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Abstract

Full Text

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THERMODYNAMIC PROPERTIES OF INDIUM ANTIMONIDE

Indium and antimony form one intermetallic compound, InSb, with a melting point of $530 \pm 5^\circ$ ([1]). The phase diagram of the In–Sb system is shown in Fig. 1.

Indium antimonide belongs to the group of semiconductor compounds of the type $A^{III}B^{V}$, possessing the zinc-blende structure; in connection with its semiconductor properties, many physical characteristics of this compound have been studied rather extensively (for an extensive bibliography, see ([2])).

Studies of the thermodynamic properties of indium antimonide have been carried out in ([3–6]). In ([3,4]), the heat of formation of this compound was studied by the method of tin calorimetry. In ([4]), the standard isobaric-isothermal potential (ΔZ°) and the entropy of formation (ΔS°), obtained by the authors by calculation, are also given. Work ([5]) is devoted to the study of the heat capacity of indium antimonide in the temperature range 20–500°C and to the determination of the heat of fusion of the compound. In ([6]), the heat capacities of a number of semiconductor compounds, including indium antimonide, were studied; the investigation was carried out in the temperature range 80–300°K.

The aim of our investigation was to calculate the thermodynamic properties of indium antimonide on the basis of experimentally obtained values of the electromotive forces of electrochemical cells. The e.m.f. of concentration (with respect to the electrodes) cells was studied:

$$\text{In (liq)} \mid \text{(KCl—LiCl)} + \text{InCl} \mid \text{(InSb + Sb) (solid)}.$$

The change in the isobaric-isothermal potential ΔZ as a result of the reaction proceeding in the cell

$$\text{In (liq)} + \text{Sb (solid)} = \text{InSb (solid)}$$

is proportional to the magnitude of the e.m.f. of the cell

$$\Delta Z = -zFE; \tag{1}$$

F is the Faraday number, equal to 26062 cal/g-equiv.; E is the e.m.f. in volts, and z is the valence of the ion (In^+), in the present case $z = 1$.

Study of the dependence of the e.m.f. on temperature makes it possible to establish the functional dependence of ΔZ on T, and consequently to find the change in enthalpy and entropy upon formation of InSb from the equations

$$\Delta S = -\frac{d\Delta Z}{dT} = zF\frac{dE}{dT}; \tag{2a}$$

$$\Delta H = \Delta Z + T\Delta S. \tag{2b}$$

Experimental Part

The investigation was carried out in the temperature range 390–490°C. Alloys of composition 59.9 and 67.2 at. % Sb, belonging to the heterogeneous region InSb–Sb, were studied.

Indium alloys with antimony were prepared by melting weighed portions of the metals; this is the usual method for preparing indium and gallium antimonides and arsenides, described in studies of their electrical properties (see, for example, (7)).

In our work the melting was carried out in evacuated quartz ampoules at a temperature of 635-650° C. Metals of 99.99% purity were used. The ampoule with the molten metals was inverted several times to improve mixing of the metals; then, after some holding at 635-650° C, the alloy was cooled to 450° C, at which it was held for several hours.

The resulting alloy was thoroughly ground in an agate mortar, and alloy electrodes were pressed from the powder; during this operation a current lead—a tungsten wire 0.5 mm in diameter—was pressed into the alloy. The electrodes were cylindrical in shape, with cylinder length 10-15 mm and diameter 6 mm.

The electrolyte was a melt of the eutectic mixture of lithium and potassium chlorides with a small addition (0.1%) of indium monochloride.

Indium monochloride was prepared according to the procedure described in (8). First indium trichloride was prepared by burning metallic indium in a stream of chlorine; then a mixture of indium trichloride and metallic indium was fused in an evacuated quartz ampoule, during which the reaction occurred

$$InCl_3 + 2In = 3InCl.$$

Fig. 1. Phase diagram of the system

The cell was assembled in a specially made quartz vessel, shown in Fig. 2. At the bottom, in the narrowed part, there was liquid indium, and the alloy electrode

Fig. 1. Phase diagram of the system

Figure 1: Fig. 1. Phase diagram of the system

Fig. 2. External view of the cell

Figure 2: Fig. 2. External view of the cell

was fixed above it. The cell was immersed in a cylindrical quartz apparatus 450 mm long and 40 mm in diameter, closed by a wide ground stopper with sealed-in tungsten current leads and a platinum–platinum-rhodium thermocouple, which measured the temperature of the cell. The cylindrical apparatus served as a casing for the cell and made it possible to conduct the experiment in an atmosphere of inert gas (pure argon). The cell was heated in a special electric furnace with a metal tube. The cell was immersed to the center of the furnace to a depth of 300 mm, where the zone of constant temperature extended over a section 50 mm long; the danger of thermoe.m.f. arising under these conditions was reduced to a minimum. The furnace temperature was regulated; constancy of temperature in the cell was maintained to an accuracy of $±$1°. The equilibrium value of the e.m.f. was established 10–12 h after the start of the experiment; subsequently, on transition to another temperature, equilibrium was reached more rapidly. The dependence of e.m.f. on temperature was studied both on increasing and on decreasing temperature. The reproducibility of the data lies within $±$1.0 mV. The experimental results are shown in Fig. 3.

Fig. 2. External view of the cell

The experimental data were treated by the method of least squares; the equation obtained was

$$E = (0.3455 - 0.241 \cdot 10^{-3}T) \text{ V},$$

from which, according to equations (1) and (2), the changes in the isobaric–

of the isothermal potential, enthalpy, and entropy corresponding to the formation of 1 mole of InSb from liquid indium and solid antimony*:

$$\Delta Z = -FE = 23.066\,(0.345 - 0.241 \cdot 10^{-3}T) = 7.97 + 5.56 \cdot 10^{-3}T \text{ kcal/g-mol}.$$

Hence, for the temperature interval studied,

$$\Delta H = -3.98 \pm 0.20 \text{ kcal/g-at},$$

$$\Delta S = -2.78 \pm 0.25 \text{ cal/g-at} \cdot \text{deg}.$$

Fig. 3. Dependence of e.m.f. on temperature at different gross compositions of the alloy electrode. *a*—alloy of composition 59.9 at.% Sb; *b*—alloy of composition 67.2 at.% Sb

Figure 3: Fig. 3. Dependence of e.m.f. on temperature at different gross compositions of the alloy electrode. *a*—alloy of composition 59.9 at.% Sb; *b*—alloy of composition 67.2 at.% Sb

The accuracy of ΔZ is determined by the reproducibility of the e.m.f. data; it is ± 1 mV, which corresponds to an error of ± 0.01 kcal/g-at.

Using our experimental data, the heat capacities of the pure metals ([9]) and of indium antimonide ([5]), and also the heat of fusion of indium ([9]), we calculated the standard values of the thermodynamic functions. The values obtained are:

$$\Delta Z_{298} = -3.07 \pm 0.01 \text{ kcal/g-at},$$

$$\Delta H_{298} = -3.67 \pm 0.20 \text{ kcal/g-at},$$

$$\Delta S_{298} = -2.01 \pm 0.25 \text{ cal/g-at} \cdot \text{deg}.$$

Fig. 3. Dependence of e.m.f. on temperature at different gross compositions of the alloy electrode. *a*—alloy of composition 59.9 at.% Sb; *b*—alloy of composition 67.2 at.% Sb.

Comparison with literature data

Table 1 compares the results of our work with literature data for indium antimonide.

In row 1 of Table 1, the value ΔH_{723} was obtained by Kleppa by the method of tin calorimetry; ΔH_{298} was calculated by us from Kleppa' s value ΔH_{723}, using the same literature data on heat capacities that we used in recalculating the results of our work to standard temperature. Rows 2 and 3 contain the results of calculating the standard isobaric-isothermal potential by two independent routes ([4]). In row 2 the calculation was carried out by Wagner' s method ([10]); the liquidus curve of the phase diagram of the In–Sb system, corresponding to the equilibrium of melts with the solid InSb phase, is used; the heat and temperature of fusion of the compound are also included in the calculation,

Table 1

No.	$-\Delta H_{723}$, kcal/g-at	$-\Delta H_{298}$, kcal/g-at	$-\Delta H_{273}$, kcal/g-at	$-\Delta Z$, kcal/g-at	$-\Delta S_{298}$, cal/g-at · deg	Method	Author
1	4.30	4.00				Calorimeter	(3)
2				3.02		Calculation by ([10])	
3			3.47	2.88	1.99	Calorim. calculation	([4])
4	3.98	3.67	–	3.07	2.01	E.m.f.	Present study

* 1 cal. = 4.1840 abs. joules.

where the heat of fusion was determined by the authors experimentally by a calorimetric method. In line 3 are the results of the calculation carried out from the basic equation $\Delta Z = \Delta H - T\Delta S$; in this calculation the heat of formation found by the authors from calorimetric measurements was used, as well as the value of the standard entropy of formation calculated from literature data on absolute entropies. The latter quantity for InSb was found from tabulated data for θ/T, where θ is the Debye temperature, taken by the authors as equal to $200 \pm 5°$.

It is seen from Table 1 that the heats of formation of indium antimonide obtained by us agree, within the accuracy of our experiment, with the results obtained in ([4]). The change in thermodynamic potential and entropy, calculated from e.m.f. data, also agree fairly well with the calculation of Schottky and Bever ([4]).

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