
230	16.6	8.3	0.7	−9.3	−0.3
240	17.9	8.0	0.4	(−10.9)	0.5
250	18.6	8.6	0.5	(−11.2)	0.2
260	19.1	8.9	0.5	(−11.0)	0.3
270	19.9	9.6	0.5	(−11.4)	0.0
280	20.2	9.9	0.6	(−11.5)	0.1
290	20.9	10.6	0.7	(−12.1)	−0.3
298.15	21.3	10.8	0.7	(−11.8)	−0.1
300	21.5	11.2	0.7	(−12.5)	−0.5
310	22.1	11.7	0.8	(−12.7)	−0.7
320	22.4	12.0	0.9	(−12.2)	−0.4

Example 3. (1,1-Dimethylethyl)urea (tert-Butylurea).



$P[NH_2CONHC(CH_3)_3] = P(NH_2CONH_2) + \Delta P(CH_3)_N + [\Delta P(CH_3)_C + \Delta P(CCN)] + [\Delta P(CH_3)_C + \Delta P(CCN) + \Delta P(CCC)] + [\Delta P(CH_3)_C + \Delta P(CCN) + 2\Delta P(CCC)] = P(\text{urea}) + \Delta P(CH_3)_N + 3\Delta P(CH_3)_C + 3\Delta P(CCN) + 3\Delta P(CCC) = P(\text{urea}) + P_i + 3P_j + 3P_l + 3P_k$

Table 16. Additive Constants for Calculation of Reduced Enthalpy $[H°(T) - H°(0)]/T$ of Crystalline Alkylureas Ignoring Phase Changes

	J·K^{-1}·mol^{-1}				
T/K	H_i	H_j	H_l	H_m	H_k
5	0.03	−0.01	0.02	−0.04	0.02
10	0.19	−0.06	0.14	−0.25	0.11
15	0.5	0.0	0.3	−0.6	0.2
20	0.8	0.0	0.5	−0.8	0.2
25	1.2	0.2	0.6	−1.1	0.2
30	1.6	0.4	0.7	−1.3	0.2
35	2.1	0.6	0.8	−1.5	0.2
40	2.6	0.9	0.8	−1.9	0.1
45	3.1	1.3	0.7	−2.2	0.0
50	3.6	1.6	0.7	−2.5	−0.1
60	4.5	2.4	0.5	−2.8	−0.3
70	5.7	3.1	0.2	−3.8	−0.4
80	6.7	3.7	0.0	−4.3	−0.5
90	7.7	4.2	−0.2	−4.8	−0.6
100	8.7	4.7	−0.4	−5.2	−0.6
110	9.5	5.2	−0.5	−5.5	−0.5
120	10.3	5.6	−0.6	−5.8	−0.5
130	11.0	5.9	−0.6	−5.9	−0.4
140	11.7	6.3	−0.6	−6.0	−0.3
150	12.3	6.6	−0.5	−6.1	−0.3
160	12.9	6.9	−0.5	−6.1	−0.2
170	13.8	7.1	−0.5	−6.7	−0.1
180	14.2	7.4	−0.4	−6.5	−0.1
190	14.6	7.7	−0.3	−6.3	0.0
200	14.5	8.7	0.0	−4.9	−0.7
210	14.9	9.0	0.1	−4.7	−0.7
220	15.3	9.3	0.2	−4.5	−0.7
230	15.7	9.7	0.3	−4.2	−0.7
240	15.3	11.1	0.7	(−1.9)	−1.9
250	15.7	11.3	0.8	(−1.7)	−1.9
260	16.1	11.7	0.8	(−1.5)	−1.9
270	16.7	12.2	0.9	(−1.7)	−2.2
280	16.3	13.1	1.2	(−3.7)	−2.7
290	16.7	14.4	1.6	(−5.4)	−3.9
298.15	17.1	15.8	1.0	(−6.4)	−4.4
300	17.4	16.3	1.0	(−7.4)	−5.0
310	17.7	16.0	1.8	(−7.7_	−4.3
320	18.0	17.3	1.9	(−9.0)	−5.4

Table 17. Average Percentage Deviation of Thermodynamic Functions of Crystalline Alkylureas Calculated Ignoring Phase Changes from Those Based on Experiment

T/K	C	S	G	H
5	19.1	19.1	18.9	19.1
10	18.3	19.7	19.8	19.6
15	13.2	16.5	18.3	15.8
20	9.6	13.5	15.8	12.6
25	6.7	11.3	13.7	10.1
30	4.8	9.3	12.0	8.1
35	3.4	7.8	10.6	6.6
40	2.4	6.6	9.4	5.4
45	1.9	5.7	8.4	4.4
50	1.8	5.0	7.5	3.6
60	2.0	3.9	6.2	3.9
70	2.1	3.2	5.3	2.1
80	2.0	2.7	4.6	2.0
90	1.9	2.4	4.0	1.9
100	1.8	2.1	3.6	1.9
110	1.7	2.0	3.2	1.9
120	1.7	1.9	3.0	1.8
130	1.7	1.9	2.7	1.8
140	1.7	1.8	2.5	1.7
150	1.7	1.8	2.4	1.7
160	1.8	1.8	2.2	1.7
170	2.2	1.8	2.2	1.8
180	2.5	1.8	2.1	1.7
190	2.8	1.7	2.0	1.6
200	3.2	1.5	2.0	2.2
210	3.8	1.4	1.9	2.0
220	4.3	1.3	1.8	2.0
230	4.8	1.3	1.7	2.0
240	5.6	1.4	1.4	1.6
250	6.0	1.5	1.2	1.7
260	6.4	1.6	1.4	2.0
270	7.3	1.6	1.2	2.1
280	3.9	1.6	1.5	1.8
290	3.7	1.2	1.2	1.2
298.15	3.8	2.2	1.5	3.0
300	4.2	2.0	1.3	2.8
310	3.5	2.3	1.4	3.2
320	3.0	2.4	1.3	3.7

The n_i, n_j, n_k, n_l, and n_m coefficient matrix of the equations systems for the compounds **I**–**XIV** is given in Table 6.

It was established from solution of some particular subsets of equation systems from Table 6 that the obtained equation system yields a steady solution; i.e., removing any equation from the system or changing a property value for any compound by a tripled experimental uncertainty should not lead to substantial changes of additive constant values. Rigorous criteria of steadiness for systems of linear equations do not exist (*8*). However, some simple practical recommendations may help to obtain systems with steady solutions:

1. The number of equations should be at least 1.5–2 times more than the number of variables.

2. The matrix of coefficients for a system of linear equations (Table 6) should be filled over the area uniformly as far as possible.

A small value of error in determination of free terms of equations (differences between property of substituted and unsubstituted urea) also stabilizes the systems of equations.

The values of the additive constants to estimate thermodynamic properties of substituted urea derivatives (Tables 7–10) were calculated from the complete sets of equations by a least-squares method. However, the number of equations to determine the additive constants was decreased when the temperature was changed from 5 K to room temperature, because the equations for the compounds that showed solid-to-solid transitions were excluded from the set. This reduction of the systems of equations was one of the causes of an appearance of unstable solutions, given in parentheses in Tables 7–10.

The agreement between calculated values of thermodynamic properties and experimental ones for particular compounds is shown in Table 11 for three compounds at three different temperatures. The average percent deviations of calculated values of the thermodynamic functions from experimental ones are given in Table 12. On the basis of this table we can make the following conclusions concerning semiempirical methods for calculation of thermodynamic properties of the crystalline state.

A simple additive substitution scheme, equivalent to using 1,3-interactions of polyvalent atoms in the molecules, provides an average accuracy within 2–5% in additive calculations of C_s, $S°(T)$, $[H°(T) - H°(0)]/T$, and $[G°(T) - H°(0)]/T$ of urea derivatives in the crystalline state in a temperature range from 50 to 300 K. The agreement between calculated and experimental values of heat capacities and entropies is significantly better.

According to ref 1, the corrections concerning the molecular symmetry and mixing of stereoisomers were not included in the additive calculations of $S°(T)$ and $G°(T)$.

The average errors in the additive calculations of C_p, $S°(T)$, and other functions reached some 10% at temperatures lower 30 K. However, the absolute values of the thermodynamic functions at $T < 30$ K are small in magnitude, and the absolute error of thermodynamic functions is also small.

Table 18. Experimental Heat Capacity Data Obtained from Vacuum Adiabatic Calorimetry Measurements (Data Series in Regions of Phase Transitions Are Also Included, Which May Be Used for Determination of Shapes of Heat Capacity Curves Near Transitions)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K
					I. Urea (Figure 2)						
					Series 1						
40.24	18.17	0.9663	50.90	23.75	1.6797	67.19	30.87	2.7838	86.96	37.10	3.4802
41.62	18.76	1.7901	52.83	24.73	2.1547	69.91	31.81	2.6489	90.37	38.12	3.3425
44.99	20.77	1.5749	54.93	25.74	2.0325	72.51	32.81	2.5332	93.66	39.10	3.2231
46.53	21.56	1.4939	56.91	26.65	1.9278	75.45	33.60	3.3362	96.84	39.92	3.1208
47.99	22.32	1.4194	58.80	27.48	1.8361	78.71	34.73	3.1856	99.92	40.72	3.0304
49.39	23.15	1.3504	61.28	28.53	3.1231	82.76	35.59	4.9035			
					Series 2						
4.61	0.0189	0.2953	9.70	0.5730	0.4590	17.12	3.367	0.6716	28.69	10.65	1.0561
4.89	0.0476	0.2710	10.14	0.6613	0.4213	17.76	3.708	0.6053	29.84	11.47	1.2281
5.15	0.0723	0.2510	10.65	0.7873	0.5764	18.35	4.053	0.5681	31.02	12.58	1.1234
5.39	0.0886	0.2360	11.20	0.9330	0.5191	18.90	4.349	0.5350	32.18	13.03	1.1947
5.67	0.1068	0.3303	11.70	1.084	0.4723	19.48	4.699	0.6173	33.35	13.87	1.1212
6.06	0.1316	0.4697	12.22	1.247	0.5603	20.08	5.065	0.5786	34.56	14.68	1.2943
6.51	0.1683	0.4206	12.76	1.427	0.5095	20.76	5.546	0.7725	35.82	15.46	1.2120
6.91	0.1979	0.3840	13.29	1.621	0.5589	21.51	6.017	0.7156	37.12	16.29	1.3735
7.28	0.2293	0.3537	13.83	1.832	0.5120	22.33	6.543	0.9008	38.45	17.10	1.2867
7.65	0.2683	0.3800	14.33	2.043	0.4733	23.20	7.114	0.8298	39.82	17.97	1.4380
8.02	0.3152	0.3499	14.83	2.244	0.5133	24.23	7.761	1.2278	41.40	18.81	1.6908
8.36	0.3607	0.3250	15.32	2.504	0.4741	25.41	8.510	1.1182	43.05	19.75	1.6065
8.77	0.4118	0.4929	15.88	2.767	0.6257	26.49	9.155	1.0323	44.62	20.58	1.5173
9.25	0.4860	0.4479	16.49	3.072	0.5751	27.58	9.937	1.1407	46.10	21.45	1.4355
					III. 1,1-Dimethylurea						
					Series 1						
111.61	76.88	4.2024	123.69	81.99	3.8785	134.95	86.43	3.6460	146.80	90.53	4.2513
115.75	78.74	4.0789	127.52	83.60	3.7923	138.56	87.72	3.5834	155.16	93.38	4.1125
119.77	80.47	3.9715	131.27	85.02	3.7163	142.51	89.05	4.3304			
					Series 2						
170.34	98.09	3.9063	183.00	101.9	6.0886	200.84	107.0	5.8226			
174.22	99.33	3.8595	189.03	103.8	5.9896						
178.05	100.5	3.8158	194.98	105.4	5.9020						
					Series 3						
156.39	93.77	4.0958	164.44	96.44	3.9795						
160.44	95.08	4.0366	168.39	97.68	3.9257						
					Series 4						
207.26	108.8	5.9726	230.61	115.4	5.6945	259.78	123.4	5.4241	286.12	131.0	6.5430
213.20	110.6	5.8958	243.17	118.7	5.5740	265.91	125.2	6.7370	292.79	132.8	6.4850
219.06	112.2	5.8255	248.75	120.3	5.5215	272.70	127.1	6.6711	299.42	134.9	6.4260
224.86	113.8	5.7594	254.28	121.8	5.4719	279.43	128.8	6.6116	306.01	136.6	6.3752
					Series 5						
5.30	0.0935	0.2616	12.12	1.381	0.4425	24.95	10.43	1.2665	59.87	45.29	3.2299
5.60	0.1092	0.2446	12.56	1.551	0.4098	26.16	11.63	1.1395	62.96	47.86	2.9505
5.88	0.1256	0.2297	12.97	1.687	0.3868	27.25	12.69	1.0433	65.82	50.15	2.7748
6.19	0.1533	0.2908	13.37	1.860	0.3631	28.26	13.71	0.9655	68.53	52.22	2.6348
6.51	0.1784	0.2704	13.87	2.120	0.5738	29.42	14.96	1.3364	71.67	54.39	3.6471
6.86	0.2057	0.3605	14.44	2.387	0.5285	30.78	16.48	1.3849	75.20	56.94	3.4259
7.24	0.2467	0.3306	14.96	2.674	0.4873	32.57	18.40	2.1882	78.54	59.22	3.2489
7.59	0.2849	0.3064	15.44	2.950	0.4532	34.63	20.68	1.9250	81.72	61.21	3.1034
7.92	0.3271	0.2853	15.89	3.210	0.4246	36.47	22.67	1.7364	85.18	63.33	3.8375
8.31	0.3735	0.4186	16.52	3.605	0.8101	38.27	24.54	1.8529	88.96	65.45	3.6674
8.73	0.4533	0.3776	17.30	4.075	0.7339	40.04	26.45	1.6976	92.53	67.50	3.5193
9.13	0.5276	0.3500	18.01	4.547	0.6697	42.05	28.57	2.3197	95.98	69.35	3.3928
9.49	0.6099	0.3255	18.78	5.151	0.8725	44.27	30.79	2.1152	99.32	71.09	3.2856
9.83	0.6909	0.3018	19.62	5.806	0.7900	46.31	32.86	1.9512	102.55	72.69	3.1900
10.25	0.7964	0.4851	20.38	6.408	0.7248	48.20	34.68	1.8220	105.70	74.24	3.1057
10.73	0.9318	0.4405	21.31	7.197	1.1118	49.97	36.39	1.7145	108.76	75.74	3.0288
11.18	1.064	0.4062	22.37	8.110	0.9956	52.78	38.97	3.9077	111.76	77.12	2.9600
11.64	1.210	0.4815	23.60	9.201	1.4305	56.49	42.40	3.5173			
					IV. 1,3-Dimethylurea (Figure 3)						
					Series 1 (Crystal **III**, **II**)						
122.69	85.03	3.2448	150.79	94.69	4.0246	176.67	100.2	3.7207	205.78	104.7	4.3061
125.90	86.11	3.1847	154.77	97.87	3.9397	180.38	99.86	3.6986	210.08	105.9	4.2646
129.71	87.38	4.4290	158.50	131.1	3.5265	184.07	99.98	3.6719	214.36	107.0	4.2295
134.10	88.68	4.3404	161.97	132.7	3.4836	188.15	100.6	4.4772			
138.39	90.16	4.2485	165.53	113.7	3.6655	192.62	101.4	4.4374			
142.60	91.63	4.1685	169.21	105.6	3.7157	197.04	102.6	4.3870			
146.73	93.01	4.0953	172.95	101.3	3.7367	201.43	103.6	4.3475			

Table 18 (Continued)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K
					Series 2 (Crystal II, I)						
216.42	107.5	4.2121	241.35	114.8	4.0160	269.70	123.7	5.5025	302.81	141.7	5.1542
220.65	108.8	4.1752	245.42	116.0	3.9888	275.32	125.6	5.4545	307.35	163.1	4.8887
224.84	109.8	4.1456	249.47	117.2	3.9624	280.91	127.4	5.4091	312.66	135.6	5.2072
229.01	111.1	4.1091	253.50	118.5	3.9344	286.47	129.5	5.3598	318.17	137.5	5.1707
233.15	112.3	4.0774	258.37	120.1	5.6011	292.01	131.2	5.3215	323.66	139.9	5.1282
237.26	113.6	4.0456	264.05	122.0	5.5505	297.51	132.0	5.3014	329.15	142.5	5.0853
					Series 3 (Crystal III)						
5.57	0.4975	0.1909	10.93	3.140	0.3702	17.86	8.771	0.4729	31.11	22.58	1.0551
5.78	0.5435	0.1804	11.30	3.395	0.3516	18.40	9.330	0.6052	32.34	23.86	1.3942
6.08	0.6404	0.3702	11.77	3.745	0.5719	19.00	9.876	0.5721	33.69	25.31	1.2949
6.45	0.7770	0.3301	12.33	4.148	0.5247	19.70	10.56	0.8203	34.94	26.77	1.2079
6.79	0.9012	0.2998	12.84	4.537	0.4854	20.49	11.32	0.7622	36.42	28.37	1.7395
7.10	1.022	0.2756	13.32	4.931	0.4499	21.43	12.21	1.1051	38.09	30.18	1.6037
7.54	1.196	0.5474	13.76	5.253	0.4258	22.49	13.30	1.0088	39.65	31.81	1.4958
8.07	1.438	0.4801	14.18	5.580	0.4033	23.47	14.29	0.9324	41.43	33.66	2.0739
8.54	1.670	0.4305	14.58	5.906	0.3837	24.37	15.22	0.8692	43.43	35.61	1.9153
8.97	1.888	0.3923	15.09	6.375	0.6432	25.50	16.36	1.3434	45.51	37.72	2.2292
9.35	2.126	0.3592	15.72	6.935	0.5922	26.79	17.73	1.2281	47.66	39.80	2.0663
9.71	2.350	0.3322	16.30	7.423	0.5576	27.97	19.02	1.3336	49.66	41.71	1.9338
10.11	2.584	0.4324	16.85	7.884	0.5255	29.07	20.22	1.0529	52.85	44.61	4.4367
10.54	2.870	0.3984	17.37	8.341	0.4974	30.09	21.44	0.9819	57.04	48.41	3.9509
					Series 4 (Crystal III)						
65.53	55.41	4.2038	77.33	64.03	4.4044	89.47	71.59	3.7467	102.27	77.80	4.1164
69.57	58.55	3.8793	81.61	66.71	4.1432	93.60	73.76	4.5152	106.36	79.40	4.0322
73.32	61.26	3.6284	85.64	69.25	3.9263	98.03	75.81	4.3269			
					Series 5 (Crystal III)						
108.41	80.23	2.6646	117.50	83.64	5.1794						
111.05	81.30	2.6128	122.60	85.29	5.0250						
113.63	82.36	2.5644									
					Series 6 (Crystal III, II)						
154.56	96.25	0.6890	160.56	133.8	1.0431	166.80	111.0	1.1001	173.39	101.2	1.1172
155.24	96.68	0.6847	161.57	131.3	1.0491	167.89	107.3	1.1098	174.75	100.5	1.1519
156.16	97.81	1.1759	162.58	130.6	1.0480	168.98	104.8	1.1156	176.15	100.4	1.1154
157.31	101.6	1.1584	163.60	122.5	1.0705	170.08	103.5	1.1184	177.81	100.1	1.1098
158.44	109.8	1.1257	164.65	116.9	1.0859	171.18	102.5	1.1184	178.91	99.95	1.1091
159.52	123.2	1.0783	165.71	115.6	1.0876	172.29	101.6	1.1189			
					Series 7 (Crystal II, I)						
298.00	133.4	0.9027	301.55	157.2	0.9288	305.98	133.0	0.9824	310.56	134.6	0.9763
298.97	134.5	0.9955	302.54	144.6	0.9564	307.14	133.7	0.9804	311.70	135.0	0.9721
299.87	138.2	0.9729	303.66	135.8	0.9766	308.28	133.8	0.9790	312.85	135.4	0.9759
300.70	153.9	0.9364	304.82	133.5	0.9822	309.42	134.2	0.9772			
					V. Ethylurea (Figure 4)						
					Series 1						
112.63	68.90	6.8451	126.87	74.28	4.1970	142.94	79.99	3.8698	156.38	85.05	4.3800
118.26	71.01	4.4265	131.02	75.81	4.1013	147.18	81.60	4.6456			
122.62	72.62	4.3056	135.07	77.20	4.0171	151.98	83.34	4.4388			
					Series 2						
4.86	0.2126	0.3483	12.14	2.841	0.4695	24.75	12.90	0.6942	55.66	40.60	2.5518
5.20	0.2558	0.3265	12.60	3.111	0.4377	25.43	13.55	0.6583	58.13	42.36	2.3969
5.50	0.3025	0.2949	13.02	3.356	0.4111	26.20	14.32	0.8838	60.75	44.12	2.8369
5.78	0.3645	0.2685	13.42	3.603	0.3883	27.05	15.15	0.8298	63.50	45.90	2.6721
6.11	0.4200	0.3726	13.79	3.867	0.3668	27.93	16.04	0.9215	66.35	47.64	3.0418
6.46	0.4851	0.3423	14.15	4.073	0.3500	28.82	16.97	0.8656	69.31	49.41	2.8838
6.78	0.5778	0.3096	14.56	4.322	0.4631	29.72	17.96	0.9341	72.62	51.24	3.7305
7.13	0.6784	0.3933	15.01	4.639	0.4350	31.54	19.78	0.9761	76.24	53.14	3.5272
7.50	0.7741	0.3549	15.43	4.900	0.4146	32.62	20.91	1.1939	79.69	54.81	3.3597
7.83	0.9050	0.3173	15.83	5.167	0.3953	33.78	22.05	1.1207	83.26	56.51	3.8034
8.15	0.9828	0.3091	16.35	5.583	0.6516	35.12	23.45	1.5714	87.24	58.37	4.1557
8.51	1.121	0.4175	16.98	6.066	0.6044	36.63	24.90	1.4649	91.29	60.43	3.9663
8.91	1.260	0.3843	17.69	6.622	0.8309	38.04	26.23	1.3624	96.69	62.45	4.8254
9.27	1.405	0.3574	18.48	7.261	0.7606	39.35	27.50	1.2816	102.46	64.96	5.0747
9.61	1.577	0.3322	19.31	7.968	0.8948	40.60	28.61	1.2147	107.12	66.83	4.2644
9.93	1.718	0.3121	20.17	8.729	0.8220	42.09	29.89	1.7805	111.31	68.40	4.1283
10.24	1.855	0.2963	20.96	9.388	0.7693	43.81	31.45	1.6593	115.38	70.03	4.0101
10.56	2.018	0.3631	21.70	10.10	0.7151	45.42	32.83	1.5601	119.61	71.66	4.4603
10.91	2.212	0.3396	22.48	10.80	0.8372	47.22	34.27	2.0350	124.01	73.30	4.3405
11.24	2.383	0.3203	23.28	11.54	0.7816	49.18	35.83	1.9041			
11.66	2.560	0.5084	24.04	12.28	0.7322	52.26	38.15	2.2516			

Table 18 (Continued)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K
					Series 3						
162.35	87.12	5.3328	202.77	103.1	5.5874	245.50	123.9	5.0286	289.53	161.2	6.0449
167.63	89.18	5.2325	208.34	105.4	5.5090	250.59	126.9	4.9673	295.68	171.2	5.8899
172.82	91.31	5.1413	213.83	107.8	5.4321	255.62	130.1	4.9070	301.68	181.9	5.7356
177.91	93.10	5.0565	219.26	110.4	5.3575	261.03	133.9	5.6748			
182.93	95.11	4.9779	224.63	113.0	5.2851	266.80	138.2	5.5910			
187.88	97.07	4.9049	229.93	115.5	5.2192	272.49	142.8	5.5065			
192.76	98.99	4.8371	235.17	118.5	5.1498	278.11	148.1	5.4172			
197.57	101.0	4.7717	240.36	121.2	5.0874	283.65	154.1	5.3243			
					VI. (1-Methylethyl)urea (Figure 5)						
					Series 1 (Crystal **II**)						
13.19	4.508	0.4960	16.06	7.041	0.5613	19.52	10.67	0.5546	22.98	14.32	0.6607
13.67	4.908	0.4654	16.60	7.553	0.5272	20.06	11.31	0.5237	23.62	15.01	0.6264
14.12	5.300	0.4576	17.11	8.069	0.4971	20.57	11.80	0.5002	24.23	15.82	0.5933
14.57	5.686	0.4318	17.70	8.666	0.6731	21.14	12.43	0.6458	24.89	16.43	0.7214
14.98	6.064	0.4078	18.34	9.380	0.6254	21.77	13.07	0.6103	25.59	17.14	0.6875
15.49	6.489	0.6023	18.95	10.04	0.5867	22.36	13.73	0.5780	26.26	17.86	0.6535
					Series 2 (Crystal **II**)						
27.58	19.42	0.7396	45.58	37.13	1.4966	82.10	61.73	3.0931	143.96	92.40	4.0870
28.30	20.19	0.7024	47.03	38.32	1.4155	85.13	63.47	2.9658	148.43	94.38	4.8400
29.16	21.08	1.0074	48.41	39.39	1.3476	88.61	65.38	4.0137	153.23	96.56	4.7447
30.13	22.16	0.9433	49.25	40.05	1.3222	92.53	67.52	3.8297	157.94	98.75	4.6566
31.10	23.32	1.0089	51.13	41.44	2.4355	96.29	69.59	3.6744	162.57	100.9	4.5787
32.09	24.31	0.9624	53.49	43.12	2.3081	99.89	71.54	3.5410	167.13	103.0	4.5068
33.07	25.43	1.0096	55.73	44.81	2.1584	103.82	73.45	4.2990	171.63	105.1	4.4400
34.05	26.49	0.9520	57.82	46.28	2.0391	108.04	75.66	4.1434	176.06	107.0	4.3798
35.07	27.57	1.1041	59.81	47.64	1.9441	112.12	77.54	4.0127	180.43	109.0	4.3211
36.15	28.66	1.0402	62.06	49.15	2.5468	116.07	79.53	3.8968	184.76	110.9	4.2689
37.38	29.90	1.4226	64.54	50.82	2.4133	119.92	81.27	3.7955	189.03	112.9	4.2197
38.75	31.13	1.3312	66.89	52.38	2.2983	123.88	83.11	4.1152	193.26	114.7	4.1730
40.04	32.43	1.2501	69.14	53.82	2.1976	127.95	85.17	4.0144	197.45	116.6	4.1287
41.40	33.68	1.4705	72.06	55.71	3.6467	131.92	87.04	3.9240	201.60	118.4	4.0881
42.83	34.92	1.3840	75.59	57.86	3.4257	135.81	88.81	3.8454			
44.17	36.01	1.3095	78.93	59.92	3.2435	139.82	90.66	4.1652			
					Series 3 (Crystal **II**)						
205.72	120.4	4.0466	225.21	129.6	5.1965	246.07	139.5	4.9962	266.45	152.4	4.8106
209.81	122.0	4.0151	230.48	131.9	5.1436	251.20	142.2	4.9501	271.45	162.3	4.7205
214.54	124.3	5.3176	235.71	134.6	5.0897	256.31	144.9	4.9054			
219.90	126.8	5.2580	240.90	137.1	5.0417	261.39	147.5	4.8630			
					Series 4 (Crystal **II**, **I**)						
265.75	151.3	2.9681	280.26	312.9	1.1875	287.54	215.5	1.3192	299.00	171.5	1.3886
268.88	155.9	2.9415	280.79	320.8	0.4065	289.11	194.1	1.3551	300.68	171.6	1.3834
272.00	165.0	2.8990	281.24	310.1	0.3098	290.72	179.7	1.3787	302.36	171.7	1.3818
274.35	178.8	1.3958	281.64	293.8	0.3160	292.35	173.2	1.3877	304.06	172.6	1.3790
275.90	202.2	1.3524	283.06	260.6	1.2526	294.00	171.6	1.3896			
277.41	228.1	1.3090	284.52	240.3	1.2843	295.66	171.4	1.3891			
278.87	270.7	1.2455	286.02	227.3	1.3022	297.32	171.1	1.3870			
					Series 5 (Crystal **I**)						
303.00	172.2	4.1442	311.32	175.3	4.0655						
304.47	172.7	4.5511	315.76	177.1	4.0460						
307.47	174.0	4.1233									
					Series 6 (Crystal **II**)						
5.71	0.4419	0.2246	7.43	1.001	0.4097	9.73	2.010	0.4631	11.99	3.548	0.3138
5.95	0.4990	0.2620	7.82	1.129	0.3788	10.18	2.311	0.4241	12.30	3.782	0.2993
6.21	0.5783	0.2451	8.19	1.268	0.3525	10.59	2.550	0.3962	12.65	4.037	0.3989
6.44	0.6566	0.2300	8.53	1.446	0.3260	10.97	2.829	0.3696	13.05	4.359	0.3764
6.66	0.7369	0.2173	8.84	1.549	0.3084	11.33	3.062	0.3491			
7.00	0.8416	0.4537	9.25	1.750	0.5058	11.67	3.305	0.3309			
					VII. Tetramethylurea (Figure 6)						
					Series 1 (Crystal)						
99.46	91.30	2.9819									
103.29	94.03	4.6695									
107.87	97.40	4.4870									
					Series 2 (Crystal)						
129.89	112.3	4.8621	143.94	120.6	4.5223	158.58	130.2	5.2257			
134.69	115.2	4.7333	148.41	123.4	4.4291						
139.36	118.0	4.6188	153.29	126.5	5.3393						
					Series 3 (Crystal)						
173.77	143.3	4.8711	188.09	152.0	4.6669						
178.61	146.7	4.7987	192.74	154.3	4.6092						
183.38	149.6	4.7279									

Table 18 (Continued)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K
					Series 4 (Crystal)						
204.50	162.6	4.4616	218.11	176.3	5.1245	233.16	192.7	4.8247	247.49	235.8	5.0923
208.96	166.9	4.3883	223.23	181.6	5.0378	237.95	200.5	4.6872			
213.35	171.6	4.3118	228.24	186.8	4.9261	242.61	213.2	4.5268			
					Series 5 (Crystal)						
110.44	99.20	5.5483	121.11	106.5	5.1328						
115.88	102.9	5.3239	126.16	110.0	4.9687						
					Series 6 (Crystal)						
136.55	116.3	4.6903	145.73	121.7	4.4874						
141.18	119.0	4.5746	150.17	124.5	4.3988						
					Series 7 (Crystal)						
195.10	155.7	4.5850									
199.69	158.3	4.5319									
					Series 8 (Liquid)						
280.46	225.4	4.4534	294.22	228.7	4.3950						
285.06	226.4	4.4342	298.80	229.9	4.3757						
289.64	227.6	4.4139									
					Series 9 (Liquid)						
282.39	225.8	5.2802									
287.81	227.0	5.2532									
					Series 10 (Crystal)						
254.93	355.8	3.6545									
258.40	461.7	3.1535									
261.32	639.6	2.5665									
					Series 11 (Liquid)						
272.91	223.8	1.4612	277.54	224.9	1.5450	282.18	226.6	1.4453			
274.45	223.0	1.4615	279.09	225.5	1.4510						
276.00	223.9	1.4579	280.64	226.0	1.4482						
					Series 12 (Liquid)						
291.22	227.8	5.2357									
296.64	228.9	5.2122									
302.04	230.5	5.1841									
					Series 13 (Crystal)						
4.93	0.1825	0.2248	11.26	2.630	0.6160	23.91	16.42	1.0773	55.41	52.30	2.7008
5.17	0.2156	0.2751	12.01	3.148	0.8872	24.95	17.71	0.9922	58.02	54.91	2.5234
5.44	0.2503	0.2788	12.83	3.845	0.7670	25.98	19.00	1.0830	62.11	58.75	5.6601
5.71	0.2927	0.2698	13.55	4.501	0.6799	27.29	20.66	1.5298	67.48	64.10	5.0932
5.97	0.3409	0.2529	14.20	5.089	0.6162	28.73	22.53	1.3797	72.36	68.64	4.6662
6.21	0.3826	0.2402	14.90	5.748	0.7929	30.05	24.26	1.2580	77.63	73.21	5.8879
6.44	0.4470	0.2243	15.65	6.530	0.7140	31.64	26.24	1.9129	83.58	78.37	6.0046
6.71	0.4998	0.3298	16.33	7.316	0.6473	33.47	28.40	1.7358	89.37	83.22	5.7788
7.03	0.5755	0.3050	16.96	7.972	0.6013	35.26	30.57	1.8496	94.78	87.74	5.2487
7.37	0.6908	0.4009	17.53	8.657	0.5586	37.03	32.65	1.6943	99.56	91.13	4.3112
7.76	0.8130	0.3661	18.31	9.544	1.0017	41.20	37.19	2.4114	103.79	94.68	4.1414
8.20	0.9680	0.5306	19.26	10.66	0.9032	43.51	39.69	2.1990	107.86	97.55	4.0003
8.69	1.180	0.4671	20.12	11.74	0.8213	45.61	42.03	2.0267	111.79	100.4	3.8748
9.19	1.399	0.5284	20.91	12.71	0.7646	47.79	44.42	2.3440	115.60	103.1	3.7545
9.86	1.760	0.8109	21.75	13.74	0.9081	50.05	46.67	2.1782	119.32	105.7	3.6652
10.61	2.209	0.6964	22.78	15.05	1.1783	52.60	49.34	2.9289	122.94	108.1	3.5809
					VIII. 1,1-Diethylurea (Figure 7)						
					Series 1 (Crystal **II**)						
10.79	1.793	0.2803	17.68	6.830	0.7991	31.74	22.62	1.4105	56.59	48.93	2.6297
11.08	1.935	0.2660	18.46	7.541	0.7326	33.10	24.31	1.2966	59.14	51.30	2.4660
11.35	2.099	0.2525	19.17	8.257	0.6738	34.35	25.78	1.2076	61.57	53.50	2.3854
11.71	2.287	0.4465	20.45	9.514	0.5909	35.53	27.18	1.1320	64.63	56.11	3.7272
12.16	2.558	0.4109	21.24	10.44	0.9773	36.63	28.45	1.0672	68.22	59.11	3.4583
12.57	2.813	0.3834	22.18	11.53	0.8890	37.81	29.79	1.2697	72.44	62.17	4.9785
12.95	3.062	0.3597	23.14	12.54	0.9808	39.04	31.07	1.2005	77.23	65.86	4.5965
13.71	3.520	0.4215	24.09	13.65	0.9013	40.22	32.44	1.1368	81.68	69.07	4.2998
14.13	3.800	0.3963	24.97	14.70	0.8354	41.59	33.99	1.6042	86.41	72.29	5.1560
14.52	4.125	0.3728	25.79	15.59	0.7846	43.15	35.64	1.5039	91.42	75.82	4.8507
14.90	4.356	0.3554	26.56	16.50	0.7417	44.77	37.27	1.7370	96.14	79.09	4.6043
15.25	4.677	0.3361	27.48	17.59	1.1017	46.46	39.03	1.6322	100.65	82.08	4.4020
15.76	5.058	0.6576	28.55	18.86	1.0177	48.04	40.67	1.5408	104.97	84.77	4.2322
16.40	5.581	0.6062	29.54	20.09	0.9452	49.55	42.23	1.4638	109.13	87.28	4.0883
16.99	6.160	0.5586	30.52	21.29	1.0101	51.37	43.97	2.1651	113.15	89.94	3.9580
					Series 2 (Crystal **II**)						
110.06	88.01	4.0979	134.99	102.6	3.9923	158.07	115.6	4.7273	182.97	131.0	5.7946
118.21	92.78	4.4217	138.95	104.7	3.9128	162.75	118.4	4.6396	188.73	135.4	5.6738
122.57	95.36	4.2950	143.42	107.1	5.0471	167.36	121.1	4.5579	194.18	168.0	5.2021
126.82	97.78	4.1838	148.41	110.0	4.9296	171.89	123.6	4.4859			
130.95	100.2	4.0831	153.29	113.1	4.8206	177.10	127.1	5.9158			

Table 18 (Continued)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K
					Series 3 (Crystal **II**, **I**)						
189.19	136.0	2.2690	197.73	922.8	0.3255	203.03	156.2	0.9552	210.05	143.2	0.9763
191.46	139.1	2.2459	198.12	600.1	0.4645	204.01	154.5	0.9578	211.07	143.2	0.9745
193.71	144.4	2.2107	198.65	398.6	0.5916	205.01	150.2	0.9663	212.09	143.1	0.9741
195.76	217.0	1.8704	199.39	242.4	0.7978	206.01	148.0	0.9701	213.10	143.5	0.9734
196.90	820.9	0.3641	200.21	211.3	0.8487	207.01	146.8	0.9716	216.48	145.2	2.6280
197.21	1230.	0.2495	201.11	175.2	0.9166	208.02	144.5	0.9758			
197.45	1202.	0.2566	202.06	161.5	0.9448	209.03	143.8	0.9761			
					Series 4 (Crystal **I**)						
216.52	145.3	2.1374	222.30	148.1	2.8223						
218.68	146.6	2.1259	225.15	149.7	2.8000						
219.15	146.7	2.6124	227.77	150.8	5.1976						
					Series 5 (Crystal **I**)						
238.25	155.3	5.0932	265.47	167.8	6.7480	292.75	180.6	6.4605	324.48	197.7	8.1775
244.41	158.2	7.0059	272.37	171.2	6.6692	299.46	183.8	6.3964			
251.49	161.4	6.9157	279.21	174.2	6.5971	307.17	187.8	8.4001			
258.51	164.5	6.8318	286.00	177.4	6.5273	315.86	192.6	8.2901			
					IX. 1,3-Diethylurea (Figure 8)						
					Series 1						
92.89	88.61	1.1682	105.34	96.66	3.9838	130.65	112.4	3.3408	152.66	126.1	3.0069
94.05	89.48	1.1535	109.25	98.94	3.8578	133.95	114.5	3.2805	155.62	128.0	2.9699
95.19	90.45	1.1390	113.05	101.3	3.7529	137.19	116.3	3.2285	158.92	130.0	3.6816
96.74	91.31	1.9526	116.74	103.7	3.6450	140.37	118.4	3.1768	162.55	132.6	3.6290
98.67	92.61	1.9155	120.34	105.9	3.5574	143.51	120.3	3.1298	166.13	134.7	3.5839
100.57	93.91	1.8812	123.85	108.0	3.4792	146.60	122.4	3.0847	169.66	137.0	3.5411
102.43	94.98	1.8500	127.28	110.2	3.4067	149.65	124.1	3.0461	173.15	139.4	3.4966
					Series 2						
171.51	138.1	4.7001	194.04	153.4	4.3873	219.88	171.4	5.1773	244.85	189.2	4.9169
176.15	141.0	4.6322	198.82	156.7	5.4484	224.98	174.8	5.1218	249.70	192.8	4.8707
180.71	144.3	4.5608	204.19	160.5	5.3722	230.03	178.7	5.0643	254.50	195.7	4.8310
185.22	147.4	4.4982	209.48	164.2	5.3029	235.02	182.4	5.0106	259.26	199.1	4.7906
189.66	150.5	4.4410	214.71	168.0	5.2368	239.96	185.7	4.9637	261.43	200.4	4.7730
					Series 3						
261.68	200.4	5.5263	283.17	212.4	5.3571	304.09	220.9	5.2355	324.75	229.2	5.1268
267.12	203.9	5.4766	288.44	215.2	5.3192	309.28	222.8	5.2082	329.88	232.1	5.0983
272.51	207.2	5.4303	293.68	217.4	5.2887	314.45	224.7	5.1823			
277.86	210.0	5.3927	298.90	219.2	5.2610	319.61	226.7	5.1567			
					Series 4						
5.44	0.3493	0.4203	10.19	2.416	0.6894	15.54	7.309	0.7252	21.17	14.17	1.2706
5.98	0.4861	0.6092	10.98	3.013	0.8628	16.24	8.073	0.6660	22.38	15.77	1.1380
6.57	0.6520	0.5281	11.79	3.668	0.7540	16.88	8.810	0.6170	23.47	17.18	1.0368
7.09	0.7975	0.4704	12.51	4.315	0.6725	17.67	9.750	0.9525	24.46	18.49	0.9553
7.71	1.042	0.7251	13.16	4.906	0.6110	18.58	10.85	0.8630	25.38	19.76	0.8863
8.56	1.426	0.9468	13.92	5.615	0.8977	19.41	11.90	0.7911	26.53	21.21	1.4013
9.44	1.919	0.7942	14.77	6.499	0.7992	20.17	12.85	0.7334	29.09	24.75	1.1658
					Series 5						
32.38	29.47	1.2929	41.21	41.40	1.4013	52.36	53.86	1.8778	65.70	67.18	2.6016
33.63	31.26	1.1990	42.57	42.97	1.3211	54.19	55.82	1.7757	68.23	69.58	2.4672
34.79	33.00	1.1175	43.86	44.47	1.2511	55.92	57.66	1.6888	70.64	71.49	2.3557
35.87	34.51	1.0537	45.08	45.92	1.1907	57.57	59.34	1.6141	72.94	73.37	2.2586
36.90	36.01	0.9967	46.48	47.42	1.6060	59.15	60.87	1.5501	75.86	75.68	3.5816
38.20	37.60	1.6166	48.35	49.41	2.1500	60.67	62.48	1.4868	79.34	78.40	3.3907
39.76	39.68	1.4968	50.43	51.77	1.9997	63.63	65.37	1.5454	82.65	80.96	3.2327
					Series 6						
5.34	0.3349	0.4296	9.18	1.768	0.7221	15.35	7.115	0.6183	25.04	19.28	1.1537
5.75	0.4354	0.3861	9.86	2.205	0.6326	16.17	8.044	1.0221	26.15	20.69	1.0617
6.12	0.5257	0.3529	10.46	2.624	0.5666	17.32	9.345	1.2915	27.17	22.11	0.9824
6.46	0.6257	0.3246	11.30	3.271	1.1106	18.54	10.79	1.1316	28.48	23.86	1.6425
6.96	0.7680	0.6520	12.33	4.131	0.9429	19.61	12.16	1.0117	32.72	30.00	1.2413
7.57	0.9883	0.5681	13.22	4.947	0.8256	20.94	13.91	1.6432	33.92	31.71	1.1557
8.11	1.198	0.5072	14.00	5.703	0.7387	22.48	15.91	1.4277	35.04	33.28	1.0845
8.59	1.450	0.4570	14.71	6.436	0.6715	23.83	17.70	1.2716			
					Series 7						
79.19	78.42	2.6161	87.83	84.98	2.8124						
82.01	80.55	3.0331	90.59	86.99	2.7238						
84.97	82.79	2.9153									

Table 18 (Continued)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/J·K^{-1}·mol^{-1})	ΔT/K
X. *n*-Butylurea (Figure 10)											
Series 1 (Crystal **III**)											
5.85	0.5201	0.4257	9.84	2.321	0.8952	16.17	7.425	0.7372	23.48	15.23	0.9159
6.26	0.6284	0.3818	10.67	2.867	0.7361	17.00	8.213	0.9114	24.46	16.32	1.0391
6.62	0.7600	0.3425	11.38	3.383	0.6709	17.87	9.043	0.8310	25.91	18.02	1.3242
7.03	0.8958	0.4635	12.10	3.941	0.7429	18.77	10.01	0.9645	27.18	19.53	1.2117
7.47	1.045	0.4174	12.94	4.580	0.9429	19.69	10.99	0.8796	28.44	21.06	1.2983
8.00	1.291	0.6464	13.83	5.308	0.8304	20.53	11.96	0.8081	29.68	22.66	1.1908
8.60	1.591	0.5612	14.62	6.004	0.7454	21.48	12.96	1.0878			
9.13	1.901	0.4968	15.40	6.703	0.8101	22.52	14.12	0.9938			
Series 2 (Crystal **III**)											
32.32	25.86	1.5323	55.04	51.24	2.2897	91.81	80.04	3.3682	142.94	107.9	3.9679
33.89	27.79	1.6220	57.26	53.22	2.1636	95.12	82.21	3.2500	147.06	110.2	4.2920
35.44	29.69	1.4881	59.37	55.17	2.0571	98.49	84.18	3.4950	151.31	111.9	4.2188
36.87	31.42	1.3836	61.73	57.41	2.6683	101.92	86.30	3.3851	155.48	114.0	4.1479
38.21	33.07	1.2940	64.33	59.80	2.5245	105.25	88.09	3.2893	159.58	116.1	4.0811
39.47	34.60	1.2166	66.79	61.80	2.4040	108.48	89.84	3.2044	163.81	118.2	4.4020
40.72	36.01	1.2813	69.14	63.85	2.2991	111.81	91.81	3.4483	163.06	117.8	4.3936
42.18	37.54	1.6344	71.39	65.68	2.2021	115.21	93.74	3.3643	168.17	120.5	4.3355
43.76	39.33	1.5329	73.82	67.64	2.6505	118.86	95.79	3.9499	172.46	122.6	4.2726
45.53	41.30	2.0156	76.77	69.70	3.2680	122.76	97.75	3.8548	176.69	124.7	4.2125
47.47	43.41	1.8772	79.96	72.07	3.1151	126.43	99.37	4.3237	180.86	127.0	4.1568
49.30	45.34	1.7651	83.01	74.24	2.9853	130.70	101.7	4.2204	184.98	129.3	4.1038
51.04	47.10	1.7137	85.93	76.28	2.8722	134.87	103.7	4.1299	189.42	131.4	4.8084
52.89	48.98	2.0050	88.75	78.17	2.7740	138.95	105.8	4.0460			
Series 3 (Crystal **III**)											
198.88	137.2	4.6730	221.41	152.7	4.3737	247.33	167.5	5.9374	277.58	198.4	6.3994
203.51	140.2	4.6156	226.08	155.3	4.9645	253.25	172.1	5.8529	283.87	228.8	6.0223
208.08	143.2	4.5525	231.01	158.2	4.9121	259.09	176.8	5.7698	289.36	353.5	4.8906
212.59	146.7	4.4802	235.90	160.9	4.8592	264.87	181.9	5.6868			
217.03	149.7	4.4172	241.34	164.6	6.0084	271.04	188.4	6.5552			
Series 4 (Crystal **III**, **II**)											
273.22	194.3	5.5230	288.57	315.6	1.9131	293.00	578.9	1.1112	296.04	516.1	1.3052
278.87	204.2	5.3987	290.09	399.1	1.3022	293.71	617.1	1.0753	297.15	445.7	1.3575
283.15	227.2	3.0681	291.20	464.2	1.2232	294.39	640.2	1.1234	298.40	350.9	1.3944
286.18	248.5	2.9475	292.17	528.5	1.1500	295.13	577.9	1.1791	299.77	230.9	1.4186
Series 5 (Crystal **II**)											
303.34	212.2	4.1801	310.89	218.0	4.1236						
307.64	215.0	4.1559	315.17	221.3	4.0905						
Series 6 (Crystal **II**)											
307.17	214.2	4.1415									
309.51	216.5	4.1448									
311.45	218.2	4.1026									
XI. (1,1-Dimethylethyl)urea (Figure 11)											
Series 1 (Crystal **II**)											
6.19	0.6965	0.1635	10.75	3.340	0.4479	16.66	8.920	0.5394	22.66	15.69	0.4951
6.45	0.7929	0.2968	11.19	3.680	0.4143	17.18	9.460	0.5095	23.15	16.19	0.4778
6.75	0.9032	0.2734	11.70	4.098	0.5932	17.68	9.981	0.4836	23.61	16.81	0.4585
7.09	1.044	0.3595	12.27	4.597	0.5398	18.16	10.50	0.4597	24.01	17.31	0.4438
7.45	1.207	0.3271	12.80	5.066	0.4973	18.65	11.10	0.5227	24.50	17.84	0.4281
7.81	1.371	0.3596	13.28	5.525	0.4620	19.16	11.64	0.4979	25.01	18.35	0.5772
8.16	1.556	0.3297	13.73	5.970	0.4324	19.65	12.22	0.4743	25.57	19.01	0.5562
8.49	1.776	0.3033	14.16	6.401	0.4070	20.12	12.71	0.4549	26.12	19.64	0.5346
8.90	2.014	0.4901	14.64	6.821	0.5534	20.56	13.27	0.4351	26.64	20.26	0.5170
9.38	2.306	0.4432	15.18	7.355	0.5162	21.07	13.82	0.5672	27.15	21.05	0.4984
9.81	2.604	0.4050	15.68	7.905	0.4857	21.62	14.42	0.5413	27.64	21.47	0.4793
10.27	2.927	0.4937	16.16	8.401	0.4572	22.14	15.11	0.5071	28.11	21.95	0.4673
Series 2 (Crystal **II**)											
29.87	24.06	0.5796	47.51	41.74	1.2027	89.39	75.35	3.3875	145.23	110.1	3.6901
30.49	24.84	0.6440	48.68	42.82	1.1558	92.71	77.68	3.2587	149.29	112.6	4.4536
31.28	25.69	0.9381	49.82	43.87	1.1139	95.91	79.97	3.1460	153.70	115.0	4.3674
32.26	26.68	1.0032	51.67	45.41	2.5965	99.00	82.10	3.0474	158.02	117.3	4.2906
33.24	27.79	0.9514	54.18	47.68	2.4237	102.38	84.34	3.7145	162.27	119.5	4.2234
34.17	28.80	0.9067	56.53	49.66	2.7773	106.02	86.86	3.5927	166.46	121.6	4.1628
35.20	29.87	1.1467	58.74	51.56	2.1539	109.56	89.29	3.4860	170.59	123.5	4.1070
36.31	31.08	1.0861	62.05	54.24	4.7408	112.99	91.51	3.3865	174.66	125.4	4.0526
37.37	32.19	1.0334	65.87	57.50	3.1793	116.55	93.80	3.2973	178.69	127.4	4.0025
38.38	33.25	0.9860	68.95	60.03	2.9881	119.91	95.70	3.7001	183.37	129.7	5.3720
39.41	34.25	1.0727	71.85	62.35	2.8292	123.57	97.91	3.6235	188.70	132.4	5.2893
40.73	35.46	1.5504	74.61	64.46	2.6960	127.15	99.79	3.5535	193.94	135.2	5.2090
42.23	36.89	1.4585	77.25	66.38	2.5834	130.66	101.9	3.4812	199.12	137.7	5.1391
43.65	38.25	1.3798	80.13	68.61	3.1920	134.11	103.8	3.4155	204.22	140.4	5.0699
45.00	39.44	1.3133	83.25	70.89	3.0528	137.72	105.9	3.8325			
46.28	40.72	1.2529	86.24	73.04	2.9333	141.51	108.0	3.7588			

Table 18 (Continued)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/J·K^{-1}·mol^{-1})	ΔT/K
					Series 3 (Crystal **II**, **I**)						
206.50	141.5	5.9903	224.10	151.0	5.7377	241.51	163.0	6.4433	260.60	169.4	6.2594
212.45	144.8	5.8989	229.82	154.2	5.6634	247.93	170.0	6.3150	266.89	171.4	6.2075
218.32	147.8	5.8173	235.47	158.0	5.5864	254.27	169.5	6.2882			
					Series 4 (Crystal **II**, **I**)						
231.41	155.1	5.6452	253.51	169.3	5.3703	278.16	176.5	6.0978	302.59	187.5	5.8870
237.04	159.4	5.5580	259.38	169.2	6.2708	284.33	179.4	6.0394	309.47	190.6	7.5179
242.62	164.2	5.4794	265.68	171.1	6.2173	290.45	182.2	5.9858	317.15	194.5	7.4383
248.09	170.1	5.3860	271.94	173.6	6.1582	296.54	184.7	5.9367	324.77	198.3	7.3641
					Series 5 (Crystal **II**, **I**)						
240.77	161.8	1.3702	251.00	170.0	2.0606	258.67	168.6	0.7566	263.44	170.2	1.5011
242.57	164.1	2.1006	253.10	168.8	2.0617	259.86	168.6	0.7546	265.63	171.0	1.5003
244.70	167.1	2.0836	255.20	168.5	2.0607	260.66	169.2	0.7533			
246.80	169.4	2.0696	256.66	168.8	0.7567	261.46	169.3	0.7533			
248.91	171.2	2.0587	257.46	168.6	0.7566	262.25	170.1	0.7499			
					XII. 1,3-Di-*tert*-butylurea (Figure 12)						
					Series 1 (Crystal **II**)						
113.25	133.9	3.7807	135.61	155.6	4.1222	158.98	177.2	3.6982	184.65	200.1	4.1534
116.98	137.5	3.6810	139.69	159.4	4.0352	163.08	180.2	4.4792	193.30	206.4	4.9105
120.61	141.1	3.5837	143.69	163.3	3.9543	167.52	184.1	4.4064	198.18	210.4	4.8470
124.15	144.8	3.4980	147.62	166.3	3.8851	171.90	187.9	4.3400			
127.62	148.0	3.4244	151.47	169.9	3.8177	176.21	191.7	4.2763			
131.44	151.3	4.2215	155.25	173.3	3.7421	180.46	195.6	4.2172			
					Series 2 (Crystal **II**, **I**)						
201.50	212.8	4.8111	232.49	238.2	5.3167	263.78	265.4	5.0024	296.51	315.6	5.4326
206.30	216.6	4.7526	237.82	242.6	5.2584	268.85	269.7	4.9592	301.69	465.0	4.6691
211.04	220.6	4.6973	243.10	247.3	5.2015	273.89	274.6	4.9140	305.66	357.5	3.0750
216.16	224.9	5.5092	248.33	251.3	5.1523	279.32	279.9	5.7067			
221.67	229.5	5.4405	253.52	255.8	5.1016	285.13	285.8	5.6482			
227.11	233.9	5.3756	258.67	260.7	5.0507	290.87	294.1	5.5764			
					Series 3 (Crystal **II**, **I**)						
280.96	280.5	2.0567	293.90	299.7	1.9978	305.66	336.2	1.9091	318.36	297.0	1.9776
283.12	283.3	2.0473	296.04	306.7	1.9825	307.72	324.9	1.9299	320.57	295.2	1.9798
285.28	285.3	2.0396	298.14	325.9	1.9398	309.79	318.9	1.9402	322.79	296.2	1.9763
287.44	287.6	2.0329	300.40	526.0	1.5975	311.89	309.1	1.9584	325.01	296.5	1.9732
289.60	291.0	2.0222	301.70	626.0	1.6616	314.02	303.6	1.9675	327.25	298.4	1.9687
291.75	294.1	2.0150	303.65	361.8	1.8616	316.18	298.7	1.9760			
					Series 4 (Crystal **I**)						
320.76	294.5	2.6522	326.53	297.8	2.6362						
323.64	295.3	2.6453	329.42	300.8	2.6252						
					Series 5 (Crystal **I**)						
322.40	294.5	3.4880									
326.14	297.3	3.4708									
					Series 6 (Crystal **II**, **I**)						
292.09	294.9	2.0111	299.60	497.5	0.4922	302.27	392.9	0.5425	304.90	327.2	0.5795
294.20	301.1	1.9950	300.14	685.4	0.4212	302.90	361.9	0.5595	305.59	318.1	0.5850
296.27	326.0	1.9398	300.64	668.3	0.4344	303.55	349.2	0.5667	306.30	309.7	0.5899
298.33	366.3	1.8584	301.73	745.9	0.4023	304.22	335.6	0.5746			
					Series 7 (Crystal **II**)						
5.66	1.480	0.4742	13.70	11.76	0.6342	22.71	26.91	0.7972	41.73	54.65	1.8413
6.13	1.840	0.4137	14.31	12.74	0.5867	23.64	28.48	1.0487	43.68	57.09	2.0410
6.54	2.147	0.3713	14.94	13.68	0.6381	24.67	30.09	0.9768	45.66	59.48	1.8965
7.03	2.618	0.5750	15.60	14.77	0.6764	25.62	31.61	0.9165	47.92	62.21	2.6075
7.58	3.170	0.5001	16.26	15.90	0.6287	28.03	35.37	1.2170	50.44	64.98	2.4048
8.15	3.769	0.6145	16.98	17.13	0.5858	29.21	37.23	1.1341	53.48	68.40	3.6614
8.73	4.488	0.5370	17.50	17.91	0.6257	30.46	39.32	1.3455	56.98	72.40	3.3299
9.29	5.156	0.5488	18.14	19.05	0.6520	31.77	41.10	1.2662	60.19	76.07	3.0733
10.04	6.190	0.9254	18.79	20.22	0.6125	33.10	43.08	1.3590	63.64	80.02	3.8038
10.91	7.438	0.7935	19.52	21.46	0.8276	34.77	45.40	1.9737	67.32	84.14	3.5455
11.67	8.545	0.7035	20.32	22.90	0.7706	36.66	48.26	1.7977	70.77	87.93	3.3290
12.35	9.566	0.6362	21.08	24.07	0.7257	38.41	50.51	1.6627			
13.02	10.63	0.6944	21.87	25.51	0.8491	40.02	52.64	1.5471			
					Series 8 (Crystal **II**)						
77.74	95.65	2.8573	89.86	109.0	4.2354	101.75	122.0	3.7209	112.83	133.5	4.2566
81.21	99.29	4.0789	94.00	113.5	4.0345	105.41	126.1	3.5941	117.02	137.8	4.1236
85.50	104.0	4.4837	97.95	117.9	3.8650	108.95	129.8	3.4845	121.09	141.7	4.0099

Table 18 (Continued)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K
XIII. Tetraethylurea (Figures 13 and 14)											
Series 1 (Glass)											
5.90	1.424	0.2940	14.87	12.58	0.5327	31.92	41.55	1.0516	70.13	95.65	2.2020
6.18	1.620	0.2701	15.39	13.40	0.5006	32.94	43.14	1.0012	72.83	98.67	2.8138
6.50	1.843	0.3654	15.98	14.39	0.6726	34.02	44.87	1.1474	75.58	102.0	2.6928
6.85	2.136	0.3252	16.63	14.47	0.6259	35.40	47.11	1.6033	78.50	105.5	3.1661
7.22	2.481	0.4153	17.30	16.64	0.7265	36.95	49.64	1.4962	81.54	109.1	2.9479
7.61	2.842	0.3709	18.01	17.82	0.6772	38.40	51.94	1.4073	84.73	112.6	3.4361
8.02	3.239	0.4426	18.81	19.16	0.9117	39.97	54.41	1.7383	88.10	116.3	3.3129
8.51	3.759	0.5309	19.69	20.61	0.8420	41.82	57.19	1.9612	91.35	119.9	3.1978
9.02	4.302	0.4715	20.50	22.13	0.7826	43.72	60.07	1.8312	94.50	123.4	3.0986
9.47	4.861	0.4240	21.35	23.59	0.9392	45.64	62.77	1.9951	97.55	126.8	3.0103
9.88	5.373	0.3879	22.27	25.19	0.8744	47.57	65.56	1.8761	100.78	130.3	3.4690
10.31	5.881	0.4649	23.12	26.60	0.8222	49.40	68.13	1.7761	104.19	133.9	3.3668
10.75	6.463	0.4266	23.92	27.96	0.7774	51.60	71.32	2.6444	107.51	137.3	3.2751
11.17	7.050	0.3944	24.68	29.26	0.7378	54.16	74.93	2.4681	110.73	140.6	3.1929
11.65	7.751	0.5724	25.59	30.84	1.0922	56.56	78.13	2.3258	113.88	143.8	3.1188
12.20	8.526	0.5234	26.65	32.71	1.0164	58.82	81.19	2.2054	116.96	146.8	3.0498
12.71	9.278	0.4833	27.64	34.42	0.9562	60.98	83.95	2.1040	119.97	149.8	2.9883
13.18	9.960	0.4515	28.68	36.09	1.1131	63.28	86.96	2.5115			
13.72	10.81	0.6183	29.76	38.01	1.0394	65.73	90.06	2.3941			
14.32	11.69	0.5722	30.83	39.77	1.1123	68.07	93.05	2.2910			
Series 2 (Glass, Liquid)											
124.97	154.1	3.4229	144.33	173.2	3.0574	159.49	312.5	2.5849	178.75	312.5	4.7965
128.35	157.4	3.3510	147.61	178.2	3.5101	162.05	312.2	2.5754	183.51	313.0	4.7653
131.67	160.6	3.2864	151.07	187.6	3.4034	165.02	312.3	3.4000			
134.92	163.7	3.2239	154.29	232.5	3.0535	169.13	312.3	4.8632			
141.24	170.0	3.1080	156.92	317.7	2.5712	173.96	312.3	4.8293			
Series 3 (Crystal)											
19.97	18.84	0.6110	27.03	31.50	1.0275	35.92	46.92	1.2517	46.43	63.40	1.3611
20.57	19.91	0.5770	28.03	33.30	0.9640	37.24	49.15	1.3801	48.09	65.82	1.9607
21.31	21.19	0.8827	28.97	34.87	0.9125	38.59	51.39	1.3021	50.00	68.62	1.8515
22.16	22.72	0.8198	29.95	36.76	1.0490	39.86	53.44	1.2356	52.11	71.54	2.3663
23.00	24.22	0.8507	30.98	38.55	0.9930	41.07	55.39	1.1777	54.41	74.74	2.2306
23.94	25.88	1.0204	32.04	40.37	1.2766	42.34	57.38	1.3589			
24.93	27.63	0.9491	33.36	42.59	1.1957	43.67	59.43	1.2942			
25.96	29.53	1.1064	34.63	44.72	1.3319	45.03	61.47	1.4225			
Series 4 (Crystal)											
56.58	77.77	2.1124	74.28	99.36	2.8678	99.52	125.4	3.5499	126.41	150.0	4.5606
58.65	80.54	2.0128	77.32	102.8	3.2149	103.03	128.9	3.4388	130.92	153.8	4.4458
60.63	83.08	1.9295	80.48	106.3	3.0773	106.43	132.0	3.3442	135.33	157.7	4.3407
62.96	86.00	2.7381	84.12	109.9	4.1950	110.04	135.4	3.8549	139.64	161.2	4.2474
65.63	89.22	2.5993	88.22	114.1	3.9934	113.86	138.8	3.7503	143.85	164.7	4.1664
68.39	92.56	2.9092	92.14	118.1	3.8219	117.57	142.2	3.6520	147.99	168.0	4.0873
71.34	95.95	3.0049	95.90	121.7	3.6793	121.77	145.7	4.6901	152.05	171.4	4.0143
Series 5 (Crystal)											
156.53	175.3	4.2612	176.89	194.6	3.9086	197.00	216.0	3.8968	218.06	250.2	4.0679
160.74	179.1	4.1826	180.91	198.1	4.1411	201.15	221.0	4.4022	222.02	268.7	3.9276
164.89	183.3	4.0926	185.03	202.3	4.0839	205.50	226.6	4.3292	225.81	296.1	3.7270
168.95	187.0	4.0213	189.08	206.6	4.0202	209.78	232.0	4.2516			
172.95	190.7	3.9651	193.08	211.3	3.9555	213.97	239.5	4.1669			
Series 6 (Liquid)											
288.37	341.4	4.3829	299.09	345.9	5.8187						
293.37	343.3	5.8588	304.76	349.0	5.7765						
Series 7 (Liquid)											
202.99	316.3	4.5545	230.25	320.7	4.6601	252.58	326.4	4.4532	276.06	336.3	4.8373
207.54	316.7	4.5848	234.77	321.7	4.5431	256.98	327.9	4.4565	280.81	338.3	4.8115
212.08	317.2	4.5618	239.26	322.6	4.5225	261.61	329.7	4.9335	285.53	340.3	4.7856
216.60	318.8	4.6148	243.72	324.1	4.4955	266.46	332.1	4.8999			
225.71	319.6	4.5918	248.16	325.1	4.4759	271.28	334.4	4.8660			
Series 8 (Crystal, Liquid)											
220.07	265.6	3.9787	233.77	549.5	2.5844	243.32	325.8	3.5156			
223.93	285.8	3.8223	235.81	961.4	1.7246						
227.58	319.2	3.5967	240.48	655.6	2.2832						
Series 9 (Crystal)											
4.74	0.2766	0.3529	6.34	0.7659	0.2012	8.11	1.827	0.2710	10.69	4.279	0.3527
5.07	0.3420	0.3106	6.58	0.8858	0.2765	8.38	2.026	0.2494	11.03	4.709	0.3273
5.37	0.4105	0.2822	6.85	1.014	0.2538	8.72	2.310	0.4313	11.45	5.224	0.4948
5.64	0.4945	0.2543	7.16	1.177	0.3626	9.14	2.698	0.3568			
5.90	0.5823	0.2301	7.51	1.400	0.3256	9.91	3.435	0.4201			
6.13	0.6659	0.2167	7.83	1.601	0.2947	10.32	3.874	0.3793			

Table 18 (Continued)

T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K	T/K	C_s/(J·K^{-1}·mol^{-1})	ΔT/K
					Series 9						
11.93	5.811	0.4521	14.86	10.12	0.3642	18.00	15.31	0.4529	21.52	21.50	0.6369
12.36	6.427	0.4162	15.22	10.70	0.3448	18.44	16.13	0.4307	22.14	22.60	0.6080
12.77	6.980	0.3852	15.64	11.33	0.4871	18.87	16.94	0.4096	22.92	24.00	0.9455
13.20	7.552	0.4737	16.12	12.14	0.4578	19.36	17.73	0.5685	23.84	25.69	0.8822
13.66	8.293	0.4354	16.56	12.87	0.4334	19.92	18.73	0.5386	24.70	27.23	0.8291
14.08	8.940	0.4076	17.03	13.67	0.5056	20.45	19.63	0.5133			
14.48	9.511	0.3858	17.53	14.50	0.4779	20.95	20.52	0.4904			
					XIV. *n*-Octylurea						
					Series 1						
4.80	0.3182	0.3781	11.82	4.119	0.4399	23.08	18.41	1.0050	43.54	52.00	1.7693
5.17	0.3826	0.3387	12.33	4.583	0.5728	24.06	19.81	0.9324	45.26	54.76	1.6581
5.49	0.4729	0.3015	12.88	5.117	0.5204	24.96	21.30	0.8618	46.88	57.30	1.5654
5.78	0.5491	0.2747	13.39	5.635	0.4785	25.80	22.71	0.8062	48.41	59.66	1.4867
6.12	0.6359	0.3890	13.98	6.220	0.6851	26.68	24.18	0.9459	49.87	61.86	1.4191
6.49	0.7540	0.3487	14.64	6.947	0.6208	27.61	25.62	0.8884	51.51	64.27	1.8524
6.83	0.8989	0.3122	15.23	7.652	0.5645	28.47	26.97	0.8429	53.31	66.98	1.7591
7.17	1.027	0.3554	15.79	8.302	0.5204	29.40	28.62	0.9921	55.20	69.81	2.0201
7.57	1.222	0.4424	16.50	9.176	0.9059	30.42	30.34	1.0472	57.18	72.66	1.9232
8.00	1.418	0.3965	17.37	10.27	0.8190	31.67	32.35	1.4476	59.06	75.50	1.8320
8.46	1.673	0.5065	18.17	11.27	0.7511	33.39	35.16	1.9703	60.86	78.00	1.7587
8.94	1.930	0.4531	18.89	12.30	0.6920	35.27	38.34	1.7831	62.59	80.31	1.6971
9.38	2.210	0.4093	19.71	13.52	0.9309	36.98	41.20	1.6355	64.26	82.50	1.6400
9.84	2.562	0.4995	20.61	14.76	0.8547	38.56	43.85	1.5171	66.25	84.91	2.3429
10.32	2.900	0.4523	21.44	15.92	0.7919	40.04	46.38	1.4170	68.55	87.96	2.2431
11.35	3.709	0.4795	22.21	17.10	0.7373	41.70	48.93	1.9068			
					Series 2						
68.07	87.23	3.2623	104.83	124.7	3.4821	145.04	155.1	3.6872	187.59	183.8	4.2885
71.21	91.11	3.0118	108.27	127.6	3.3884	148.69	157.6	3.6287	191.83	186.6	4.2351
74.38	94.85	3.3368	111.62	130.3	3.3045	152.28	160.3	3.5707	196.01	189.7	4.1819
77.64	98.62	3.1717	115.11	133.1	3.6920	155.83	162.4	3.5229	200.15	192.6	4.1327
80.75	102.1	3.0325	118.75	136.2	3.6008	159.32	164.6	3.4769	203.35	195.6	4.0004
83.72	105.2	2.9137	122.61	139.0	3.4901	163.06	167.0	4.0203	207.31	198.2	3.9666
86.90	108.3	3.4460	126.06	141.3	3.4212	167.03	169.6	3.9628	211.22	200.9	3.9289
90.28	111.5	3.3149	129.76	144.1	3.9784	170.95	172.4	3.9076	215.38	204.2	4.4578
93.87	114.8	3.8553	133.69	146.9	3.8960	174.82	174.9	3.8581	219.77	207.6	4.4074
97.65	118.3	3.7128	137.55	149.7	3.8206	178.94	177.7	4.4066			
101.30	121.5	3.5906	141.33	152.2	3.7535	183.29	180.7	4.3454			
					Series 3						
228.62	213.9	4.8885	242.90	225.3	4.7323						
233.43	217.8	4.8350	247.55	229.5	4.6762						
238.19	221.4	4.7841									
					Series 4						
256.72	237.1	4.6050	274.36	254.6	4.3829	291.36	271.5	4.6817	309.16	291.2	4.4925
261.22	241.2	4.5308	278.63	258.4	4.3376	295.89	276.3	4.6331	313.48	296.7	4.4413
265.66	245.4	4.4812	282.85	262.7	4.2917	300.36	281.1	4.5856	317.75	302.3	4.3914
270.04	249.8	4.4307	287.02	266.9	4.2527	304.79	285.9	4.5426			

Furthermore, the additive calculations of the crystal thermodynamic properties at T = 5−298.15 K for compounds **I**−**XII** and **XIV** were made without taking into consideration the solid-to-solid transitions, which occur for some of the named compounds at temperatures lower than 298.15 K (Tables 13−16). Those calculations show that neglecting the individual solid-to-solid transitions does not result in a great loss of the accuracy of the additive calculation method. Average divergences between the experimental and calculated C_p and $S°(T)$ values for the crystals **I**−**XIV** are, at T = 298.15 K, 3.8% and 2.2%, respectively (Table 17). Probably, it may be explained by the fact that the system of linear equations used to calculate the additive constants becomes more steady due to the extension of the equation systems when we ignore the phase distinctions in the crystals of urea alkyl derivatives (see explanation above). However, tetrasubstituted ureas fuse at T > 230 K, thus reducing the number of equations containing parameters ΔP(CNC). Hence solutions for these parameters are not reliable at T > 230 K, and they are given in parentheses in Tables 13−16.

Literature Cited

(1) Kabo, G. J.; Kozyro, A. A.; Diky, V. V. *J. Chem. Eng. Data* **1995**, *40*, 160.

(2) Vishnyakova, T. P.; Golubeva, I. A.; Glebova, E. V. *Usp. Khim.* **1985**, *54*, 429.

(3) Simirsky, V. V.; Kabo, G. J.; Frenkel, M. L. *J. Chem. Thermodyn.* **1987**, *19*, 1121.

(4) Buck, J. S.; Ferry, C. W. *J. Am. Chem. Soc.* **1936**, *58*, 854.

(5) Michler, W. *Chem. Ber.* **1875**, *8*, 1774.

(6) Rossini, F. D. *Experimental Thermochemistry*; Plenum Press: London, 1956; p 326.

(7) Ruehrwein, R. A.; Huffman, H. M. *J. Am. Chem. Soc.* **1946**, *68*, 1759.

(8) Yarovoi, S. S. *Methods of calculations of physico-chemical properties for hydrocarbons*; Khimia: Moscow, 1978.

(9) Kabo, G. J.; Miroshnichenko, E. A.; Frenkel, M. L.; Kozyro, A. A.; Simirsky, V. V.; Krasulin, A. P.; Vorob'eva, V. P.; Lebedev, Yu. A. *Izv. AN SSSR Ser. Khim.* **1990**, *55*, 750.

(10) Della Gatta, G.; Ferro, D. *Thermochim. Acta* **1987**, *122*, 143.

(11) Zordan, T. A.; Hurkot, D. G.; Peterson, M.; Hepler, L. G.; *Thermochim. Acta* **1972**, *5*, 21.

(12) Vorob'eva, V. P.; Miroshnichenko, E. A. 5 Vses. Konf. po Term. Org. Soed. Tez. Dokl. Sept 22−24, 1987, Kuibyshev (USSR); p 20.

(13) Kozyro, A. A.; Dalidovich, S. V.; Krasulin, A. P. *Zh. Prikl. Khim. (Leningrad)* **1986**, *59*, 1456.
(14) Gambino, M.; Bros, J. P. *Thermochim. Acta* **1988**, *127*, 223.
(15) Kozyro, A. A.; Kabo, G. J.; Krasulin, A. P.; Sevruk, V. M.; Simirsky, V. V.; Sheiman, M. S.; Frenkel, M. L. *J. Chem. Thermodyn.* **1993**, *25*, 1409.
(16) Krasulin, A. P.; Kozyro, A. A.; Dalidovich, S. V. *Zh. Fiz. Khim.* **1986**, *60*, 2580.

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