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Abstract

Full Text

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Thermodynamics of the Formation of the Higher Antimonide of Iron

To investigate the thermodynamics of the formation of the compound $FeSb_2$ from the elements according to the reaction:

$$\mathrm{Fe(s)} + 2\mathrm{Sb(s)} = \mathrm{FeSb_2} \tag{1}$$

the method of electromotive forces (e.m.f.) was used. The dependence of the e.m.f. of the cell

$$\mathrm{Fe} \,|\, \mathrm{Fe}^{2+},\ \mathrm{KCl} + \mathrm{LiCl}\ (\mathrm{melt}) \,|\, \mathrm{FeSb_2} + \mathrm{Sb}$$

on temperature was studied in the interval 410–610°. Twelve alloys of seven different compositions were investigated, lying within the heterogeneous region $FeSb_2 + Sb$ of the phase diagram of the Fe–Sb system (see Fig. 1 ([1])).

Fig. 1. Section of the melting diagram of the Fe–Sb system

The experimental procedure has been described in detail earlier. The electrodes were protected from oxidation by a slow stream of nitrogen, previously passed through a layer of copper at 500–600° to remove oxygen. The e.m.f. value became established within 20–30 hours, after which it remained constant at each temperature within 1 mV and was well reproduced during repeated passage through the temperature interval upward and downward. The potentials of individual electrode alloys relative to the same reference electrode differed by 0–3 mV.

The results of all experiments were processed by the method of least squares. For the dependence $E = f(T)$, the following equation was found:

$$E = 0.1497 - 0.00004T \ (\text{volts}), \tag{2}$$

using which one can calculate the changes in the isobaric-isothermal potential, enthalpy, and entropy in the formation of $FeSb_2$ from iron and antimony according to reaction (1).

$$\Delta Z = -nFE = -6.9 + 0.0018T \text{ (kcal/mol)}. \tag{3}$$

For $T = 800°K$

$$\Delta Z_{800^\circ} = -5.4 \pm 0.1 \text{ (kcal/mole)} = -1.8 \pm 0.03 \text{ (kcal/g-atom)}.$$

From (3) and $\Delta Z = \Delta H - T\Delta S$, we obtain:

$$\Delta H = -6.9 \pm 0.4 \text{ (kcal/mole)} = -2.30 \pm 0.1 \text{ (kcal/g-atom)},$$

$$\Delta S = -1.8 \pm 0.4 \text{ (cal/deg} \cdot \text{mole)} = -0.6 \pm 0.1 \text{ (cal/deg} \cdot \text{g-atom)}.$$

Discussion of the results. In the literature there is only one value of ΔH for the formation of $FeSb_2$, namely $\Delta H = -1.2$ kcal/g-atom, obtained by Körber and Elsen ([2,3]) by the method of mixing liquid metals in a calorimeter. This value differs from the heat of formation of $FeSb_2$ obtained by us by approximately 1 kcal/g-atom. The reason for this discrepancy probably lies in the following. Körber and Elsen determined ΔH of alloy formation as the difference between the heat evolved on mixing liquid iron and antimony and cooling the resulting alloy, and the heat evolved on cooling the same quantities of metals over the same temperature interval without alloy formation. This difference amounted to only a few percent of the measured quantity of heat and may be determined with considerable error, as Elsen himself indicates ([3]). On the other hand, Körber ([4]) points out that the method they used permits errors due to insufficient homogenization of the alloy during rapid cooling. These errors of the mixing method may be especially significant in determining the heats of formation of compounds that melt incongruently, as Wagner indicates ([5]). O. S. Ivanov ([6]) notes the inaccuracy of Körber' s data on the heats of formation of alloys in the systems Fe–Sb, Co–Sb, and Ni–Sb because of excessively rapid solidification of the alloys, leading to the formation of a nonequilibrium mixture. Indeed, Kurnakov and Konstantinov ([7]) found that a melt of composition $FeSb_2$ solidifies in the form of a three-phase mixture of crystals of the compound $FeSb_2$, the ε-phase, and antimony. The interaction of the ε-phase with antimony with formation of $FeSb_2$ proceeds completely only as a result of 30-hour annealing at a temperature of 710°C. Consequently, in Körber and Elsen' s calorimeter the heat of formation of $FeSb_2$ could hardly have been completely evolved.

Theoretical calculation. If it is assumed that a dilute liquid solution of iron in antimony has the properties of an ideal solution, then $\Delta Z'$ for the formation of solid $FeSb_2$ from liquid iron and antimony can be calculated from the equation for the liquidus branch (bounded by the dotted line in the figure) of the melting diagram of the Fe–Sb system (see Fig. 1), found by us from the data of Kurnakov and Konstantinov (^{7}).

$$\lg N_{\mathrm{Fe}} = -7.023 + 6.135 \cdot 10^{-3} T, \tag{4}$$

$$\lg N_{\mathrm{Sb}} = 0.428 - 0.490 \cdot 10^{-3} T. \tag{5}$$

For the equilibrium between the liquid and solid phases we have:

$$\Delta Z'_{\mathrm{FeSb}_{(s)}} - \Delta\mu_{\mathrm{Fe(l)}} + 2\Delta\mu_{\mathrm{Sb(l)}} = 4.575T\left(\lg N_{\mathrm{Fe}} + 2\lg N_{\mathrm{Sb}}\right).$$

Substituting (4) and (5), we obtain: $\Delta Z' = -28.21T + 23.58 \cdot 10^{-3} T^2$. For 950°K, $\Delta Z'_{950^\circ} = -5.5$ kcal/mole.

To calculate ΔZ for the formation of solid $FeSb_2$ from solid iron and antimony, it is necessary to take into account ΔZ of melting of iron and antimony and of the phase transitions of iron, which we do using the values given in (^{8}) for the heats of melting of iron and antimony and of phase transitions in solid iron:

$$\Delta Z_{\mathrm{FeSb}_{2(s)}} = \Delta Z'_{\mathrm{FeSb}_{2(s)}} - \sum \Delta Z \text{ of melting and transitions} =$$

$$= -5.5 - 1.4 = -6.9 \text{ kcal/mole}.$$

The calculated value of ΔZ belongs approximately to the same temperature region and is close to the experimentally found value.

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References

1. M. Hansen, *Structures of Binary Alloys*, 2, 1941, p. 697.
2. F. Körber, W. Oelsen, Mitt. Kaiser Wilhelm Inst. Eisenforsch. Düsseldorf, **19**, 209 (1937).
3. W. Oelsen, Zs. Elektrochem., **43**, No. 8, 530 (1937).

4. F. Körber, *Stahl und Eisen*, **56**, No. 48, 1401 (1936).

5. K. Wagner, *Thermodynamics of Alloys*, 1957, pp. 99, 102.

6. O. S. Ivanov, Izv. AN SSSR, OKhN, **1944**, p. 192.

7. N. S. Kurnakov, N. S. Konstantinov, in: N. S. Kurnakov, *Collected Selected Works*, **2**, 1939, p. 60.

8. O. Kubaschewski, E. Evans, *Thermochemistry in Metallurgy*, IL, 1954, p. 302.

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