

## Thermodynamic properties and phase transitions of 1-methylcyclohexanol and 1-chloro-1-methylcyclohexane

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### Abstract

Comprehensive investigations of thermodynamic properties of 1-methylcyclohexanol (I) and 1-chloro-1-methylcyclohexane (II) were carried out. The heat capacities and enthalpies of transitions of I and II in the condensed state between 5 and 320 K were measured by vacuum adiabatic calorimetry. It was found that II exists in the plastic crystal state over a narrow temperature interval from 214.37 to 234.52 K. The enthalpies of sublimation of I and vaporization of II and their saturated vapor pressures were obtained. Infrared (IR) and Raman spectra of both compounds were recorded and vibrational analyses were made. Thermodynamic functions of I and II in the ideal gas state were calculated by the statistical thermodynamics methods. It was shown by the low-temperature IR spectroscopy that only one 'chair'-conformer of II with equatorial methyl group exists in rigid crystal phase at  $T < 214.37$  K. The nature of molecular rotation in the plastic crystal state of II is discussed.  
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### 1. Introduction

Some organic compounds are capable to transform reversibly into the plastic crystal state [1]. Densities, mechanical, optical, dielectric and other properties of crystals change at such transitions. This fact creates a potential possibility to work out their practical applications. The forming of plastic crystals is caused by a partial removing of prohibitions of reorientational motion of molecules in the solid state and the appearance of conformers which are characteristic for the liquid state of substances near their melting points [1,2].

To predict an ability to form plastic crystals is difficult even in a series of compounds with molecules of similar structure. The temperature limits of existence of plastic crystals, the enthalpies and entropies of transitions from rigid to plastic crystals are also considerably individualized. These facts define the interest to investigate thermodynamic properties of substances in order to determine their ability to form plastic crystals on the basis of a thermodynamic criterion ( $\Delta_{\text{trs}}S_m^0/\Delta_{\text{fus}}S_m^0 \cong 3 - 5$ ) suggested earlier [1] and to analyze the nature of molecular motions in their crystals.

It is known that chlorocyclohexane [3] and cyclohexanol [4] form plastic crystals, but methylcyclo-

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hexane [5] melts without undergoing transition into the plastic phase. In the present work, thermodynamic properties of two tertiary cyclohexane derivatives: 1-methylcyclohexanol (1-MeCHol) and 1-chloro-1-methylcyclohexane (1,1-CIMeCH) were investigated. Methyl group and hydroxyl group or chlorine are combined in pairs in their molecules. We think that it is necessary to investigate these compounds in order to study the possibility to predict an ability of substances to form plastic crystals on the basis of their molecular structure.

In the present study, isobaric heat capacities of 1-MeCHol and 1,1-CIMeCH between 5 and 320 K and their enthalpies of phase transitions and saturated vapor pressures are reported. In order to reach agreement between entropies of ideal gases calculated by statistical thermodynamics methods and obtained on the basis of experimental data, the molecular constants were selected. The character of rotation and inversion of 1,1-CIMeCH molecules in the plastic crystal state was investigated by the methods of statistical thermodynamics and IR spectroscopy.

## 2. Experimental

1-MeCHol was synthesized from methylmagnesiumiodide and cyclohexanone by Grignard reaction. After washing, draining and twice distillations at 343 K/4 kPa the purity of 1-MeCHol was 99.95 (mass.%) as determined in a gas-liquid chromatograph CHROM-5.

1,1-CIMeCH was synthesized by action of  $ZnCl_2$  solution in concentrated hydrochloric acid on 1-MeCHol. After twice distillations at 341 K/5.3 kPa, the purity of 1,1-CIMeCH was 99.93 (mass.%) as determined by gas-liquid chromatography.

The low-temperature heat capacities and enthalpies of transitions of the compounds in the condensed state between 5 and 320 K were measured in a Model TAU-1 vacuum adiabatic calorimeter, described earlier [6]. The probable error of the heat capacity values  $C_{sat,m}$  is considered to be  $\pm 4 \cdot 10^{-3} \cdot C_{sat,m}$  between 40 and 320 K and becomes more considerable when measurements are performed at  $T < 40$  K, and it is  $\pm 2 \cdot 10^{-2} \cdot C_{sat,m}$  at the liquid-He temperatures.

The enthalpies of sublimation and vaporization of the compounds under study were determined

in a differential heat-conducting microcalorimeter of the Calvet type MID-200 with special calorimetric cells [7]. The saturated vapor pressures were measured by the integral effusion Knudsen method. The apparatus construction and the measuring procedure were reported earlier [8,9]. It was assumed for calculations that vapors have a monomolecular composition.

The IR spectra of liquid 1-MeCHol and 1,1-CIMeCH over the wavenumber range from 75 to  $450 \text{ cm}^{-1}$  were recorded with an FT spectrometer LAFS 1000 with resolution of  $2.9 \text{ cm}^{-1}$ . The IR spectra in the range from 4000 to  $400 \text{ cm}^{-1}$  were obtained with a Specord-75 IR spectrometer using thin films of liquids between KBr plates. The Raman spectra between 4000 and  $50 \text{ cm}^{-1}$  were recorded by a Ramalog-4 spectrometer with argon laser ( $B=514.5 \text{ nm}$ ). 'Karl Zeiss' multipass gas cell with length of optical way 1 m was used to obtain IR spectrum of gaseous 1,1-CIMeCH which was in the state of saturated vapor at 293 K. The studies of IR spectra of liquid and crystal 1,1-CIMeCH between 293 and 205 K were made in 'Karl Zeiss' low-temperature chamber. The IR spectra were periodically recorded while cooling the sample at the rate  $0.02 \text{ K} \cdot \text{s}^{-1}$ .

## 3. Results and discussion

### 3.1. Thermodynamic properties of 1-methylcyclohexanol and 1-chloro-1-methylcyclohexane

The experimental heat capacities of 1-MeCHol and 1,1-CIMeCH in the condensed state are represented in Figs. 1 and 2, respectively. Extrapolation of the heat capacities to 0 K was made using Debye equation:  $C_{V,m} = 3 \cdot R \cdot D \cdot (\Theta_D/T)$ . The characteristic Debye temperatures  $\Theta_D$  were determined from  $C_{sat,m}$  values near 5 K and they are  $\Theta_D = 94.6 \text{ K}$  for 1-MeCHol and  $\Theta_D = 91.2 \text{ K}$  for 1,1-CIMeCH.

Thermodynamic characteristics of phase transitions of 1-MeCHol and 1,1-CIMeCH in the condensed state are given in Table 1. The entropy of solid-to-solid transition of 1,1-CIMeCH  $\Delta_{crII}^{crI} S_m^0 = 43.76 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is more than six times as much as its entropy of fusion  $\Delta_{crI}^1 S_m^0 = 6.95 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . According to [1,2], it means that the plastic crystal phase of

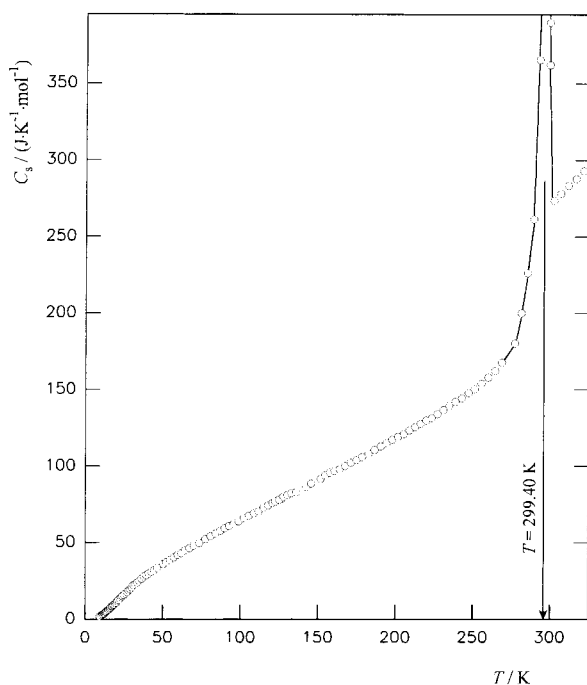


Fig. 1. Experimental molar heat capacities of 1-methylcyclohexanol in the condensed state at the saturated vapor pressure.

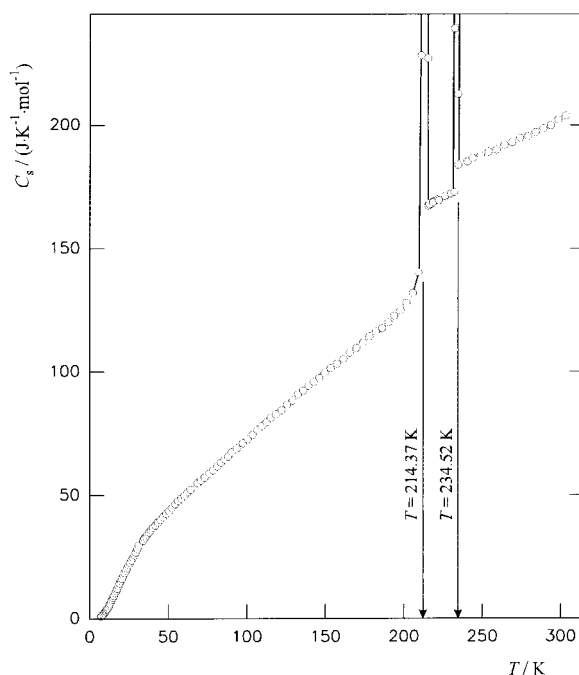


Fig. 2. Experimental molar heat capacities of 1-chloro-1-methylcyclohexane in the condensed state at the saturated vapor pressure.

1,1-ClMeCH exists over the temperature interval from 214.37 to 234.52 K.

The smoothed molar heat capacities and derived molar thermodynamic functions of 1-MeCHol and 1,1-ClMeCH in the condensed state are given in Tables 2 and 3, respectively.

In spite of similarity of the chemical nature and molecular geometrical parameters 1-MeCHol, cyclohexanol and methylcyclohexane, thermal behaviors of these substances are very different. Thus, 1-MeCHol, in contrast to cyclohexanol [4], does not exist in the plastic crystal state. As a result, the fusion entropy of 1-MeCHol is approximately 8 times as much as the fusion entropy of cyclohexanol  $\Delta_{\text{crI}}^1 S_m^0 =$

$5.96 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (though their temperatures are almost the same: 299.40 and 299.09 K [4], respectively). On the other hand, both 1-MeCHol and methylcyclohexane [5] do not form plastic crystals. The fusion temperatures of these compounds are different by more than 150 K (299.40 and 146.58 K [5]), but their fusion entropies are close: 47.84 and  $46.05 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively.

1,1-ClMeCH, like chlorocyclohexane [3], exists in the plastic crystal state, and their entropies of transitions  $\text{crII} \rightarrow \text{crI}$  differ by about  $7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  ( $43.76$  and  $36.42 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively). Somewhat larger value of  $\Delta_{\text{crII}}^{\text{crI}} S_m^0$  for 1,1-ClMeCH is probably caused by the presence of  $\text{CH}_3$  - top in its molecule

Table 1

Temperatures, the molar enthalpies and entropies of phase transitions of 1-methylcyclohexanol (1-MeCHol) and 1-chloro-1-methylcyclohexane (1,1-ClMeCH) in the condensed state

Compounds	Transition	$T_{\text{trs}}$ (K)	$\Delta H_m^0$ ( $\text{J}\cdot\text{mol}^{-1}$ )	$\Delta S_m^0$ ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )
1-MeCHol	$\text{cr} \rightarrow \text{l}$	299.40	(14322±19)	(47.84±0.07)
1,1-ClMeCH	$\text{crII} \rightarrow \text{crI}$	214.37	(9381±28)	(43.76±0.13)
	$\text{crI} \rightarrow \text{l}$	234.52	(1630±4)	(6.95±0.02)

Table 2  
Molar thermodynamic functions for 1-methylcyclohexanol

$T/K$	$C_{p,m}^0/R$	$\Delta_0^T S_m^0/R$	$\Delta_0^T H_m^0/RT$	$\Phi_m^0/R$
Crystal				
5	0.03352	0.01119	0.008419	0.002766
10	0.2696	0.09032	0.06783	0.02249
15	0.7468	0.2840	0.2098	0.07421
20	1.331	0.5779	0.4163	0.1616
25	1.917	0.9386	0.6585	0.2801
30	2.500	1.340	0.9173	0.4229
35	3.031	1.767	1.182	0.5842
40	3.499	2.202	1.443	0.7592
45	3.917	2.639	1.695	0.9438
50	4.308	3.072	1.938	1.135
60	5.060	3.924	2.396	1.529
70	5.787	4.759	2.829	1.931
80	6.472	5.577	3.241	2.336
90	7.132	6.378	3.637	2.741
100	7.784	7.163	4.019	3.144
110	8.427	7.935	4.391	3.544
120	9.063	8.696	4.754	3.942
130	9.694	9.446	5.110	4.337
140	10.32	10.19	5.459	4.728
150	10.95	10.92	5.805	5.117
160	11.58	11.65	6.146	5.502
170	12.20	12.37	6.484	5.885
180	12.85	13.08	6.820	6.265
190	13.52	13.80	7.155	6.643
200	14.20	14.51	7.490	7.018
210	14.90	15.22	7.826	7.392
220	15.61	15.93	8.164	7.764
230	16.35	16.64	8.503	8.134
240	17.17	17.35	8.847	8.503
250	17.98	18.07	9.196	8.871
260	18.80	18.79	9.550	9.239
270	19.62	19.51	9.908	9.606
280	20.44	20.24	10.27	9.973
290	21.26	20.97	10.63	10.34
298.15	21.92	21.57	10.93	10.64
299.40	22.02	21.66	10.98	10.69
Liquid				
299.40	32.56	27.42	16.73	10.68
300	32.63	27.48	16.76	10.72
310	33.86	28.57	17.30	11.28
320	35.08	29.67	17.83	11.83

( $M=114.188 \text{ g}\cdot\text{mol}^{-1}$ ;  $R=8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )

Table 3  
Molar thermodynamic functions for 1-chloro-1-methylcyclohexane

$T/K$	$C_{p,m}^0/R$	$\Delta_0^T S_m^0/R$	$\Delta_0^T H_m^0/RT$	$\Phi_m^0/R$
Crystal II				
5	0.03852	0.01284	0.009629	0.003210
10	0.3791	0.1168	0.08928	0.02755
15	1.094	0.3952	0.2968	0.09841
20	1.897	0.8180	0.6115	0.2064
25	2.657	1.324	0.9459	0.3785
30	3.334	1.870	1.289	0.5813
35	3.922	2.429	1.624	0.8052
40	4.424	2.987	1.944	1.043
45	4.855	3.533	2.244	1.290
50	5.239	4.065	2.524	1.541
60	5.974	5.086	3.038	2.047
70	6.680	6.060	3.508	2.551
80	7.377	6.997	3.948	3.049
90	8.064	7.906	4.368	3.538
100	8.743	8.791	4.771	4.019
110	9.412	9.655	5.163	4.493
120	10.07	10.50	5.544	4.958
130	10.72	11.33	5.918	5.417
140	11.36	12.15	6.284	5.869
150	11.98	12.96	6.643	6.315
160	12.59	13.75	6.996	6.755
170	13.21	14.53	7.343	7.189
180	13.82	15.30	7.685	7.619
190	14.43	16.07	8.025	8.043
200	15.05	16.82	8.360	8.463
210	15.66	17.57	8.693	8.879
214.37	15.93	17.90	8.838	9.060
Crystal I				
214.37	20.11	23.16	14.10	9.060
220	20.34	23.69	14.26	9.427
230	20.74	24.60	14.53	10.07
234.52	20.93	25.00	14.65	10.35
Liquid				
234.52	22.08	25.84	15.49	10.35
240	22.27	26.35	15.64	10.71
250	22.62	27.27	12.91	11.35
260	22.96	28.16	16.18	11.98
270	23.30	29.04	16.44	12.60
280	23.65	29.89	16.69	13.20
290	23.99	30.72	16.93	16.79
298.15	24.27	31.39	17.13	14.26
300	24.34	31.54	17.17	14.37

( $M=132.633 \text{ g}\cdot\text{mol}^{-1}$ ,  $R=8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

which makes an additional contribution to entropy change by a removing prohibition of hindered internal rotation at the transition rigid crystal  $\rightarrow$  plastic crystal.

To obtain the experimental entropies of 1-MeCHol and 1,1-ClMeCH in the gas state, their saturated vapor pressures and enthalpies of evaporation were measured.

The experimental saturated vapor pressures of crystal 1-MeCHol and liquid 1,1-ClMeCH are given in Table 4. The temperature dependence of saturated vapor pressure of 1-MeCHol between 273 and 295 K can be described by Eq. (1):

Table 4

Saturated vapor pressures  $P$  for crystal 1-methylcyclohexanol (1-MeCHol) and for liquid 1-chloro-1-methylcyclohexane (1,1-ClMeCH):  $\Delta m$  is the sample mass decrease;  $\tau$  is the duration of effusion

Compounds	$T$ (K)	$\tau$ (s)	$\Delta m$ (mg)	$P$ (Pa)
1-MeCHol	273.23	19854	8.69	12.11
	276.27	12654	7.97	17.51
	279.05	9954	8.81	25.50
	281.55	7554	9.08	34.16
	284.13	6354	10.57	46.93
	286.96	5454	12.54	65.18
	289.71	4254	13.31	89.12
	292.15	3054	12.62	118.20
1,1-ClMeCH	273.17	1854	45.75	416.6
	273.17	1854	45.11	410.8
	273.17	1884	46.20	414.0
	273.17	1854	44.49	405.2
	273.17	1854	44.93	409.2
	273.17	1854	45.61	415.4
	$\langle P(273.17 \text{ K}) \rangle = (411.9 \pm 4.5) \text{ Pa}$			

$$\ln(P/\text{Pa}) = (37.650 \pm 0.281) - (9606 \pm 80)/(T/\text{K}) \quad (1)$$

The saturated vapor pressure of liquid 1,1-ClMeCH at  $T = 273.17 \text{ K}$  is  $P_{\text{sat}} = 411.9 \text{ Pa}$ .

The enthalpies of sublimation of 1-MeCHol and vaporization of 1,1-ClMeCH, including the values obtained calorimetrically (Table 5), are given in Table 6. The weight-averaged sublimation enthalpy of 1-MeCHol  $\Delta_{\text{cr}}^{\text{g}} H_m^0(284.07 \text{ K}) = (77.08 \pm 0.34) \text{ kJ} \cdot \text{mol}^{-1}$  was used in further calculations. The standard evaporation entropies and the experimental entropies of ideal gases for the compounds under investigation are given in Table 7.

### 3.2. Statistical calculations of thermodynamic functions of 1-methylcyclohexanol and 1-chloro-1-methylcyclohexane in the ideal gas state.

Statistical calculations of thermodynamic properties of 1-MeCHol and 1,1-ClMeCH in the ideal gas

Table 5

Results of calorimetric determinations of the enthalpies of evaporation for 1-methylcyclohexanol and for 1-chloro-1-methylcyclohexane.

No.	$m$ (g)	$T$ (K)	$\int_{\tau=0}^{\tau} \Delta E \cdot d\tau$ (mV·s)	Type of cell	$\Delta H$ (J)	$\Delta H_m^0$ (kJ·mol <sup>-1</sup> )
Sublimation of 1-methylcyclohexanol ( $K_A = 198.52 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$ and $K_D = 186.53 \text{ mV} \cdot \text{s} \cdot \text{J}^{-1}$ )						
1	0.11888	290.70	15642.0	A	78.793	75.68
2	0.08205	290.91	10777.9	A	54.291	75.56
3	0.16316	290.43	20309.0	B	108.878	76.20
4	0.12259	290.89	15280.2	B	81.918	76.30
5	0.14802	290.77	18364.7	B	98.454	75.95
$\langle \Delta_{\text{cr}}^{\text{g}} H_m^0(290.74) \rangle = (75.94 \pm 0.39) \text{ kJ} \cdot \text{mol}^{-1}$						
Vaporization of 1-chloro-1-methylcyclohexane ( $K_A = \text{mV} \cdot \text{s} \cdot \text{J}^{-1}$ and $K_B = \text{mV} \cdot \text{s} \cdot \text{J}^{-1}$ )						
1	0.07144	297.37	5199.0	A	22.648	42.05
2	0.10183	299.63	7461.3	A	32.503	42.33
3	0.09651	299.82	7092.7	A	30.897	42.46
4	0.06811	297.66	4745.3	B	21.814	42.48
5	0.08148	299.72	5689.2	B	26.152	42.57
6	0.09904	299.93	6867.1	B	31.567	42.27
$\langle \Delta_1^{\text{g}} H_m^0(299.02) \rangle = (42.36 \pm 0.20) \text{ kJ} \cdot \text{mol}^{-1}$						

The calorimetrically measured enthalpy change  $\Delta H$  of specimens and the molar enthalpies  $\Delta H_m^0$  were calculated from the expressions:

$$\Delta H = K^{-1} \cdot \int_{\tau=0}^{\tau} \Delta E \cdot d\tau; \Delta H_m^0 = \Delta H \cdot M/m,$$

where  $m$  is the mass of a specimen;  $M$  is the molar mass;  $K$  is the calorimetric constant;  $\Delta E$  is the thermocouple potential difference corresponding to the temperature imbalance between the cell and the calorimeter thermostat at time  $\tau$ ;  $\tau$  is the experiment duration;  $T$  is the temperature of the calorimeter. The value of  $m$  is corrected for the mass of saturated vapor in the free volume of the ampoule immediately before the experiment.

Table 6

Temperatures and molar enthalpies of evaporation of 1-methylcyclohexanol (1-MeCHol) and of 1-chloro-1-methylcyclohexane (1,1-C1MeCH)

Compounds	Transition	<i>T</i> (K)	$\Delta_{\text{cr}(l)}^g H_m^0$ (kJ·mol <sup>-1</sup> )	Methods of determination
1-MeCHol	cr → g	284.07	(79.87±0.67)	from effusion data Eq. (1)
		290.74	(75.94±0.39)	microcalorimetry
		284.07	(76.13±0.39)	reduced value <sup>a</sup>
		284.07	(77.08±0.34)	weight-averaged value <sup>b</sup>
1,1-C1MeCH	l → g	299.02	(42.36±0.20)	microcalorimetry
		273.17	(43.83±0.20)	reduced value <sup>c</sup>

<sup>a</sup> It was obtained from the sublimation enthalpy, found microcalorimetrically by using the heat capacity difference  $\Delta_{\text{cr}}^g C_{p,m} = -28 \text{ J·K}^{-1}\cdot\text{mol}^{-1}$  between 290.74 and 284.07 K.

<sup>b</sup> It was calculated from the sublimation enthalpy, obtained from Eq. (1), and the reduced sublimation enthalpy, found microcalorimetrically.

<sup>c</sup> It was obtained from the vaporization enthalpy, found microcalorimetrically, by using the heat capacity difference  $\Delta_1^g C_{p,m} = -57 \text{ J·K}^{-1}\cdot\text{mol}^{-1}$  between 299.02 and 273.17 K.

Table 7

The molar entropies of sublimation for 1-methylcyclohexanol and of vaporization for 1-chloro-1-methylcyclohexane and the experimental molar entropies of these compounds in the gas state

Compound	Transition	<i>T</i> (K)	$\Delta_{\text{cr}(l)}^g S_m^0$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> ) <sup>a</sup>	$S_m^0(g)$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> ) <sup>b</sup>
1-MeCHol	cr → g	284.07	(207.39±1.22)	(378.15±1.43)
1,1-C1MeCH	l → g	273.17	(114.68±0.75)	(358.37±1.29)

<sup>a</sup> The standard molar entropies of evaporation were obtained using the enthalpies of evaporation  $\Delta_{\text{cr}}^g H_m^0 = 77.08 \text{ kJ·mol}^{-1}$  and  $\Delta_1^g H_m^0 = 43.83 \text{ kJ·mol}^{-1}$  (Table 8) and the saturated vapor pressures 46.27 Pa (Eq. (1)) and 411.9 Pa (Table 6) for 1-MeCHol and 1,1-C1MeCH, respectively.

<sup>b</sup> The experimental entropies of gaseous compounds were calculated from their standard entropies of evaporation and the molar entropies of crystal 1-MeCHol  $\Delta_0^T S_m^0$  (170.76±0.74) J·K<sup>-1</sup>·mol<sup>-1</sup> (Table 4) and liquid 1,1-C1MeCH  $\Delta_0^T S_m^0 = (243.69±1.05) \text{ J·K}^{-1}\cdot\text{mol}^{-1}$  (Table 5).

state were made by the procedures and relations given in [10]. To analyze the conformational compositions of gaseous compounds as well as to obtain the geometrical parameters of their conformers and to determine the energetic characteristics of molecular internal rotation and ring inversion, the molecular mechanics methods [11] were used by the MM2(87) program.

It was found that, similarly to chlorocyclohexane [3], eight potential minima for molecular ring inversion exist for both 1-MeCHol and 1,1-C1MeCH. Two 'chair'-conformers with equatorial (conformer A) and

axial (conformer B) methyl group and three pairs of chiral 'twist'-conformers correspond to these minima. Conformer A is more stable than conformer B for both compounds. Principal moments of inertia products and reduced moments of inertia of molecular tops for conformers A and B of the present substances (Table 8) were calculated on the basis of geometrical parameters obtained by the MM2(87) program.

The energetics of molecular internal rotation of compounds was investigated by the procedure 'dihedral driver' of the MM2(87) program. This procedure

Table 8

Principal moments of inertia products ( $I_{AIBIC}$ ) and reduced moments of inertia of the tops ( $I_{\text{red}}$ ) for 'chair'-conformers with equatorial (A) and axial (B) methyl group of 1-methylcyclohexanol (1-MeCHol) and 1-chloro-1-methylcyclohexane (1,1-C1MeCH)

Compound	Conformer	$I_{AIBIC} \cdot 10^{114}$ (g <sup>3</sup> ·cm <sup>6</sup> )	$I_{\text{red}}(\text{CH}_3) \cdot 10^{40}$ (g·cm <sup>2</sup> )	$I_{\text{red}}(\text{OH}) \cdot 10^{40}$ (g·cm <sup>2</sup> )
1-MeCHol	A	74.308	5.31	1.30
	B	77.063	5.32	1.29
1,1-C1MeCH	A	144.390	5.33	–
	B	160.935	5.32	–

allowed to study the alteration of molecular energy as a function of dihedral angles. The potential barriers of  $\text{CH}_3$ -top rotation  $V_0$  in molecules of 1-MeCHol and 1,1-ClMeCH are 14.6 and 19.2  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. The molecular energy changes of 1-MeCHol at OH-top rotation were approximated by the potential function (2):

$$V(f) = \{1.99 + 0.45 \cos f + 0.17 \cos 2f - 1.70 \cos 3f\} \text{ kJ} \cdot \text{mol}^{-1}$$

where  $f$  is the rotation angle of OH-top.

Vibrational contributions to the thermodynamic properties of 1-MeCHol and 1,1-ClMeCH were obtained from wavenumbers (Tables 9 and 10), selected on the basis of analyses of their vibrational spectra and calculations of normal vibrations forms and wavenumbers of their molecules using the procedures given in [12]. The bands 353 and 310  $\text{cm}^{-1}$  corresponding to torsional vibrations of methyl and hydroxyl groups were excluded from full wavenumbers set of 1-MeCHol. Contributions of hindered rotations of molecular tops were determined from quantum energy levels, calculated for above potential functions.

Conformational contributions to thermodynamic functions were obtained from vibrations with wavenumbers 170  $\text{cm}^{-1}$  for 1-MeCHol (Table 9) and 125  $\text{cm}^{-1}$  for 1,1-ClMeCH (Table 10) taking into account the corrections on conformers mixing [10]. The differences between energies of formation of 'chair' and 'twist'-conformers of compounds were determined by the MM2(87) program giving 25  $\text{kJ}\cdot\text{mol}^{-1}$  on average. That's why, as for chlorocyclohexane [3], the total fraction of 'twist'-forms in equilibrium gaseous conformers mixture becomes appreciable only above 400 K for the both compounds.

Formerly [13] studies of the low-temperature NMR spectra of isopentane solution of 1-MeCHol have shown that on lowering the temperature down to 222 K the signal of hydroxyl proton splits into two components with difference of chemical shifts  $\Delta\sigma=51$  Hz. The potential barrier of cyclohexyl ring inversion determined from this difference is  $G^\ddagger = 43.8 \text{ kJ}\cdot\text{mol}^{-1}$ . The value  $\Delta_{a\rightarrow e}G^0(200 \text{ K}) = 1.65 \text{ kJ}\cdot\text{mol}^{-1}$  for conformational equilibrium  $A\leftrightarrow B$  was obtained by conformers relation, found

from the integrated intensity of signals. Then  $\Delta_{a\rightarrow e}H^0 = \Delta_{a\rightarrow e}G^0(200 \text{ K}) = 1.65 \text{ kJ}\cdot\text{mol}^{-1}$ , because it was assumed in the statistical calculations that the entropies and the heat capacities of all the 1-MeCHol conformers in the gas state are the same.

IR spectrum of gaseous 1,1-ClMeCH between 900 and 400  $\text{cm}^{-1}$  at 293 K is presented in Fig. 3. Based on the vibrational assignment of 1,1-ClMeCH (Table 10), the areas of doublet 545–565  $\text{cm}^{-1}$  and band 658  $\text{cm}^{-1}$  are consistent with the amounts of conformers A and B, respectively, in their equilibrium mixture. The separation of the profiles of bands 545 and 565  $\text{cm}^{-1}$  was performed under assumption that they have gaussian forms, because these bands overlap strongly in IR spectrum involved. It was found that at 293 K 72% of gaseous 1,1-ClMeCH molecules are in 'chair'-conformation with equatorial methyl group (conformer A). Then  $\Delta_{a\rightarrow e}G^0(293 \text{ K}) = 2.30 \text{ kJ}\cdot\text{mol}^{-1}$ .

Taking into consideration the above characteristics of conformational transitions, the entropies of gaseous 1-MeCHol  $S_m^0(\text{g}; 284.07 \text{ K}) = 378.09 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and 1,1-ClMeCH  $S_m^0(\text{g}; 273.17 \text{ K}) = 358.01 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

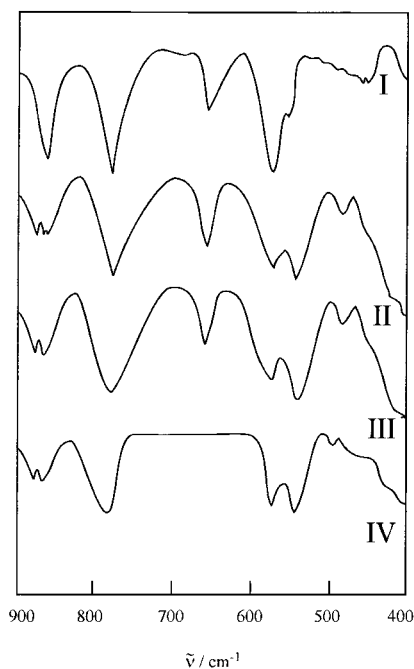


Fig. 3. Infrared spectra of 1-chloro-1-methylcyclohexane: I, gas at  $T=293 \text{ K}$ ; II, liquid at  $T=293 \text{ K}$ ; III, plastic crystal at  $T=223 \text{ K}$ ; IV, rigid crystal at  $T=205 \text{ K}$ .

Table 9

Experimental and calculated vibrational wavenumbers  $\tilde{\nu}$  of 1-methylcyclohexanol<sup>a</sup>; *t* is torsional mode, P.E.D.(%) is potential energy distribution

$\tilde{\nu}$ (cm <sup>-1</sup> )		P.E.D.(%)		$\tilde{\nu}$ (cm <sup>-1</sup> ) selected for statistical calculations
Calc.	IR	Raman		
1470	1460 s	1463 s	CO(9),CCH(22),HCH(62)	1463
1461			CCH(24), HCH(72)	1463
1460			CCH(33), HCH(65)	1463
1455			CCH(18), HCH(78)	1463
1453			CCH(31), HCH(68)	1463
1447	1448 vs	1443 s	CCH(37), HCH(60)	1443
1446			CCH(33), HCH(66)	1443
1427		1428 s	CO(15), CCH(45); HCH(24)	1428
1390	1400 m	1394 w	CC(13), CO(9); CCH(69)	1394
1385	1373 s		CC(7), CCH(89)	1394
1379			CC(23), CCH(25), HCH(5)	1373
1375	1350 m		CC(16), CCH(79)	1350
1367	1340 m	1347 m	CC(30), CCH(68)	1347
1358	1320 m		CC(5), CCH(64), HCH(30)	1320
1269	1278 m	1275 s	CC(8), CCH(44), COH(42)	1275
1250	1260 vs	1262 s	CC(19), CCC(6), CCH(70)	1260
1219	1212 s	1212 m	CCH(98)	1212
1216			CC(5), CCH(91)	1212
1191	1168 vs	1167 s	CCH(99)	1167
1176	1140 m	1137 m	CCH(83), COH(5)	1137
1152	1123 vs	1121 m	CC(14), CCH(79)	1121
1078	1090 m	1088 m	CC(42), COH(18), CCH(28)	1088
1069	1072 m	1071 m	CC(48), CCH(48)	1071
1039	1042 vs	1041 m	CC(42), CCC(7), CCH(41)	1041
1019	1012 s	1009 s	CC(15), CCH(74)	1009
991	990 s	993 w	CC(20), CCH(74)	993
957	968 vs	971 s	CO(10), CCH(81)	971
919	925 m	923 m	CC(9), CCC(5), CCH(82)	923
908	910 vs	905 m	CC(21), CCC(23), CCH(53)	905
885	890 m		CC(49), CCC(6), CCH(40)	890
832	850 s	844 m	CC(45), CCH(50)	844
808	833 s	829 s	CC(22), CO(5), CCH(67)	829
760	783 w	765 m	CC(9), CCH(88)	765
698	718 s	718 s	CC(54), CO(16), CCH(23)	718
575	560 m	566 s	CC(11), CCC(29), CCH(56)	566
494	478 m	491 w	CCC(60), CCH(23), CCO(11)	478
473	453 w	468 w	CCC(49), CCH(18), CCO(15)	453
402		433 w	CCC(39), CCH(10), CCO(41)	433
398	428 w	424 m	CCC(36), CCH(25), tCCr(18)	424
340		353 w	tCC(96)	-
326	325 w	310 vw	CCC(36), tCCr(15), CCO(36)	310
323	325 w	310 vw	tCC(5), tCO(94)	-
289		295 w	CCC(55), CCO(19), tCO(19)	295
269	220 w		CCC(25), tCCr(21), CCO(43)	220
212	170 vw		CCC(27), tCCr(44), CCO(18)	170
127	120 vw	120 m	CCC(49), CCO(14), tCCr(35)	120

<sup>a</sup> Experimental and calculated wavenumbers of O–H and C–H valence vibrations between 3600 and 2800 cm<sup>-1</sup> are not included in this Table. The wavenumbers {3600, 2965(2), 2930(5), 2900, 2855(5)} cm<sup>-1</sup> were chosen for statistical calculations.



Table 10  
 Experimental and calculated vibrational wavenumbers  $\tilde{\nu}$  of 1-chloro-1-methylcyclohexane <sup>a</sup>,  $t$  is torsional mode, P.E.D.(%) is potential energy distribution. Torsional coordinate of methyl group was not taken into consideration in wavenumbers calculations

CH <sub>3</sub> (e)Cl(a)-'chair' conformer			CH <sub>3</sub> (a)Cl(e)'chair' conformer		
$\tilde{\nu}$ (cm <sup>-1</sup> )	Raman	Calc.	P.E.D. (%)	$\tilde{\nu}^b$ (cm <sup>-1</sup> )	$\tilde{\nu}^b$ (cm <sup>-1</sup> )
1460 m		1483	CCH(40),CCHm(14)	1460	1460
		1464	CCHm(12),HCHm(82)	1460	1460
		1458	CCH(20),HCH(76)	1460	1460
1450 s	1455 s	1454	CCH(21),HCH(76)	1455	1455
		1450	CCH(20),HCH(73)	1455	1455
		1447	HCHm(75)	1455	1455
		1444	CCH(20),HCH(77)	1455	1455
		1440	CCH(18),HCH(79)	1455	1455
1428 w	1435 m	1426	CC(37),CCH(61)	1435	1435
1380 s	1390 w	1423	CC(27),CCH(50),HCHm(10)	1390	1390
1363 m		1380	CC(20),CCH(76)	1363	1363
1350 w	1355 w	1379	CCH(28),CCHm(55)	1355	1355
1340 w		1348	CC(10),CCH(67),CCHm(10)	1340	1340
1330 w		1307	CCH(87)	1330	1330
1278 m	1285 s	1290	CC(17),CCH(64)	1285	1285
1255 s	1265 m	1265	CCH(90)	1265	1265
		1259	CCH(92)	1265	1265
1240 w	1240 w	1251	CCH(81)	1240	1240
1167 sh	1175 w	1203	CC(29),CCH(43),CCHm(12)	1175	1175
1145 s	1150 m	1139	CCH(86)	1150	1150
1090 s	1090 m	1087	CCm(47),CCC(17),CCH(14)	1090	1090
		1084	CC(65),CCH(31)	1090	1090
1014 m	1020 m	1073	CC(28),CCH(44),CCHm(13)	1090	1090
980 m	990 m	1033	CC(29),CCH(31),CCHm(25)	1020	1020
960 vs	965 w	938	CC(30),CCH(17),CCHm(40)	980	980
920 m	930 w	933	CCC(21),CCH(49),CCHm(18)	965	965
		886	CCH(89)	930	930
878 m	855 m	868	CC(40),CCm(19),CCH(16)	878	883
845 m		836	CC(61),CCHm(16)	855	883
		802	CC(44),CCH(46)	845	835
780 sh	780 sh	802	CC(45),CCH(45)	780	780
770 s	780 vs	745	CC(16),CCH(78)	780	780
570 s	670 m	583	CC(32),CCH(39),CCH(13)	670	658 m.
545 s	520 w	552	CCm(15),CCC(25),CCH(42)	520	515 w
462 w	470 w	484	CCC(60),CCH(26)	470	462 w
445 w	450 m	474	CCC(42),CCH(40)	445	445 w
390 m	400 m	393	tCCr(20),CCC(33),CCH(26)	390	390 m
			CCC(11),CCCm(49),CCH(16)	390	390 m
			CCC(32),CCC(34),tCCr(15)	450	445 w
			CCC(54),CCCm(13),CCH(24)	470	470 w
			CCC(38),CCH(54)	520	520 w
			CCl(27),CCm(16),CCH(21)	670	670 m
			CC(16),CCH(78)	770 s	780 vs
			CC(22),CCm(17),CCH(55)	780 sh	798
			CC(67),CCH(24)	830 vw	831
			CC(41),CCm(14),CCH(16)	883 sh	885
			CC(67),CCH(10)	883	885
			CC(62),CCH(24)	885	885
			CC(22),CCm(17),CCH(55)	830 vw	831
			CC(16),CCH(78)	780 sh	798
			CC(27),CCm(16),CCH(21)	658 m.	669
			CCC(38),CCH(54)	515 w	499
			CCC(54),CCCm(13),CCH(24)	462 w	480
			CCC(32),CCC(34),tCCr(15)	445 w	435
			CCC(11),CCCm(49),CCH(16)	390 m	386

Table 10  
(continued)

CH <sub>3</sub> (e)Cl(a)-'chair' conformer		CH <sub>3</sub> (a)Cl(e)'chair' conformer	
$\tilde{\nu}$ (cm <sup>-1</sup> )	Calc.	$\tilde{\nu}^b$ (cm <sup>-1</sup> )	P.E.D. (%)
IR	Raman	IR	Raman
370 m	373	370	CCCm(40),CCH(11),CCCCI(31)
325 m	334	325	CCI(16),CCCm(19),CCCCI(26)
290 w	301	290	CCC(29),tCCr(21),CCCCI(31)
280 m	296	270	CCC(13),CCCm(45),tCCr(22)
200 m	202	220	CCC(17),CCCCI(47),tCCr(21)
130 m	118	125	CCC(28),CCCm(20),tCCr(30)

<sup>a</sup> Experimental and calculated wavenumbers of C–H valence vibrations between 3000 and 2800 cm<sup>-1</sup> are not included in this Table.

The wavenumbers {2970(2), 2945, 2930(4), 2905, 2870(3), 2840(2)} cm<sup>-1</sup> were chosen for statistical calculations.

<sup>b</sup> Experimental vibrational wavenumbers selected for statistical calculations.

were calculated. These values are in a good agreement with the experimental entropies for the compounds under study in the gas state: 378.15 and 358.37 J·K<sup>-1</sup>·mol<sup>-1</sup> (Table 7), respectively. Standard molar thermodynamic functions of 1-MeCHol and 1,1-C1MeCH in the ideal gas state are listed in Tables 11 and 12.

### 3.3. The rotation of 1-chloro-1-methylcyclohexane molecules in the plastic crystal state

According to conventional knowledge [1,2], the transition of organic compounds into the plastic crystal state can be caused by the onset of internal rotation and over-all reorientation of molecules in the nodes of

Table 11

Standard molar thermodynamic functions for 1-methylcyclohexanol in the ideal gas state

T/K	$C_{p,m}^0/R$	$\Delta_0^T S_m^0/R$	$\Delta_0^T H_m^0/RT$	$\Phi_m^0/R$
100	8.245	33.08	5.688	27.39
200	12.90	40.23	8.133	32.10
298.15	18.24	46.34	10.55	35.79
300	18.35	46.46	10.60	35.86
400	24.28	52.55	13.28	39.27
500	29.71	58.57	16.04	42.53
600	34.36	64.41	18.71	45.69
700	38.27	70.00	21.24	48.77
800	41.53	75.33	23.58	51.76
900	44.27	80.39	25.73	54.66
1000	46.57	85.18	27.70	57.48

( $R=8.31451$  J·K<sup>-1</sup>·mol<sup>-1</sup>;  $p^0=101325$  Pa).

Table 12

Standard molar thermodynamic functions for 1-chloro-1-methylcyclohexane in the gas state

T/K	$C_{p,m}^0/R$	$\Delta_0^T S_m^0/R$	$\Delta_0^T H_m^0/RT$	$\Phi_m^0/R$
100	7.320	31.97	5.063	26.90
200	12.40	38.63	7.483	31.15
298.15	17.70	44.55	9.954	34.59
300	17.81	44.65	10.00	34.65
400	23.53	50.56	12.67	37.89
500	28.78	56.39	15.38	41.01
600	33.30	62.05	18.00	44.05
700	37.11	67.48	20.47	47.01
800	40.32	72.65	22.75	49.90
900	43.01	77.56	24.86	52.70
1000	45.27	82.21	26.79	55.42

( $R=8.31451$  J·K<sup>-1</sup>·mol<sup>-1</sup>;  $p^0=101325$  Pa).

crystal lattice. Previously, Agaev et al [14,15] found when studying the IR spectra of 1,1-ClMeCH that band  $660\text{ cm}^{-1}$  assigned to C–Cl stretching vibration disappears at freezing of 1,1-ClMeCH sample near 200 K. Then, only the most stable conformer with the axial chlorine remains in this freezed sample at 200 K. To adjust the temperature, when an abrupt change of conformational composition of the compound under study takes place, the IR spectra of 1,1-ClMeCH in the condensed state were recorded over the temperature interval from 293 to 200 K (Fig. 3). It can be seen from these spectra that the intensity of band  $658\text{ cm}^{-1}$  does not almost change on lowering the temperature from 293 to 214 K. However, this band disappears almost completely just after formation of the rigid crystal phase of 1,1-ClMeCH at below 214 K. So, it may be considered that only one, thermodynamically more stable  $\text{CH}_3(\text{e})\text{Cl}(\text{a})$ -‘chair’-conformer of 1,1-ClMeCH retains in its rigid crystal.

Such a change of conformational composition at the plastic crystal  $\rightarrow$  rigid crystal transition occurs also in the chlorocyclohexane [3] and in the chlorocyclopentane [16]. Consequently, the prohibition of cyclohexyl ring inversion with potential barrier of about  $50\text{ kJ}\cdot\text{mol}^{-1}$  obtained by the MM2(87) program is removed at the rigid crystal  $\rightarrow$  plastic crystal transition. So, it is very probable that the methyl group rotation is also excited at this transition, because potential barrier of this rotation is  $19.2\text{ kJ}\cdot\text{mol}^{-1}$  as obtained from MM2(87) calculations. The contributions of ring inversion ( $S_{m\text{inv}}^0 = 14.61\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and  $\text{CH}_3$ -top rotation ( $S_m^0(\text{CH}_3) = 4.76\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) to the entropy of 1,1-ClMeCH at temperature of transition  $\text{crII} \rightarrow \text{crI}$  (214.37 K) were performed by the statistical thermodynamics methods (system of non-interacted molecules). As the sum of these two values is considerably less than the value  $\Delta_{\text{crII}}^{\text{crI}} S_m^0 = 43.76\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , it is necessary to accept, as for chlorocyclohexane [3], a possibility of existence of both internal rotation and over-all rotation of molecules in the plastic crystals of 1,1-ClMeCH.

The over-all rotation of molecule is expected to be significantly hindered, because the total contribution of the free rotation of molecules to the entropy of 1,1-ClMeCH at 214.37 K is  $116.19\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (system of non-interacted molecules) and it is considerably more than the entropy of transition  $\Delta_{\text{crII}}^{\text{crI}} S_m^0$ . It is very probable that the over-all rotation of 1,1-ClMeCH

molecules takes place only along one rotational axis. This supposition is in agreement with the results of investigation of cyclohexane in its crystals by the molecular dynamics methods reported by Wurfinger [17]. It was shown [17] that the rotation of cyclohexane molecules along one  $\text{C}_3$ -axis is connected with significantly less van der Waals atomic radii overlapping of neighbouring molecules in crystal lattice in comparison with the rotation of these molecules along other axes.

To interpret the nature of molecular motion in plastic crystals it is very important to note that a large heat capacity jump  $\Delta_{\text{crII}}^{\text{crI}} C_{s,m} = 34.7\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  takes place at transition of 1,1-ClMeCH into the plastic crystal state. This fact testifies that some stable states with different  $\Delta E_i$  appear in plastic crystal because  $\Delta_{\text{orient}} C_{s,m} \neq 0$  only at  $\Delta E_i \neq 0$  in conformity with correlation from [18]:

$$\begin{aligned} \Delta_{\text{orient}} C_{s,m} &= \sum_{i=1}^n \frac{\partial x_i}{\partial T} \Delta E_i \\ &= \frac{1}{RT^2} \sum_{i=1}^n x_i \sum_{j>i}^n x_j (\Delta E_i)^2 \end{aligned} \quad (3)$$

where  $x_i, x_j$  - are the mole fractions of molecules in  $i, j$ -‘plastic orientations’ ( $x_i = \text{const}$  for all  $i = (2, 3 \dots n)$  for each plastic crystal accordingly accepted assumptions);  $\Delta E_i = E_{\text{plast}} - E_{\text{bas}}$  is the energy difference between the plastic and basic orientations (Fig. 4);  $T$  is the temperature;  $\Delta_{\text{orient}} C_{s,m}$  is the heat capacity change caused by changing the molecular orientations in plastic crystals. We estimated possible values  $\Delta E_i$  and numbers of distinguished orientational states  $n$  using correlation (3) which approximately corresponds to  $\Delta_{\text{orient}} C_{s,m} = \Delta_{\text{crII}}^{\text{crI}} C_{s,m} - C_{s,m\text{inv}} - C_{s,m}(\text{CH}_3) = 18.0\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The calculated values, close to the experimental ones, are obtained at moderate values  $\Delta E_i$  and sufficiently large numbers of non-equivalent orientational states  $n$  (Fig. 5).

It should be mentioned that these estimations supplement greatly the conception of Guthrie and McCullough who suggests a relation  $\Delta_{\text{orient}} S_m^0 = R \ln N$  for orientational disorder in plastic crystal, where  $N$  is numbers of non-equivalent orientations. It is supposed in this case that all non-equivalent states with different molecular orientation are of equal energetical value. But, accordingly to Eq. (3),  $\Delta_{\text{orient}} C_{s,m} = 0$  at  $\Delta E_i = 0$ . This fact is in contradiction with our mea-

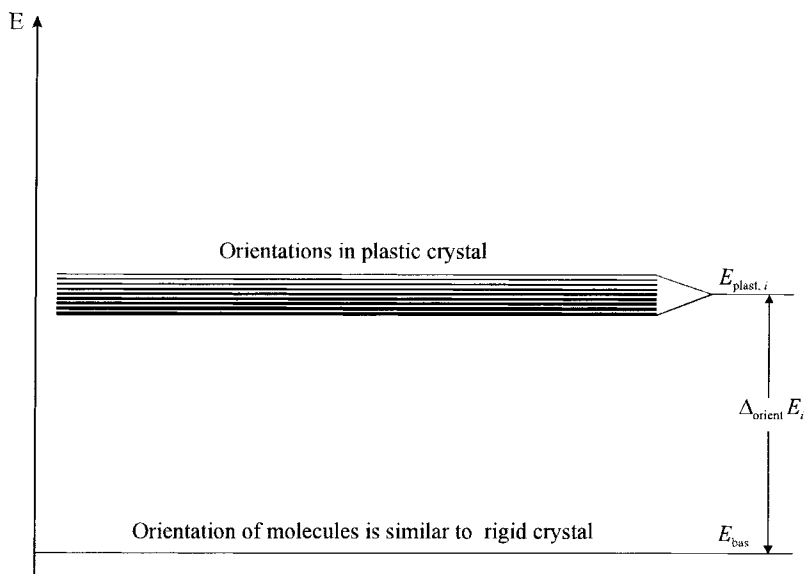


Fig. 4. The model of energetical states with different orientations of molecular groups in the plastic crystal state:  $\Delta_{\text{orient}}E_i$  is the energy difference between the plastic and basic orientations of molecules.

surements ( $\Delta_{\text{orient}}C_{s,m \text{ exp}} = 18 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and with the existence of the heat capacity jumps at the transitions into the plastic crystal state for some other cyclohexane derivatives:  $\Delta_{\text{crII}}^{\text{crI}}C_{s,m}(186.09\text{K})=13.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for cyclohexane [5],  $\Delta_{\text{crII}}^{\text{crI}}C_{s,m}(220.4 \text{ K})=17.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for chlorocyclohexane [3],  $\Delta_{\text{crII}}^{\text{crI}}C_{s,m}(265.50 \text{ K})=22.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for cyclohexanol [4],  $\Delta_{\text{crII}}^{\text{crI}}C_{s,m}(153.15 \text{ K})=32.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for 1,1-dimethylcyclohexane [5]. Therefore, a more strict method of estimations of the contribution of orientational disorder to the entropy of crystals is the following relation:

$$\Delta_{\text{orient}}S_m^0 = -R \sum_{i=1}^n x_i \ln x_i$$

where  $x_i$  is the mole fraction of molecules in  $i$ -orientation.

Closer to experimental value  $\Delta_{\text{orient}}S_m^0 = \Delta_{\text{crII}}^{\text{crI}}S_m^0 - S_{m \text{ inv}}^0 - S_m^0(\text{CH}_3) = 24.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  the orientational entropies of 1,1-CIMeCH are obtained with values of  $\Delta E_i$  and  $n$  shown in Fig. 6.

The general agreement between the experimental and calculated values  $\Delta_{\text{orient}}C_{s,m}$  and  $\Delta_{\text{orient}}S_m^0$  for 1,1-CIMeCH is obtained with values of

$\Delta E_i \approx 5.5 \text{ kJ}\cdot\text{mol}^{-1}$  and numbers of  $n$  from 32 to 44. Sufficiently large numbers of non-equivalent configurations  $n$  can be probably explained by the fact that the non-equivalent states are formed by groups of coordinated molecules in crystal. In this case, large values of  $n$  are physically justified.

So, it can be suggested that in the plastic crystal phase of 1,1-CIMeCH:

1. Rotation of molecules can possibly happen along one axis mainly.
2. Rotation of molecules is hindered in the plastic crystal state.
3. Preferable co-ordinated configurations of molecular groups are formed at simultaneous rotation of molecules. The energetical minima correspond to these configurations.
4. It is very probable that the global energetical minimum corresponds to the molecular orientation which is equivalent to the molecular arrangement in the rigid crystal state.

This model makes possible to get a satisfactory interpretation of values of  $\Delta_{\text{crII}}^{\text{crI}}S_m^0$  and of  $\Delta_{\text{crII}}^{\text{crI}}C_{s,m}$  for the transition of 1,1-CIMeCH into the plastic crystal state.

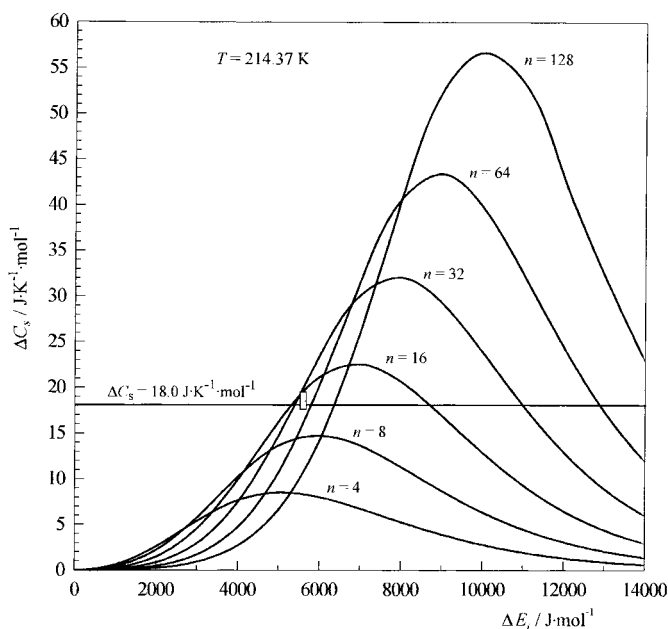


Fig. 5. The dependence of the orientational heat capacity on the energy difference between plastic and basic molecular orientations (see Fig. 4) and on the numbers of non-equivalent states for 1-chloro-1-methylcyclohexane:  $\square$  is the interval of general agreement between the experimental and calculated values  $\Delta_{\text{orient}}C_{s,m}$  and  $\Delta_{\text{orient}}S_m^0$ .

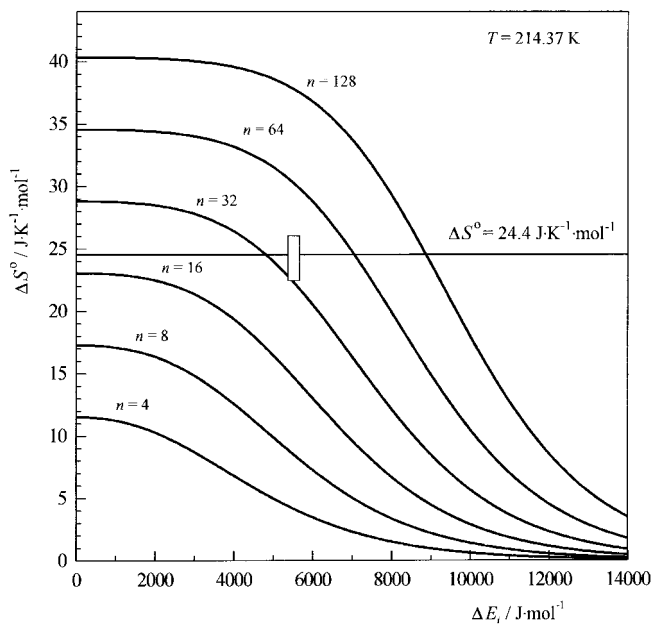


Fig. 6. The dependence of the orientational entropy on the energy difference between plastic and basic molecular orientations (see Fig. 4) and on the numbers of non-equivalent states for 1-chloro-1-methylcyclohexane:  $\square$  is the interval of general agreement between the experimental and calculated values and  $\Delta_{\text{orient}}C_{s,m}$  and  $\Delta_{\text{orient}}S_m^0$ .

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