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Abstract

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PHYSICAL CHEMISTRY

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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF GALLIUM ANTIMONIDE BY THE ELECTROMOTIVE-FORCE METHOD

Gallium antimonide (GaSb) is the only compound formed in the gallium–antimony system (^{1}); it melts at 703°C, crystallizes in the sphalerite structure, and belongs to the group of semiconductor compounds $A^{III}B^{V}$.

According to the literature, the possibility is allowed of a slight deviation of the chemical composition of gallium antimonide from the stoichiometric one, although there is as yet no direct proof of such an assumption. There are indications that the width of the homogeneity range of gallium antimonide is not determined even by the precision X-ray method (^{2}).

The thermodynamic properties of gallium antimonide are considered by Renner in his article devoted to a review of literature data on compounds of the $A^{III}B^{V}$ group up to and including 1959 (^{3}). By that time, for gallium antimonide, the standard enthalpy of formation had been determined by means of tin calorimetry (^{4}), as well as the vapor pressure over solid gallium antimonide using mass-spectrometric analysis of the vapor composition (^{5}). In work (^{4}), in addition to the heat of formation of the compound, the heat of its melting was also determined by the method of quantitative thermal analysis. On the basis of the results of their investigation and the value of the phase diagram of the gallium–antimony system, the authors (^{4}), using Wagner' s equation (^{6}), calculated the isobaric potential (ΔG°_{298}) and the entropy of formation of gallium antimonide.

The literature also contains data on the mean heat capacities of gallium antimonide in the temperature interval 293—980°K (^{7}).

From the work of Piesbergen (^{8}), devoted to the study of the heat capacities of $A^{III}B^{V}$ compounds in the interval 11—273°K, the standard entropy of gallium antimonide is known, calculated by the author (^{8}) by graphical integration of the temperature dependence of the heat capacity.

Our objective was the experimental study of the principal thermodynamic properties of gallium antimonide: the isobaric-isothermal potential, entropy, and enthalpy of formation. As in our previous investigations ($^{9-11}$), we used the electromotive-force method for this purpose.

The investigation was carried out in the temperature interval 360—560°C. The e.m.f. of cells was studied

$$(-)\ \mathrm{Ga}_{(\ell)} \mid (\mathrm{KCl—LiCl}) + \mathrm{GaCl_3} \mid (\mathrm{GaSb} + \mathrm{Sb})^{(+)}_{(\mathrm{s})}.$$

melt

The e.m.f. of the cells corresponds to the reaction

$$\mathrm{Ga}_{(\ell)} + \mathrm{Sb}_{(\mathrm{s})} = \mathrm{GaSb}_{(\mathrm{s})}. \tag{1}$$

Directly from the magnitude of the e.m.f. there is calculated the change in the isobaric-isothermal potential of reaction (1)

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

z is the charge of the potential-forming metal; for gallium $z = 3$, F is the Faraday number $= 23062$ cal/V · g-equiv., E is the e.m.f. in volts.

The temperature coefficient of the e.m.f. makes it possible to calculate the change in enthalpy and entropy of the process

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

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

High-purity metals were used in the work: gallium −99.999%, and zone-melted antimony −99.999%.

Gallium antimonide with an excess of antimony was prepared by melting the components in evacuated quartz ampoules. In some experiments, previously prepared gallium antimonide (lattice constant $a = 6.09$ Å) mixed with antimony was used.

Fig. 1

Fig. 1

Figure 1: Fig. 1

As electrolyte there served a eutectic mixture of KCl—LiCl with a small addition of gallium chloride. Gallium chloride was prepared under a melt of the KCl—LiCl electrolyte by burning metallic gallium in a stream of chlorine. The concentrated electrolyte thus prepared with respect to gallium chloride was then added in a small portion to the cell electrolyte. The details of the method are described in papers (9, 10); a description of the cell apparatus is given in (11). Recording the e.m.f.-temperature curve during direct and reverse temperature runs usually required a period of 5-6 days of round-the-clock operation. Figure 1 presents the experimental results obtained for 7 electrodes of different methods of preparation and different excess antimony contents.

By the method of least squares, with joint treatment of all points, the equation obtained was:

$$E = 161.1 - 0.095\,T \text{ mV.} \tag{II}$$

The straight line in Fig. 1 corresponds to this equation. The method we used of joint treatment of all points is possible in the present case, since all the alloys studied belong to one and the same two-phase region GaSb—Sb.

Table 1

633-833 °K	633-833 °K	633-833 °K	298°K	298°K	298°K	298°K
$-\Delta H$, kcal/g-at.	$-\Delta S$, e.u./g-at.	$-\Delta G$, 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.
5.6 ± 0.5	3.3 ± 0.7	3.2 ± 0.3	$4.7 \pm 0.54.97 \pm 0.22$(4)	$0.7 \pm 0.71.4 \pm 0.3$(4)	$4.5 \pm 0.34.56 \pm 0.35$(4)	$9.67 \pm 0.69.09 \pm 0.05$(8)

On the basis of the equation $E = f(T)$, in accordance with relations 1-3, the thermodynamic functions for the temperature interval 360-560°C were calculated; they are summarized in Table 1. The accuracy of the quantities presented is determined by the error in determining E and the coefficients of equation (II); it is calculated by least-squares formulas as twice the sample variance (12).

Using literature data on the heat capacities of gallium, antimony, and gallium antimonide in the temperature interval 293-980°K (7), we recalculated the thermodynamic functions from their values in the interval 633-833°K to the standard temperature (298°K); they are also collected in Table 1.

Table 2 gives the thermodynamic functions of formation of gallium antimonide from monatomic gaseous atoms, calculated from the results of our work and the atomization energies of gallium and antimony according to (^{13}). Table 2 also includes the values of the same functions reported in Renner' s paper (^{3}); there the heat of atomization of gallium arsenide calculated by Folbert and the entropy of atomization calculated from the vapor pressure over gallium antimonide at 900°K according to (^{5}) are given.

Table 2

ΔH°_{298}, kcal/g-at.	ΔS°_{298}, e.u./g-at.	ΔG°_{298}, kcal/g-at.	Source
68.5	32.1	59.0	Present study
69.2	33.05	59.35	(^{3})

From the data of Table 1 it is clear that there is good agreement between the results of our work on the heat of formation of gallium antimonide and the calorimetric determinations of Schottky and Bever. The entropy of the compound, within the accuracy of the experimental data, agrees with (^{8}).

The atomization energies calculated on the basis of results obtained by various research methods, as is seen from Table 2, agree well with one another.

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