

SOME RECENT ADDITIONS TO THE CHEMISTRY OF INDIUM

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Although indium was discovered in 1863, its extreme scarcity has prevented extensive investigations of its properties and those of its compounds. Within the past decade, however, the metal has been made available, and of the many papers published, only a few can be considered here.

Indium is produced commercially from electrolytic zinc concentrates and from an ore, of undisclosed location, controlled by the Indium Corporation of America and assaying 1.93 ounces of indium per ton. This ore is ground and concentrated by flotation. The concentrate is roasted and leached with sulfuric acid. The indium is then displaced or precipitated by neutralization and purified. From zinc process residues, the indium is recovered by solution in sulfuric acid and repeated replacement with zinc. No primary ore of indium is known, and although widely distributed, indium constitutes only 0.1 to 0.2% of other ores.

Pure indium is prepared by electrolysis. A stable bath developed by Gray of the Indium Corporation is made by dissolving freshly precipitated indium hydroxide in concentrated sodium cyanide solution containing 0.5 gram of d-glucose per gram of indium. From this bath indium deposits in a satin-like silvery condition. Westbrook of Grasselli Chemicals obtains compact deposits of indium from a sulfuric acid bath containing 250 grams of sodium citrate per liter. In the absence of some "stabilizing" compound, the indium deposit is spongy and undesirable. Sucrose, glycine, formic acid, etc., can be used.

Indium of atomic weight purity has been obtained by repeated electrolytic transport of the metal through indium chloride solution. Analyses of the trihalides from this product gave 114.76 as the atomic weight. Two isotopes, 113 and 115, are known.

Indium with a molal electrode potential of 0.336 volt lies between cadmium

and tin in the electromotive series.

A brown hydride, decomposing at 330°C., is said to form when hydrogen is passed over molten indium. A salt-like hydride apparently forms when atomic hydrogen contacts indium at 100-170°C.

Isobaric dehydration experiments and x-ray examinations have shown that the gelatinous precipitate produced at low temperatures by the addition of alkali to indium salt solutions and the granular precipitate produced by digestion at 100°C are identical and have the composition $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, or $\text{In}(\text{OH})_3$. The granular form contains larger particles. Colloidal sols also contain $\text{In}(\text{OH})_3$ particles. Information on the effects of polyhydroxy compounds on the precipitation of the hydroxide and on the solution of the latter in strong alkalis is still lacking.

Indium forms basic salts of the type $(\text{RCOO})_2\text{InOH}$ with several organic acids, and a number of double salts of the trichloride and tribromide with substituted ammonium halides and substituted sulfonium chloride are known. Double substituted ammonium sulfates have also been prepared.

Trimethyl indium, a white solid liberating two methyl groups as methane with water or alcohol and the third with dilute acids, has been prepared by digesting indium, dimethyl mercury, and mercuric chloride. Triphenyl indium has been obtained in a similar fashion. From it substituted bromides and iodides can be made. All react with water to give indium hydroxide. A dioxane complex forms with indium tribromide and a tripyridine salt with the triiodide.

Indium sulfate solutions containing sulfuric acid on evaporation deposit $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ which on heating gives $\text{In}_2(\text{SO}_4)_3$, a convenient water-soluble salt. The thermodynamics and hydrolysis of indium sulfate solutions have been investigated.

Indium trifluoride forms by the action of fluorine on the sesqui-oxide or on warming ammonium hexafluorindate. Heated with indium it gives indium difluoride. Indium dichloride is a glassy solid resembling anhydrous stannous chloride. Selenides and tellurides or both di- and tri-valent indium have been prepared. A nitride, InN , is formed by cathodic volatilization of indium in nitrogen at low pressures.

New qualitative tests include the production of a bright green fluorescence with an alcoholic solution of morine (sensitivity, 1γ), the formation of a red color when a filter paper moistened with solutions of complex indium cyanide and alcoholic alizarin is dipped in saturated boric acid, and the precipitation of as little as 0.7γ with quinalizarin in ammonium hydroxide.

Recent quantitative methods involve precipitation with 8-hydroxyquinoline from a buffered acetic acid solution, titration in acetic acid solution with potassium ferrocyanide using diphenylbenzidine as indicator, precipitation with sodium nitrite and sodium hydroxide or with potassium cyanate, and polarographic analyses.

A 42 per cent indium alloy with silver appears to completely resist alkali sulfide tarnishing but is extremely hard and brittle. Smaller amounts of indium are said to render silver tarnish-resistant, but this is disputed. A better procedure involves plating with indium and diffusing the plate in at higher temperatures. Dental amalgams with 10 to 20 per cent indium as well as alloys containing indium, gold, palladium, silver, and copper are tarnish-resistant and free from objectionable expansion and contraction effects. Gallium and indium give a 24 per cent indium eutectic melting at 16°C .

Adding 18 per cent indium to Lipowitz metal gives an alloy melting at 46.5°C . Cadmium-silver-copper and copper-lead bearings are rendered resistant to acid corrosion by diffused indium plate.

Indium salts are highly toxic to mice and rabbits when given sub-cutaneously but less so on oral administration. Toxicity may be delayed and results in anemia. Treatment of experimental syphilis has been reported.

Indium appears most promising in dental alloys, jewelry, fusible alloys, and bearing metals. Indium plate could be used in reflectors and mirrors. Indium or low melting indium alloys in quartz tubes could be used for high temperature thermometry. Indium oxide (0.05 per cent or more) gives yellow glass.

Pure indium metal can now be obtained for \$1.00 to \$2.50 a gram. Between 1924 and 1934, some 1000 kg. of the metal were produced, and Gray has stated that 50,000 to 100,000 ounces could be furnished annually if necessary.

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Because of the number of papers referred to, only a few general references can be given. These contain complete literature citations.

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