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Thermodynamic properties of 2-adamantanone in the condensed and ideal gaseous states

Ala B. Bazyleva*, Andrey V. Blokhin, Gennady J. Kabo, Andrey G. Kabo, Viktor M. Sevruk

Chemistry Faculty, Belarusian State University, Leningradskaya 14, Minsk 220050, Belarus

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Abstract

The results of a comprehensive study of thermodynamic properties of 2-adamantanone in different phase states are reported. The heat capacity of the compound in the condensed state was measured from 5 to 310 K with an adiabatic calorimeter and between 290 and 610 K with a differential scanning calorimeter of the heat-bridge type. Adamantanone undergoes a solid-to-solid phase transition at 216.4 ± 0.1 K with $\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\circ} = 7.627 \pm 0.014\,\mathrm{kJ\,mol^{-1}}$ and fusion at 557.5 ± 0.2 K with $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\circ} = 11.77 \pm 0.24\,\mathrm{kJ\,mol^{-1}}$. The solid-phase transition is associated with formation of orientationally disordered (plastic) crystal. The thermodynamic functions of the compound in the crystalline and liquid states were obtained. The saturated vapour pressure for crystalline adamantanone between 280 and 333 K was determined by the Knudsen effusion method, the undersaturation of the vapours in the effusion cell being taken into account. The sublimation enthalpy of the compound was measured with a differential Calvet-type calorimeter. The weighted average value of the sublimation enthalpy was $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\circ}(298.15\,\mathrm{K}) = 66.38 \pm 0.25\,\mathrm{kJ\,mol^{-1}}$. The thermodynamic properties of the compound in the ideal gaseous state were calculated by statistical thermodynamics.

Keywords: 2-Adamantanone; Heat capacity; Phase transitions; Plastic crystals; Thermodynamics of sublimation; Statistical thermodynamics; Thermodynamic properties

1. Introduction

Adamantane-based drugs have attracted considerable attention in medicine. Certain of the medications based on 2-substituted adamantanes (kemantan, bromantan, etc.) exhibit characteristics of actoprotectors, adaptogens and even immunostimulants [1]. It was thought earlier [2] that it was complicated to obtain 2-substituted adamantanes because hydrogen attached to a secondary carbon atom in adamantane was much more inert than that of a tertiary carbon atom. However, at present there are a number of fairly selective methods of direct oxidation of adamantane to 2-adamantanone with high yields [2,3]. That is why 2-adamantanone is widely used in syntheses of some pharmacologically active substances.

Detailed and reliable data on the physical and physicochemical properties of initial substances, intermediates and target compounds are necessary for development of the technology of medicine production. Information on the thermodynamic properties of 2-adamantanone is scanty and, in some cases, ambiguous. For example, Butler et al. [4] investigated the thermal behaviour of the compound by DSC in the range from 120 to 400 K and found only one solid-to-solid transition at 221 K with $\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\circ} = 7.93 \pm 0.10\,\mathrm{kJ\,mol^{-1}}$. However, heat capacities in the condensed state as well as the parameters of fusion have not been determined. In addition, some thermochemical properties measured earlier for 2-adamantanone disagree. For example, the values of the sublimation enthalpy, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\circ}(298.15\,\mathrm{K})$, are different: $66.1 \pm 1.3\,\mathrm{kJ\,mol^{-1}}$ (calorimetry) [5], $60.7 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$ (chromatography) [6], $80.3 \pm 2.5\,\mathrm{kJ\,mol^{-1}}$ (from vapour pressures by static method) [7] and $76.1 \pm 1.5\,\mathrm{kJ\,mol^{-1}}$ (the method is not clearly indicated: either by calorimetry or from vapour pressures by Knudsen's method) [8]. Data on the enthalpy of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ (cr, 298.15 K), are also inconsistent: $-310.9 \pm 3.8\,\mathrm{kJ\,mol^{-1}}$ [7] and $-319.7 \pm 1.2\,\mathrm{kJ\,mol^{-1}}$ [8] (bomb calorimetry in both cases).

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* Corresponding author. Tel.: +375 17 209 5197; fax: +375 17 200 3916.
E-mail address: BazylevaAB@bsu.by (A.B. Bazyleva).

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Special interest in 2-adamantanone is also connected with the formation of a plastic crystal characterized by positional order but dynamical orientational disorder [9–12]. Besides the calorimetric investigation by Butler et al. [4] mentioned above, the plastic crystal of the compound has been studied by X-ray diffraction scattering [13], nuclear magnetic resonance (NMR) [14,15] and incoherent quasi-elastic neutron scattering (IQNS) [16].

A transition from ordered to orientationally disordered crystal is normally accompanied by a substantial increase in entropy of a substance and therefore the melting entropy of plastic crystals is much less ($\Delta_{\rm fus}S^{\circ}_{\rm m} < 21\,{\rm J\,mol^{-1}\,K^{-1}}$). There are also noticeable changes in heat capacity, crystal structure, molar volume, dielectric and optical properties at this transition [10]. Taken together, these suggest potential applications of plastic phases in different devices—heat storage systems, mechanical and optical locks, etc.

The present paper gives the results of an investigation of the thermodynamic properties of 2-adamantanone in the condensed and gaseous states: the heat capacity and the enthalpies of the phase transitions in the condensed state, the sublimation enthalpy, the saturated vapour pressure, and the thermodynamic properties of the compound in the ideal gaseous state. The orientational molecular disorder in its plastic crystal form is considered in terms of the model of the energy states of molecules in plastic crystals described in detail earlier [17–19].

2. Experimental

2.1. Materials

A commercial sample of 2-adamantanone (Aldrich Chem. Co., Inc.) with initial mass-fraction purity >0.99 was thrice recrystallized from acetone and then purified additionally by sublimation at 333 K and 0.4 kPa. The final mass-fraction purity was 0.9996 as determined by GLC (a steel column of 3 m length filled with the stationary phase OV-1 (0.03 mass fraction) on Inerton N Super, and a flame ionization detector).

Benzoic acid (VNIIFTRI, Moscow, Russia; K-1 grade with mass-fraction purity >0.99995), naphthalene (REACHEM, Russia; with chromatographic purity—mass fraction >0.9999) and high-purity copper (mass-fraction purity >0.99995) were used without additional purification.

2.2. Heat capacity and phase-transition parameters

2.2.1. Adiabatic calorimetry

The heat capacity at saturated vapour pressure ($C_{\rm s,m}$) for 2-adamantanone in the crystalline state from 5 to 310 K and the enthalpy of its solid-to-solid transition were measured with a vacuum adiabatic calorimeter TAU-1 made by VNIIFTRI (Moscow, Russia). The solid samples of masses 0.86340 and 0.83578 g were used for the measurements in the helium ($T < 110$ K) and nitrogen baths ($T > 100$ K), respectively. The apparatus construction and the procedures of sample loading and measurements were described in detail earlier [19–22].

The reliability of the heat-capacity measurements with the adiabatic calorimeter was verified in experiments with benzoic acid [23,24] and high-purity copper [25]. The uncertainty was estimated to be $\pm 4 \times 10^{-3}\,C_{\rm s,m}$ from 40 to 320 K and not more than $\pm 2 \times 10^{-2}\,C_{\rm s,m}$ near 5 K. The corrections for adjustment of $C_{\rm s,m}$ to $C_{p,{\rm m}}$ and for sublimation of adamantanone (the total contribution was less than $10^{-4}\,C_{\rm s,m}$ near 300 K) were negligible compared with the experimental uncertainty and, hence, were not considered. The correction for helium was estimated to give a minor contribution to the total heat capacity even at low temperatures and consequently was not taken into account.

The temperature corresponding to the peak value of the effective heat capacity in the transition region was assumed to be the temperature of the solid-to-solid transition ($T_{\rm trs}$). The transition enthalpy was determined by averaging the results of single-step experiments. The initial ($T_{\rm start}$) and final ($T_{\rm end}$) temperatures of these experiments lay outside the phase-transition range. The $\Delta_{\rm trs}H^{\circ}_{\rm m}$ value was calculated according to

$$\Delta_{\rm trs}H^{\circ}_{\rm m} = Q - \int_{T_{\rm start}}^{T_{\rm trs}} C_{p,{\rm m}}({\rm crII})\,{\rm d}T - \int_{T_{\rm trs}}^{T_{\rm end}} C_{p,{\rm m}}({\rm crI})\,{\rm d}T, \quad (1)$$

where Q is the energy required for heating 1 mol of the compound from $T_{\rm start}$ to $T_{\rm end}$; $C_{p,{\rm m}}$(crII) and $C_{p,{\rm m}}$(crI) are the normal molar heat capacities of the low- and high-temperature phases in the phase-transition region, respectively.

2.2.2. Differential scanning calorimetry

The measurements of the heat capacity for adamantanone between 290 and 610 K in the condensed state were conducted with a differential scanning calorimeter of the heat-bridge type described in Ref. [26]. The temperature scale of the device was verified with the melting points of tin, lead, indium, and benzoic acid. The calorimeter was calibrated with the heat capacity of high-purity copper (mass fraction ≥0.99995). A sample of 2-adamantanone of 0.7167 g mass was used in these measurements. The average scanning rate was $0.8\,{\rm K\,min^{-1}}$. The uncertainty of the heat-capacity determination is estimated to be $\pm 2 \times 10^{-2}\,C_{p,{\rm m}}$.

The results of the heat-capacity measurements by scanning calorimetry were used to obtain the thermodynamic parameters of fusion of 2-adamantanone. In this case, the temperature corresponding to the intersection point of the heat-capacity baseline for crI before the transition and the tangent to the rising side of the phase-transition peak (the onset temperature) was assumed to be the melting point ($T_{\rm fus}$). The enthalpy of the crI → liq transition was determined by integration of the excess heat capacities in the phase-transition region.

2.3. Thermodynamics of sublimation

2.3.1. Calorimetric determination of the sublimation enthalpy

The sublimation enthalpy for 2-adamantanone was measured with a differential heat-conduction calorimeter of the Calvet type MID-200 equipped with special calorimetric cells described in detail in Ref. [27]. The uncertainty of the sublimation-enthalpy measurements was estimated to be $\pm 5 \times 10^{-3}\,\Delta_{\rm sub}H^{\circ}_{\rm m}$.

The molar sublimation enthalpy for the compound was calculated according to

$$\Delta_{\rm sub} H_{\rm m}^\circ = (Km)^{-1} M \int_{t=0}^{\tau} \Delta E \, {\rm d}t, \tag{2}$$

where m is the mass of the sample (adjusted to vacuum conditions); M the molar mass of the substance; K the calorimetric constant of the cell at the given temperature; ΔE the thermocouple voltage corresponding to the temperature difference between the cell and the thermostat at the point in time t; τ is the elapsed time. The integrated signal of ΔE was recorded by a voltmeter during the whole experiment.

Calibration of the cells was carried out with naphthalene. The recommended data on the thermodynamics of naphthalene sublimation at 298.15 K are [28,29]: $\Delta_{\rm sub} H_{\rm m}^\circ = 72.60 \pm 0.60\,{\rm kJ\,mol^{-1}}$ and $\overline{\Delta_{\rm cr}^{\rm g} C_{\rm p}^\circ} = -34 \pm 2\,{\rm J\,K^{-1}\,mol^{-1}}$.

2.3.2. The integral Knudsen effusion method

The saturated vapour pressure for solid 2-adamantanone in the temperature range from 280 to 333 K was measured by the integral Knudsen effusion method, with the uncertainty of the technique amounting to $\pm 5 \times 10^{-2}\, p_{\rm sat}$. The device construction and the measurement procedure were presented in Refs. [27,30]. The modified effusion cell with the enlarged surfaces of contact and of evaporation described earlier [31] was used in the present work. Three nickel membranes were applied: two of thickness $50 \pm 1\,\mu{\rm m}$ with diameters of the effusion orifices of 0.1833 ± 0.0004 mm and 0.8370 ± 0.0004 mm and one of $84 \pm 1\,\mu{\rm m}$ thickness with average orifice diameter of 0.4467 ± 0.0005 mm.

The equations for calculating the $p_{\rm sat}$ values from the results of the effusion measurements are discussed in Section 3.2. It should be emphasized that the vapours in the cell were assumed to be monomers.

3. Results and discussion

3.1. The thermodynamic properties in the condensed state

The temperature dependence of the molar heat capacity at saturated vapour pressure for 2-adamantanone between 5 and 610 K is presented in Fig. 1. The experimental values of $C_{\rm s,m}$ determined by adiabatic calorimetry are listed in Table S1 of the Supplementary Data. In these measurements the low-temperature phase (crII) of the compound was obtained by slow cooling of the sample from ambient temperature at 0.03–0.01 K s^{-1} and one or two orders of magnitude slower over the phase-transition region.

Extrapolation of the heat capacities of crII to 0 K was performed with the Debye approximation with three degrees of freedom:

$$C_{p,{\rm m}} \approx C_{V,m} = 3RD\left(\frac{\langle \Theta_{\rm D} \rangle}{T}\right), \tag{3}$$

where $D(x)$ is the Debye function, $\langle \Theta_{\rm D} \rangle$ the average Debye characteristic temperature, and R is the gas constant. The value $\langle \Theta_{\rm D} \rangle = 110.1 \pm 0.1$ K was obtained from the experimental heat capacities in the region from 5.1 to 7.2 K.

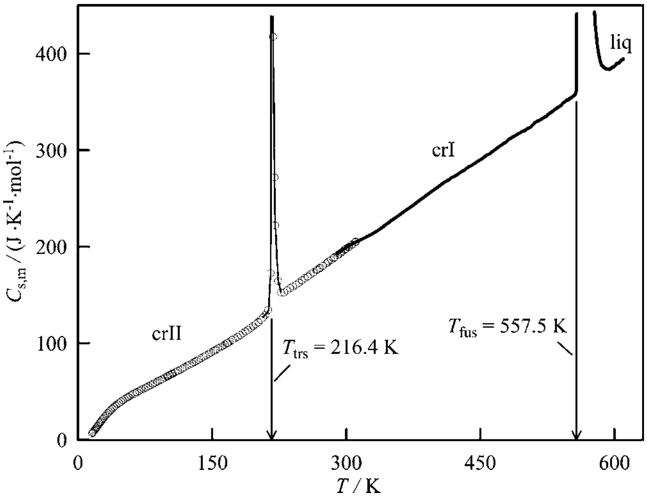

Fig. 1. The temperature dependence of the molar heat capacity of 2-adamantanone in the condensed state: ○ are the results of measurements by adiabatic calorimetry; solid lines are the results obtained by DSC.

Adamantanone was found to undergo a solid-to-solid transition at 216.4 ± 0.1 K and fusion at 557.5 ± 0.2 K. The enthalpy and the entropy of the crII → crI transition:

$$\Delta_{\rm trs} H_{\rm m}^\circ = (7.627 \pm 0.014)\,{\rm kJ\,mol^{-1}} \quad \text{and}$$

$$\Delta_{\rm trs} S_{\rm m}^\circ = (35.24 \pm 0.06)\,{\rm J\,mol^{-1}\,K^{-1}},$$

were obtained by averaging the results of the single-step experiments in the adiabatic calorimeter (Table 1). The baselines of the phases crII and crI:

$$C_{p,{\rm m}}({\rm crII})\,({\rm J\,K^{-1}\,mol^{-1}}) = 80.48 - 0.2934\,T\,({\rm K}) + 2.469 \times 10^{-3}\,T^2\,({\rm K}), \tag{4}$$

$$C_{p,{\rm m}}({\rm crI})\,({\rm J\,K^{-1}\,mol^{-1}}) = 37.09 + 0.3861 T\,({\rm K}) + 4.992 \times 10^{-4} T^2\,({\rm K}), \tag{5}$$

were obtained from the experimental heat capacities from the ranges 170–202 K and 231–310 K for crII and crI, respectively.

On the determination of the fusion enthalpy from the results of the DSC measurements, the common heat-capacity baseline

Table 1
The enthalpy of the solid-to-solid phase transition (crII → crI) for 2-adamantanone[a]

$T_{\rm start}$ (K)	$T_{\rm end}$ (K)	Q (J mol^{-1})	$\Delta_{\rm trs} H_{\rm m}^\circ$ (J mol^{-1})
199.36	231.77	12,050	7613
199.04	233.20	12,336	7641
199.64	231.98	12,061	7626
198.46	230.86	12,037	7633
197.16	232.80	12,477	7620

The average value is $\langle \Delta_{\rm trs} H_{\rm m}^\circ \rangle = 7627 \pm 14\,{\rm J\,mol^{-1}}$.

[a] The heat-capacity baselines for crII and crI used for the calculation of $\Delta_{\rm trs} H_{\rm m}^\circ$ are Eqs. (4) and (5), respectively.

for crI and liquid,

$$C_{p,\mathrm{m}}(\mathrm{liq})\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = -16.76 + 0.6735T\,(\mathrm{K}), \tag{6}$$

was used. It was derived from the experimental $C_{p,\mathrm{m}}$ values from the ranges 500 to 556 K (crI) and 594 to 610 K (liquid). The thermodynamic parameters of fusion were obtained to be

$$\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}} = (11.77 \pm 0.24)\,\mathrm{kJ\,mol^{-1}} \quad \text{and}$$
$$\Delta_{\mathrm{fus}}S^{\circ}_{\mathrm{m}} = (21.1 \pm 0.4)\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

The low-temperature crystalline phase crII obtained was thermodynamically stable in the temperature range 0–216.4 K. This conclusion was made on the basis of the following: in the low-temperature region there was only one repeatable heat-capacity anomaly related to the crII → crI transition; the enthalpy of this transition was reproduced in the series of the single-step experiments (Table 1). This thermal behaviour of adamantanone differs from that observed by Butler et al. [4] who found different DSC-curves for samples investigated immediately after sublimation ($T_{\mathrm{trs}} = 205$ K, $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}} = 3.7\,\mathrm{kJ\,mol^{-1}}$) and subjected to a number of ‘cooling-heating’ cycles between 150 and 250 K ($T_{\mathrm{trs}} = 221$ K, $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}} = 7.93\,\mathrm{kJ\,mol^{-1}}$).

Butler et al. [4] also pointed out a large hysteresis both for T_{trs} and $\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}$: 178 K and 7.39 kJ mol^{-1} on cooling and 221 K and 7.93 kJ mol^{-1} on heating. Such behaviour is likely to be connected with difficulty of conversion of one phase into another, which becomes noticeable at high scanning rates. Thus, equilibrium was not achieved in the system due to the dynamic nature of the measurements carried out in the work presented in Ref. [4]. However, the adiabatic calorimetry used in this work makes it possible to obtain parameters of phase transitions corresponding closely to equilibrium.

The low value of the fusion entropy and the ratio $\Delta_{\mathrm{trs}}S^{\circ}_{\mathrm{m}}/\Delta_{\mathrm{fus}}S^{\circ}_{\mathrm{m}} = 1.7$ are evidence that crI of 2-adamantanone is a plastic crystal. This phase has a lattice with cubic symmetry ($Fm3m$, $Z = 4$, $a = 0.9524$ nm) [13]. There is no information on the crystal structure of crII as well as on the molar volume change at the crII → crI transition at standard pressure. Nevertheless, Hara et al. [32] obtained the values of the relative volume change at the solid-to-solid phase transition at pressures from 5 to 9 kbar. If these values are extrapolated to $p = 1$ bar, the molar volume rises by almost 6% at the crII → crI transition. This is also an inherent feature of the transition from ordered to plastic crystal [33].

A model of the energy states of molecules in plastic crystals was proposed earlier [17–19]. This model gives a reasonable quantitative description of both the entropy change ($\Delta_{\mathrm{trs}}S$) and the essential heat-capacity jump ($\Delta_{\mathrm{trs}}C_p$) at the ‘ordered crystal → plastic crystal’ transition. On the basis of these parameters for 2-adamantanone, the number of non-equivalent orientations, $n_{\mathrm{orient}} = 24$, and the average energy difference between the lowest ‘basic’ orientation and the higher ‘plastic’ ones, $\Delta_{\mathrm{orient}}H = 4.9\,\mathrm{kJ\,mol^{-1}}$, were calculated for the plastic crystal (crI). The obtained value of n_{orient} is twice that taken as the most probable upon the interpretation of the NMR [14,15] and IQNS [16] data. A possible reason of this discrepancy could be the formation of rotational ensembles composed of several molecules in such orientations that do not correspond to energy minima in the crystal provided that only one molecule rotates, but become stabilized if neighbouring molecules undergo cooperative rotation. This process is not considered in the treatment of the results of the NMR and IQNS studies, although such a situation could be realized in the case of molecules with essential dipole moments.

The heat-capacity data for the compound in the range from 290 to 310 K were obtained by both adiabatic calorimetry and DSC (Fig. 1). In this interval there is good agreement (within 1.3%) between the two methods, which serves as verification of the reliability of the $C_{p,\mathrm{m}}$ values measured with the scanning calorimeter.

On the basis of all the data presented above, the smoothed molar heat capacity and the standard thermodynamic functions of 2-adamantanone in the condensed state between 5 and 610 K were derived (Table 2).

3.2. The saturated vapour pressure and the sublimation enthalpy

The results of the effusion measurements for 2-adamantanone from 280 to 333 K are summarized in Table 3.

A detailed analysis of the mass transfer in effusion experiments was performed by Nesmeyanov [34]. It was shown that the undersaturation of vapours in an effusion cell should be taken into account, especially in the case of solid substances. Thus, if this phenomenon is considered, the resulting equation for the saturated vapour pressure, p_{sat}, can be written as

$$\begin{aligned} p_{\mathrm{sat}} &= \frac{\Delta m}{kS_{\mathrm{or}}\tau}\sqrt{\frac{2\pi RT}{M}}\{1 + kS_{\mathrm{or}}(\alpha\gamma S_{\mathrm{sub}})^{-1}\} \\ &= p^{*}\{1 + kS_{\mathrm{or}}(\alpha\gamma S_{\mathrm{sub}})^{-1}\}, \end{aligned} \tag{7}$$

where Δm is the mass loss of the sample during the effusion time, τ, in vacuum; k the probability of the transmission of the molecules through the orifice; S_{or} the area of the effusion orifice; R the gas constant; T the average temperature during the experiment; M the molar mass of the effusing vapour; S_{sub} the ideal geometrical surface of the sample from which the sublimation occurs; γ the roughness coefficient; α is the condensation coefficient. The first two multipliers can be combined into p^{*} representing the apparent values of the vapour pressure calculated if complete saturation is assumed.

It was shown previously [27,30] that the failure of gas isotropy near to the orifice of an effusion cell must be taken into consideration in calculations of k coefficients. In the present work the iterative computational procedure for the calculation of k, which was developed in Ref. [27] according to Wahlbeck’s theory [35], was applied. In terms of this theory, the transmission probability depends on the membrane parameters l (membrane thickness) and d (diameter of an effusion orifice) as well as on λ (mean free path of molecules). The effective diameter of 2-adamantanone ($d_{\mathrm{eff}} = 0.684$ nm) necessary for calculations of λ was evaluated from the van-der-Waals molecular volume obtained by the molecular mechanics method using the MM3 force field [36] in the Tinker 4.0 package [37].

Table 2
The molar thermodynamic functions of 2-adamantanone in the condensed state

T (K)	$C^\circ_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$\Delta_0^T H^\circ_\mathrm{m}/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$\Delta_0^T S^\circ_\mathrm{m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Φ°_m ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
Crystal II				
5	0.1823	0.04553	0.06070	0.01518
10	1.656	0.3850	0.5082	0.1232
15	5.822	1.436	1.885	0.4498
20	11.78	3.253	4.349	1.096
25	18.17	5.601	7.667	2.067
30	24.08	8.198	11.51	3.315
35	29.25	10.84	15.62	4.778
40	33.72	13.43	19.83	6.396
45	37.58	15.90	24.03	8.122
50	40.93	18.24	28.16	9.920
60	46.54	22.51	36.14	13.63
70	51.40	26.29	43.68	17.39
80	56.13	29.73	50.86	21.13
90	60.88	32.92	57.74	24.82
100	65.70	35.96	64.40	28.44
110	70.62	38.89	70.90	32.01
120	75.56	41.74	77.25	35.52
130	80.56	44.53	83.50	38.97
140	85.65	47.29	89.65	42.37
150	90.88	50.02	95.74	45.72
160	96.28	52.74	101.8	49.04
170	101.9	55.46	107.8	52.32
180	107.7	58.20	113.8	55.57
190	113.9	60.97	119.8	58.79
200	120.5	63.78	125.8	61.98
210	127.7	66.65	131.8	65.17
216.4	132.6	68.53	135.7	67.19
Crystal I				
216.4	144.0	103.8	171.0	67.19
220	146.2	104.4	173.4	68.91
230	152.3	106.4	180.0	73.60
240	158.5	108.4	186.6	78.17
250	164.8	110.6	193.2	82.64
260	171.2	112.8	199.8	87.02
270	177.7	115.1	206.4	91.32
280	184.3	117.4	213.0	95.54
290	191.0	119.8	219.5	99.70
298.15	196.6	121.9	224.9	103.1
300	197.8	122.3	226.1	103.8
320	211	127.5	239.3	111.9
340	224	132.7	252.5	119.8
360	236	138.1	265.6	127.5
380	248	143.6	278.7	135.1
400	260	149.1	291.8	142.6
420	272	155	305	150
440	285	160	318	157
460	297	166	331	165
480	309	172	344	172
500	322	178	356	179
520	334	183	369	186
540	347	189	382	193
557.5	359	194	393	199
Liquid				
557.5	359	215	414	199
570	367	219	423	204
590	381	224	435	212
610	394	229	448	219

The following equation for the vapour pressure of 2-adamantanone from 280 to 333 K was used:

$$\ln p_\mathrm{sat}\,(\mathrm{Pa}) = A + BT^{-1}\,(\mathrm{K}) + C\ln T\,(\mathrm{K}), \tag{8}$$

where A, B and C are the fitting parameters.

$$B = [\overline{\Delta^\mathrm{g}_\mathrm{crI}C^\circ_{p,\mathrm{m}}}T_0 - \Delta_\mathrm{sub}H^\circ_\mathrm{m}(T_0)]R^{-1}, \tag{9}$$

$$C = \overline{\Delta^\mathrm{g}_\mathrm{crI}C^\circ_{p,\mathrm{m}}}R^{-1}, \tag{10}$$

where $\Delta_\mathrm{sub}H^\circ_\mathrm{m}(T_0)$ is the sublimation enthalpy at temperature T_0; $\overline{\Delta^\mathrm{g}_\mathrm{crI}C^\circ_{p,\mathrm{m}}}$ is the average difference between the heat capacities of gas and crystal (crI). The parameter $C = 4.71 \pm 0.14$ was calculated by averaging the data on the heat capacities of adamantanone in the condensed and ideal gaseous states between 280 and 333 K obtained in this work.

It can be seen from Fig. 2a that the use of p^*, i.e. the neglect of the undersaturation phenomenon, leads to inconsistency between the vapour-pressure data obtained with the use of membranes with diverse effusion orifices. Additional measurements were carried out for benzoic acid and the same observation was made (Fig. S1a and Table S2 of Supplementary Data), indicating the existence of vapour undersaturation in these effusion experiments.

Combining Eqs. (7) and (8), one can obtain:

$$\begin{aligned}&\ln p^*\,(\mathrm{Pa}) - C\ln T\,(\mathrm{K})\\ &\quad = A + BT^{-1}\,(\mathrm{K}) - \ln\{1 + kS_\mathrm{or}(\alpha\gamma S_\mathrm{sub})^{-1}\}.\end{aligned} \tag{11}$$

Since it is rather complicated to find α, γ and S_sub separately, it is reasonable to determine their product. The parameters A, B and the product $(\alpha\gamma S_\mathrm{sub})$ for 2-adamantanone were found by least-squares fitting: $(\alpha\gamma S_\mathrm{sub}) = (3.2 \pm 0.8) \times 10^{-6}\,\mathrm{m}^2$ and the temperature dependence of the saturated vapour pressure between 280 and 333 K was described by the equation:

$$\begin{aligned}\ln p_\mathrm{sat}\,(\mathrm{Pa}) &= (58.81 \pm 0.28) - (9375 \pm 90)T^{-1}\,(\mathrm{K})\\ &\quad -(4.71 \pm 0.14)\ln T\,(\mathrm{K}).\end{aligned} \tag{12}$$

It is evident from Fig. 2b that consideration of undersaturation could provide consistent vapour-pressure data for 2-adamantanone. The same procedure was successfully applied to benzoic acid (Table S2 and Fig. S1b).

The results of the determination of the sublimation enthalpy for 2-adamantanone by calorimetry are presented in Table 4. Adjustment of the obtained value to 298.15 K with the use of the average difference between the heat capacities of gas and crystal from 298.15 to 313.7 K, $\overline{\Delta^\mathrm{g}_\mathrm{crI}C^\circ_{p,\mathrm{m}}} = 39.3 \pm 1.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$, gives:

$$\Delta_\mathrm{sub}H^\circ_\mathrm{m}(\mathrm{cal.},\ 298.15\,\mathrm{K}) = (66.41 \pm 0.27)\,\mathrm{kJ\,mol^{-1}}.$$

The calorimetric value agrees within the experimental errors with the value, $\Delta_\mathrm{sub}H^\circ_\mathrm{m}(\mathrm{eff.},\ 298.15\,\mathrm{K}) = 66.27 \pm 0.75\,\mathrm{kJ\,mol^{-1}}$, calculated from the saturated vapour pressure given by Eq. (12), and with the literature value, $66.1 \pm 1.3\,\mathrm{kJ\,mol^{-1}}$, determined by calorimetry [5]. However, there are essential discrepancies between these values and

Table 3
The saturated vapour pressure for crystalline 2-adamantanone ($d_{\mathrm{eff}} = 0.684$ nm, $M = 150.220$ g mol^{-1}, $R = 8.31447$ J K^{-1} mol^{-1})[a]

T (K)	τ (s)	Δm (mg)	d_{or} (mm)	k	p^* (Pa)	Kn	p_{sat} (Pa)[b]
280.00	23,400	10.04	0.8370	0.9738	0.2499	8.90	0.2919
283.47	18,000	11.11	0.8370	0.9850	0.3576	6.30	0.4184
288.42	10,814	11.05	0.8370	1.006	0.5844	3.92	0.6860
293.34	5,400	8.97	0.8370	1.035	0.9317	2.50	1.098
295.90	6,600	14.04	0.8370	1.053	1.178	1.99	1.393
293.48	21,600	10.05	0.4467	0.8923	1.063	4.11	1.110
295.94	18,000	10.90	0.4467	0.9037	1.372	3.21	1.433
298.39	14,400	10.73	0.4467	0.9139	1.676	2.65	1.751
303.32	9,000	10.32	0.4467	0.9389	2.531	1.78	2.648
308.33	6,000	10.93	0.4467	0.9711	3.919	1.17	4.107
310.80	4,500	10.58	0.4467	0.9909	4.977	0.93	5.220
313.24	3,600	9.93	0.4467	1.004	5.788	0.81	6.074
315.71	3,600	12.73	0.4467	1.024	7.301	0.64	7.669
310.80	23,400	8.00	0.1833	0.8598	4.954	2.28	4.989
313.26	23,400	9.85	0.1833	0.8709	6.046	1.88	6.089
315.72	19,800	10.22	0.1833	0.8827	7.343	1.56	7.396
318.18	16,200	10.26	0.1833	0.8955	8.915	1.29	8.981
323.06	10,800	10.00	0.1833	0.9213	12.77	0.92	12.86
327.99	7,200	9.94	0.1833	0.9502	18.60	0.64	18.74
332.90	6,300	12.79	0.1833	0.9779	26.77	0.45	26.99

[a] Δm is the experimental mass loss of the sample in the vacuum during time τ at temperature T; d_{or} is the diameter of the effusion orifice; k is the transmission probability according to Wahlbeck [27,35]; p^* are the values of the vapour pressure calculated without taking into account vapour undersaturation in the effusion cell; Kn is the Knudsen number.

[b] p_{sat} are the equilibrium saturated vapour pressures calculated by Eqs. (12) with $(\alpha\gamma S_{\mathrm{sub}}) = (3.2 \pm 0.8) \times 10^{-6}$ m^2.

others: 60.7 ± 0.2 kJ mol^{-1} [6], 80.3 ± 2.5 kJ mol^{-1} [7], and 76.1 ± 1.5 kJ mol^{-1} [8].

The disagreement of the present $\Delta_{\mathrm{sub}} H_{\mathrm{m}}^{\circ}$ values with that obtained by gas-liquid chromatography [6], could be ascribed to the following: only *n*-alkanes were used as reference substances in Ref. [6] and, therefore, it did not take into consideration different chromatographic behaviour of polar and non-polar compounds. This leads to a shift of their value due to differences between the enthalpies of dissolution of n-alkanes and adamantanone in the stationary phase.

In Refs. [27,30] it was shown that neglect of the failure of gas isotropy in an effusion cell results in overstated values of saturated vapour pressure as well as sublimation (vaporization) enthalpy. However, there is no indication in Ref. [8] whether this phenomenon was taken in consideration in the sublimation-enthalpy determination. Moreover, it is not even clear from the paper [8] whether $\Delta_{\mathrm{sub}} H_{\mathrm{m}}^{\circ}$ for 2-adamantanone was measured by Knudsen's method or by Calvet-type calorimetry.

The reason for the large discrepancy between the sublimation-enthalpy values obtained in the present work and by Arora and Steele [7] is unknown.

Thus, the calculation of the average weighted value of $\Delta_{\mathrm{sub}} H_{\mathrm{m}}^{\circ}$ was performed using the results from the present work and from Ref. [5]: $\Delta_{\mathrm{sub}} H_{\mathrm{m}}^{\circ}(298.15\,\mathrm{K}) = 66.38 \pm 0.25$ kJ mol^{-1}.

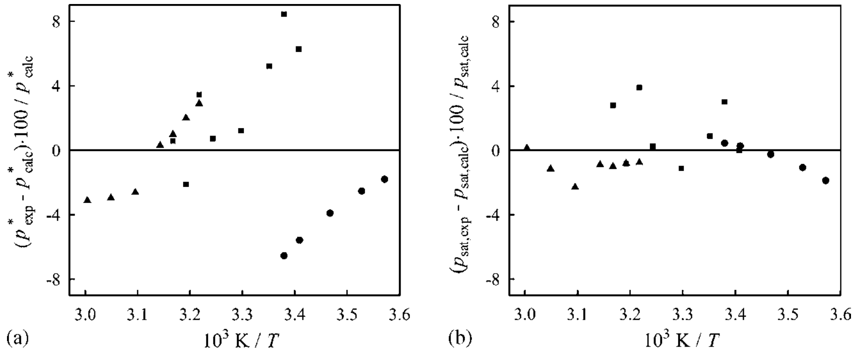

Fig. 2. The relative deviation between the experimental vapour-pressure values and the smoothed curve for 2-adamantanone: (a) complete saturation of the vapours in the Knudsen cell was assumed; (b) undersaturation of the vapours in the Knudsen cell was taken into account. Symbols ▲ are the results obtained with the membrane of $l = 50 \pm 1$ μm thickness and the orifice diameter of $d = 0.1833 \pm 0.0004$ mm; ■ are the vapour pressures measured with the membrane with $l = 84 \pm 1$ μm and $d = 0.4467 \pm 0.0005$ mm; ● are the values obtained with the membrane having $l = 50 \pm 1$ μm and $d = 0.8370 \pm 0.0004$ mm.

Table 4
The results of calorimetric measurements of the sublimation enthalpy ($\Delta_{\rm sub}H^\circ_{\rm m}$) for 2-adamantanone ($M$ = 150.220 g mol^{-1})[a]

T (K)	m (mg)	$\int_{t=0}^{\tau}\Delta E\,{\rm d}t$ (mV s)	Type of cell	$\Delta_{\rm sub}H^\circ_{\rm m}$ (kJ mol^{-1})
313.29	17.25	1415.08	A	65.64
313.70	24.44	1995.30	A	65.33
313.79	30.68	2514.77	A	65.58
313.56	25.47	2086.95	A	65.57
313.81	27.45	2266.30	A	66.06
313.31	17.17	1440.20	B	66.32
313.77	30.04	2488.19	B	65.48
313.92	35.39	2956.33	B	66.05
313.63	26.36	2186.26	B	65.58
313.83	26.04	2185.79	B	66.37

The average value is $\langle\Delta_{\rm sub}H^\circ_{\rm m}$ (crI, 313.7 K)$\rangle$ = 65.80 ± 0.26 kJ mol^{-1}.

[a] The calorimetric constants of cells A and B are: $K_{\rm A}$ = 187.7 ± 0.7 mV s J^{-1} and $K_{\rm B}$ = 190.0 ± 1.4 mV s J^{-1}. The values of m are adjusted to the vacuum conditions (the density of adamantanone is ρ = 1.08 g cm^{-3} as determined by Arora and Steele [7]).

3.3. The thermodynamic properties in the ideal gaseous state

The procedure for the calculation of the thermodynamic properties of organic substances in the ideal gaseous state by statistical thermodynamics was described in detail in Ref. [38].

There are no internal rotations and conformational transformations in the molecule of 2-adamantanone. The symmetry number of the molecule is $\sigma = 2$. The product of the principal moments of inertia for the molecule of 2-adamantanone ($I_{\rm A}I_{\rm B}I_{\rm C}$ = 2.3605 × 10^{-133} kg^3 m^6) was obtained from its geometry optimised by molecular mechanics with the MM3 force field [36] in the Tinker 4.0 computer package [37]. The vibrational contributions to the thermodynamic properties were calculated with the complete set of the fundamentals presented in Ref. [39] (numbers of the normal modes having the same wave numbers are given in parentheses): 2950 (2), 2940 (4), 2920 (2), 2910, 2900, 2880 (3), 2860, 1723, 1473, 1460 (2), 1446, 1434, 1360, 1355, 1349, 1340 (2), 1320 (2), 1300 (2), 1284, 1265, 1255, 1248, 1240, 1205, 1121, 1105, 1098, 1090, 1078, 1065 (2), 1051, 1035, 1006, 971, 960, 955, 894, 884, 875, 860, 835, 810, 776 (2), 715, 620 (2), 596, 470, 440 (2), 391, 369 (2), 283, 273, 123.

The thermodynamic properties of adamantanone in the ideal gaseous state between 100 and 1000 K are summarized in Table 5. The experimental and calculated values of the standard entropy of gaseous 2-adamantanone are closely consistent with each other:

$$\Delta_0^T S^\circ_{\rm m,calc.}\,({\rm g},\ 298.15\,{\rm K}) = (356.0 \pm 1.8)\,{\rm J\,K^{-1}\,mol^{-1}},$$

$$\Delta_0^T S^\circ_{\rm m,exp}\,({\rm g},\ 298.15\,{\rm K}) = (356.2 \pm 1.3)\,{\rm J\,K^{-1}\,mol^{-1}}.$$

The value of $\Delta_0^T S^\circ_{\rm m,exp}$ (g, 298.15 K) was obtained from

$$\Delta_0^T S^\circ_{\rm m,exp}\,({\rm g}, T) = \Delta_0^T S^\circ_{\rm m}({\rm cr}, T) + \frac{\Delta_{\rm sub}H^\circ_{\rm m}(T)}{T} + R\ln\left(\frac{p_{\rm sat}(T)}{p^{\rm o}}\right) \qquad (13)$$

Table 5
The standard molar thermodynamic functions of 2-adamantanone in the ideal gaseous state ($p^{\rm o}$ = 10^5 Pa)

T (K)	$C^\circ_{p,\rm m}$ (J K^{-1} mol^{-1})	$\Delta_0^T H^\circ_{\rm m}$/T (J K^{-1} mol^{-1})	$\Delta_0^T S^\circ_{\rm m}$ (J K^{-1} mol^{-1})	$\Phi^\circ_{\rm m}$ (J K^{-1} mol^{-1})
100	50.09	38.43	258.8	220.4
150	70.76	45.62	282.9	237.2
200	96.11	54.98	306.6	251.6
273.15	140.7	71.80	342.9	271.1
298.15	157.2	78.26	356.0	277.7
300	158.4	78.75	356.9	278.2
400	223.6	106.9	411.5	304.6
500	280.6	136.1	467.7	331.6
600	327.5	164.2	523.2	359.0
700	365.8	190.4	576.6	386.3
800	397.6	214.4	627.6	413.3
900	424.0	236.2	676.0	439.8
1000	446.3	256.2	721.9	465.7

with the data on the entropy of the compound in the condensed state, $\Delta_0^T S^\circ_{\rm m}({\rm cr},\ 298.15\,{\rm K}) = 224.9 \pm 1.0\,{\rm J\,K^{-1}\,mol^{-1}}$, the sublimation enthalpy, $\Delta_{\rm sub}H^\circ_{\rm m}\,(298.15\,{\rm K}) = 66.38 \pm 0.25\,{\rm kJ\,mol^{-1}}$, and the saturated vapour pressure, $p_{\rm sat}$ (298.15 K) = 1.669 ± 0.038 Pa, which were measured in this work.

The agreement between experimental and calculated values of $\Delta_0^T S^\circ_{\rm m}$ is evidence of the reliability of the molecular parameters as well as the fact that the residual entropy of the low-temperature crystal (crII) at $T \to 0$ K is equal to 0 and, hence, that there is no disorder in crII.

4. Conclusions

The comprehensive thermodynamic study of 2-adamantanone in different phase states was carried out. It should be emphasised that there is good agreement between the data of the different methods and techniques, which is evidence of their reliability. It was calorimetrically confirmed that the compound formed orientationally disordered crystal. Further investigation of the plastic crystalline phase of 2-adamantanone could promote a deeper insight into the nature of molecular disorder in organic crystals.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.08.018.

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