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Abstract

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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF INDIUM ARSENIDE BY THE METHOD OF ELECTROMOTIVE FORCES

Indium arsenide (InAs) belongs to the group of semiconductor compounds $A^{III}B^{V}$, and the various physical properties of this group are widely studied. Our task was to investigate the basic thermodynamic properties, such as the isobaric-isothermal potential, entropy, and enthalpy of formation of indium arsenide. At the beginning of our investigation, only the standard enthalpy of formation of indium arsenide was known from the literature. In the work of Schottky and Bever (^{1}) the heat of formation was determined by the method of tin calorimetry; Gadzhiev and Sharifov (^{2,3}) used for this purpose the method of direct synthesis from the components in a calorimetric bomb (^{4}); Gutbier (^{5,6}) calculated the standard heat of formation of indium arsenide from the results of a mass-spectrometric study of the evaporation process of solid indium arsenide at 1000–1100° K. Recently the work of Piesbergen (^{7}) has become known, concerning the study of the atomic heat capacities of compounds of the $A^{III}B^{V}$ group in the temperature interval 11–273°K. From the results of work (^{1}), by graphical integration, the author calculated the standard (298° K) entropy of a number of the compounds studied, including indium arsenide.

In our investigation of the thermodynamic properties of indium arsenide, the method of electromotive forces (e.m.f.) was used. For this purpose we studied the e.m.f. of cells of the type:

$$(-)\mathrm{In}\,(\ell)\ /\ \text{chloride melt}\ /\ (\mathrm{InAs}+\mathrm{As})\,(\mathrm{s})(+).$$

$$+\mathrm{InCl}$$

The investigation was carried out in the temperature interval 240–510°C. From the phase diagram of the indium–arsenic system (^{8}) it is seen that the electrodes —arsenide alloys with arsenic, irrespective of the excess content of arsenic, fall in one two-phase field, arsenide–arsenic. The e.m.f. of such cells corresponds to the formation of arsenide from the components

$$\mathrm{In}\,(\ell) + \mathrm{As}\,(\mathrm{s}) = \mathrm{InAs}\,(\mathrm{s}). \tag{1}$$

Directly from the value of the e.m.f. the change in the isobaric-isothermal potential (ΔG^0) of reaction (I) is calculated:

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

z is the charge of the potential-forming metal; for indium $z = 1$; F is the Faraday number, equal to 23062 cal/V • g-eq; E is the e.m.f. in volts.

The changes in entropy and enthalpy of the process are calculated from the temperature dependence of the e.m.f.:

$$\Delta S = -\frac{d(\Delta G)}{dT} = zF\frac{dE}{dT}; \tag{2}$$

$$\Delta H = \Delta G + T\Delta S. \tag{3}$$

In the work, metals of semiconductor purity were used: indium 99.999% and arsenic 99.99%. Indium arsenide was prepared at the Institute of Rare Elements according to procedures developed there* (concentration of carri-

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current carriers $n = 2.3$—$5.8 \cdot 10^{16}$. To prepare the electrode, arsenide was mixed with freshly sublimed arsenic. Tablets 6 mm in diameter and 6-8 mm long were pressed from the mixture; at the same time, a current lead made of tungsten wire 0.5 mm in diameter was pressed into the electrode. For each experiment the mixture was prepared anew, since arsenic oxidizes during storage.

The electrolyte in the cells was chloride melts: in the temperature interval 360—550°C, a mixture of KCl–LiCl of eutectic composition, and at 220—380°, a mixture of $ZnCl_2$–KCl–NaCl. Indium chloride was added to the melt in the form of previously prepared monochloride (InCl) in an amount of 0.1-0.2%. The basic details of the method are described in works (^{9,10}); a description of the devices—cells—is given in (^{11}). The study of the e.m.f. as a function of temperature occupied a period of round-the-clock operation for 5-6 days.

Fig. 1. $(-)\mathrm{In}(\ell)/\mathrm{melt}/(\mathrm{InAs} + \mathrm{As})(+)$.
Numbers of points are numbers of experiments

Fig. 1

Figure 1: Fig. 1

The entire set of experimental points obtained in all experiments was processed jointly; the equation of the linear e.m.f.-temperature dependence was derived by the method of least squares. Such a method of joint treatment of all points is possible because all the alloys studied fall into the same two-phase region.

The experimental results are shown in Fig. 1. The straight line on the graph corresponds to the calculated equation

$$E = 586.3 - 0.232\,T \text{ mV}.$$

On the basis of this equation, in accordance with relations (1)—(3), the thermodynamic functions were calculated in the temperature interval 240—510°C.

Table 1

513–783°K	513–783°K	513–783°K	298°K	298°K	298°K	298°K
$-\Delta H^\circ$, kcal/g-at	$-\Delta S^\circ$, e.u./g-at	$-\Delta S^\circ_{648}$, kcal/g-at	$-\Delta H^\circ$, kcal/g-at*	$-\Delta S^\circ$, e.u./g-at*	$-\Delta G^\circ$, kcal/g-at*	S°, e.u./g-at
6.8 ± 0.4	2.7 ± 0.6	5.1 ± 0.4	6.2 ± 0.4	1.3 ± 0.6	5.8 ± 0.4	9.8 ± 0.6
			6.9 ± 0.4(3)			9.05 ± 0.05(7)
			6.9 ± 0.5(6)			
			7.4 ± 0.65(1)			
			6.9 ± 0.4	2.17 ± 0.05	6.3 ± 0.5	

* Calculated according to (3,7,13).

The results of the calculation are summarized in Table 1 (row 1). The error values given were estimated as the magnitudes of confidence intervals within which the results of 95% of possible measurements of the given quantity should lie (twice the sample variance) (12).

Table 1 also summarizes the standard quantities obtained by calculation from our data at high temperatures; there, too, a summary of standard quantities from literature sources is given. In the last row of the tab-

the value of the isobaric potential was calculated from the enthalpy of formation (3) and the entropy change, calculated from data (7, 13).

The recalculation of our data to standard quantities was carried out under the assumption that Δc_p is constant. In the absence of experimental data on the heat capacity of indium arsenide above 273°K, for the purposes of our calculation we assumed for the change in the heat capacity of indium arsenide in the interval 298–648°K the same course of the heat capacity with temperature as is observed for gallium antimonide according to the work of Kochetkova and Rezukhina (14). The curves of heat capacity versus temperature for these two compounds in the interval 11-273°K (7) show an analogy in the course of the dependence. With some approximation we extended this analogy also to higher temperatures. The heat capacities of indium and arsenic were taken from (13). Hence Δc_p is equal to -0.41 cal/g-at in the interval 298–429°K and -0.76 cal/g-at after the transition to liquid indium in the interval 429–648°K.

From a review of the data in Table 1 it is seen that both the enthalpy and the entropy of formation of indium arsenide, calculated from the results of our study, are somewhat lower than those obtained from calorimetric determinations of these quantities separately (3, 7).

The entropy and enthalpy calculated through the derivatives of the emf with respect to temperature are, naturally, determined less accurately than the isobaric potential ΔG, which is calculated directly from the measured value of the emf.

The recalculation of thermodynamic functions from higher temperatures to the standard temperature may introduce a certain share of error. The assumptions made by us in carrying out such a recalculation were indicated above. The isobaric potential ΔG_{298}, as was to be expected, is in better agreement with that calculated from the literature data.

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