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LETTERS TO THE EDITOR

Determination of the Enthalpy of Ammonia Borane Sublimation

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Ammonia borane (BH_3NH_3) is a promising carrying agent for the hydrogen power engineering (hydrogen content of 19.6 wt %) [1]. In this connection the study of ammonia borane thermochemical properties is of a special interest.

Solid ammonia borane decomposes on heating to evolve hydrogen and to form polymeric amidoborane.

$$BH_3NH_3(solid) = 1/n(BH_2NH_2)_n(solid) + H_2(gas).$$

Decomposition of ammonia borane in a condensed phase was studied by differential scanning calorimetry [2–4] and thermogravimetry [5]. Publications on the study of ammonia borane behavior in gas phase are few in number. The structure of its molecule was determined by the rotation spectroscopy method [6, 7]. The IR spectroscopic studies of gaseous ammine-borane are reported in [8]. In the same work the partial pressure of ammonia borane saturated vapor was found to be 10^{-4} mmHg at 295 K, which points to its low volatility. This value is in agreement with the upper limit (10^{-3} mmHg at 298 K) determined by the Knudsen effusion method [9].

It was found in [5] that thermal decomposition of ammonia borane with hydrogen evolution proceeds rather slowly at 318–348 K (within tens of hours) but is accelerated noticeably at 368 K. This fact allows us to select optimal conditions for measuring heat effect of ammonia borane sublimation in a vacuum by a direct calorimetric method.

The optimal temperature for the calorimetric experiment was selected experimentally. At 339 K the measured heat effect corresponds to heating an ampule with ammonia borane, no additional heat effect being recorded (experiment duration of 21 h). In this case no sublimate was observed on walls of the tube cold region. Thus, the saturated vapor pressure of ammonia borane at 339 K is insufficient for calorimetric measurements.

When temperature was increased up to 357 K, a noticeable endothermic effect was recorded in addition to the effect of dropping the ampule, white crystals settled in the cold region of the tube, and a small amount of a non-volatile residue was found in the cell after the experiment termination. The IR spectrum of sublimated material is identical to the IR spectrum of initial ammonia borane. The IR spectrum of the non-volatile residue is analogous to the spectrum of polyamidoborane [3], which points to a partial thermal decomposition of ammonia borane during the experiment.

To minimize the contribution of the thermal decomposition at 357 K, we used small weighted samples of ammonia borane, which has allowed the duration of calorimetric experiments to be reduced. The heat of sublimation Q_{sub} was calculated as a difference between measured overall effect Q_{meas} and the heats spent for heating the cell (Q_{cell}) and ammonia borane (Q_{amm} calculated using the heat capacity of solid ammonia borane at 298.15 K, 75.37 J mol^{-1} K^{-1} [11]) and taking into account the contribution of the exothermic decomposition by the reaction Q_{reac}. The last contribution was calculated by the weight of the non-volatile residue m_{poly} using the published value of the process enthalpy of –21.7±1.2 kJ/mol in the range 343–363 K [4]. Results of the calorimetric study are presented in the table (m is a sample weight, t is the experiment duration, m_1 is the weight of sublimated ammonia borane, and $\Delta_{sub}H^0_{357}$ is the standard enthalpy

Data of calorimetric experiments

Exp. no.	m, mg	t, h	Q_{meas}, J	Q_{cuv}, J	Q_{amm}, J	m_{poly}, mg	Q_{reac}, J	m_1, mg	Q_{sub}, J	$\Delta_{sub}H^0_{357}$, kJ/mol
1	10.9	5.0	44.0	17.3	1.6	0.5	–0.4	10.4	25.5	75.9
2	13.8	3.8	52.7	17.9	2.1	0.9	–0.7	12.8	33.4	80.3
3	13.1	2.7	45.5	16.7	2.0	1.3	–1.0	11.7	27.7	73.1
4	11.0	2.7	40.0	15.3	1.7	1.2	–0.9	9.7	23.9	75.9

of ammonia borane sublimation). The average value of four experiments was 76.3±3.0 kJ/mol (see table).

Thus, we have found optimal conditions for the determination of the enthalpy of ammonia borane sublimation by a direct calorimetric method. The experimental value of $\Delta_{sub}H^0_{357}(BH_3NH_3)$ was 76.3±3.0 kJ/mol.

According to the X-ray analysis, commercial ammineborane (97%, Aldrich) contained a small amount of a crystal phase of $(NH_4)HB_4O_7{\cdot}3H_2O$. The purification was carried out by dissolution in anhydrous diethyl ether, insoluble admixture was filtered off on a glass frit filter, and a solvent was distilled off under a reduced pressure within 1 h at 25°C. According to the X-ray analysis and IR spectroscopy thus purified specimen was free from impurities.

A DAK-1a calorimeter with a modified system of substance input was used in the work. The construction of the installation allowed us to carry out experiments in deep vacuum. In the course of an experiment a cell with an ammonia borane weighted sample was placed in a dropping system, and the system was evacuated. After reaching a thermal equilibrium (reaching basic line) the cell with the ammonia borane weighted sample was dropped in a preheated calorimetric vessel, and a heat effect was measured up to reaching a basic line. As cells we used glass ampules of height 2–3 cm and diameter 1 cm with width of walls ~1 mm. A heat capacity of each cell was measured in a blank run when an empty cell with a known weight m_{cell} was dropped in a calorimetric cell. The heat capacity of the cell C_{cell} was calculated by the formula: $C_{cell} = Q/(m_{cell}\Delta T)$, where Q is a heat effect of dropping (J), ΔT is a difference between temperatures of the calorimeter and the cell before dropping. The calorimeter was calibrated against current. The calorimeter constant K was calculated by the formula: $K = Q/S$, where S is the area limited by a heat-release curve and prolongation of a calorimeter basic line [10]. The signal from the calorimeter was transmitted to a computer, and the data were treated using the Origin 7.0 program.

Compounds were identified by IR spectroscopy (KBr) on a Fourier IR Prestige-21 Shimadzu spectrophotometer. The X-ray analysis was fulfilled in the Center of X-ray diffraction studies at St. Petersburg State University.

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