[CONTRIBUTION OF THE METALLURGY LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The System InAs–InSb

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A phase diagram for the system InAs–InSb, obtained by thermal analysis, X-ray and metallographic studies, is presented. The liquidus runs in an uninterrupted line from the freezing point of InAs (952°) to a eutectic point experimentally indistinguishable from the freezing point of InSb (525°). In the solid state a small single-phase region exists near the InAs end of the diagram.

In the Metallurgy Laboratories of the University of Notre Dame a program was initiated several years ago to investigate the alloying nature of indium. When the present work was started, there had been determined and published as part of this program the phase relationships in the systems In–Bi,[1] In–Sb,[2] In–Cd–Zn[3] and In–As.[4] Preliminary work in the ternary system In–As–Sb showed that the valid tie lines were those joining Sb and InSb with the intermediate phase InAs, dividing the In–As–Sb system into three sub-ternaries: namely, In–InAs–InSb, InAs–InSb–Sb and InAs–Sb–As. Of the terminal binary phase diagrams for the three sub-ternaries, all have been investigated and reported in the literature except InAs–Sb and InAs–InSb. The determination of the latter is the subject of this report.

Experimental Procedure

The indium used was obtained from the Indium Corporation of America and had a guaranteed purity of 99.97% with the following chemical analysis: Cu, 0.002%; Pb, 0.006%; Sn, 0.01%; and Zn, 0.01%. This was received in the form of shot, and before use the metal surface was cleaned with dilute nitric acid, followed by a thorough washing and an alcohol rinse.

The antimony was obtained from the J. T. Baker Chemical Company. The lot analysis was as follows: Fe, 0.007%; S, 0.03%; As, 0.005%; Pb, 0.02%; Cu, 0.002%.

A semi-quantitative spectrographic analysis of J. T. Baker purified lump arsenic crystals showed the following impurities to be present: Sn, 0.00X%; Pb, 0.00X%; Sb, 0.0X%; Fe, 0.000X%; and Bi, 0.0X%. The arsenic was further purified by heating *in vacuo* at 350° to sublime oxides. The element was then sealed in Pyrex tubes *in vacuo* and the arsenic sublimed at 600°. The arsenic condensed in the cooler portions of the tube, and it was stored in the air-free tube to avoid oxidation before alloying.

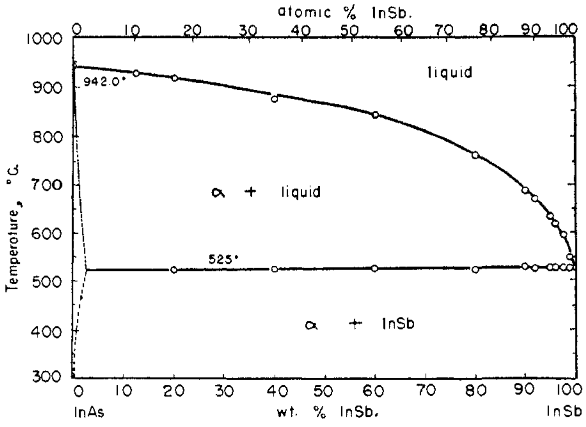

Fig. 1.—Phase diagram of the system InAs–InSb.

Alloys were prepared by sealing into evacuated Vycor or quartz tubes accurately weighed portions of the three elements to produce an ingot of the desired composition. Frequent agitation was necessary to produce homogeneous melts, and each molten alloy was held at a temperature above its freezing point for at least 30 minutes to ensure complete solution. After this treatment, the tubes were quenched to produce an ingot for thermal analysis.

Continued cooling and heating curves were obtained at rates of from 0.5 to 5° per minute, using either Vycor or graphite as a crucible material. The alloys were protected from oxidation by maintaining an atmosphere of dried, purified argon. Each melt was stirred vigorously during the course of the run. Temperatures were measured with a platinum *vs.* 10% platinum–rhodium thermocouple which was calibrated periodically against the freezing points of indium, silver, antimony, zinc and tin. The thermocouple readings were taken with a precision White single potentiometer with a high-sensitivity galvanometer. This instrument is readily adaptable to inverse rate thermal measurements since the e.m.f. can be changed in regular intervals of 0.01 mv. The time required for a given e.m.f. change was recorded by an electrical stop clock which records to 0.01 minute.

Conventional polishing techniques gave satisfactory results in preparing specimens for microscopic examination. Vilella's reagent, with 400 ml. of ethyl alcohol, 20 ml. of HCl and 40 g. of picric acid and Eden etchant (containing 20 g. of $Fe(NO_3)_3$, 20 g. of NH_4NO_3, 2 ml. of HNO_3 plus 500 ml. of water) were used to detail the microconstituents. These were used singly and in solutions containing 1 part Vilella and 1 part Eden reagent.

In order to confirm the conclusions deduced from the thermal analysis and microscopic examination, each alloy was X-rayed on a Debye–Scherrer camera using Cr–K α-radiation.

Results and Discussion

The thermal data obtained are given in Table I, and the phase diagram is shown in Fig. 1. The liquidus consists of an uninterrupted line running from the freezing point of InAs (942°) to a eutectic point experimentally indistinguishable from the freezing point of InSb (525°). The X-ray determinations showed that a single-phase region exists

TABLE I

THERMAL VALUES OF THE InAs–InSb SYSTEM

InSb, wt. %	InSb, atomic %	Liquidus, °C.	Solidus, °C.
0.0	0.0	942.0	...
12.5	10.1	926.3	...
20.0	16.8	917.5	524.8
40.0	34.7	875.1	525.3
60.0	54.3	844.6	526.2
80.0	76.6	760.6	524.8
90.0	87.9	684.7	527.3
92.0	90.5	670.5	524.9
95.0	94.0	632.0	525.8
96.0	95.1	618.3	526.3
97.5	97.2	595.2	524.2
100.0	100.0	525.0	...

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(1) E. A. Peretti and S. C. Carapella, Jr., *Trans. A.S.M.*, **41**, 947 (1949).

(2) T. S. Liu and E. A. Peretti, *ibid.*, **44**, 539 (1952).

(3) S. C. Carapella, Jr., and E. A. Peretti, *ibid.*, **43**, 853 (1951).

(4) T. S. Liu and E. A. Peretti, *ibid.*, **45**, in press (1952).

in the InAs end of the diagram. Attempts to determine the extent of this field were not very successful due to the inability to attain equilibrium in the solid alloys, even after heating for three months. The alloys were too brittle to permit acceleration of homogenization by working before heat treatment. Extrapolation of the solidus in this area gives an approximate value of 2% InSb as the maximum extent of the one-phase region.

Thus, all alloys in the system form a solid solution as the primary phase upon freezing, and practically all alloys complete freezing at 525° with the formation of InSb.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Complex Ions of Chromium. II. *trans–cis* Isomerization of Potassium Dioxalatodiaquochromate(III)[1]

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The absorption spectra of *trans*- and *cis*-potassium dioxalatodiaquochromate(III) were determined, the *cis* form absorbing considerably more at peaks slightly shifted toward the red. Using this difference in absorption at a wave length of 415 mμ, the rate of the *trans–cis* isomerization was followed spectrophotometrically. The rate was found to be first order with respect to the chromium salt and independent of added hydrogen ion. The rate varied only slightly with ionic strength. Rates determined at different temperatures enabled calculation of heat and entropy of activation for the isomerization.

Methods of preparation of the solid salts of dioxalatodiaquochromate(III) were reported by Croft,[2] Rosenheim and Cohn,[3] and E. A. Werner[4] but it was A. Werner[5] who first recognized that both *trans* and *cis* isomers should exist and that all previous workers had prepared only the *trans* isomer because of the very much smaller solubility of that isomer. Werner described a procedure for preparing the *cis* isomer.

In a solution of dioxalatodiaquochromate(III), the equilibrium between the isomers is such that the *cis* isomer is the main species present; however, the solubility of the *trans* isomer is so small that it crystallizes out first when a solution is allowed to evaporate slowly. Since there have been no reports on the exact relationships existing between these isomers in solution, it was the purpose of this investigation to study the kinetics of the *trans–cis* isomerization of potassium dioxalatodiaquochromate(III). This was possible by spectrophotometric methods since in solution the *cis* isomer absorbs much more strongly than the *trans* isomer. This was first recognized by observation of the color of the fresh *cis* and *trans* solutions at equivalent concentrations. Under these conditions the solution of the *trans* isomer is much less intensely colored.

Experimental

Reagents.—The *trans*- and *cis*-potassium dioxalatodiaquochromate(III) were prepared by the methods of Werner[5] using reagent grade oxalic acid and potassium dichromate. The ionic strength was controlled by adding reagent grade sodium nitrate, and the acidity was controlled by addition of reagent grade perchloric acid.

Procedure.—The salts used were analyzed for both oxalate and chromium. The reference standard for both analyses was a cerium(IV) sulfate solution prepared from Certified Ceric Ammonium Nitrate from the G. Frederick Smith Chemical Company. This ensured that the salts used had two moles of oxalate for each mole of chromium.

To analyze for oxalate a weighed sample was boiled with excess potassium hydroxide to precipitate the chromium(III) hydroxide, the solution was acidified, treated with excess standard cerium(IV) solution, boiled, cooled, and the excess cerium back-titrated with standard ferrous solution. To analyze for chromium a weighed sample was acidified, boiled with excess ammonium persulfate for 15 minutes in the presence of silver nitrate as catalyst. The chromate produced was titrated with standard ferrous solution.

The absorption spectra and rates were determined by use of a Model DU Beckman spectrophotometer, using 2-cm. cells. The solutions were suspended in a constant temperature bath except while making the measurements. The rate measurements were made by the method of Guggenheim[6] as modified by King.[7] Two identical samples were weighed out. The first was dissolved, diluted to volume and allowed to stand in the constant temperature bath for several times the half-life of the reaction. The second weighed sample was dissolved, diluted and the absorbancy[8] of the first sample measured as a function of time after putting the second sample into solution, using the second solution in the reference cell.

The reaction was considered to be

$$\textit{trans} \xrightarrow{k_1} \textit{cis}$$

and the equation that was applied to treat the data was

$$A_s' = (A_s)_{t+\gamma} - (A_s)_t = b(T)_0(1 - e^{-k_1\gamma})[(a_M)_C - (a_M)_T]e^{-k_1 t}$$

where A_s' was the measured absorbancy of the first, more strongly absorbing solution with reference to the second solution, b was the cell thickness, $(T)_0$ was the molar concentration of the starting *trans* compound, $(a_M)_T$ and $(a_M)_C$ were the molar absorbancy indexes of the *trans* and *cis* species, γ was the time between mixing the first and second solutions, and t was the time since mixing the second solution. By plotting $\log A_s'$ against t the slope of the straight line obtained was $-k_1/2.303$, where k_1 was the specific reaction rate constant. By plotting in this manner

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[1] The work on this investigation was supported by National Science Foundation Research Grant NSF-G62. The first paper of this series is considered to be THIS JOURNAL, **73**, 1240 (1951).

[2] H. Croft, *Phil. Mag.*, **21**, 197 (1842).

[3] A. Rosenheim and R. Cohn, *Z. anorg. Chem.*, **28**, 337 (1901).

[4] E. A. Werner, *J. Chem. Soc.*, **53**, 404 (1888).

[5] A. Werner, *Ann.*, **406**, 261 (1914).

[6] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

[7] E. L. King, THIS JOURNAL, **74**, 563 (1952).

[8] The terms used for spectrophotometric data are those recommended by the National Bureau of Standards, Letter Circular, LC-857 (1947).