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Thermodynamic properties of adamantane and the energy states of molecules in plastic crystals for some cage hydrocarbons

G.J. Kabo*, A.V. Blokhin, M.B. Charapennikau, A.G. Kabo, V.M. Sevruk

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

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Abstract

Thermodynamic properties of adamantane (I) were investigated in this paper. Heat capacities of I in the condensed state between 340 and 600 K were measured by a scanning calorimeter of triple heat bridge type, and characteristics of the fusion of I were determined. The measurements of the enthalpy of sublimation and the saturated vapor pressure for I were made. Thermodynamic functions of I in the ideal gas state were calculated by the statistical thermodynamics methods. The energy states of molecules in the plastic crystals for some cage hydrocarbons (adamantane, bicyclo[2.2.2]octane, pentacycloundecane, heptacyclotetradecane and diamantane) are discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Adamantane; Cage hydrocarbons; Thermodynamics; Phase transitions; Plastic crystals

1. Introduction

There are a few attempts of the interpretation of orientational disorder in crystals [1–3]. In our previous investigations [4,5] it was shown that the test of suggested models has essential meaning not only for the interpretation of the $\Delta_{\mathrm{r.cr}}^{\mathrm{pl.cr}}S$ (entropy changes corresponding to the rigid crystal-to-plastic crystal transitions), but also, simultaneously, of the heat capacity changes $\Delta_{\mathrm{r.cr}}^{\mathrm{pl.cr}}C_{\mathrm{s}}$ at this transition. Value of $\Delta_{\mathrm{r.cr}}^{\mathrm{pl.cr}}C_{\mathrm{s}}$ is not zero only with presence of energy differences between stable ('pseudorigid') and 'plastic' molecular orientations in crystal. The procedure of calculation of the mean energy differences between basic and 'plastic' orientations $\Delta_{\mathrm{orient}}H$ and the numbers of non-equivalent orientations of molecules n_{orient} in plastic crystals was proposed for some cyclohexane derivatives [5]. The estimation of $\Delta_{\mathrm{orient}}S$ and $\Delta_{\mathrm{orient}}C_{\mathrm{s}}$ from the experimental values of $\Delta_{\mathrm{trs}}S$ and $\Delta_{\mathrm{trs}}C_{\mathrm{s}}$ was complicated by necessary account of the contributions arising from removal of prohibitions for internal rotation and ring inversion in molecules during the transition into the orientational disordered crystal state. As it was noted [3], cage hydrocarbons give an unique opportunity to investigate the orientational disorder in plastic crystals which have not been complicated by the ring inversion in molecules.

In this study the heat capacity in the condensed state between 340 and 600 K, the enthalpies of fusion and sublimation and the saturated vapor pressure of adamantane were measured. The statistical calculations of thermodynamical properties of adamantane in the ideal gas state were performed and the results agree with the experimental value of entropy obtained from the low-temperature investigations by Chang and Westrum [6] and our data.

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* Corresponding author. Fax: +375-17-2203916.
E-mail address: kabo@fhp.bsu.unibel.by (G.J. Kabo).

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The values of $\Delta_{\mathrm{orient}}H$ and numbers of non-equivalent orientations n_{orient} were estimated for adamantane and cage hydrocarbons $C_{11}H_{14}$ and $C_{14}H_{16}$ investigated earlier in our laboratory [7,8], and also for some related substances.

2. Experimental

Adamantane was purified by triple recrystallization from acetone and subsequent sublimation at 333 K/0.5 kPa. The purity of the sample was 99.98 (mass%) as determined by gas–liquid chromatography (chromatograph Chrom-5, FID detection, steel column with length 3 m and diameter 7 mm was filled with 5 mass% of PEG on Inerton AW-DMCS, carrier gas was nitrogen at pressure 76 kPa, temperature of column was 333 K).

The measurements of the heat capacity between 340 and 600 K were carried out using an advanced and automated [9,10] scanning calorimeter of the triple heat bridge type. By heating the device with constant speed, there were temperature differences between the heater block and containers. These differences were proportional to individual thermal fluxes and, hence, to the total heat capacity of containers with contents. The temperature difference was measured through electrical potential difference generated in the copper-to-(0.550 Cu + 0.450 Ni) differential thermocouple. Containers were hermetically sealed and an internal space of the device was filled by argon at pressure 6.5 KPa. Investigated substance was placed in one of the containers, the other container was filled with a standard substance having a well-known temperature dependence of the heat capacity (copper with purity of 99.995%) and the third one remained empty. Specific heat capacity of the compound under study is calculated from the formula

$$c_x = c_{\mathrm{Cu}}\frac{m_{\mathrm{Cu}}}{m_x}\frac{V_1}{V_2} - \frac{c_k\,m_k}{m_x},$$

where c_x is the specific heat capacity of substance in question; c_{Cu} is the specific heat capacity of copper; c_k is the specific heat capacity of the container material; m_x is the mass of substance; m_{Cu} is the mass of copper; m_k is the mass of the container; V_1 is a potential difference between the empty cup and the cup with sample under investigation; V_2 is a potential difference between the empty cup and the cup with copper.

The calorimeter was calibrated by a high-purity copper (99.995%). The uncertainty in heat capacity determination is estimated approximately to be ± 2% [10].

The saturated vapor pressure was determined by integral effusion Knudsen method. The sample was placed in a stainless steel chamber, which was sealed with a Teflon gasket. Membrane of nickel foil (thickness 0.05 mm) with diameters of effusion orifice (0.2265 ± 0.0004 mm) was used. It was assumed for calculation that the vapor has a monomolecular composition. The uncertainty in vapor pressures determination did not exceed ±5%. The apparatus construction and measuring procedure were described earlier [11,12].

The sublimation enthalpy was determined in a differential heat-conducting microcalorimeter of Calvet type MID-200 with special calorimetric cells, described earlier [13]. The modernized MID-200 included a voltmeter with limits of measurements between 1×10^{-9} and 2 V and relaxation time between 2 and 30 s combined with an IBM PC. The samples were placed in hermetic cells of stainless steel supplied with a nickel membrane. After preliminary thermostating of the calorimeter, the membrane was pierced by a special demountable rod and the heating flux needed for evaporation was recorded. The calorimeter was calibrated by sublimation of benzoic acid (K-1) and naphthalene and by vaporization of *n*-decane and doubly distilled water. As a result, it was found that the uncertainty of evaporation enthalpy measurements did not exceed ±0.5%.

3. Thermodynamic properties of adamantane

The temperature dependence of the heat capacity of adamantane in the condensed state between 5 and 600 K obtained from the results of measurements [6] and our investigations is represented in Fig. 1. (The smoothed values of the molar heat capacity and the standard thermodynamic functions of adamantane in the interval from 340 to 600 K are listed in Table 1). Thermodynamic quantities associated with the phase transitions of the compound are given in Table 2.

The enthalpy of sublimation of adamantane was determined in a series of calorimetric experiments (Table 3). The experimental saturated vapor pressures over crystal adamantane are given in Table 4.

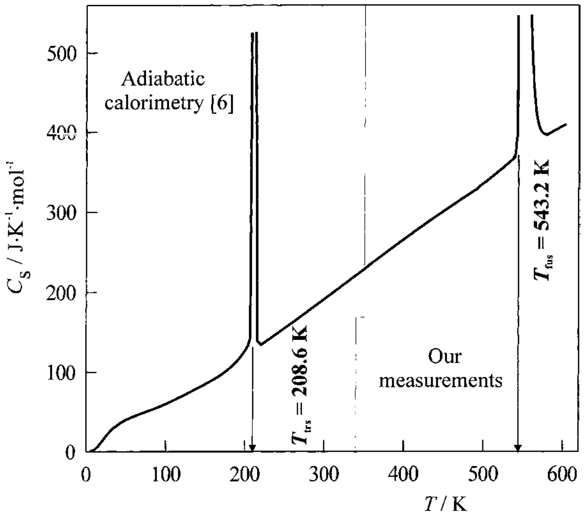

Fig. 1. The temperature dependence of the heat capacity in the condensed state for adamantane.

The entropy of crystal adamantane from the low-temperature measurements [6] is $\Delta_0^T S_m^0$ (crI; 303.54 K) = (199.27 ± 0.40) J K^{-1} mol^{-1}. Thermodynamic parameters of sublimation $\Delta_{crI}^{g} H_m$ (303.54 K) = (58.52 ± 0.15) kJ mol^{-1} and $\Delta_{crI}^{g} S_m$ (303.54 K) = (192.79 ± 0.49) J K^{-1} mol^{-1} were calculated on the basis of results given in Table 3 and the mean value $\Delta_{crI}^{g} C_p = -44.35$ J K^{-1} mol^{-1}. The experimental standard entropy of adamantane in the ideal gas state S_m^0 (g; 303.54 K) = (324.62 ± 0.76) J K^{-1} mol^{-1} was obtained using the value of P_{sat} = (30.4 ± 1.5) Pa (Table 4).

The molar mass M = 136.2364 g mol^{-1} was used for the statistical calculation of thermodynamic functions of adamantane in the gas state. The principal moments-of-inertia product $I_{ABC} = 124.647 \times 10^{-135}$ kg^3 m^6 was calculated from geometrical parameters obtained by the molecular mechanics method [14]. The adamantane molecule belongs to the symmetry groups T_d and has the symmetry number for external rotation $\sigma = 12$. Numerical values of wave numbers for the normal modes of intermolecular vibrations were taken from [15] (2957 2957 2950 2940 2940 2940 2927 2913 2910 2910 2910 2900 2900 2850 2850 2850 1472 1455 1455 1455 1439 1439 1370 1370 1359 1359 1359 1321 1321 1321 1310 1310 1310 1288 1288 1288 1217 1217 1189 1128 1128 1128 1101 1101 1101 1043 1043 1043 990 970 970 970 953 953 873 873 873 800 800 800 756 638 638 638 444 444 444 402 402 312 312 312), in which the normal vibrational assignment for adamantane molecules was made on the basis of comparison IR and Raman spectra for adamantane and some its H-substituted isotopomers (-1-d$_1$, -2-d$_1$, -2,2-d$_2$, -d$_{16}$).

Table 1
Molar thermodynamics functions for adamantane[a]

T (K)	$C^0_{s,m}/R$	$\Delta_0^T S^0_m/R$	$\Delta_0^T H^0_m/RT$	Φ^0_m/R
Crystal I				
340	26.26	26.64	13.66	12.98
350	27.38	27.42	14.04	13.38
360	28.41	28.21	14.42	13.78
370	29.37	29.00	14.82	14.18
380	30.27	29.79	15.21	14.58
390	31.14	30.59	15.61	14.98
400	31.98	31.39	16.01	15.38
410	32.80	32.19	16.41	15.78
420	33.61	32.99	16.81	16.18
430	34.42	33.79	17.21	16.58
440	35.24	34.59	17.61	16.98
450	36.07	35.39	18.01	17.38
460	36.91	36.19	18.41	17.78
470	37.77	37.00	18.81	18.19
480	38.65	37.80	19.22	18.59
490	39.55	38.61	19.62	18.99
500	40.46	39.42	20.03	19.39
510	41.38	40.23	20.44	19.79
520	42.32	41.04	20.85	20.19
530	43.25	41.85	21.26	20.59
540	44.18	42.67	21.68	20.99
543.2	44.48	42.93	21.81	21.12
Liquid				
543.2	44.48	46.02	24.81	21.21
550	45.10	46.58	25.06	21.52
560	45.99	47.40	25.42	21.98
570	46.84	48.22	25.79	22.43
580	47.65	49.04	26.16	22.88
590	48.39	49.87	26.53	23.33
600	49.05	50.68	26.90	23.78

[a] M = 136.236 g mol^{-1}; R = 8.31451 J K^{-1} mol^{-1}.

Table 2
Temperatures, the molar enthalpies and entropies of phase transitions of adamantane

Transition	T_{trs} (K)	ΔH_m^0 (J mol^{-1})	ΔS_m^0 (J K^{-1} mol^{-1})	Reference
CrII → crI	208.60	3376	16.19	[4]
CrI → l	543.20	13958 ± 279	25.7 ± 0.5	This work

Table 3
The results of calorimetric determination of the enthalpy of sublimation for adamantane[a]

No.	m (g)	T (K)	$\int_{\tau=0}^{\tau}\Delta V\,\mathrm{d}\tau$ (mV s)	Type of cell	ΔH (J)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}$ (kJ mol^{-1})
1	0.05016	306.14	4790.37	A	20.50	58.40
2	0.06792	305.86	6498.38	A	29.17	58.51
3	0.07126	306.52	6854.55	A	30.77	58.82
4	0.07615	309.06	7211.37	A	32.37	57.91
5	0.09246	309.14	8852.84	A	39.74	58.55
6	0.07291	309.47	6953.20	A	31.21	58.32
7	0.06815	308.11	6494.41	A	29.15	58.28
8	0.11800	308.40	11278.84	A	50.63	58.45
9	0.06363	309.04	5702.89	B	26.95	57.70
10	0.08484	309.09	7659.34	B	36.19	58.12
11	0.07283	309.37	6611.68	B	31.24	58.45
12	0.10855	308.51	9819.18	B	46.40	58.24
13	0.04533	306.08	4104.92	B	18.52	58.29
14	0.07410	305.81	6703.16	B	30.25	58.24
15	0.05741	306.50	5226.57	B	23.58	58.61

$\langle\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}\langle 307.81\rangle\rangle = (58.33 \pm 0.15)$ kJ mol^{-1}

[a] The calorimetrically measured enthalpy change ΔH and molar enthalpies $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}$ were calculated from expressions: $\Delta H = K^{-1}\int_{\tau=0}^{\tau}\Delta V\,\mathrm{d}\tau$; $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0} = \Delta H(M/m)$, where m is the mass of a specimen; M is the molar mass; K is the calorimetric constant ($K_{\mathrm{A}} = 228.78$ mV s K^{-1} and $K_{\mathrm{B}} = 211.62$ mV s K^{-1}); ΔV is the thermocouple potential difference corresponding to the temperature difference between the cell and the calorimetric thermostat at time τ; τ 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.

The entropy of gaseous adamantane at $T = 303.54$ K, S_{m}^{0} (g) $= (324.83 \pm 1.62)$ J K^{-1} mol^{-1} 1 determined from the above-mentioned data is in very good agreement with the experimental value. Thermodynamic functions of adamantane in the ideal gas state between 100 and 1000 K are given in Table 5.

Using the results of the previous normal vibrational assignment for adamantane [18], another value of S_{m}^{0} (g; 303.54 K) $= (323.93 \pm 1.62)$ J K^{-1} mol^{-1} was obtained, which also agrees well with the experimental entropy of the gaseous compound.

Table 4
Saturated vapor pressures P_{sat} over crystal adamantane; Δm is the sample mass decrease; τ is the duration of effusion

T (K)	τ (s)	Δm (mg)	P_{sat} (Pa)
303.58	5454	19.57	30.37
303.52	3054	10.87	30.14
303.46	3054	11.06	30.65
303.53	3054	10.90	30.21
303.56	3054	10.72	29.71
303.59	3054	11.24	31.15

$\langle P_{\mathrm{sat}}(303.54\ \mathrm{K})\rangle = (30.4 \pm 1.5)$ Pa

4. States of molecules of some cage hydrocarbons in plastic crystals

Thermodynamic characteristics of solid-to-solid transition and fusion of adamantane and some cage hydrocarbons (Fig. 2) are given in Table 6. All represented cage hydrocarbons exist in the plastic crystal state over wide temperature intervals T_{fus}–$T_{\mathrm{tr}} \approx$ (85–330) K. There is an approximate constancy of the sums of the entropies of all the solid-to-solid transitions and fusion $\sum_i \Delta_{\mathrm{cr}}^{1}S_i \cong (47 \pm 7)$ J K^{-1} mol^{-1} for these compounds which was also noted in our previous studies [4,5] for the cyclohexane and cyclopentane derivatives. However, the values $\sum_i \Delta_{\mathrm{cr}}^{1}S_i$ are more exactly described by the correlation equation between $\sum_i \Delta_{\mathrm{cr}}^{1}S_i$ and the symmetry number of external rotation σ and the principal moments-of-inertia products I_{ABC} (kg^3 m^6) of cage hydrocarbons (Table 7):

$$\sum_i \Delta_{\mathrm{cr}}^{1}S_i = -0.153\ln(I_{\mathrm{ABC}}) - 0.035\ln(\sigma). \tag{1}$$

Table 5
Standard molar thermodynamic functions for adamantane in the ideal gas state ($R = 8.31451$ J K^{-1} mol^{-1}; $p^0 = 101\,325$ Pa)

T (K)	$C^0_{p,m}/R$	$\Delta_0^T S^0_m/R$	$\Delta_0^T H^0_m/RT$	Φ^0_m/R	$\Delta_f H^0_m$ (kJ mol^{-1})[a]	$\Delta_f G^0_m$ (kJ mol^{-1})[a]
100	5.144	28.26	4.225	24.04	−98.57	−40.54
200	10.38	33.29	5.887	27.40	−117.1	24.76
298.15	17.73	38.75	8.530	30.22	−134.6	98.16
300	17.88	38.86	8.587	30.27	−134.9	99.61
303.54	18.17	39.07	8.697	30.37	−135.4[b]	102.5[b]
400	26.01	45.12	11.93	33.19	−150.1	180.2
500	33.23	51.73	15.49	36.23	−162.1	264.2
600	39.24	58.33	18.97	39.37	−171.1	350.3
700	44.19	64.77	22.23	42.54	−177.5	437.8
800	48.31	70.94	25.24	45.71	−181.9	526.5
900	51.76	76.84	28.00	48.84	−184.4	614.6
1000	54.68	82.45	30.52	51.92	−185.3	703.5

[a] Calculated on the basis of $\Delta_f H^0_m$ (g; 298.15) = (134.6 ± 2.2) kJ mol^{-1} [16]. The thermodynamic properties of C (graphite) and H_2 (gas) between 100 and 1000 K were taken from [17].

[b] Obtained by linear interpolation.

The values of $\sum_i \Delta^1_{cr} S_i$ calculated from Eq. (1) agree with the experimental values within ±10% (Table 7) which is satisfactory for such kind of correlations.

The entropies of solid-to-solid transition from rigid to plastic crystal differ by the factor from 1.5 to 2.5 for hydrocarbons under study (Table 6). The differences in $\Delta_{trs}C_s$ between cage hydrocarbons are very great and the determination of any correlation between the heat capacity changes at the transition in question and the structural parameters of molecules was unsuccessful.

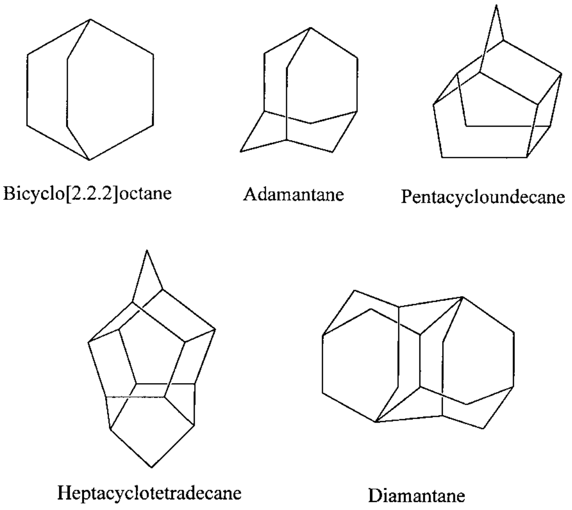
Bicyclo[2.2.2]octane
Adamantane
Pentacycloundecane
Heptacyclotetradecane
Diamantane

Fig. 2. The molecular structures of cage hydrocarbons.

For cage hydrocarbons, when there are no internal rotation and ring inversion in molecules, parameters of the transitions into the plastic crystal state can be represented as the following sums [5]:

$$\Delta_{trs}S = \Delta_v S + \Delta_{orient}S, \tag{2}$$

$$\Delta_{trs}C_s = \Delta_v C_s + \Delta_{orient}C_s, \tag{3}$$

where $\Delta_v S$ and $\Delta_v C_s$ are the volume-change contributions at the phase transitions, $\Delta_{orient}S$ and $\Delta_{orient}C$ are the contributions due to orientational disordering of molecules in the plastic crystals.

The volume-change contributions to $\Delta_{trs}S$ can be calculated on the basis of (p–V_m–T)-data by the following equation [5]:

$$\Delta_v S = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V = \int_{V_1}^{V_2} (\beta_v(V))\,\mathrm{d}V = \beta_v \Delta_{trs} V, \tag{4}$$

where V_1 and V_2 are the mole volumes of rigid crystal and plastic crystal, respectively, at the temperature of the solid-to-solid transition, $\beta_v = (\partial p/\partial T)_V$ are the mean pressure coefficient in the range from V_1 to V_2, $\Delta_{trs}V = V_2 - V_1$. There are no experimental data for the estimation of $\beta_v(V)$. It was shown [5] that the ratio $\Delta_v S/\Delta_{trs}S$ was 0.42 on the average for the transitions from rigid crystal to plastic crystal observed in some cyclohexane derivatives.

Table 6

The temperatures, molar enthalpies and molar entropies of phase transitions of same cage hydrocarbons in the condensed state

Formula	Compound	Transition type	T (K)	$\Delta_{trs}H^0_m$ (kJ mol^{-1})	$\Delta_{trs}S^0_m$ (J K^{-1} mol^{-1})	$\sum_i \Delta^1_{cr}S_i$ (J K^{-1} mol^{-1})	Reference
C_8H_{14}	Bicyclo[2.2.2]octane	CrII → crI	164.25	4.59	27.9		[19]
		CrI → liq	447.48	8.35	18.7	46.6	
$C_{10}H_{16}$	Adamantane	CrII → crI	208.60	3.38	16.2		[6]
		CrI → liq	543.20	13.80	25.4	41.6	This work
$C_{11}H_{14}$	Pentacycloundecane	CrII → crI	164.40	4.86	29.6		[7]
		CrI → liq	475.80	6.38	13.5	43.1	
$C_{14}H_{16}$	Heptacyclotetradecane	CrII → crI	355.00	14.67	41.4		[8]
		CrI → liq	440.00	5.57	12.6	54.0	
$C_{14}H_{20}$	Diamantane	CrIII → crII	407.22	4.46	10.8		
		CrII → crI	440.43	8.96	20.2		
		CrI → liq	517.92	8.64	16.8	47.8	[20]

This value was used for the present cage hydrocarbons to estimate the orientational entropy during the formation of plastic crystals: $\Delta_{orient}S = \Delta_{trs}S - \Delta_v S = 0.58\Delta_{trs}S$.

Since the (V_m, T)-isobars of organic crystals are nearly linear [21] and, hence, $(\partial^2 V/\partial T^2) \approx 0$, the volume-change contributions $\Delta_v C_s$ may be ignored when considering the phase transitions under study. In view of the above-mentioned assumptions the values of $\Delta_{orient}S$ and $\Delta_{orient}C_s$ were determined for plastic crystals of some hydrocarbons (Table 7).

The correlation ratio for $\Delta_{orient}S$ was also obtained from the data of Table 7:

$$\Delta_{orient}S = -6.020 \times 10^{-3} R\ln(I_{ABC}) + 8.325\chi - 0.311R\ln(\sigma), \qquad (5)$$

where I_{ABC} (kg^3 m^6) is the principal moments-of-inertia products of molecules, $\chi = (2B - A - C)/(A - C)$ is the acentricity parameter where A, B, C (Hz) are the rotational constants [22], σ is the symmetry number for overall rotation of molecules. It should be mentioned that distribution of correlation ratios (1) and (5) on other classes of substances can result in large errors.

It was shown in our previous studies [4,5] that the modified model of Guthrie and McCullough [1] is fruitful for interpretations of numerical values $\Delta_{orient}S$ and $\Delta_{orient}C_s$ in plastic crystals. It is accepted in this model that:

1. The molecules in the plastic crystalline phases undergo hindered overall rotation from one

Table 7

The contributions of orientational disordering of molecules to the heat capacity ($\Delta_{orient}C_s$) and entropy ($\Delta_{orient}S$) of plastic crystals, sums of entropies of all phase transitions between the low-temperature 'rigid' crystal and the liquid ($\sum_i \Delta^1_{cr}S_i$), principal moments of inertia products (I_{ABC}), symmetry numbers (σ) and acentricity parameters 'kappa' (χ) for some cage hydrocarbons

Compoud	T (K)	$\Delta_{orient}C_s$ (J K^{-1} mol^{-1})	$\sum_i \Delta^1_{cr}S_i$ (J K^{-1} mol^{-1})	$\sum_i \Delta^1_{cr}S_{i\,calc}$ (J K^{-1} mol^{-1})^a	$\Delta_{orient}S$ (J K^{-1} mol^{-1})	$\Delta_{orient}S_{calc}$ (J K^{-1} mol^{-1})^b	$I_{ABC} \times 10^{135}$ (kg^3 m^6)	σ	χ
Bicyclo[2.2.2]octane	164.25	10.4	46.6	46.8	16.2	19.1	43.774	6	−1.00
Adamantane	208.60	8.9	41.6	46.6	9.4	8.9	124.647	12	0.00
Pentacycloundecane	164.40	36.8	43.1	46.7	17.2	17.9	139.381	1	−0.31
Heptacyclotetradecane	355.00	49.1	54.0	46.5	24.0	20.0	495.864	4	−1.00
Diamantane^c	440.43	12.5	47.8	46.4	18.0	18.9	755.594	6	−1.00

[a] Calculated by Eq. (1).

[b] Calculated by Eq. (5).

[c] It was suggested for diamantane that only crI is 'plastic crystal', therefore the sum of the changes of the heat capacity and the entropy during the transitions crIII → crII and crII → crI was used (the temperature of rigid-to-plastic crystal transition is 440.43 K).

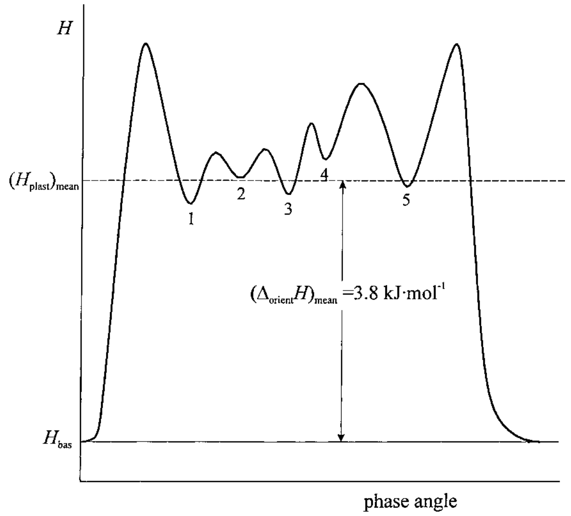

Fig. 3. The diagram of energy levels corresponding to different orientations of adamantane molecules in the plastic crystal state.

preferable orientation to another orientation having the local minima of energy.

2. The frequencies of the lattice vibrations (vibrations with respect to the centers of gravity of the molecules) are close enough for the rigid and plastic crystals to cause practically no difference in their contributions to thermodynamic properties of these two crystalline phases. The normal vibrational frequencies of molecules are also practically the same in the rigid and plastic crystalline phases.
3. The lowest energy ('basic') orientation in the plastic crystal is the one existing in the rigid crystal. All other orientations of the molecules ('plastic' orientations) have higher energy. The molecules may turn through sufficiently large angle φ (in the limit of 2π) along one or several rotational axes in the plastic crystal lattice forming a variety of orientationally stable positions with the energy minima of the order of H_{plast}.

Therefore, the energy states of molecules in the plastic crystal of adamantane can be represented in Fig. 3 which will be self-explanatory.

The following assumptions were used for estimations of the number of non-equivalent orientations of molecules in the plastic crystals n_{orient} and the energy difference between 'rigid' (basic — H_{bas}) and 'plastic' (H_{plast}) orientations $\Delta_{orient}H = H_{plast} - H_{bas}$:

1. All values of H_{plast} are very close to each other. So, the energy levels of all 'plastic' orientations might be characterized by a single (mean) value $(H_{plast})_{mean}$.
2. The entropies of all 'plastic' orientations are the same.
3. The mole fractions of the 'plastic' orientations in the crystalline phase may be estimated from the following equations:

$$K_{plast} = \frac{(n_{orient} - 1)x_{plast}}{x_{bas}}, \qquad (6)$$

$$\Delta_{orient}G = \Delta_{orient}H - T\Delta S = (H_{plast})_{mean} - H_{bas} - RT\ln(n_{orient} - 1), \qquad (7)$$

where x_{plast} is the mole fraction of molecules having one of the 'plastic' orientation, x_{bas} is the mole fraction of molecules having 'basic' orientation.
4. The changes of the thermodynamic properties due to the occurrence of orientational disorder at the rigid crystal-to-plastic crystal transition can be determined from the equations which are similar to the relations obtained for the calculation of the contributions of conformational conversions [23]. For our model these relations transform to the following equations:

$$\Delta_{orient}S = -R[x_{bas}\ln x_{bas} + (n_{orient} - 1)x_{plast}\ln x_{plast}] \qquad (8)$$

$$\Delta_{orient}C_s = \frac{1}{RT^2}(n_{orient} - 1)x_{bas}x_{plast}(\Delta_{orient}H)^2 \qquad (9)$$

where $\Delta_{orient}H = (H_{plast})_{mean} - H_{bas}$ is the mean energy difference between the plastic and basic orientations; T is the temperature; $\Delta_{orient}S$, and $\Delta_{orient}C$ are the entropy and heat capacity changes, respectively, arising from the orientational degree of freedom of molecules in the plastic crystalline phase.

One variant to calculate n_{orient} and $\Delta_{orient}H$ was described in our previous work [4]. In our present work the parameters n_{orient} and $\Delta_{orient}H$ were obtained by the entropy $\Delta_{orient}S(T_{trs})$ and the heat capacity $\Delta_{orient}C_s(T_{trs})$ iso-curves, constructed from the ratios (8) and (9) in coordinates $\Delta_{orient}H - n_{orient}$ (Fig. 4). The

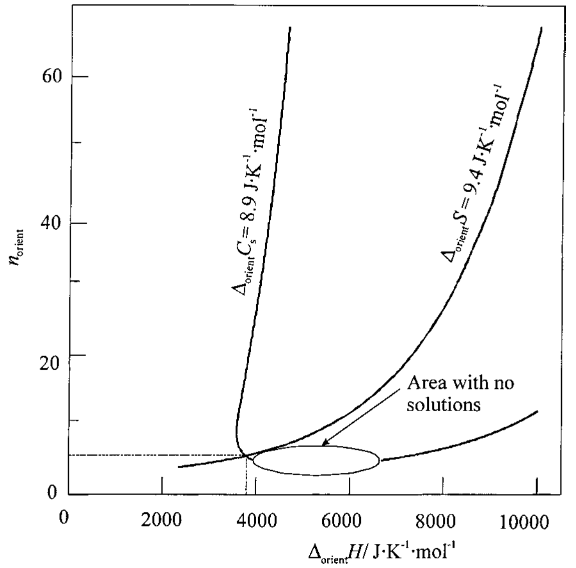

Fig. 4. The number of orientations of adamantane molecules in plastic crystal n_{orient} as a function of the mean energy difference between 'plastic' and 'basic' molecular orientations $\Delta_{\mathrm{orient}}H$ for $\Delta_{\mathrm{orient}}S^0_{\mathrm{m}} = 9.4$ J K^{-1} mol^{-1} and $\Delta_{\mathrm{orient}}C_{\mathrm{s}} = 8.9$ J K^{-1} mol^{-1} at $T = 208.6$ K.

values of $\Delta_{\mathrm{orient}}H$ and n_{orient} for the cage hydrocarbons are given in Table 8. It is completely obvious that the values of n_{orient} and $\Delta_{\mathrm{orient}}H$ change very irregularly in a series of cage hydrocarbons (Table 8).

It is clear that the question concerning the physical interpretation of sufficiently large numbers of n_{orient} is of interest (for example, $n_{\mathrm{orient}} = 47$ for $C_{11}H_{14}$ and $n_{\mathrm{orient}} = 114$ for $C_{14}H_{16}$). The large values of n_{orient} may be interpreted by mutual coordination of the rotations of different molecules in the nodes of the crystalline lattice. Indeed, if there are m positions corresponding to the minima of the potential energy during the rotation of each molecule and l is the number of molecules in rotational ensemble, then the total number of non-identical orientations of the ensemble is $n = m^{(l+1)}$. This fact indicates the possibility of the existence of large numbers of n_{orient}.

Table 8
The numbers of non-equivalent molecular orientational n_{orient} and the mean energy differences between 'plastic' and 'basic' molecular orientations $\Delta_{\mathrm{orient}}H$ for some cage hydrocarbons

Compound	T_{trs} (K)	n_{orient}	$\Delta_{\mathrm{orient}}H$ (kJ mol^{-1})
Bicyclo[2.2.2]octane	164.25	12	3.1
Adamantane	208.60	5	3.8
Pentacycloundecane	164.40	47	6.0
Heptacyclotetradecane	355.00	114	14.4
Diamantane	440.43	16	9.1

5. Conclusion

Cage hydrocarbons with various symmetry exist in the plastic crystal state over wide temperature intervals. The modified model of Guthrie–McCullough of energy states of molecules in the plastic crystals allows to estimate the number of non-equivalent orientations of molecules and the mean energy difference between 'basic' and 'plastic' orientations on the basis of the thermodynamic parameters of rigid-to-plastic crystal transitions.

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