Determination of the Heat of Formation of Indium Antimonide by Fusion in a Calorimetric Bomb

1961

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Chemistry

S. N. Gadzhiev and K. A. Sharifov

Determination of the Heat of Formation of Indium Antimonide by Fusion in a Calorimetric Bomb

(Presented by Academician V. N. Kondrat' ev on 6 October 1960)

Existing methods for determining the heat of formation are not always suitable for semiconductor substances (combustion, dissolution), or else are cumbersome (metallic calorimetry), and some give low accuracy (e.g., vapor elasticities, etc.).

The aim of the present investigation was to develop a new procedure for determining the heat of formation of binary semiconductor compounds. The experiments were carried out on a calorimetric apparatus with an isothermal jacket (1). In a bomb of the type used by the thermal laboratory of Moscow University, a small electric furnace was installed (Fig. 1), consisting of a quartz ampoule 11 mm in diameter and 45 mm long. A heating element was wound on the ampoule —nichrome wire 0.15 mm in diameter, with a resistance of 110 ohms. To prevent the turns of the wire from slipping during heating, a thin layer of a paste-like mixture consisting of kaolin, borax, and water was applied to them; this was dried at the synthesis temperature. Current of about 1 ampere and a voltage of 120 volts was supplied to the furnace through a voltage stabilizer. The work of the current was measured by means of a high-accuracy alternating-current meter (manufactured by the "Etalon" plant). The change in the temperature of the calorimeter was determined by an MMT-4 thermistor.

An electric motor with a reduction gear and a connecting-rod-and-crank device was inserted into the bomb for stirring the alloyed mixture by rocking the ampoule; the speed was 10 oscillations per minute. The motor was switched on in parallel with the furnace, and consequently stirring took place only during its heating.

Fig. 1. 1 —calorimetric bomb; 2 —quartz ampoule—furnace; 3 —rubber jacket; 4 —silver screen; 5 —electric motor; 6 —connecting-rod-and-crank device; 7 — reduction gear; 8 —current-supplying wires

The heat value of the calorimeter, equal to 2904.4 ± 0.6 cal_{15}, was determined

using benzoic acid, with the appropriate correction introduced for the item–

parts inserted into the bomb (motor, furnace, etc.), which were absent during the combustion of benzoic acid. The electric-energy meter was then calibrated by heating an empty ampoule in the bomb; one revolution of the meter pointer corresponded to 41.40 ± 0.02 cal.

Heating of both the empty and the filled ampoule was continued for 4 min (meter reading–150 revolutions). About 6000 cal was released; the temperature rise of the calorimeter was 2.15° with the empty ampoule and 2.30° with the filled ampoule. Consequently, the thermal effect of the reaction accounts for 0.15°, and therefore, in order to obtain sufficiently accurate results, the experiments must be carried out at a high level.

Separate experiments established that 50 sec after the current was switched on, the temperature inside the furnace reached 700°. A silver screen was installed between the electric motor and the furnace, the edges of which fitted tightly against the walls of the bomb. The screen protects the motor from the heat of the furnace by reflecting it and conducting it away to the walls of the bomb. Owing to this, the main period of the experiment is shortened by 6–7 min. The bomb was filled with nitrogen to 30 atm. This, in turn, shortens the main period by another 8–9 min and brings it to 15 min (30 readings). To check the reliability of the method, indium antimonide, which has been studied comparatively well, was chosen as the object.

A stoichiometric mixture of indium and antimony (of purities 99.999 and 99.992, respectively) in an amount of 12 g was placed in the ampoule-furnace. After evacuation to 10^{-3} mm Hg, the ampoule was sealed. To prevent fusion of the contents of the ampoule during sealing, it was cooled by a thin stream of water directed close to the sealing point. The ampoule was then dried in air and inserted into a metallic (tantalum) jacket connected to the rod for stirring.

Small pieces of glass capillary were slipped onto the leads of the furnace, made of platinum wire of 0.25 mm cross section, for electrical insulation. The degree of conversion was checked by X-ray diffraction and by chemical analysis.

Table 1

Experiment No.	Amount of reacting substance, g In	Amount of reacting substance, g Sb	Number of revolutions of the electric-meter pointer	ΔT corr.	Q, cal. total	Q, cal. due to reaction	$-\Delta H^0_{298}$

Experiment No.	Amount of reacting substance, g	Amount of reacting substance, g	Number of revolutions of the electric-meter pointer	ΔT corr.	Q, cal.	Q, cal.	$-\Delta H^0_{298}$
1	5.8262	6.1816	150.25	2.2734	6605.20	385.55	3.78
2	5.8273	6.1827	150.06	2.2778	6615.46	403.55	3.97
3	5.8274	6.1828	150.70	2.2846	6635.46	397.05	3.91

Indium and antimony form one compound, InSb ([2]). X-ray analysis* of the reaction products established the presence only of cubic InSb. Lines belonging to the individual components and to the hexagonal modification of the substance were not found. Chemical analysis of the reaction products was carried out by treating them with 12 N hydrochloric acid saturated with hydrogen sulfide ([5]), which dissolves only free indium. It was thereby found that the extent of combination is 96–100%.

The results of the experiments are given in Table 1.

Thus, the standard heat of formation of indium antimonide is

$$\Delta H^0_{298}\,\mathrm{InSb_{cubic}} = -3.89 \pm 0.04 \text{ kcal/g-at.}$$

Table 2 presents the results of the present work and literature values for InSb.

As can be seen from Table 2, our results agree well with the data of other authors. ΔH of InSb is small, and in this respect it is closer to alloys than to

* The X-ray analysis was carried out by K. P. Mamedov and Z. D. Nurieva.

Table 2

No.	$-\Delta H_{723}$, kcal/g-atom	$-\Delta H_{273}$, kcal/g-atom	$-\Delta H_{298}$, kcal/g-atom	Method of determination	Source
1	4.30	–	4.00	Tin calorim.	(3)
2	–	3.47	3.49	Tin calorim.	(4)
3	–	–	3.4	Direct fusion	(5)
4	3.98	–	3.67	E.d.s.	(6)

No.	$-\Delta H_{723}$, kcal/g-atom	$-\Delta H_{273}$, kcal/g-atom	$-\Delta H_{298}$, kcal/g-atom	Method of determination	Source
5	–	–	3.89	Fusion in a bomb	Present study

salt-like compounds. Obviously, for compounds with a comparatively larger ΔH, a higher accuracy can be achieved.

Apparently, this method can also be applied to multicomponent systems.

It should also be noted that, by creating a back pressure of nitrogen in the bomb, explosions that often occur in the synthesis of compounds whose components have a high vapor pressure can be prevented.

Institute of Physics, Academy of Sciences
Azerbaijan SSR

Received
5 X 1960

CITED LITERATURE

1. S. N. Gadzhiev, K. A. Sharifov, *Dokl. AN AzerbSSR*, **15**, No. 8, 667 (1959).

2. M. Hansen, K. Anderko, *Constitution of Binary Alloys*, N. Y.–London, 1958.

3. O. J. Kleppa, *J. Am. Chem. Soc.*, **77**, 897 (1955).

4. W. Schottky, M. Bever, *Acta Metallurgica*, **6**, No. 5, 320 (1958).

5. A. Schneider, H. Klotz, *Naturwiss.*, **46**, No. 4, 141 (1959).

6. A. V. Nikolskaya, V. A. Geiderikh, Ya. I. Gerasimov, *DAN*, **130**, No. 5, 1074 (1960).

Note: Figure translations are in progress. See original paper for figures.