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Thermal Analysis of the Indium–Iodine System

BY E. A. PERETTI

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A complete phase diagram for the system Indium–Iodine is presented. Three intermediate compounds exist; InI, InI_2 and InI_3, with congruent melting points of 365, 224.6 and 207°, respectively. InI forms a eutectic with In at 0.2 wt. % iodine and 155°. The solubility of solid and liquid InI in In is low, and at 365° a monotectic is formed with a composition indistinguishable from that of InI. The InI–InI_2 portion has a eutectic at 68.2 wt. % I and melting at 216°. In a similar fashion InI_2 and InI_3 form a eutectic at 147° with 71.8 wt. % I. The triiodide forms a eutectic with iodine at 96.8° and 90.2 wt. % iodine.

Thermal Analysis of the Indium–Iodine System.—The only reference in the literature to the indium–iodine phase diagram is that of Thiel and Koelsch[1] who investigated only the portion of the system between 50 and 75 atomic % iodine. It was our original intention to determine the nature of the system for compositions lying in the 0 to 50% and 75 to 100% iodine regions, but we could not check melting points reported by Thiel and Koelsch, and so we reinvestigated the 50–75% iodine field.

Experimental Procedure

The iodine used was Fisher's "Certified Reagent" grade which, according to the certificate of analysis, contained 0.001% non-volatile matter and 0.003% chlorine and bromine.

The indium came from two sources. Metal-shot from the Indium Corporation of America had a guaranteed purity of 99.97% with the following chemical analysis: Sn, 0.01%; Zn, 0.01%; Cu, 0.002%; Pb, 0.006%. Before being combined with the iodine the surface of the shot was cleaned with dilute nitric acid, and then by a thorough washing and an alcohol rinse. For certain critical compositions we used indium supplied by the American Smelting and Refining Company Central Research Laboratories. It was in the form of 0.25 inch extruded stick and had a purity of 99.999%.

All of the compositions studied were made by direct union of the elements in sealed, nitrogen-filled, glass tubes having an i.d. of 12 mm. If improperly carried out, the reaction between iodine and indium became sufficiently explosive to shatter the glass container and scatter its contents. This was particularly true for combinations containing more than about 40 atomic % iodine. Explosions were prevented completely by heating the glass tubes in an upright position so that the indium would all be on the bottom, overlain with the iodine. The temperature was brought slowly to the melting point of iodine, (113.6°) held constant for about one-half hour, gradually increased to above the melting point of the indium (156.4°), and finally held for at least one-half hour at a temperature about 50° above the liquidus. Successful melts also were made by heating the glass tubes in a position slightly inclined from the horizontal with the solid indium and iodine again unmixed and with the indium at the highest section of the tube. Upon heating to above the melting point of iodine, the tube could be carefully

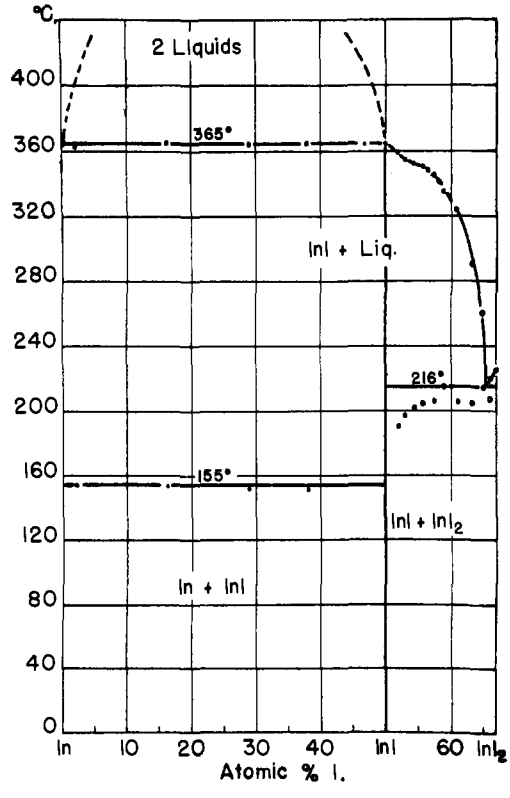

Fig. 1.—The In–InI_2 portion of the system In–I.

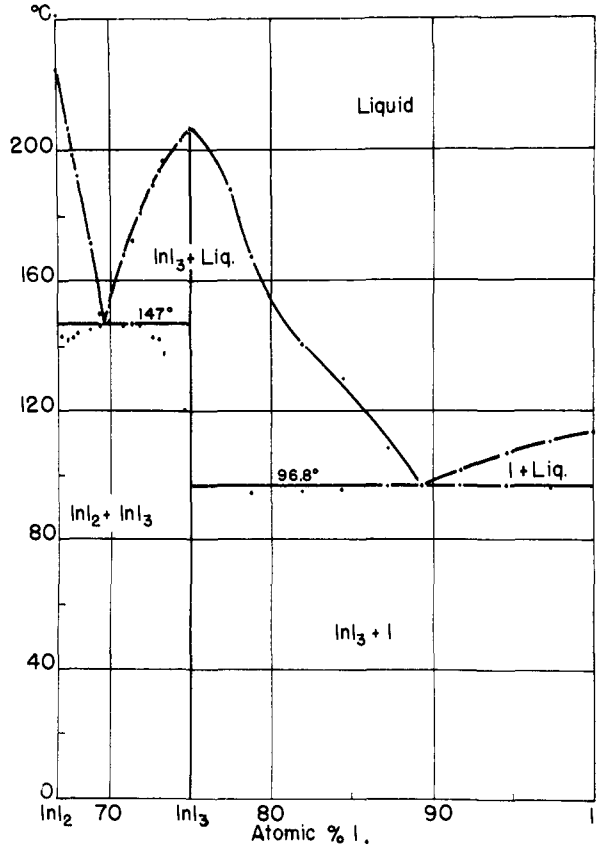

Fig. 2.—The InI_2–I portion of the system In–I.

(1) A. Thiel and H. Koelsch, *Z. anorg. allgem. Chem.*, **66**, 317 (1910).

tilted back and forth so that a limited amount of iodine could be run into the indium for reaction, and explosion could thus be prevented.

The course of the reaction could be followed easily through the glass tubes, and it was found necessary to employ vigorous shaking of the contents after the initial reaction had taken place, to insure complete dissolution of the ingredients, even when the contents were at a temperature of 50 to 100° above the liquidus. The melts were finally allowed to freeze rapidly in the tube, where they could be stored free from contamination until they could be used for thermal analysis.

Cooling and heating curves were taken of each composition in a 19 mm. i.d. glass tube, using about 50 g. of material for each determination.

A protective atmosphere of purified nitrogen was used, and the melts were stirred vigorously while cooling at rates of from 0.5 to 3° per minute. Temperatures were measured with an iron–constantan thermocouple which was calibrated periodically against the boiling point of water and the freezing points of iodine, indium, tin, bismuth and zinc.

Compositions containing more than 50 atomic % iodine were hygroscopic and could not be examined by the usual microscopic techniques, but structures often could be determined by observation of a specimen under the microscope through the glass tube immediately after freezing. The high-indium mixtures responded to conventional polishing and etching procedures.

Results

The complete phase diagram is shown in Figs. 1 and 2. Between 0 and 50 atomic % iodine (Fig. 1) indium and InI form a eutectic which melts at 155° and contains 0.2% iodine. At 365° a two-liquid region is encountered with a monotectic occuring at a temperature indistinguishable from the melting point of InI. At this temperature the two liquids are close to In and to InI, respectively, in composition.

The portions of the system lying between 50 and 75 atomic % encompass the intermediate compounds InI, InI_2 and InI_3 as established by Thiel and Koelsch.[1] The general shape of the diagram in this region as herein reported agrees with the latter investigations; however great differences exist in the reported compound melting points and the liquidus and solvus temperatures. As can be seen from Fig. 1, we obtain melting points at 365 and 224.6° for InI and InI_2, respectively, as compared to 351 and 212° reported by Thiel and Koelsch. Furthermore, we place the eutectic of InI and InI_2 at 68.2 weight % iodine (31.8% indium or 93.4 mole % InI plus 6.6 mole % I) and 216° *versus* Thiel and Koelsch's 205° and 67.8% iodine. Many of our eutectic arrests occurred at 205°; however, they were accompanied by severe under-cooling, and as 216° was the arrest point when supercooling was prevented, this is considered to be the true eutectic temperature. Thiel and Koelsch do not state the purity of their ingredients, but it is quite probable that the indium which was available to them (the year 1910) was rather impure. This would account for the differences observed.

The InI_2–InI_3 area also differs somewhat in detail from the previous investigation. We obtain a eutectic at 71.8 weight % iodine (28.2% indium or 30.6 mole % InI_3 plus 69.4 mole % InI_2) melting at 147°. The melting point of InI is 207°. These are in good agreement with Thiel and Koelsch's eutectic at 72 weight % iodine and 147° and in fair agreement with their melting point for InI_3 of 200°.

As was the case with the In–InI portion, the InI_3–I binary (Fig. 2) is reported here for the first time; it is a simple system with a eutectic at 96.8°, containing 90.2 weight % iodine (9.8% indium or 84.4 mole % iodine and 15.6 mole % InI_3).

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NOTRE DAME, INDIANA