out that the determination of k_r is not very accurate and that the precision on the value of log k_r is probably of the order of ±0.01. Furthermore, the same value of D_{A^-} was used in the calculations of k_r at different ionic strengths, whereas D_{A^-} actually decreases with increasing ionic strength. Measurements at ionic strengths lower than 0.01 were not carried out because it would have been necessary to decrease the concentrations of the buffer mixtures and pyruvic acid to values at which the accuracy of the polarographic measurements becomes too low.

Conclusion.—The agreement between the values of the rate constant for ionic recombination, as obtained by the polarographic method and from Onsager's theory, is fair.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND METALLURGY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY, SOCORRO]

The In–In$_2$S$_3$ System[1]

BY M. F. STUBBS, J. A. SCHUFLE, A. J. THOMPSON AND J. M. DUNCAN

A phase diagram for the In–In$_2$S$_3$ system obtained by thermal analysis, metallographic and X-ray studies is presented. Compounds In$_2$S$_3$, (In$_3$S$_4$), (In$_5$S$_6$) and InS are found to exist, but not the previously reported compound In$_2$S. The melting point of In$_2$S$_3$ is found to be 1090–1100° with decomposition. X-Ray evidence has been obtained to supplement the thermal analysis, and compounds In$_2$S$_3$, (In$_5$S$_6$) and InS are found to be stable at room temperature.

Data obtained during the determination of equilibrium constants in the reduction of indium trisulfide with hydrogen (work in progress) showed that the In–In$_2$S$_3$ system was probably more complex than shown by Thiel and Luckmann[2] in their study of the same system. These authors made visual observations of the melting points and so-called "sintering points" of various mixtures of indium and sulfur. Their results gave limited information about the internal structure of the phase diagram. With indium metal now available in commercial quantities, we have again carried out a thermal analysis of the In–In$_2$S$_3$ system, and have supplemented these data with metallographic and X-ray examinations.

Apparatus.—In contrast to Thiel and Luckmann, who used only enough material to fill a capillary melting point tube, we were able to use sufficient material (40–50 g. for each cooling curve) to give sizeable heats of fusion and reaction which could be recorded readily on cooling curves. This required a fairly large melting point tube. The high temperatures (600–1100°) at which the sulfides of indium melt required the use of a tube constructed of high-melting material such as Vycor (96% silica) glass. Metal cannot be used since sulfur reacts with almost any metal at these temperatures. Helium gas at atmospheric pressure was passed over the melt to prevent oxidation. A thermocouple well was imbedded in the melt and sealed into the top of the melting point tube with Sauereisen heat resistant cement.

The high temperatures required were reached quickly and conveniently by use of an Ajax–Northrup Induction Furnace. The Vycor tube containing the material to be melted was placed in a snug-fitting carbon crucible which was heated by induced current.

The temperatures were recorded by means of a chromel-alumel thermocouple and a General Electric thermocouple potentiometer, type P. J. — 1 B 4. The thermocouple was calibrated against the following standards: (1) U. S. Bureau of Standards copper ingot, m.p. 1083.2°; (2) silver foil, 99.9975% Ag, m.p. 960.5°; (3) 28.1% copper, 71.9% silver alloy, which gives a eutectic melting at 779°; (4) antimony, 99.8–99.83% Sb, m.p. 630.5°; and (5) zinc, 99.98% Zn, m.p. 419.4°.

The space between the carbon crucible and the induction coil in the induction furnace was packed with calcium oxide as an insulating material to slow down the rate of cooling.

Preparation of Materials Used.—The best method for preparing pure In$_2$S$_3$ proved to be that of precipitation from aqueous solution. Pure indium metal (99.96+% indium) was dissolved in hydrochloric acid and the excess acid evaporated off on a hot plate. The resulting solid InCl$_3$ was dissolved in water, the *p*H of the solution adjusted to approximately 3, and pure hydrogen sulfide gas from a cylinder was bubbled through it. It was found necessary to maintain the *p*H of the solution between 1.5 and 3.0. This was done by dropwise addition of a 3.0 *M* solution of ammonium acetate. In$_2$S$_3$ will not precipitate at *p*H values below 1.5, while at *p*H values above 3.4, there is danger of contamination with hydrous indium oxide.[3] The orange-yellow precipitate of In$_2$S$_3$ was washed by decantation, filtered, washed with H$_2$S water and dried in an oven for several hours at 130°. The sulfide was then pulverized in an agate mortar, digested with hot water, filtered, washed and dried overnight at 130°. The sulfide finally was heated in a vacuum or atmosphere of H$_2$S at approximately 350° for at least an hour to remove traces of ammonium salts, sulfur and water. In$_2$S$_3$ prepared by this method gave the following typical analyses after conversion to hydroxide and ignition to oxide at 800°: In, 70.49%, 70.14%, 70.36%; theoretical for In$_2$S$_3$, 70.48%. Spectrographic analysis of the precipitated sulfide showed it to be free of all but traces of impurities.

An attempt was made to prepare fairly large amounts of In$_2$S$_3$ by heating indium shot with excess sulfur in a sealed evacuated Pyrex tube. Although heating was controlled carefully and the temperature raised very slowly, the heat of reaction was so large that an explosion always resulted. Apparently, this method is satisfactory only for the preparation of small quantities, or if used for preparation of larger quantities (50–100 g.) would require specially strengthened reaction tubes of glass or other inert material.

Experimental Procedure.—Indium–sulfur mixtures of varying composition were made by melting together weighed amounts of pure In$_2$S$_3$ and In in the Vycor melting point tube, under an atmosphere of helium gas, in the induction furnace. Each mixture was melted thoroughly and held above the melting point with shaking for 10–15 minutes to assure complete reaction and mixing before the cooling curve was run. Temperature readings were taken every ten seconds. The melt was agitated during cooling to prevent supercooling, both hand shaking and mechanical vibration being used. A total of 77 such cooling curves were run on different In–In$_2$S$_3$ mixtures. Temperature was plotted against time to obtain the cooling curves.

As an aid to interpretation of the cooling curves, portions of the cooled melt in each case were polished and etched as

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[1] Presented at the XIIth International Congress of Pure and Applied Chemistry at New York City, September, 1951.

[2] A. Thiel and H. Luckmann, *Z. anorg. allgem. Chem.*, **172**, 353 (1928).

[3] T. Moeller, THIS JOURNAL, **63**, 2626 (1941).

metallographic specimens and examined under a crystallographic microscope. Observation of the various crystal forms present in the melt made it possible to identify a particular crystalline form with a definite reaction or fusion temperature in the phase diagram. For example, in In–In_2S_3 mixtures containing as high as 99% In, red crystals, later identified as InS, were observed in the colored melt. The fact that no compound besides InS (78.16% In) was found to crystallize from 78–99% In melts helped to eliminate the possibility of the existence of a compound In_2S (87.75% In) under the conditions at which our studies were made.

Melts containing more than 84–85% In always contained two layers: (1) melt 2, the lower layer, being metallic looking, but carrying a few dispersed crystals of red InS; (2) melt 1, the upper layer, being composed of red crystals, but carrying a few dispersed globules of metallic looking material (In metal or melt 2).

The melt of composition corresponding to InS (78.16% In) showed two crystalline phases, red and black, plus some metallic-looking residue. However, when the melt was ground to a powder, mixed, remelted, and held just below 680° (660–675°) (see phase diagram Fig. 1) for one hour, equilibrium conditions resulted and the cooled melt, on microscopic examination, showed only red crystals of InS, the black crystals and melt having reacted to form red crystals of InS.

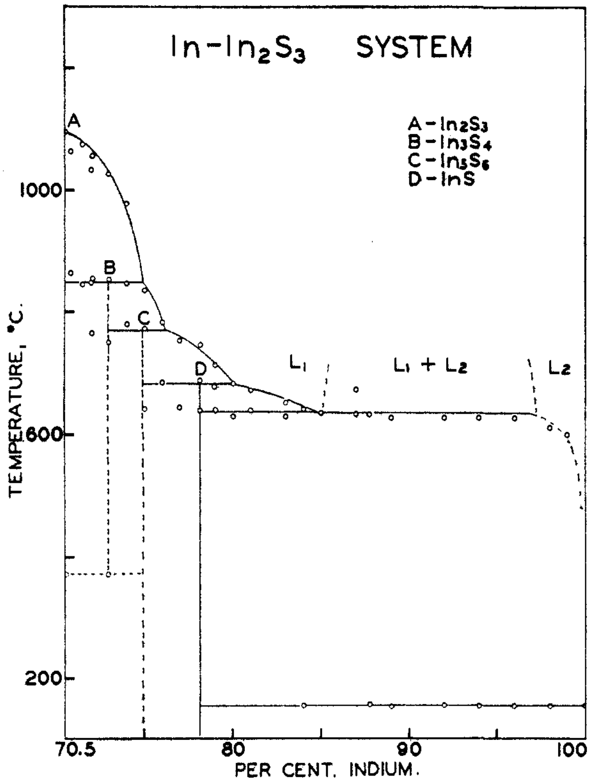

Fig. 1.

Melt of composition 75.00% In, corresponding roughly to In_5S_6 (74.89% In), likewise was held just below 760° (740–760°) for 30 minutes. Examination of the cooled melt showed almost pure black crystals with just a trace of red crystals (InS).

Pure In_2S_3 decomposes at or near its melting point so that the cooled melt usually appears as black crystals. However, when melted In_2S_3 is cooled under an atmosphere of sulfur the main body of the melt appears black, but the top surface of the melt has a layer of dark red crystalline material, probably the true crystalline form of pure In_2S_3. A sample of black crystalline In_2S_3 melt was held at 900° for 30 minutes with excess sulfur and the cooled melt appeared to be composed almost entirely of red crystalline In_2S_3 on examination under the microscope.

The area of immiscibility of melts 1 and 2 (see Fig. 1) between approximately 85 and 98% In was also investigated. Small Vycor tubes (5 mm. i.d.) containing an In_2S_3–In mixture made up to contain 90% In were heated to 1300° in the induction furnace. The tubes were removed from the cooling furnace at 1300, 1200, 1100 and 1000° and quenched by immediate immersion in water. The cooled melts then were cut in half along the vertical axis and examined for layering. Two phases were found to exist at all the temperatures studied, up to and including 1300°. Apparently, the 90% In mixture shows immiscibility between melts 1 and 2 up to and beyond 1300°, or else the separation into two phases is so rapid that even quenching in water does not prevent it completely.

The determination of the melting point of pure In_2S_3 was attempted by sealing In_2S_3 in an evacuated tube with excess sulfur. Several such attempts resulted in explosion of the Vycor tube because of the pressure of the sulfur vapor, but one run was successful and showed a melting point of 1098° for the pure In_2S_3. This value is considerably higher than the previously reported 1050°.[2]

The two experimental points at about 370° and compositions of 70.5 and 73% indium (see Fig. 1) were determined by differential thermal analysis on an apparatus manufactured by Eberbach[4] for mineral analysis. The material to be tested is placed in a receptacle in a metal block which is heated electrically. Two thermocouples are used, one in an air space within the heating block, the other imbedded in the sample being tested. The differential rate of heating between the two thermocouples shows a sharp change for any change in heat capacity in the substance being tested due to phase changes in the material tested.

Samples of various fused In–In_2S_3 mixtures were powdered and X-ray powder diffraction photographs were prepared from these samples. A North American Phillips Co. X-ray tube and powder camera were used, using the $Cu_{K\alpha_1\alpha_2}$ radiation with a nickel filter.

Four different phases appear in the In–In_2S_3 system according to the X-ray examination. In addition to In_2S_3 and In, which have characteristic X-ray spectra, two other phases appear, one at 75–76% In, the other at 78% In. The phase at 75–76% would seem to correspond to In_5S_6 (74.89% In), and the phase at 78% In to InS (78.16% In). No new spectral lines were found between the composition of InS and pure In, which would have indicated a compound of formula In_2S (87.75% In). Klemm and von Vogel[5] had previously presented an X-ray spectrum for this compound (In_2S) as well as for InS and In_2S_3.

Preliminary studies of the crystal structure of various phases in the In–In_2S_3 system based on X-ray powder diagrams were being made when the report of Hahn and Klinger[6] came to our attention. The high and low temperature forms, α-In_2S_3 and β-In_2S_3, reported by these authors were confirmed by us. A communication from one of these authors[7] indicated that they likewise had been unable to prepare the compound In_2S by the methods of Thiel and Luckmann[2] and Klemm and von Vogel[5] or to detect it roentgenographically.

The Phase Diagram.—The various temperatures of fusion and reaction indicated by the cooling curves were plotted against composition of mixture in obtaining the phase diagram (Fig. 1). Four compounds of indium and sulfur are indicated, In_2S_3, (In_3S_4), (In_5S_6) and InS, the second and third formulas being in parentheses to indicate uncertainty with regard to composition. All components, except probably In_2S_3, have incongruent melting points, *i.e.*, the crystalline solid compound is at no time in equilibrium with a melt of its same composition. The maximum in the phase diagram found by Thiel and Luckmann[2] at the composition of InS was not found by us. No evidence for the existence of the compound In_2S (87.75% In) was found. Rather InS was found to solidify at 640° in this area, the monotectic at 155°, and the cooled

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[4] Eberbach and Son Co., Ann Arbor, Michigan.

[5] W. Klemm and U. H. von Vogel, *Z. anorg. allgem. Chem.*, **219**, 45 (1934).

[6] H. Hahn and W. Klinger, *Z. anorg. Chem.*, **260**, 97 (1949).

[7] Harry Hahn, *Inorg. Chem. Inst.*, Kiel University, Kiel, Germany.

melt to consist of two separate phases which exist in the molten state as immiscible liquids probably as high as 1300°.

The melting point of pure In_2S_3 is found to be considerably higher than the 1050° reported by Thiel and Luckmann.[2] A true melting point is difficult to obtain because the compound melts with decomposition. A melting point of between 1090 and 1100° is indicated for the pure compound.

Meritectic temperatures were recorded as

$$840°\text{: } In_2S_3 + \text{melt} \rightleftarrows (In_3S_4) \qquad (1)$$

$$770°\text{: } (In_3S_4) + \text{melt} \rightleftarrows (In_5S_6) \qquad (2)$$

$$680°\text{: } (In_5S_6) + \text{melt} \rightleftarrows InS \qquad (3)$$

The monotectic intersects the miscibility gap at 640°. The reaction line at 370° is believed to be due to the decomposition of the In_3S_4 phase into In_2S_3 and In_5S_6. The In_3S_4 phase apparently exists only above this temperature. No evidence for its existence at room temperature was found in the X-ray studies. The compounds In_3S_4 and In_5S_6 probably are spinel-like compounds and should be written as $InS{\cdot}In_2S_3$ and $3InS{\cdot}In_2S_3$, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary and Quaternary Aqueous Systems Involving Thallous, Ammonium, Potassium and Cupric Sulfates

BY JOHN E. RICCI AND JACK FISCHER

Some aqueous salt systems involving thallous sulfate have been studied at 25° in order to compare the behavior of the thallous with that of the corresponding silver and alkali metal salts. Continuous solid solution is formed between Tl_2SO_4 and both $(NH_4)_2SO_4$ and K_2SO_4. Both systems apparently belong to Type I of the Roozeboom classification in respect to the distribution between the aqueous solution and the crystalline phase. The Tl_2SO_4–K_2SO_4–H_2O system, studied at 10, 25 and 45°, is unusual in that while the vapor pressure of the saturated aqueous solution has, according to the observed distribution, no minimum for the entire system, the analytical water content has a very distinct minimum. In the system Tl_2SO_4–$CuSO_4$–H_2O the hydrated double salt $Tl_2SO_4{\cdot}CuSO_4{\cdot}6H_2O$ was found to be just incongruently soluble at 25°. The equilibrium relations at 25° for the corresponding congruently soluble double salts in the systems $(NH_4)_2SO_4$–$CuSO_4$–H_2O and K_2SO_4–$CuSO_4$–H_2O were reinvestigated, in part, and in both cases the maximum water content of the solubility curve was found not to occur in the pure aqueous solution of the double salt but in a solution containing excess of the univalent sulfate. The 25° isotherms of the two quaternary systems Tl_2SO_4–$(NH_4)_2SO_4$–$CuSO_4$–H_2O and Tl_2SO_4–K_2SO_4–$CuSO_4$–H_2O were determined. In each case there is no isothermally invariant point of threefold saturation, since each involves only the three solid phases $CuSO_4{\cdot}5H_2O$, a continuous anhydrous solid solution of the univalent sulfates, and a continuous hydrated solid solution of two double salts, one congruently and one incongruently soluble. Jänecke diagrams of the isotherms, with (approximate) contours of water content, are given for both systems.

In order to add to the information on the relations between thallous salts and the salts of other univalent cations, the solubility isotherms at 25° of a number of aqueous systems of thallous sulfate and other sulfates were investigated. The systems chosen involve the salts Tl_2SO_4, $(NH_4)_2SO_4$, K_2SO_4 and $CuSO_4$. Despite certain similarities between argentous and thallous salts, we find continuous solid solution formed between Tl_2SO_4 and both $(NH_4)_2SO_4$ and K_2SO_4 at room temperature, while Ag_2SO_4 forms solid solution with neither of these salts.[1] Moreover, thallous sulfate forms the double salt $Tl_2SO_4{\cdot}CuSO_4{\cdot}6H_2O$, a schoenite, isomorphous with the corresponding double salts $(NH_4)_2SO_4{\cdot}CuSO_4{\cdot}6H_2O$ and $K_2SO_4{\cdot}CuSO_4{\cdot}6H_2O$.

Of the four quaternary aqueous systems involving the four salts under discussion, that consisting of water and the three univalent sulfates, or the system Tl_2SO_4–$(NH_4)_2SO_4$–K_2SO_4–H_2O, has not here been investigated. Every pair of these three salts forms continuous solid solution at room temperature,[2] and it may safely be expected, therefore, that the quaternary isotherm would involve but one solid phase, a ternary anhydrous solid solution of the three simple sulfates. Another of the possible quaternary systems, namely, $(NH_4)_2SO_4$–K_2SO_4–$CuSO_4$–H_2O, has already been investigated.[3] This involves the two isomorphous double salts $(NH_4)_2SO_4{\cdot}CuSO_4{\cdot}6H_2O$ and $K_2SO_4{\cdot}CuSO_4{\cdot}6H_2O$, both congruently soluble and forming continuous solid solution with each other. The isotherm (25°) has two curves of twofold saturation, one for quaternary liquid saturated with $CuSO_4{\cdot}5H_2O$ and the solid solution of the hydrated double salts, and one for saturation with this solid solution and the continuous anhydrous solid solution of $(NH_4)_2SO_4$ and K_2SO_4. Between these curves, or on the solubility surface of the double salt solid solution, there is a ridge of maximum vapor pressure falling from the solubility of the potassium double salt to that of the ammonium double salt. The 25° isotherms of the remaining two quaternary systems are here reported. Their phase relations differ from the preceding in that in each of them one double salt is congruently soluble and the other incongruently soluble.

Materials and General Procedure.—Some of the thallous sulfate used was a pure sample remaining from previous work in this Laboratory,[4] some of it was prepared by purification of commercial C.P. material, and some from Tl_2CO_3 and sulfuric acid. In these preparations the thallous sulfate was heated to dryness and partial melting with excess of H_2SO_4 and then again with ammonium carbonate, finally being recrystallized from water two or three times. The

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[1] E. L. Simons and J. E. Ricci, THIS JOURNAL, **68**, 2194 (1946).

[2] For the system $(NH_4)_2SO_4$–K_2SO_4–H_2O at 25° see A. Weston, *J. Chem. Soc.*, **121**, 1223 (1922), and A. E. Hill and C. M. Loucks, THIS JOURNAL, **59**, 2094 (1937).

[3] R. Hayami, *Mem. Col. Sci. Kyoto Imp. Univ.*, **4**, 359 (1921).

[4] A. E. Hill, N. O. Smith and J. E. Ricci THIS JOURNAL, **62**, 858 (1940).