ELSEVIER

Thermochimica Acta 290 (1996) 13–30

thermochimica
acta

Heat capacities and enthalpies of transitions of 1-methylcyclopentanol and 1-chloro-1-methylcyclopentane in the condensed state

G.J. Kabo *, A.V. Blokhin, A.A. Kozyro, V.V. Diky

Department of Chemistry, Belorussian State University, Leningradskaya 14, Minsk 220080, Belarus

Received 7 May 1996; accepted 8 July 1996

Abstract

Heat capacities and enthalpies of transitions for 1-methylcyclopentanol (I) and 1-chloro-1-methylcyclopentane (II) in the condensed state were measured by vacuum adiabatic calorimetry in interval from 5 to 315 K. It was found that these compounds formed glasses by their cooling from 310 K at a rate $(0.03-0.05)\,\mathrm{K \cdot s^{-1}}$. The crystal I undergoes two solid-to-solid transitions at 281.72 K and 301.47 K and melts at 308.53 K. The correlation between the entropies of transitions of I testifies that it does not form the plastic crystal phase. Two solid-to-solid transitions at 164.20 K and 178.82 K occurred in the crystal II. The fusion temperature of II is 189.05 K. The ratio of the entropy of transition crII → crI to that of fusion for II exceeds 8. This fact confirms that II forms the plastic crystal state even in a very narrow interval from 178.82 to 189.05 K. The thermodynamic characteristics of glassy I and II were obtained and the thermodynamic analysis of the heat capacity jump at T_g and the residual entropies was made for both compounds on the base of possible structural changes of molecules and substances at T_g.

Keywords: 1-chloro-1-methylcyclopentane; Glassy state; 1-methylcyclopentanol; Plastic crystals; Thermodynamic properties

1. Introduction

The present work continues our investigations [1,2,3,4] concerning the influence of ring inversion and internal rotation in molecules of cyclohexane and cyclopentane derivatives on physical, chemical and thermodynamic properties of substances. It was shown in our previous works [3,4] that the approximative constancy for the sum of solid-to-solid transitions and fusion entropies is observed in a series of cyclohexane and cyclopentane derivatives. This rule can be used in some cases to predict thermal behaviour of a number of similar organic crystals. At the same time it was noted that the predicting of an ability to form plastic crystals is very difficult on the base of simple structure analogies in a series of similar substances. Therefore the study of low temperature heat capacity of compounds with potential formation of the plastic crystalline phase is of great interest. Such an investigation is also stimulated by the fact that transition into the plastic crystal state is accompanied by the changings in densities, electric

---

* Corresponding author.

PII S0040-6031(96)03061-4

and optical properties, and conformational compositions of compounds, and these changes, probably, can have practical applications.

The results of measurements of heat capacities and phase transitions enthalpies of 1-methylcyclopentanol (1-MeCPol) and 1-chloro-1-methylcyclopentane (1,1-ClMeCP) in the condensed state at the temperature 5–315 K are represented in this work. The comparison of thermal behaviours of crystals of some structurally similar derivatives of cyclohexane and cyclopentane and their abilities to form plastic crystals was carried out. The thermodynamic data of 1-MeCPol and 1,1-ClMeCP confirm the rule of approximative constancy of sums of all transitions entropies in the condensed state for cyclopentane derivatives. Thermodynamic analysis of the heat capacity changes at glass transition $\Delta_{gl}^{l} C_s$ and the residual entropies $\Delta_{cr}^{gl} S_m^0(0K)$ for 1-MeCPol and 1,1-ClMeCP was made on the base of possible structural changes of molecules at T_g.

2. Experimental.

1-MeCPol was synthesized from methylmagnesiumiodide and cyclopentanone by Grignard reaction. The product of reaction was washed several times with a saturated aqueous solution of sodium bisulfite to remove any unchanged ketone and was dried over anhydrous sodium carbonate during 24h. The yield of 1-MeCPol was about 70%. After twice distillations under reduced pressure at 354 K and 13.3 kPa the purity of 1-MeCPol was determined by g.l.c. (carrier gas–N_2) with a flame-ionization detector and a steel column (l = 3 m; d = 0.004 m; containing 5% polyethylenglycol-1500 on inerton AV-DMCS; at column temperature 323 K). The samples of 1-1MeCPol were previously heated up to 323 K to convert the substance in liquid state. The purity of 1-MeCPol was 99.96% (mass.).

1,1-ClMeCP was synthesized by action of $ZnCl_2$ solution in concentrated hydrochloric acid on 1-MeCPol. Organic layer was washed with an ice-cold concentrated sulphuric acid to remove any olefins formed, then it was washed with 2% sodium carbonate aqueous solution and several times with water. The product obtained was dried by anydrous $CaCl_2$. The yield of 1,1-ClMeCP was about 60%. After twice distillations under reduced pressure at 310 K and 4.6 kPa the purity of 1,1-ClMeCP was 99.94% (mass.) as determined by g.l.c.

The low temperature heat capacities and enthalpies of phase transitions of the compounds at temperatures between 5 and 315 K were measured in a Model TAU-1 vacuum adiabatic calorimeter fabricated by VNIIFTRI (Moscow). The temperature was measured by iron-rhodium resistance thermometer of capsule type ($R_0 = 45.32\,\Omega$), calibrated also in VNIIFTRI (Moscow). The probable error of the molar heat capacity values $C_{sat,m}$ is considered to be $\pm 4 \cdot 10^{-3} \cdot C_{sat,m}$ over the temperature range 40 to 315 K. This error becomes larger when measurements are performed at $T < 40$ K, and it is $2 \cdot 10^{-2} \cdot C_{sat.m}$ at liquid-He temperatures. The sample masses imployed in these studies are 0.76019 g for 1-MeCPol and 0.52757 g for 1,1-ClMeCP. The accuracy of the calorimeter was verified by measurements of heat capacity of benzoic acid (K–1) and of high-purity copper. The reliability of our calorimeter is also confirmed by a good agreement of independent experimental results of heat capacities and transitions enthalpies of chlorocyclohexane [1,5]. A more detailed description of the calorimeter was made in an earlier publication [6].

3. Results.

It was found through the present experiments that these compounds formed glasses by cooling of their liquids from 310 K at a rate (0.03 to $0.05\,K \cdot s^{-1}$). Experimental values of the molar heat capacities at saturated vapour pressure $C_{sat,m}$ of 1-MeCPol and 1,1-ClMCP are represented in Tables 1 and 2 and in Figs. 1, 2 and 3, respectively. Extrapolation of the heat capacities of the investigated compounds to 0 K was made using Debye equation: $C_{v,m} = 3 \cdot R \cdot D.\ (\theta_D/T)$. The characteristic Debye temperature values were determined from $C_{sat,m}$ values near 5 K and they are $\theta_D = 91.6$ K and $\theta_D = 93.8$ K for crystalline and glassy 1-MeCPol, respectively, and $\theta_D = 89.4$ K and $\theta_D = 69.7$ K for crystalline and glassy 1,1-ClMeCP, respectively.

It was established that a spontaneous crystallization of glassy 1-MeCPol took place at temperatures

Table 1
Experimental molar heat capacities at vapour-saturation pressure for 1-methylcyclopentanol. (R = 8.31451 J·K^{-1}·mol^{-1}).

$\frac{\langle T \rangle}{K}$	$\frac{C^{a}_{sat,m}}{R}$	$\frac{\langle T \rangle}{K}$	$\frac{C^{a}_{sat,m}}{R}$	$\frac{\langle T \rangle}{K}$	$\frac{C^{a}_{sat,m}}{R}$
Series 1	(glass).	48.72	4.616	180.52	12.56
6.06	0.06053	50.45	4.770	184.74	12.79
6.43	0.07462	52.03	4.899	189.18	13.23
6.84	0.09230	53.67	5.012	193.55	13.56
7.29	0.1094	55.62	5.163	197.85	13.91
7.68	0.1368	57.85	5.340	201.47	14.20
8.10	0.1567	59.50	5.457	206.26	14.67
8.55	0.1864	61.26	5.567	210.38	15.07
9.03	0.2134	63.15	5.697	214.44	15.49
9.53	0.2592	64.96	5.829	218.44	15.94
9.99	0.2916	66.76	5.944	222.67	16.41
10.47	0.3346	68.63	6.060	227.12	16.94
11.09	0.3922	70.58	6.189	231.50	17.44
11.73	0.4589	72.93	6.345	235.83	17.99
12.31	0.5165	75.68	6.526	240.12	18.52
12.84	0.5601	78.32	6.693	244.38	20.17
13.48	0.6420	80.87	6.847	Series 2	
14.22	0.7309	83.60	7.004	(crystal III)	
14.89	0.8131	86.70	7.170	5.40	0.04577
15.50	0.8846	89.49	7.324	5.79	0.05718
16.21	0.9718	92.19	7.434	6.14	0.07001
17.01	1.081	94.73	7.641	6.55	0.08278
17.89	1.205	97.10	7.763	6.99	0.1049
18.86	1.334	99.67	7.929	7.38	0.1248
19.73	1.454	102.99	8.100	7.80	0.1413
21.13	1.643	106.77	8.304	8.25	0.1729
22.01	1.761	110.44	8.524	8.82	0.2059
23.14	1.905	114.01	8.720	9.46	0.2536
24.34	2.055	115.53	8.801	10.01	0.3015
25.44	2.214	117.49	8.918	10.54	0.3478
26.46	2.329	118.77	8.994	11.05	0.3835
27.57	2.485	121.96	9.163	11.60	0.4421
28.73	2.609	125.08	9.268	12.17	0.4979
29.82	2.751	128.15	9.483	12.81	0.5651
30.96	2.900	131.51	9.674	13.50	0.6402
32.19	3.017	135.15	9.880	14.22	0.7188
33.49	3.158	142.13	10.26	14.97	0.8054
34.85	3.309	145.38	10.43	15.65	0.8884
36.26	3.470	148.59	10.63	16.38	0.9854
37.59	2.922	152.05	10.80	17.17	1.080
38.85	3.731	155.75	11.04	17.89	1.168
40.06	3.870	159.39	11.25	18.70	1.259
41.43	3.985	162.98	11.45	19.58	1.386
43.09	4.142	166.52	11.68	20.39	1.491
44.98	4.301	170.01	11.90	21.15	1.589
46.90	4.458	176.87	12.34	22.09	1.702

Table 1 (*Continued*)

$\langle T \rangle$/K	$C^{a}_{sat,m}/R$	$\langle T \rangle$/K	$C^{a}_{sat,m}/R$	$\langle T \rangle$/K	$C^{a}_{sat,m}/R$
23.20	1.846	Series 3		281.21	42.53
24.22	1.965	(crystal III)		281.52	53.41
25.17	2.087	115.61	8.630	281.64	49.40
26.20	2.229	118.98	8.801	Series 4	
27.28	2.336	122.28	8.984	(crystal II)	
28.54	2.483	125.75	9.197	281.90	36.67
29.95	2.681	129.38	9.367	282.05	33.23
31.34	2.819	132.93	9.539	282.47	27.67
32.73	2.998	136.41	9.780	283.00	26.28
34.19	3.119	139.88	9.917	284.41	26.53
35.69	3.291	143.34	10.11	285.84	26.55
37.23	3.439	146.99	10.31	287.21	26.67
38.81	3.602	150.83	10.53	289.51	27.13
40.98	3.804	154.61	10.71	291.46	27.96
44.15	4.081	158.33	10.92	293.38	28.96
47.48	4.352	162.30	11.14	295.25	30.45
50.50	4.620	166.52	11.37	297.08	32.53
54.13	4.880	170.68	11.60	298.79	35.77
57.15	5.123	174.79	11.84	300.40	41.01
59.98	5.329	178.82	12.07	301.35	53.84
62.63	5.541	182.81	12.30	Series 5	
65.46	5.720	186.74	12.56	(Crystal I)	
68.46	5.909	188.24	12.64	301.72	42.49
71.31	6.100	194.47	13.05	302.22	41.09
74.03	6.273	198.56	13.32	303.21	47.31
76.64	6.429	202.90	13.62	303.64	54.01
79.15	6.583	207.18	13.90	Series 6	
81.21	6.711	211.42	14.23	(liquid)	
82.85	6.798	215.60	14.42	308.22	50.97
85.03	6.911	220.05	14.87	308.48	39.87
87.75	7.089	224.74	15.26	308.58	29.98
91.01	7.277	229.37	15.68	309.63	30.07
93.61	7.411	233.96	16.06	311.54	30.17
96.44	7.568	238.52	16.52	313.43	30.57
99.52	7.729	243.02	16.92	315.31	30.85
102.85	7.916	247.45	17.42		
106.41	8.117	251.81	17.90		
109.88	8.310	256.40	18.29		
113.26	8.491	261.18	19.25		
116.56	8.668	265.83	20.20		
119.80	8.854	268.68	21.11		
120.79	8.859	272.52	21.74		
123.98	9.028	276.32	22.68		
127.47	9.220	278.92	23.70		
131.22	9.412	280.32	24.49		

---

[a] Average heat capacity in the temperature range ΔT with the mean temperature $\langle T \rangle$.

Table 2
Experimental molar heat capacities at vapour-saturation pressure for 1-chloro-1-methylcyclopentane ($R = 8.31451\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$).

$\langle T \rangle / \mathrm{K}$	$C^{\mathrm{a}}_{\mathrm{sat,m}} / R$	$\langle T \rangle / \mathrm{K}$	$C^{\mathrm{a}}_{\mathrm{sat,m}} / R$	$\langle T \rangle / \mathrm{K}$	$C^{\mathrm{a}}_{\mathrm{sat,m}} / R$
Series 1		38.05	4.719	9.06	0.2419
(glass).		39.34	4.846	9.52	0.2793
5.05	0.07917	42.62	5.047	10.02	0.3243
5.26	0.09663	44.28	5.279	10.54	0.3810
5.51	0.1018	45.98	5.418	11.09	0.4376
5.79	0.1313	47.73	5.517	11.59	0.4834
6.04	0.1611	49.34	5.732	12.13	0.5495
6.27	0.1668	50.89	5.847	12.70	0.6260
6.50	0.1874	53.44	6.010	13.23	0.6890
6.76	0.1969	56.40	6.235	13.82	0.7757
7.06	0.2521	58.68	6.399	14.49	0.8565
7.34	0.2581	60.85	6.537	15.10	0.9306
7.63	0.2903	63.29	6.673	15.70	1.031
7.95	0.3316	65.99	6.866	16.28	1.116
8.31	0.3694	68.51	7.080	16.97	1.227
8.69	0.4089	73.68	7.345	17.76	1.343
9.12	0.4556	76.76	7.500	18.63	1.484
9.59	0.5265	79.71	7.667	19.58	1.637
10.10	0.6009	82.56	7.914	20.59	1.812
10.63	0.6490	85.81	8.086	21.67	1.983
11.11	0.7544	89.40	8.321	22.65	2.131
11.62	0.7972	92.85	8.498	23.57	2.269
12.15	0.8940	96.22	8.741	24.43	2.412
12.64	0.9670	99.54	8.865	25.23	2.523
13.16	1.060	102.80	8.995	26.16	2.656
13.71	1.096	111.96	9.483	27.20	2.815
14.29	1.246	114.78	9.718	28.18	2.944
14.91	1.314	117.69	9.928	29.12	3.088
15.47	1.398	123.75	10.22	30.03	3.225
16.14	1.542	127.31	10.50	30.88	3.468
16.97	1.695	130.80	10.83	31.69	3.452
18.86	1.925	134.23	11.38	33.43	3.730
19.71	2.166	137.63	14.53	34.76	3.865
20.51	2.304	Series 2		36.27	4.056
21.45	2.453	(crystal III)		37.70	4.227
22.70	2.665	5.15	0.03829	39.04	4.376
25.23	3.056	5.44	0.04783	40.45	4.507
26.36	3.215	5.75	0.06110	41.92	4.655
27.42	3.366	6.09	0.07313	43.45	4.814
28.42	3.497	6.44	0.08525	45.19	4.987
29.37	3.642	6.81	0.1022	46.98	5.144
32.07	4.016	7.21	0.1223	48.68	5.273
33.72	4.238	7.67	0.1439	50.29	5.423
35.26	4.413	8.18	0.1783	52.57	5.633
36.70	4.590	8.64	0.2139	55.47	5.863

Table 2 (*Continued*)

$\langle T \rangle$ / K	$C^{a}_{sat,m}$ / R	$\langle T \rangle$ / K	$C^{a}_{sat,m}$ / R	$\langle T \rangle$ / K	$C^{a}_{sat,m}$ / R
8.64	0.2139	25.23	2.523	63.62	6.501
66.77	6.729	Series 3		164.75	14.94
69.74	6.948	(crystal III)		166.41	13.60
73.62	7.115	118.23	10.02	167.91	13.29
77.61	7.424	121.42	10.19	169.47	13.41
80.67	7.696	124.53	10.43	Series 5	
83.61	7.844	127.57	10.59	(crystal II)	
86.42	8.146	130.57	10.93	160.99	12.50
89.14	8.242	133.89	11.01	161.91	12.64
92.16	8.407	137.55	11.26	162.82	12.71
95.46	8.679	141.15	11.44	163.73	12.79
98.66	8.889	144.68	11.70	164.63	12.91
101.76	9.026	149.12	12.29	165.52	13.05
104.78	9.214	151.88	12.53	166.41	13.07
107.90	9.401	154.61	12.84	167.73	13.38
114.29	9.837	157.28	13.34	171.20	14.18
117.38	9.932	159.05	13.57	172.90	15.02
120.82	10.12	159.91	13.75	174.55	16.35
124.33	10.43	160.76	13.92	176.16	19.37
127.77	10.56	161.63	14.07	177.57	27.41
131.13	10.81	162.48	14.39	Series 6	
134.43	11.14	163.33	15.06	(crystal I)	
137.68	11.35	164.20	21.44	179.09	20.10
144.05	11.64	Series 4		180.80	18.58
147.20	11.87	(crystal II)		182.33	18.44
		164.26	18.75	183.75	19.98
184.64	21.75	246.90	20.22	293.32	21.47
185.48	25.07	251.99	20.31	299.84	21.68
186.26	29.59	Series 8		306.39	21.96
186.98	36.70	(liquid).			
187.48	43.34	193.32	19.24		
188.61	40.09	197.63	19.28		
188.90	21.23	201.93	19.29		
Series 7		206.40	19.35		
(liquid).		210.68	19.47		
189.18	19.05	215.38	19.57		
192.21	19.20	220.53	19.65		
196.49	19.29	225.64	19.79		
200.76	19.32	230.74	19.93		
205.01	19.40	235.83	20.00		
209.24	19.49	240.95	20.15		
213.46	19.57	246.87	20.30		
217.69	19.64	253.53	20.45		
221.92	19.75	260.20	20.60		
226.57	19.85	266.89	20.76		
236.73	20.04	273.60	20.79		
241.81	20.12	280.18	20.93		

[a] Average heat capacity in the temperature range ΔT with the mean temperature $\langle T \rangle$.

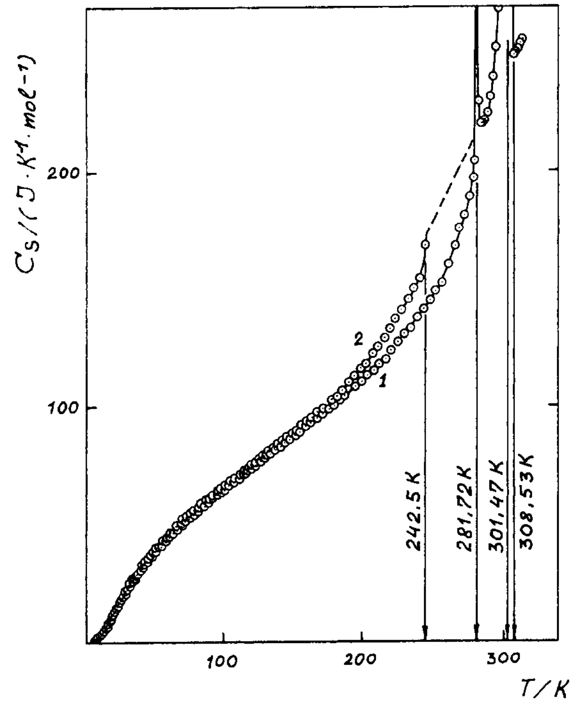

Fig. 1. The temperature dependence of the molar heat capacity of 1-methylcyclopentanol in the condensed state at saturation. Curve 1 is for crystalline 1-methylcyclopentanol and curve 2 is for glassy compound.

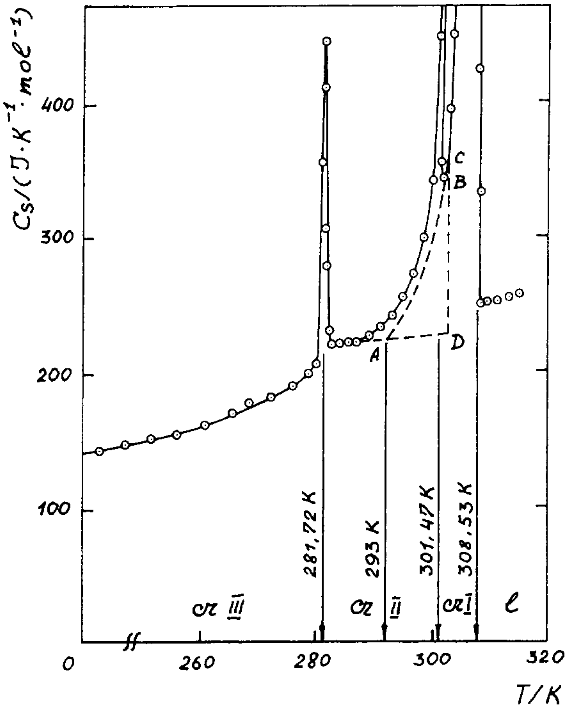

Fig. 2. The temperature dependence of the molar heat capacity of 1-methylcyclopentanol in the condensed state at saturation in interval from 240 K to 320 K and a division of enthalpies sum $(\Delta_{\mathrm{crII}}^{\mathrm{crI}}H_{\mathrm{m}}^{0} + \Delta_{\mathrm{crI}}^{\mathrm{l}}H_{\mathrm{m}}^{0})$. Points A, B and C correspond to the temperatures $T = 293$ K, $T = 302.22$ K and the final temperature T_f in experiments of determination of the molar enthalpy of solid-to-solid transition crII → crI (Table 6), respectively. Point D is the intersection point of a perpendicular dropped from point C on the absciss axis and curve of the heat capacity temperature dependence of phase crI (Eq. 2).

above $T = 244$ K. Therefore to obtain a crystalline modification of 1-MeCPol, the calorimeter was cooled from 310 K to 220–225 K, then it was heated up to 260–265 K and was maintained at these temperatures during 2 to 3 h while a complete crystallization of 1-MeCPol sample occurred.

The fusion temperature of 1-MeCPol determined from fractional-melting experiments is 308.53 K. It was found that this compound undergoes two solid-to-solid transitions at 281.72 K and 301.47 K. The results of calorimetric determinations of these transitions enthalpies for 1-MeCPol are given in Table 3. The uncertainties of the molar enthalpies of transitions for 1-MeCPol as well as for 1,1-ClMeCP were calculated as a product of standard deviations and Student coefficients corresponding to the number of measurements for a 95 per cent confidence interval. The heat-capacity baselines for crystalline phases crIII and crII and liquid of 1-MeCPol are expressed by the following equations, respectively:

$$C_{\mathrm{p,m}}(\mathrm{crIII})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = -49.33 + 7.84 \cdot 10^{-1} \cdot (T/\mathrm{K}) \quad (1)$$

$$C_{\mathrm{p,m}}(\mathrm{crII})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 21.10 + 6.99 \cdot 10^{-1} \cdot (T/\mathrm{K}) \quad (2)$$

$$C_{\mathrm{p,m}}(\mathrm{l})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = -122.56 + 1.20 \cdot (T/\mathrm{K}) \quad (3)$$

It was almost impossible to measure the heat capacity of crI because the temperatures of solid-to-solid transition crII → crI at 301.47 K and of fusion at 308.53 K for 1-MeCPol are very close (Fig. 2).

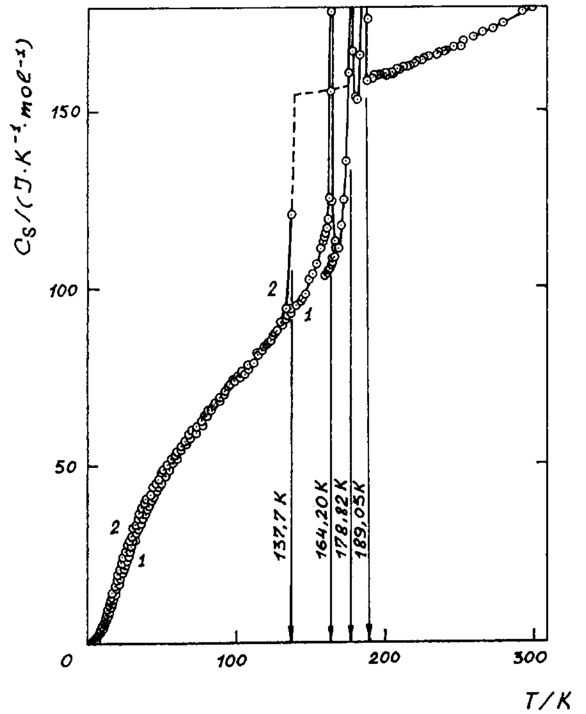

Fig. 3. The temperature dependence of the molar heat capacity of 1-chloro-1-methylcyclopentane in the condensed state at saturation. Curve 1 is for crystalline 1-chloro-1-methylcyclopentane and curve 2 is for glassy compound.

That is why it was supposed in the following calculations that the heat capacities of crII and crI of 1-MeCPol are expressed by the same Eq. (2).

Six independent experiments were made to obtain the molar enthalpies of transitions crII→crI and crI→l for 1-MeCPol. The former three calorimetric experiments were carried out to determine the sum of the molar enthalpies of these transitions (Table 3). The average value of this sum is $\langle(\Delta_{\mathrm{crII}}^{\mathrm{crI}}H_{\mathrm{m}}^{0}+\Delta_{\mathrm{crI}}^{\mathrm{l}}H_{\mathrm{m}}^{0})\rangle=(10413\pm 6)\,\mathrm{J\cdot mol^{-1}}$. Then the latter three experiments were made to obtain the molar enthalpy of transition at 301.47 K (Table 3) and thus to separate the enthalpies sum by two individual contributions. The heat quantity supplied to the calorimeter was chosen so that the final temperature T_f, corresponding to point C in Fig. 2, differs slightly from 302.22 K. The latter temperature conforms to a minimum value of the anomalous heat capacity in the region from 301.47 to 308.53 K. It was assumed that 1-MeCPol began to melt at 293 K. Then the heat quantity q_2 (Table 3), corresponding to an area of figure ABCD in Fig. 2, should be attributed to the fusion of the sample. By such a division of the enthalpies sum $(\Delta_{\mathrm{crII}}^{\mathrm{crI}}H_{\mathrm{m}}^{0}+\Delta_{\mathrm{crI}}^{\mathrm{i}}H_{\mathrm{m}}^{0})$, the following values of the molar enthalpies of transition crII→crI and of fusion of 1-MeCPol were obtained, respectively: $\Delta_{\mathrm{crII}}^{\mathrm{crI}}H_{\mathrm{m}}^{0}(301.47\,\mathrm{K})=(1820\pm 4)\,\mathrm{J\cdot mol^{-1}}$ and $\Delta_{\mathrm{crI}}^{\mathrm{l}}H_{\mathrm{m}}^{0}(308.53\,\mathrm{K})=(8593\pm 7)\,\mathrm{J\cdot mol^{-1}}$. The corresponding molar entropies of transitions are, respectively: $\Delta_{\mathrm{crII}}^{\mathrm{crI}}S_{\mathrm{m}}^{0}(301.47\,\mathrm{K})=(6.04\pm 0.01)\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and $\Delta_{\mathrm{crI}}^{\mathrm{l}}S_{\mathrm{m}}^{0}(308.53\,\mathrm{K})=(27.86\pm 0.02)\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. The relative entropy values testifies that 1-MeCPol does not form plastic crystal phase in spite of the existence of two solid-to-solid transitions because the molar entropy of fusion is substantially higher than the molar entropy of transition crII→crI [7,8].

As it was mentioned above, a spontaneous crystallization of glassy 1-MeCPol took place at $T>244\,\mathrm{K}$. It was also unable to measure the heat capacities of 1-MeCPol in the supercooled liquid state since the first calorimetric experiment induced crystallization of the supercooled phase. To obtain the complete glass transition curve and to estimate the residual entropy for 1-MeCPol it was suggested that:

1. The same Eq. (3) describes the temperature dependence of the heat capacities of suprecooled liquid from 308.52 K to 245.4 K and liquid at $T>308.53\,\mathrm{K}$.
2. The glass transition temperature $T_g=245.4\,\mathrm{K}$ was found as a point of intersection of two curves, which correspond to the function $C_{\mathrm{p,m}}=f(T)$ for supercooled liquid (Eq. (3)) and the function $C_{\mathrm{p,m}}=f(T)$ derived from the experimental heat capacities of glassy 1-MeCPol in interval from 231.5 to 244.4 K.

It is necessary to note that the heat capacities values of liquid 1-MeCPol were measured in a very narrow temperature interval from 309 to 315 K and they considerably depend on temperature values (Figs. 1 and 2). Though such a "sharp" temperature dependence of the heat capacity for liquid occurred also in the case of cyclopentanol [3], the derived characteristics of glassy 1-MeCPol, given in Table 7, should be regarded as highly approximative ones.

Table 3
Experimental determinations of the molar enthalpies of transitions for 1-methylcyclopentanol in condensed state. T_i. is the initial temperature; T_f is the final temperature; q is the heat suppplied; q_1 is the heat required to heat the calorimetric container; q_2 is the heat attributed to fusion of sample. Mass of the sample is 0.76019 g.

N	T_i/K	T_f/K	q/J	q_1/J	q_2/J	ΔH^0_m/J·mol^{-1}
Solid-to-solid transition crIII → crII at $T = 281.72$ K.						
1	257.63	284.15	92.330	38.968	—	2593
2	258.02	284.74	93.204	39.280	—	2597
3	258.17	284.82	93.190	39.164	—	2617
4	258.20	284.89	93.353	39.222	—	2621
5	258.19	284.48	92.049	38.636	—	2613
6	258.17	284.50	92.083	38.682	—	2606
$\langle \Delta_{\mathrm{crIII}}^{\mathrm{crII}} H^0_m(281.72\,\mathrm{K})\rangle = (2608 \pm 12)\,\mathrm{J\cdot mol^{-1}}$						
Solid-to-solid transition crII → crI at $T = 301.47$ K and fusion crI → l at $T = 308.53$ K						
1	288.56	311.00	152.620	34.066	—	10416
2	288.05	309.74	149.915	32.916	—	10411
3	288.10	310.89	153.686	34.594	—	10412
$\langle \Sigma \Delta H^0_m \rangle = (10414 \pm 6)\,\mathrm{J\cdot mol^{-1}}$						
Solid-to-solid transition crII → crI at $T = 301.47$ K.						
1	288.52	302.88	64.789	21.703	4.455	1820
2	288.94	303.29	65.260	21.695	4.934	1818
3	288.63	303.00	64.993	21.729	4.591	1821
$\langle \Delta_{\mathrm{crII}}^{\mathrm{crI}} H^0_m(301.47\,\mathrm{K})\rangle = (1820 \pm 4)\,\mathrm{J\cdot mol^{-1}}$						

The residual entropy of glassy 1-MeCPol is $\Delta_{\mathrm{cr}}^{\mathrm{gl}} S^0_m(0\,\mathrm{K}) = 32.01\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

The smoothed heat capacities and derived thermodynamic functions for 1-MeCPol in the condensed state are given in Table 4. Values of the basic standard molar thermodynamic functions of crystalline 1-MeCPol (crII) at 298.15 K are tabulated in Table 8.

As noted earlier, 1,1-ClMeCP turns into the glassy state at cooling of liquid. It was found that a spontaneous crystallization of glassy sample took place at temperatures above $T = 137$ K. In order to crystallize the sample completely, the calorimeter was kept in the temperature range from 150 to 155 K for 2–3 h, as in the case of 1-MeCPol.

Two solid-to-solid transitions at 164.20 K and 178.82 K occurred in crystalline 1,1-ClMeCP. Besides, it was found that the crII had a tendency towards supercooling down to 160 K at a cooling rate (0.03 to 0.05) $\mathrm{K\cdot s^{-1}}$. A spontaneous exothermic transition crII → crIII took place at $T < 160$ K. The fusion temperature of 1,1-ClMeCP was obtained from fractional-melting experiments and it is 189.05 K. Calorimetric determinations of transitions enthalpies of 1,1-ClMeCP are given in Table 5. The heat-capacity baselines for crIII, crII and liquid are expressed by the following equations, respectively:

$$C_{\mathrm{p,m}}(\mathrm{crIII})/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 17.06 + 5.57\cdot 10^{-1}\cdot (T/\mathrm{K}) \quad (4)$$

$$C_{\mathrm{p,m}}(\mathrm{crII})/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = -46.97 + 9.38\cdot 10^{-1}\cdot (T/\mathrm{K}) \quad (5)$$

$$C_{\mathrm{p,m}}(\mathrm{l})/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 157.95 - 1.10\cdot 10^{-1}\cdot (T/\mathrm{K}) + 6.16\cdot 10^{-4}\cdot (T^2/\mathrm{K}^2) \quad (6)$$

It was impossible to obtain the temperature dependence of the heat capacity of crI because of a closeness of temperatures between the transition crII → crI $T_{\mathrm{trs}} = 178.82$ K and fusion $T_{\mathrm{fus}} = 189.05$ K for 1,1-ClMeCP. It was suggested in calculations

Table 4
Molar thermodynamic functions for 1-methylcyclopentanol.
($M = 100.161\ \mathrm{g{\cdot}mol^{-1}}$; $R = 8.31451\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)

T/K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^0}{R}$	$\frac{\Delta_0^T H_m^0}{RT}$	$\frac{\Phi_m^0}{R}$
5	0.03587	0.01179	0.008900	0.003007
10	0.2942	0.09646	0.07264	0.02370
20	1.490	0.6354	0.4596	0.1758
30	2.767	1.487	1.021	0.4662
40	3.846	2.436	1.597	0.8393
50	4.732	3.392	2.138	1.255
60	5.481	4.323	2.634	1.689
80	6.763	6.081	3.511	2.570
100	7.933	7.717	4.280	3.438
120	9.057	9.264	4.983	4.281
140	10.14	10.74	5.642	5.099
160	11.31	12.17	6.276	5.894
180	12.52	13.57	6.902	6.669
200	14.10	14.97	7.539	7.429
220	16.10	16.40	8.224	8.179
240	18.52	17.90	8.978	8.927
242.5	19.30	18.10	9.080	9.020
		Supercooled liquid.		
245	20.51	18.30	9.190	9.114
260	22.83	19.60	9.915	9.681
280	25.72	21.39	10.94	10.45
300	28.61	23.27	12.02	11.24
308.53	29.84	24.09	12.50	11.59
		Crystal III.		
5	0.03854	0.01275	0.009622	0.003247
10	0.2976	0.1011	0.07577	0.02526
20	1.439	0.6307	0.4528	0.1779
30	2.666	1.452	0.9906	0.4610
40	3.706	2.365	1.543	0.8222
50	4.576	3.289	2.065	1.223
60	5.331	4.191	2.548	1.643
80	6.622	5.908	3.411	2.497
100	7.767	7.510	4.169	3.341
120	8.856	9.023	4.860	4.163
140	9.924	10.47	5.507	4.961
160	11.01	11.86	6.126	5.738
180	12.14	13.23	6.731	6.494
200	13.40	14.57	7.333	7.234
220	14.87	15.91	7.950	7.962
240	16.70	17.28	8.600	8.681
260	18.58	18.69	9.296	9.397
280	20.47	20.14	10.03	10.11
281.72	20.63	20.26	10.09	10.17
		Crystal II.		
281.72	26.22	21.38	11.20	10.17
298.15	27.60	22.90	12.07	10.83

Table 4. (*Continued*)

T/K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^0}{R}$	$\frac{\Delta_0^T H_m^0}{RT}$	$\frac{\Phi_m^0}{R}$
300	27.76	23.07	12.17	10.91
301.47	27.88	23.21	12.24	10.97
		Crystal 1.		
301.47	27.88	23.94	12.97	10.97
305	28.18	24.26	13.14	11.12
308.53	28.47	24.59	13.32	11.27
		Liquid.		
308.53	29.84	27.94	16.67	11.27
310	30.06	28.08	16.73	11.35
315	30.78	28.57	16.95	11.62

Table 5

Experimental determinations of the molar enthalpies of transitions for 1-chloro-1-methylcyclopentane in the condensed state. T_i. is the initial temperature; T_f is the final temperature; q is the heat suppplied; q_1 is the heat required to heat the calorimetric container. Mass of the sample is 0.52757 g.

N	$\frac{T_i}{K}$	$\frac{T_f}{K}$	$\frac{q}{J}$	$\frac{q_1}{J}$	$\frac{\Delta H_m^0}{J \cdot mol^{-1}}$
Solid-to-solid transition crIII → crII at T = 164.20 K.					
1	148.67	166.41	36.972	22.992	1286
2	148.16	166.83	38.636	24.193	1293
3	148.24	167.23	39.134	24.619	1274
4	148.06	166.67	38.430	24.095	1277
$\langle \Delta_{crIII}^{crII} H_m^0(164.20\ K) \rangle = (1283 \pm 14)\ J \cdot mol^{-1}$					
Solid-to-solid transition crII → crI at T = 178.82 K.					
1	166.32	183.53	58.552	23.496	5723
2	166.52	183.46	58.031	23.124	5722
3	166.97	184.34	59.070	23.829	5712
4	167.34	184.64	58.899	23.799	5675
5	166.76	184.18	58.972	23.864	5684
6	166.33	184.17	59.805	24.432	5697
$\langle \Delta_{crII}^{crI} H_m^0(178.82\ K) \rangle = (5702 \pm 21)\ J \cdot mol^{-1}$					
Fusion crI → l at T = 189.05 K.					
1	183.86	195.08	26.898	15.801	736.0
2	183.65	194.38	25.823	15.094	733.7
3	184.56	195.50	26.261	15.347	734.7
4	184.85	195.94	26.507	15.522	725.4
5	184.40	195.31	26.196	15.314	734.2
6	184.38	195.47	26.528	15.571	722.4
$\langle \Delta_{crI}^{l} H_m^0(189.05\ K) \rangle = (731 \pm 6)\ J \cdot mol^{-1}$					

Table 6
Molar thermodynamic functions for 1-chloro-1-methylcyclopentane.
($M = 118.606\,\mathrm{g\cdot mol^{-1}}$; $R = 8.31451\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$)

T/K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^0}{R}$	$\frac{\Delta_0^T H_m^0}{RT}$	$\frac{\Phi_m^0}{R}$
		Glass.		
5	0.0846	0.0286	0.0214	0.0072
10	0.5775	0.2148	0.1591	0.0557
20	2.192	1.087	0.7551	0.3324
30	3.741	2.282	1.503	0.7794
40	4.909	3.529	2.217	1.311
50	5.745	4.717	2.842	1.875
60	6.476	5.832	3.389	2.442
80	7.737	7.870	4.321	3.549
100	8.894	9.723	5.122	4.601
120	9.945	11.44	5.841	5.600
135	11.86	12.69	6.368	6.317
137.7	14.63	12.94	6.500	6.445
		Supercooled liquid.		
140	18.27	13.22	6.662	6.554
160	18.78	15.71	8.164	7.545
180	19.02	17.93	9.357	8.578
189.05	19.15	18.87	9.822	9.049
		Crystal III.		
5	0.04062	0.01359	0.01022	0.003368
10	0.3248	0.1084	0.08130	0.02706
20	1.709	0.7175	0.5197	0.1978
30	3.223	1.703	1.174	0.5293
40	4.465	2.808	1.848	0.9600
50	5.409	3.910	2.470	1.440
60	6.225	4.971	3.030	1.941
80	7.616	6.955	4.005	2.950
100	8.931	8.798	4.860	3.937
120	10.13	10.53	5.640	4.893
140	11.43	12.19	6.372	5.818
160	12.77	13.80	7.088	6.7161
164.20	13.05	14.14	7.237	6.902
		Crystal II.		
164.20	12.87	15.08	8.177	6.902
170	13.53	15.54	8.348	7.188
178.82	14.52	16.25	8.628	7.618
		Crystal I.		
178.82	18.44	20.08	12.46	7.618
180	18.44	20.20	12.50	7.700
189.05	18.44	21.11	12.79	8.320
		Liquid.		
189.05	19.15	21.57	13.25	8.320
200	19.32	22.65	13.58	9.075
220	19.67	24.51	14.12	10.40
240	20.09	26.24	14.60	11.64
260	20.57	27.87	15.04	12.83
280	21.10	29.41	15.45	13.96
298.15	21.64	30.75	15.81	14.94
300	21.70	30.89	15.85	15.04

Table 7
Thermodynamic characteristics for glassy 1-methylcyclopentanol (1-MeCPol) and 1-chloro-1-methycyclopentane (1,1-ClMeCP). T_g is the glass transition temperature, $\Delta_{gl}^{l}T$ is the temperature region of glass transition, $\Delta_{gl}^{l}C_s$ is the heat capacity jump at T_g, $\Delta_{res}S_m^0$ is the residual entropy.

Compounds	T_g/K	$\Delta_{gl}^{l}T$/K	$\Delta_{gl}^{l}C_s$/$J \cdot mol^{-1} \cdot K^{-1}$	$\Delta_{res}S_m^0$/$J \cdot mol^{-1} \cdot K^{-1}$
1-MeCPol	242.5	245.4 – 235.8	13.0	32.01
1,1-ClMeCP	137.7	140.2 – 127.3	61.1	22.45

that the heat capacity of crI remains constant in interval 178.82–189.05 K and it is the minimal heat capacity value of 1,1-ClMeCP $C_{p,m}(\mathrm{crI}) = 153.31\,J \cdot K^{-1} \cdot mol^{-1}$ measured in this interval. Average values of the molar enthalpies of transitions for 1,1-ClMeCP are, respectively: $\Delta_{crIII}^{crII}H_m^0(164.20\,K) = (1283 \pm 14)\,J \cdot mol^{-1}$, $\Delta_{crII}^{crI}H_m^0(178.82\,K) = (5702 \pm 21)\,J \cdot mol^{-1}$, and $\Delta_{crI}^{l}H_m^0(189.05\,K) = (731 \pm 6)\,J \cdot mol^{-1}$. The ratio of the molar entropy of transition $\Delta_{crII}^{crI}S_m^0(178.82\,K) = (31.89 \pm 0.02)\,J \cdot K^{-1} \cdot mol^{-1}$ to the molar entropy of fusion $\Delta_{crI}^{l}S_m^0(189.05\,K) = (3.87 \pm 0.03)\,J \cdot K^{-1}\,mol^{-1}$ exceeds 8. This fact testifies that 1,1-ClMeCP produces the plastic crystal phase [7,8], but in a very narrow temperature interval from 178.82 to 189.05 K.

As it was already mentioned, a spontaneous crystallization of glassy 1,1-ClMeCP began at $T > 137$ K. It was also impossible to measure the heat capacities of 1,1-ClMeCP supercooled liquid because the first calorimetric experiment induced crystallization of supercooled phase. Therefore to obtain the complete curve of glass transition and to estimate the residual entropy it was assumed that:
1. Both the heat capacity of supercooled liquid from 189.05 to 140.2 K and the heat capacity of liquid 1,1-ClMeCP are expressed by the same equation.
2. The glass transition temperature $T_g = 140.2$ K was determined as a point of intersection of curves corresponding to function $C_{p,m} = f(T)$ for supercooled liquid (Eq. 6) and function $C_{p,m} = f(T)$ obtained from experimental heat capacities of glassy 1,1-ClMeCP in interval 127.3–137.6 K.

The derived thermodynamic characteristics of glassy 1,1-ClMeCP are tabulated in Table 7. The residual entropy of glassy 1,1-ClMeCP is $\Delta_{cr}^{gl}S_m^0(0\,K) = 22.45\,J \cdot K^{-1}\,mol^{-1}$.

The smoothed heat capacities and derived thermodynamic functions for 1,1-ClMeCP in the condensed state are represented in Table 6. Values of the basic standard thermodynamic functions of liquid 1,1-ClMeCP at 298.15 K are given in Table 8.

4. Phase transitions of crystals of 1-methylcyclopentanol and 1-chloro-1-methylcy-clopentane.

Comparison of thermal behaviours of cyclohexane and cyclopentane derivatives is of great interest. The temperatures and the molar entropies of transitions of fifteen C_5 and C_6 cycloalkane derivatives are given in Table 9. The thermodynamic properties of half of these compounds were investigated in our laboratory [1,2,3,4, this work]. All chosen compounds can be divided either into two groups as cyclohexane derivatives and cyclopentane derivatives or (without bromocyclohexane) into seven pairs of structurally similar cycloalkane derivatives (for example, cyclohexanol and cyclopentanol, and so on). Taking into consideration the data of Table 9 and the data of analogous tables for only cyclohexane derivatives [4] and for only cyclopentane derivatives [3] it can be noted that:

1. An approximative constancy of sums of the entropies of solid-to-solid transitions and fusion is observed for the majority of cyclohexane and cyclopentane derivatives. Exceptions to this rule are cyclohexanol and especially cyclopentanol. The low sums of all transitions entropies of these cycloalkanols in the condensed state are caused, most likely, by a formation of essentially associated liquids at temperatures near T_{fus} [3].

Table 8
Values of basic standard molar thermodynamic functions at $T = 298.15$ K for crystalline 1-methylcyclopentanol (1-MeCPol) and for liquid 1-chloro-1-methylcyclopentane (1,1-ClMeCP).

Compounds	1-MeCPol	1,1-ClMeCP
Phase	crystal II	liquid
$\frac{C_{p,m}}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	(229.5 ± 0.96)	(179.9 ± 0.79)
$\frac{\Delta_0^T S_m^0}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	(190.4 ± 0.84)	(255.7 ± 1.16)
$\frac{\Delta_0^T H_m^0/T}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	(100.4 ± 0.46)	(131.5 ± 0.59)
$\frac{\Phi_m^0}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	(90.08 ± 0.40)	(124.2 ± 0.56)

2. While comparing the pairs of structurally similar derivatives of cyclohexane and cyclopentane it can be noted that, as a rule, cyclopentane derivatives possess more complicated thermal behaviours and they have larger numbers of solid-to-solid transitions. Another situation is observed for the pair of chlorocyclohexane and chlorocyclopentane.

3. Structurally similar C_5 and C_6 cycloalkane derivatives possess the same abilities to form plastic crystals. Six compounds among fourteen, included in seven pairs in Table 9, do not form the plastic phase. These six compounds make three pairs of structurally similar derivatives of cyclohexane and cyclopentane, namely: methylcy-cloalkanes, cycloalkanthiols, and 1-methylcycloalkanols. All the rest compounds form the plastic crystal phase in the large or small temperature intervals.

It can be supposed that the availability of certain substitutes or the certain combination of geminal substitutes in molecules of similar cyclohexane and cyclopentane derivatives render the same influence on thermal behaviours of these compounds and, specifically, on their abilities to form plastic crystals. So, monosubstituted derivatives of C_5 and C_6 cycloalkanes— secondary alkohols and chlorides— exist in the plastic crystal state, but methylcycloalkanes and cycloalkanthiols do not form such a phase. On the other hand, the influences of substitutes on thermal behaviours of crystals are not additive in 1,1-disubstituted derivatives of cyclopentane and cyclohexane. So, neither 1-methylcyclohexanol nor 1-methylcyclopentanol do not form plastic crystals unlike 1-chloro-1-methylcycloalkanes. It is also interesting that methylcyclohexane and methylcyclopentane do not undergo solid-to-solid transitions before fusion, but 1,1-dimethylsubstituted derivatives form the plastic phase.

Probably, it can be also expected that bromocyclopentane will not exist in the plastic crystal state because bromocyclohexane does not form plastic crystals [5].

5. Thermodynamic characteristics of glassy 1-methylcyclopentanol and 1-chloro-1-methylcyclopentane.

Thermodynamic parameters associated with the glass transitions of 1-MeCPol and 1,1-ClMeCP are collected in Table 7. Substantial distinctions of structural changes at T_g are definitely obvious for these two compounds and these distinctions are indirectly shown by the heat capacity jumps at T_g and the residual entropies of glasses. But, it is necessary to note that the determination of the values $\Delta_{gl}^{l} C_s$ and $\Delta_{cr}^{gl} S_m^0(0\ \mathrm{K})$ for 1-MeCPol is not accurate because of a complexity of estimation of the heat capacity for liquid 1-MeCPol (Eq. (3)) at $T < T_{fus}$. The values $\Delta_{gl}^{l} C_s$ and $\Delta_{cr}^{gl} S_m^0(0\ \mathrm{K})$ of 1,1-ClMeCP have usual magnitudes for organic compounds forming glassy states [9].

As is well known [10], the glass possesses "frozen" configurational disorder unlike the crystal, and this

Table 9
Temperatures and molar entropies of phase transitions of some cyclohexane and cyclopentane derivatives in the condensed state. $\Sigma\Delta_{trs}S$ is the sum of entropies of all phase transitions between low-temperature crystal and liquid.

Compound	Transition type	$\frac{T}{\mathrm{K}}$	$\frac{\Delta_{trs}S}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{\Sigma\Delta_{trs}S}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	Ref
cyclohexane	crII → crI	186.14	36.20		
	crI → l	279.82	9.57	45.77	[16]
cyclopentane	crIII → crII	122.38	29.91		
	crII → crI	138.08	2.50		
	crI → l	179.74	3.39	45.80	[16]
cyclohexanol	crIII → crI	244.80	35.29		
	crII → crI	265.50	33.25		
	crI → l	299.09	5.96	39.21	[17]
cyclopentanol*	crIV → crIII	176.0	0.324		
	crIII → crII	202.6	16.61		
	crII → crI	234.0	0.235		
	crI → l	255.60	4.80	21.97	[3]
methylcyclohexane	cr → l	146.58	46.05	46.05	[16]
methylcyclopentane	cr → l	130.7	53.0	53.0	[16]
cyclohexanethiol	cr → l	189.64	52.73	52.73	[18]
cyclopentanethiol	cr → l	155.39	50.41	50.41	[19]
bromocyclohexane	cr → l	216.87	49.80	49.80	[5]
chlorocyclohexane*	crIII → crII	120.0	0.41		[1]
	crII → crI	220.40	36.42		[1]
		220.24	36.83		[5]
	crI → l	229.34	8.98	45.81	[1]
		228.01	8.90	45.73	[5]
chlorocyclopentane*	crII → crI	169.35	45.06		
	crI → l	180.0	3.54	48.60	[2]
1,1-dimethylcyclohexane	crII → crI	153.14	39.08		
	crI → l	239.84	8.63	47.71	[16]
1,1-dimethylcyclopentane	crII → crI	146.79	44.21		
	crI → l	203.67	5.30	49.51	[16]
1-methylcyclohexanol*	cr → l	299.40	47.83	47.83	[4]
1-methylcyclopentanol*	crIII → crII	281.72	9.26		
	crII → crI	301.47	6.04		this
	crI → l	308.53	27.85	43.15	work
1-chloro-1-methyl-	crII → crI	214.37	43.73		
cyclohexane*	crI → l	234.52	6.98	50.71	[4]
1-chloro-1-methyl-	crIII → crII	164.20	7.81		
cyclopentane*	crII → crI	178.82	31.89		this
	crI → l	189.05	3.87	43.57	work

* – thermodynamic properties of these compounds were investigated in our laboratory.

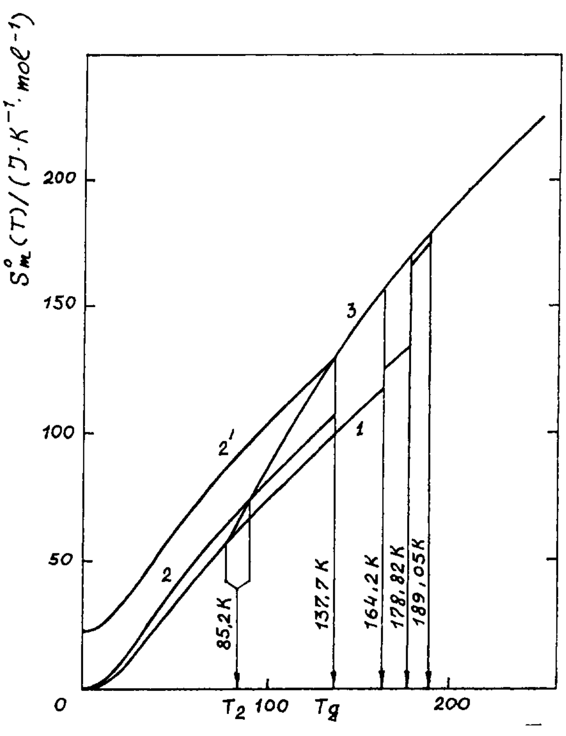

Fig. 4. The entropy diagram of 1-chloro-1-methylcyclopentane: 1, entropy of crystal; 2′, entropy of glass; 2, entropy of hypothetical glass which does not exhibit zero entropy (found as difference between $S_m^0(\mathrm{gl})$ of curve 2′ and $\Delta_{cr}^{gl}S_m^0(0\,K)$).

disorder determines to a considerable extent the residual entropy of glass. Gibbs, Dimarzio and Adam [11,12] worked out a method of calculation of configurational entropy of glass using the entropy diagram. The entropy diagram of liquid, crystalline and glassy 1,1-ClMeCP is represented in Fig. 4. The hypothetical temperature $T_2 = 85.2$ K, at which the configurational entropies of supercooled liquid and glass become equal, was determined by extrapolation of curve $3(S_m^0(\mathrm{l}) = f(T))$. In accordance with [11,12], the configurational entropy of glassy 1,1-ClMeCP is

$$S_{\mathrm{conf}}^0 = \int_{T_2}^{T_{\mathrm{gl}}} \Delta_{\mathrm{gl}}^{\mathrm{l}} C_s(T_g) \cdot T^{-1} \cdot \mathrm{d}T = 29.3\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

This value is approximately 30% larger than that of glassy 1,1-ClMeCP $\Delta_{cr}^{gl}S_m^0(0\,\mathrm{K}) = 22.45\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ (Table 7). Probably, this discrepancy is caused by imperfect extrapolation procedure for the determination of temperature T_2 in the entropy diagram.

It seems reasonable to carry out the analysis of the values $\Delta_{\mathrm{gl}}^{\mathrm{l}} C_s$ and $\Delta_{cr}^{gl}S_m^0(0\,\mathrm{K})$ for 1-MeCPol and 1,1-ClMeCP on the base of possible structural changes in molecules at T_g. According to [13,9], the heat capacity jump at T_g can be represented by the following expression:

$$\Delta_{\mathrm{gl}}^{\mathrm{l}} C_s = \Delta_{\mathrm{conf}} C_s + \Delta_{\mathrm{h}} C + \Delta_{\mathrm{vib}} C,$$

where $\Delta_{\mathrm{conf}} C_s$ is the conformational contribution to the heat capacity jump: $\Delta_{\mathrm{h}} C$ is the contribution caused by formation of "holes" at T_g; $\Delta_{\mathrm{vib}} C$ is the contribution connected with changes of vibrational spectra. It is very likely that the contribution of intermolecular vibrations changes a little at the glass transition. The contributions to entropies and heat capacities of 1-MeCPol and 1,1-ClMeCP were calculated for systems of non-interacted molecules (the ideal gas state) at respective T_g (Table 10) using the procedures and relations given in [14]. The values $\Delta_{\mathrm{conf}} C_p^0(242.5\,\mathrm{K}) = 15.1\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and $\Delta_{\mathrm{conf}} S_m^0(242.5\,\mathrm{K}) = 34.0\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for 1-MeCPol are close with experimental values $\Delta_{\mathrm{gl}}^{\mathrm{l}} C_s$ and $\Delta_{cr}^{gl}S_m^0(0\,\mathrm{K})$, respectively (Table 7). If it is assumed that the freedom of conformational conversions (internal rotation) is "frozen" at T_g, the other structural changes, probably, do not occur to a certain extent of compensate partly each other in the case of 1-MeCPol.

The contributions of internal rotation and inversion of molecules of 1,1-ClMeCP at T_g (the ideal gas state) are $\Delta_{\mathrm{conf}} C_p^0 = 6.1\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and $\Delta_{\mathrm{conf}} S_m^0 = 2.6\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. These values are substabtially lower than the obtained values $\Delta_{\mathrm{gl}}^{\mathrm{l}} C_s$ and $\Delta_{cr}^{gl}S_m^0(0\,\mathrm{K})$ of 1,1-ClMeCP. It is not possible to account for the experimental heat capacity change of 1,1-ClMeCP by the replacement of vibrations of molecules as a whole in the glassy state on translational motion and general rotation of molecules because their contributions at T_g is $C_{p,\mathrm{trans}} + C_{p,\mathrm{rot}} = 20.79 + 12.47 = 33.26\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ (Table 10) in the case of absence of potential fields (the ideal gas state). This contribution should be almost compensated by the loss of three vibrational

Table 10
Contributions of different kinds of molecular motion to entropies and heat capacities values of 1–methylcyclopentanol (1–MeCPol) and 1–chloro–1–methylcyclopentane (1,1–ClMeCP) in the gas state ($p^0 = 101.325$ kPa) at T_g

Kinds of molecular motion	1–MeCPol $T_g = 242.5$ K		1,1–ClMeCP $T_g = 137.7$ K	
	S^0_m / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	C^0_p / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	S^0_m / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	C^0_p / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
translational	161.91	20.79	152.25	20.79
rotational	111.29	12.47	107.38	12.47
vibrational	36.07	61.26	16.10	29.48
CH_3–top rotation	7.10	8.32	2.34	4.96
OH–top rotation	16.59	5.37	–	–
conformers mixing	10.36	1.43	0.25	1.12

degrees of freedom of the molecules. Therefore the heat capacity jump $\Delta^{l}_{gl}C_s$ for 1,1-ClMeCP should be largely covered by formation of "holes" at the glass transition $\Delta_h C = \Delta_h E \cdot (\partial N_h / \partial T)$, where $\Delta_h E$ is the energy of formation of 1 mole of "holes"; N_h is the amount of "holes" [9,13]. Then

$$\Delta_h C = R \cdot (V_m/V_h) \cdot (\Delta_h E/RT)^2 \cdot \exp(-\Delta_h E/RT) \qquad (7)$$

where N_h and N_m are the molar fractions of "holes" and molecules; V_h and V_m are the molar volumes of "holes" and molecules, respectively, if it is supposed, that Boltzmann equation for "holes" $(N_h/V_h)/(N_m/V_m) = \exp(-\Delta_h E/RT)$ is applicable. The dependence $\Delta_h C/(V_m/V_h) = f(\Delta_h E)$ at 137.7 K is represented in Fig. 5. The energy of formation of 1 mol of "holes" is $\Delta_h E = 2.5\,\mathrm{kJ \cdot mol^{-1}}$ for 1,1-ClMeCP if it is assumed that this energy corresponds to the maximum change of relative heat capacity at $T = 137.7$ K $\Delta_h C/(V_m/V_h) = 4.5\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ (Fig. 5). So, according to Eq. (7) and the "hole" contribution for 1,1-ClMeCP $\Delta_h C_{exp} = \Delta^{l}_{gl}C_s - \Delta_{conf}C^0_p = (61.1 - 6.1) = 55.0\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, the ratio of the molar volumes of molecules and "holes" is $V_m/V_h = 55.0/4.5 = 12.2$ for 1,1-ClMeCP.

The energy of "hole" formation can also be estimated by the following way: $\Delta_h E = \Delta_{coh} E^g/(V_m/V_h) = \Delta_{coh} E_g/12.2$, where $\Delta_{coh} E_g$ is the energy of cohesion at T_g, because it is usually

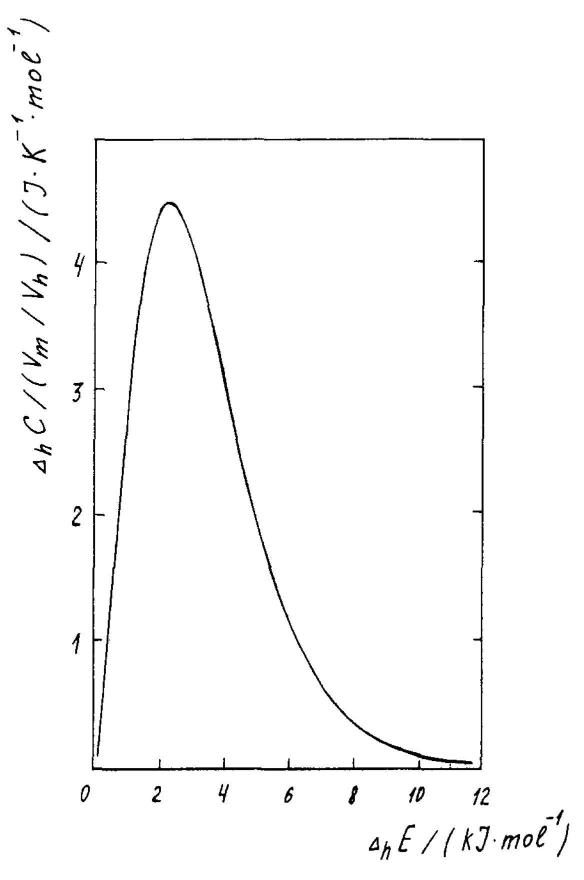

Fig. 5. Dependence $\Delta_h C/(V_m/V_h) = f(\Delta_h E)$ at $T = 137.7$ K.

assumed that $\Delta_{\mathrm{coh}}E_{\mathrm{g}}/\Delta_{\mathrm{h}}E = V_{\mathrm{m}}/V_{\mathrm{h}}$ [9]. To calculate the energy of cohesion of 1,1-ClMeCP its enthalpy of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(296.6\,\mathrm{K}) = 39.74\,\mathrm{kJ\cdot mol^{-1}}$ was determined by a differential heat-conducting microcalorimeter of Calvet type [15]. Taking into account the difference between the heat capacities of gas and liquid $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{p}(217.2\,\mathrm{K}) = -62.55\,\mathrm{J\cdot K^{-1}}$, the enthalpy of vaporization of 1,1-ClMeCP at 137.7 K was determined to be $49.68\,\mathrm{kJ\cdot mol^{-1}}$. Then $\Delta_{\mathrm{coh}}E_{\mathrm{g}} = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(137.7\,\mathrm{K}) - R\cdot T_{\mathrm{g}} = 48.53\,\mathrm{kJ\cdot mol^{-1}}$ and, consequently, $\Delta_{\mathrm{h}}E = 48.53/12.2 = 4.0\,\mathrm{kJ\cdot mol^{-1}}$. Taking into consideration the accepted assumptions, the latter value is in a satisfactory agreement with the value $\Delta_{\mathrm{h}}E = 2.5\,\mathrm{kJ\cdot mol^{-1}}$ estimated earlier on the basis of dependence $\Delta_{\mathrm{h}}C/(V_{\mathrm{m}}/V_{\mathrm{h}}) = \mathrm{f}(\Delta_{\mathrm{h}}E)$ at 137.7 K (Fig. 5). The energy of “hole” formation $\Delta_{\mathrm{h}}E = 2.5$–$4.0\,\mathrm{kJ\cdot mol^{-1}}$ obtained so is in a good accordance with the values $\Delta_{\mathrm{h}}E$ of organic compounds forming glasses [9]. Though the ratio of the molar volumes of molecules and “holes” for 1,1-ClMeCP $V_{\mathrm{m}}/V_{\mathrm{h}} = 12.2$ determined in this work is approximately twice larger than the value $(V_{\mathrm{m}}/V_{\mathrm{h}}) = 5$–$6$ adopted in [9] for organic glasses.

Acknowledgements

The authors express their thanks to the Foundation of Fundamental Research of the Republic of Belarus (Grant MP–34) and the International Science Foundation (Grant MW 4300) for sponsoring of this work.

G. J. Kabo, A. A. Kozyro and A. V. Blokhin are grateful to the International Soros Science Education Program for financial supports, promoted carrying out of the present work.

References

[1] V. V. Diky, G. J. Kabo, A. A. Kozyro, A. P. Krasulin and V. M. Sevruk, J. Chem. Thermodynamics, 26 (1994) 1001.

[2] V. V. Diky, G. J. Kabo, A. A. Kozyro, A. P. Krasulin and V. M. Sevruk, J. Chem. Thermodynamics, 25 (1993) 1169.

[3] G. J. Kabo, V. V. Diky, A. A. Kozyro, A. P. Krasulin and V. M. Sevruk, J. Chem. Thermodynamics, 27 (1995) 953.

[4] G. J. Kabo, V. V. Diky, A. A. Kozyro, A. V. Blokhin and Yu. V. Maksimuk, 14th IUPAC Conf. Chem. Thermodyn., Programm, Abstracts and Repts–Osaka, Japan, 1996, p339.

[5] K. Kobashi and M. Oguni, J. Chem. Thermodynamics, 27 (1995) 979.

[6] G. J. Kabo, A. A. Kozyro, V. S. Krouk, V. M. Sevruk, I. A. Yursha, V. V. Simirsky and V. I. Gogolinsky, J. Chem. Thermodynamics, 24 (1992) 1.

[7] J. J. Timmermans, Phys. Chem. Solids, 18 (1961) 1.

[8] D. Fox, M. M. Labes and A. Weissberger: editors, Physics and Chemistry of the organic Solid State, Interscience, New-York-London, 1965.

[9] B. Wunderlich, J. Phys. Chem., 64 (1960) 1052.

[10] A. R. Ubbelonde, Melting and Crystal Structure, Clarendon Press, Oxford, 1965.

[11] J. H. Gibbs and E. A. Dimarzio, J. Chem. Phys. 28 (1958) 373.

[12] G. Adam and J. H. Gibbs, J. Chem. Phys., 43 (1965) 139.

[13] Yu. K. Godovsky, Teplofizika polimerov, Khimiya, Moskva, 1982.

[14] M. L. Frenkel, G. J. Kabo, K. N. Marsh, G. N. Roganov and R. C. Wilhoit, Thermodynamics of Organic Compounds in the Gas State, Thermodynamics Research Center, Texas USA, 1994.

[15] V. M. Sevruk, V. V. Simirsky, G. J. Kabo, A. A. Kozyro and A. P. Krasulin, Zh. Fiz. Khim., 64 (1990) 3402.

[16] TRC Thermodynamic Tables. Hydrocarbons, K. N. March: Director, The Texas A&M University System, College Station, 1994.

[17] K. Adachi, H. Suga and S. Seki, Bull. Chem. Soc. Japan, 41 (1968) 1073.

[18] J. F. Messerly, S. S. Todd and G. B. Guthrie, J. Chem. Eng. Data, 12 (1967) 426.

[19] W. T. Berg, D. W. Scott, W. N. Hubbard, S. S. Todd, J. F. Messerly, I. A. Hossenlopp, A. G. Osborn, D. R. Douslin and J. P. McCullough, J. Phys. Chem., 65 (1961) 1425.