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Abstract

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Study of the Thermodynamic Properties of Indium Tellurides

In the indium–tellurium system four compounds are formed, of the compositions: In_2Te_5, In_2Te_3, InTe, and In_2Te. The phase diagram of the system is shown in Fig. 1 (^{1}). Of all the indium tellurides, the properties of the compound In_2Te_3 have been studied to the greatest extent. This is explained by the fact that In_2Te_3 belongs to the group of semiconductors of the type A_2^III B_3^VI, characterized by a defective sphalerite structure (^{2}). Extensive literature material on various properties of In_2Te_3 is given in (^{3}). Indium monotelluride (InTe) exhibits both metallic and semiconductor properties (^{4}). In_2Te has metallic conductivity (^{5}). As established by Schubert et al. (^{6}), the higher indium telluride should be assigned the composition In_2Te_5, and not $InTe_3$, as had previously been accepted according to the work of Klemm and Vogel (^{7}).

The aim of the present work was to study the thermodynamic properties of indium tellurides characterizing this binary system. In the work the method of electromotive forces (e.m.f.) was used. The e.m.f. of concentration chains (with respect to the electrodes) of the type

$$-\mathrm{In}_{(\mathrm{liq})}\left|\begin{array}{c}\text{electrolyte}+\mathrm{InCl}\\ \text{melt}\end{array}\right|(\mathrm{In}_x\mathrm{Te}_{1-x})^{+}_{(\mathrm{solid})},$$

were studied, where x is the mole fraction of indium.

The thermodynamic functions were calculated from the equations:

$$\Delta G = z \cdot F \cdot E,$$

where z is the charge of the potential-forming ion ($z_{\mathrm{In}*} = 1$).

F is the Faraday number, equal to 23 062 cal/equiv.

$$\Delta S = -\frac{d\Delta G}{dT} = zF\frac{dE}{dT},$$

Fig. 1. Phase diagram of the In—Te system

Figure 1: Fig. 1. Phase diagram of the In—Te system

Fig. 2. External view of the quartz apparatus

Figure 2: Fig. 2. External view of the quartz apparatus

$$\Delta H = \Delta G + T\Delta S$$

(ΔG, ΔH, and ΔS are, respectively, the change in isobaric-isothermal potential, enthalpy, and entropy).

The procedure of the work, in its main features, is set forth in papers ([8], [9]).

Fig. 1. Phase diagram of the In—Te system

Experimental Part

The study was divided into the investigation of the e.m.f. within individual phase fields. The phase diagram of the indium—tellurium system is shown

in Fig. 1 and is characterized by the following heterogeneous fields: In_2Te_5—Te; In_2Te_5—In_2Te_3; In_2Te_3—InTe and InTe—In_2Te.

All four phases are considered as stoichiometric compounds without a homogeneity range. The investigation of regions II—IV was carried out in the temperature interval 380—425°C. In this case the salt melt used was a eutectic-composition mixture of potassium and lithium chlorides. For the phase region In_2Te_5—Te (I), the temperature interval was wider—300—420°C; the salt melt was a ternary chloride mixture KCl 18; NaCl 12, $ZnCl_2$ 70 wt.%.

Fig. 2. External view of the quartz apparatus
(labels in the figure: Argon; thermocouple sheath; alloy)

Alloys of stoichiometric composition were prepared by fusing the components in evacuated quartz ampoules. The alloys were subjected to prolonged annealing. The work used indium of 99.99% purity and tellurium purified by sublimation (not less than 99.99). Chemical analysis confirmed the specified composition. The phases were identified by X-ray phase analysis. X-ray patterns were taken by the powder method in an RKD-57 camera. The exposure was carried out using CuKα—Kβ radiation. For the In_2Te_5 phase, the exposure was made in a Guinier focusing camera with a bent germanium single crystal as monochromator.

The parameters found are given below; they agree well with literature data ([10], [2], [11]):

$$\mathrm{In_2Te_5}: \quad a = 4.36\ \text{Å}; \quad b = 16.12\ \text{Å}; \quad c = 13.36\ \text{Å}; \quad \beta = 91°49'$$

$$\mathrm{In_2Te_3}: \quad a = 6.16\ \text{Å}$$

$$\mathrm{InTe}: \quad a = 8.44\ \text{Å}; \quad c = 7.17\ \text{Å}; \quad c/a = 0.849.$$

$$\mathrm{In_2Te}: \quad a = 4.45\ \text{Å}; \quad b = 12.58\ \text{Å}; \quad c = 15.36\ \text{Å}.$$

All work was performed in H-shaped cells made of quartz or refractory glass. In the first case, the quartz cells were placed in a large quartz apparatus (Fig. 2), which made it possible to work in an atmosphere of pure argon and to study several cells simultaneously (in our case, two).

Table 1

Phase region	Reaction	$E = f(T)$, V	$\Delta G = f(T)$, kcal per reaction
In_2Te_5–Te	In $+ 2.5$Te $=$ $0.5In_2Te_5$	$0.3350 + 0.176 \cdot 10^{-3}T \pm 0.012$	$-7.70 - 4.05 \cdot 10^{-3}T$
In_2Te_5–In_2Te_3	In $+ 0.75In_2Te_5 = 1.25In_2Te_3$	$0.2327 + 0.102 \cdot 10^{-3}T \pm 0.008$	$-5.37 - 2.35 \cdot 10^{-3}T$
In_2Te_3–InTe	In $+ In_2Te_3 =$ 3InTe	$0.1182 + 0.248 \cdot 10^{-3}T \pm 0.007$	$-2.72 - 5.72 \cdot 10^{-3}T$
InTe–In_2Te	In $+$ InTe $= In_2Te$	$0.2550 - 0.300 \cdot 10^{-3}T \pm 0.004$	$-5.88 + 6.92 \cdot 10^{-3}T$

A cell made of Pyrex-type glass (Fig. 3) was designed for operation in vacuum. In this case, during operation the entire cell was located in the high-temperature zone, thereby eliminating the possibility of tellurium subliming into the volume of the cold parts of the apparatus. Indium was placed in a quartz thimble inserted into one of the arms of the cell.

It was observed that the results of experiments carried out with two different cell designs did not differ from one another.

The entire set of experimental emf data for all alloys belonging to separate heterogeneous phase regions was treated by the least-squares method. For four heterogeneous regions, equations of the form $E = A + B \cdot T$ were found (Table 1).

Fig. 3. External view of the cell

Figure 3: Fig. 3. External view of the cell

Indium was in the liquid state in all reactions, while the other reaction components were in the solid state.

Combining the equations obtained made it possible to calculate the formation of all four phases from the pure components (In—liquid, Te—solid).

Fig. 3. External view of the cell

Results of the calculation are given in Table 2. The series of tellurides studied is characterized by comparatively low heats of formation.

In the literature there are data by Hahn and Burov (^{12}) on the standard heats of formation of the tellurides In_2Te_3 and InTe, obtained by combustion in a calorimetric bomb. They correspond to -47.4 and -23.0 ± 3 kcal/mole.

Because of the absence of data on the heat capacities of indium tellurides, we did not calculate standard values from our experimental data; however, it is evident that the results of our investigation give heats of formation of a different order. In this connection the question arises whether the equilibrium in the salt mixture in the presence of indium-tellurium alloys is not shifted toward the formation of $InCl_3$.

Table 2

Summary of thermodynamic data for indium tellurides

Phase	$-\Delta G_{673^\circ K}$, kcal(per 1 mole)	$-\Delta H$, kcal(per 1 mole)	ΔS, e.u.(per 1 mole)	$-\Delta G_{673^\circ K}$, kcal(per 1 atom)	$-\Delta H$, kcal(per 1 atom)	ΔS, e.u.(per 1 atom)
In_2Te_5	20.8 ± 0.5	15.4 ± 3.0	$+8.0 \pm 2.0$	3.0	2.2	+1.1
In_2Te_3	18.0 ± 0.3	13.5 ± 3.2	$+6.7 \pm 2.0$	3.6	2.7	+1.3
InTe	8.2 ± 0.2	5.4 ± 1.8	$+4.0 \pm 1.0$	4.1	2.7	+2.0
In_2Te	9.4 ± 0.3	11.3 ± 2.0	-3.0 ± 1.5	3.1	3.8	−1.0

Then the value of z in the equation $\Delta G = -z \cdot F \cdot E$ will not be equal to unity, as was assumed in works (^{8,13}) and adopted in the present work. However, this question requires additional investigation, which we intend to carry out subsequently.

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