

Thermodynamic properties of 1-aminoadamantane

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Abstract

The heat capacity of crystalline 1-aminoadamantane over the temperature range from (5 to 370) K, the temperatures and the enthalpies of its solid-to-solid phase transitions, $T_{\text{trs},1} = (241.4 \pm 0.2)$ K and $\Delta_{\text{trs},1}H_m^\circ = (1716 \pm 10)$ J · mol⁻¹; $T_{\text{trs},2} = (284.6 \pm 0.1)$ K and $\Delta_{\text{trs},2}H_m^\circ = (5309 \pm 5)$ J · mol⁻¹, were obtained by the adiabatic calorimetry. The thermodynamic functions of the compound in the crystalline state were derived. The saturated vapour pressure and the sublimation enthalpy $\{\Delta_{\text{sub}}H_m^\circ(298.15 \text{ K}) = (61.65 \pm 0.63)$ kJ · mol⁻¹ $\}$ were determined from the results of the measurements by the effusion Knudsen method and by the transpiration method. The enthalpy of combustion and the enthalpy of formation for crystalline 1-aminoadamantane were measured in a static-bomb isoperibol combustion calorimeter: $\Delta_c H_m^\circ(\text{cr}, 298.15 \text{ K}) = (-6169.2 \pm 1.9)$ kJ · mol⁻¹ and $\Delta_f H_m^\circ(\text{cr}, 298.15 \text{ K}) = (-195.4 \pm 2.3)$ kJ · mol⁻¹. The thermodynamic properties in the ideal gaseous state were calculated by the statistical thermodynamics method. The molecular and spectral data for 1-aminoadamantane were obtained from quantum-chemical calculations (B3LYP/6-31+G*) and from Raman and i.r. spectroscopic studies.

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1. Introduction

The compound 1-aminoadamantane is an intermediate compound and an effective base for drugs on the basis of 1-aminoadamantane hydrochloride (trade names – amantadine, midantan, and symmetrel), which is used for the prevention and the early-stage treatment of influenza A [1,2]. It was shown that the medication also exhibited a dopaminergic neurotransmission, which is the reason it is often applied in medical practice for treatment of dementia, Parkinson's and Alzheimer's diseases, stroke, hypoxic brain afflictions, neuroinfections, etc. [1,3]. At present, amantadine in combination with other preparations is

being intensively studied as a cure for hepatitis C in those cases where other methods are inefficient [4,5].

This multiple use of amantadine creates a special interest in the study of its physiological activity as well as of efficient technologies of its production. The latter requires a large set of thermodynamic data for all components of a technological scheme under study. In spite of the long-term application of the medication, there has not been any investigation of physicochemical properties for amantadine and its effective base – 1-aminoadamantane. The absence of thermodynamic data for the latter is probably due to the particular difficulty and complexity in studying this extremely reactive amine. For example, its high reactivity can be illustrated by the following: when exposed to the open air, the compound absorbs water vapours and carbon dioxide up to $(0.5 \text{ to } 2) \cdot 10^{-2}$ mass fraction per 10 min

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(depending on the crystal size) with the formation of 1-aminoadamantane carbonate or/and 1-aminoadamantane hydrogen carbonate. This indicates that if accurate data on its thermodynamic properties are needed, any contact by the compound with the air must be avoided.

The present work summarizes the results of a comprehensive study of thermodynamic properties of 1-aminoadamantane, the basic form of amantadine, in different phases. It also includes a thermodynamic analysis of its synthesis from 1-adamantanol.

2. Experimental

2.1. Sample preparation

A commercial sample of 1-aminoadamantane (Aldrich Chem. Co., Inc.; initial mass-fraction purity of not less than 0.97) was purified by double sublimation at $T = 310$ K and $p = 0.4$ kPa immediately prior to measurements avoiding any contact of the substance with the air and kept over ascarite.

The mass-fraction purity of 1-aminoadamantane, determined by g.l.c. (solution in hexane, stationary phase RTX-1, column length = 30 m, carrier-gas nitrogen, flame-ionisation detector) was 0.9989.

2.2. Adiabatic calorimetry

Heat capacities at vapour-pressure saturation for crystalline 1-aminoadamantane in the temperature range from (5 to 370) K and the temperatures and enthalpies of its solid-phase transitions were measured in an automatic vacuum adiabatic calorimeter TAU-10 (Termis close corporation, Moscow, Russia). The calorimeter was described in detail earlier [6]. The uncertainty of the $C_{s,m}$ measurements is $\pm 0.4\%$ between $T = (20$ and $370)$ K, $\pm 1\%$ from (10 to 20) K and does not exceed $\pm 2\%$ in the temperature range of (5 to 10) K [6]. The reproducibility for the heat-capacity measurements is better than $\pm 0.2\%$.

A titanium calorimetric cell ($V \approx 1.0$ cm³) was loaded with a solid sample of 0.5907 g. In order to avoid interaction with air components, the loading procedure was carried out in an isolated box preliminarily dried and freed of CO₂ with ascarite. The container with the sample was degassed in vacuum with residual pressure of ~ 1 Pa during 0.5 h. Helium (at $p \approx 5$ kPa and $T = 290$ K) was introduced into the internal free space of the cell for facilitation of heat transfer during the measurements. The container was sealed using an indium ring and a titanium head fixed with a copper screw.

An iron–rhodium resistance thermometer ($R_0 = 50$ Ω), which was placed on the inner surface of the adiabatic shield and calibrated for ITS-90 by VNIIFTRI (Moscow, Russia), was applied for temperature measurements. The temperature difference between the shield and the cell was gauged by a differential (copper + 0.001 iron)/chromel thermocouple. The adiabatic conditions were maintained with an accuracy of $\pm 10^{-3}$ K.

The ratio of the sample heat capacity to the total (sample + cell) was not less than 0.5 over the range of (5 to 30) K and about (0.3 to 0.4) over the remaining region.

Heating periods in the calorimetric experiments amounted to (60 to 150) s at $T < 40$ K, (200 to 250) s for $T = (40 \leq T/\text{K} \leq 80)$ K and 400 s for $T > 80$ K. The time of thermal relaxation was maintained to be (25 to 100) s at $T < 80$ K and about 150 s in the nitrogen region, except for the phase-transition ranges where this period was automatically prolonged. The periods of temperature-drift measurements were within (200 to 250) s in the helium region and 300 s at $T > 80$ K. The temperature step of the heat-capacity measurements was 1/20 of absolute temperature at $T < 40$ K and about (2.0 to 2.5) K above 40 K.

The corrections for adjustment of $C_{s,m}$ to $C_{p,m}$ and for sublimation of 1-aminoadamantane into the free space of the calorimetric cell were negligible quantities (their total contribution was less than $10^{-3} C_{s,m}$ near $T = 370$ K) and, therefore, were not taken into consideration.

2.3. Knudsen's effusion method

Saturated vapour pressures of crystalline 1-aminoadamantane over the temperature interval of (291 to 311) K were obtained by the integral effusion Knudsen method. The design of the device and the measurement procedure were described earlier [7,8]. The measurements were carried out with the effusion cell developed earlier for determination of vapour pressures over solids [9]. The following nickel membranes were used (l is the membrane thickness, d_{or} is the average effusion-orifice diameter): for membrane #1, $l = (50 \pm 2)$ μm and $d_{or} = (0.1833 \pm 0.0004)$ mm; for membrane #2, $l = (84 \pm 2)$ μm and $d_{or} = (0.4467 \pm 0.0005)$ mm. The uncertainty of the technique was estimated to be $\pm 5\%$, which was then proved in a series of vapour-pressure measurements for benzoic acid (compared with the TRC recommended data [10]).

The calculations for the saturated vapour pressure (p_{sat}) were performed by the following equation with the undersaturation correction [11,12]:

$$p_{sat} = \frac{\Delta m}{\tau} \cdot \left(\frac{1}{kS_{or}} + \frac{1}{\alpha\gamma S_{sub}} \right) \cdot \left(\frac{2\pi RT}{M} \right)^{1/2}, \quad (1)$$

where Δm is the mass loss of the sample during the time of exposure, τ , in vacuum; S_{or} is the effusion orifice area; k is the probability of the transmission of the molecules through the orifice; S_{sub} is the geometrical surface area of the sample from which the sublimation occurs; γ is the roughness coefficient; α is the condensation coefficient; T is the average temperature in the effusion experiment; M is the molar mass of the effusing vapours; R is the gas constant.

It was assumed that the vapours in the cell consisted of only monomers and, hence, $M = 0.151249$ kg \cdot mol⁻¹. The transmission-probability values for each point were computed using the iterative procedure [7,8] developed according to the Wahlbeck theory on the gas-isotropy failure [13].

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