Densities of Liquid and Solid Indium

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A recent literature survey at this Laboratory revealed a paucity of physical property data on metallic indium. Density values, being of interest to a problem at hand, were determined. The method employed involved more or less standard dilatometric practice. A 32-cc. quartz dilatometer, mercury calibrated, was used as the measuring vessel. The temperature bath consisted of silicone oil contained in a clear Pyrex Dewar flask, with appropriate heating and stirring facilities. Temperatures were controlled by a series of mercury thermoregulators, calibrated to cover a range of temperatures from 25 to 300°. The meniscus level, with respect to a zero line on the capillary of the dilatometer, was determined by differential readings on a cathetometer. These readings were directly interpolated to volumes via the mercury calibration of the dilatometer.

The metallic indium was obtained from the A. D. Mackay Company, New York, N. Y. Spectrographic analysis established a purity of 99.98% indium. The principal impurity was iron, with faint traces of nickel, copper and lead.

For liquid densities, the metal was melted under a high vacuum, and entered the dilatometer through a Corning sintered glass filter (medium porosity). A tube, extending from the filter into the main body of the dilatometer, facilitated filling, and prevented wetting of the capillary walls by the metal. To eliminate wetting and superficial oxidation, a layer of paraffin (m. p. 70°), sufficient to cover the surface of the metal, was added. Oxidation of the paraffin, at the higher temperatures, was prevented by maintaining an atmosphere of inert gas in the capillary. Experimentally determined liquid density values are given in Table I.

Table I

Density of Liquid Indium

Temp., °C.	Density, g./cc.	
	Sample A	Sample B
164	7.026	7.027
194	7.001	
228	6.974	6.974
271	6.939	6.940
300	6.916	

The average of these values result in a straight line, the equation for which is

$$d(\text{from } 156.14 \text{ to } 300°) = 7.160 - 0.000813t$$

where t is the temperature in ° C. The experimental points exhibit a deviation from this equation of less than 0.01%. Over-all accuracy is within ±0.2%.

For solid densities, a sample of air-cast indium was cut into small pieces, and inserted into the dilatometer. Void space was eliminated by the addition of sufficient n-butyl phthalate to cover the indium and provide a readable meniscus in

the capillary of the dilatometer. Residual gases were removed by prolonged evacuation.

Density values were calculated by subtracting the volume occupied by n-butyl phthalate, at a particular temperature, from the total volume at that temperature. The difference was the volume occupied by the indium.

Any error due to the possibility of void spaces in the indium chunks was obviated by the following treatments: Run 1 was made on metallic chunks; Run 2 on the same metal after it had been melted and allowed to solidify slowly at the melting point; Run 3 on the same metal after it had been melted and cooled rapidly to room temperature by quenching in water.

Experimentally determined solid density values are given in Table II.

Table II

Density of Solid Indium

Temp., °C.	Density, g./cc.		
	Run 1	Run 2	Run 3
25	7.303	7.306	7.300
70	7.274	7.270	
115		7.239	7.239
150	7.217	7.212	7.214
164 (liquid)	7.025		

Using the method of least squares, the data in Table II give the equation

$$d(\text{from } 25 \text{ to } 156.4°) = 7.321 - 0.000713t$$

where t is the temperature in ° C. The extrapolated value at 20° is in good agreement with literature values.[1,2,3]

Since all volume errors in the method used for solid density reflect on the indium volume, the solid densities show more variation than the liquid densities. However, over-all accuracy is within ±0.2%.

(1) "Mechanical Properties of Metals and Alloys," National Bureau of Standards Circular C447, 1943.

(2) "Metals Handbook," American Society for Metals, p. 78, 1939.

(3) W. A. Roth, I. Meyer and H. Zeumer, Z. anorg. Chem., 214, 315 (1933).

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NEW COMPOUNDS

Some Mercuri Cyclohexanes

α-1-Iodomercuri-2-methoxycyclohexane.—A solution of 3.49 g. (0.01 mole) of α-1-chloromercuri-2-methoxycyclohexane[1] in 18 ml. (0.015 mole) of 3.3% aqueous sodium hydroxide was added slowly to a stirred solution of 7.5 g. (0.045 mole) of potassium iodide in 20 ml. of water. After several hours 2.6 g. (60% of theoretical yield) of iodomercurial was filtered off (m.p. 76–78°) and crystallized from 3 cc. of hot acetone (m.p. 81–81.4°, wt. 1.95 g.)

(1) J. Romeyn and G. F Wright, This Journal, 69, 697 (1947).

and then by dilution of a solution in 5 cc. of cold chloroform with 20 cc. of petroleum ether (b.p. 40–60°). The pure product (wt. 1.87 g.) melted at 81.2–81.6° cor. *Anal.* Calcd. for $C_7H_{13}OHgI$: C, 19.1; H, 2.97. Found: C, 18.6; H, 3.01.

β-1-Iodomercuri-2-methoxycyclohexane.—This preparation was carried out like that for the α-diastereomer to give a 4.25 g. (96% of theoretical yield) of product, m.p. 95–96°. This was dissolved in 6 cc. of chloroform at 25° and the solution diluted with 16 cc. of petroleum ether (b.p. 40–60°). Repetition of this purification yielded 1.84 g., m.p. 96.6–97.2° cor. *Anal.* Calcd. for $C_7H_{13}OHgI$: C, 19.1; H, 2.97. Found: C, 18.6; H, 3.06.

β-1-Methoxy-2-acetoxymercuricyclohexane.—When a suspension of 3.32 g. (0.0095 mole) of $dl,ld(\beta)$1-methoxy-2-chloromercuricyclohexane and 1.64 g. (0.0098 mole) silver acetate in 50 ml. of water are stirred for forty-eight hours it gradually acquires a purplish color owing to the formation of silver chloride. This was removed by filtration, and the clear colorless filtrate concentrated under reduced pressure at 50° to a volume of 10 cc. This aqueous solution was extracted three times with 5-ml. portions of chloroform. The chloroform layers were combined and concentrated to 5-ml. volume and then diluted to 25 cc. with 90–100° petroleum ether. A white crystalline solid weighing 2.95 g. or 83 mole per cent. was filtered off which melted at 82–83.5° cor. Recrystallization from chloroform and 60–70° petroleum ether raised the melting point to 83.0–83.6° cor.

Anal. Calcd. for $C_9H_{16}O_3Hg$: C, 28.9; H, 4.3; Hg, 53.9. Found: C, 28.8; H, 4.2; Hg, 53.9.

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Gallium Citrate and Radio-gallium (Ga⁷²) Citrate[1,2]

Interest in the physiological characteristics of gallium and radiogallium (Ga⁷²) in relation to normal and neoplastic bone metabolism[3] has resulted in studies of compounds suitable for administration of this element to experimental animals. Gallium citrate was prepared and found superior in many respects to all other compounds tried, including gallium lactate.[4] Neogi and Nandi[5] mention gallium citrate but give few details of its preparation and properties.

Freshly precipitated gelatinous gallium hydroxide[2] was treated with citric acid in the ratio of 1 mole gallium to 1.2 moles citric acid. The mixture was allowed to stand at room temperature two hours, evaporated on a steam-bath to a thin sirup, filtered while warm and the clear filtrate then poured into ten volumes of cold ethanol. This precipitated the gallium citrate and dissolved the excess citric acid. The mixture was allowed to stand in the cold overnight, centrifuged and the solid washed twice with ethanol in the centrifuge cup, again centrifuged and finally the excess alcohol was removed by suction. After the excess solvent was removed the filter cake was finally dried by evaporation at reduced pressure. In order to obtain a usable product moisture must be excluded during the drying process. Such gallium as may remain in the ethanol may be easily recovered on evaporation of the solvent.

The product obtained by the above procedure without

(1) Presented at the Medicinal Chemical Section, American Chemical Society, September 20, 1949.

(2) The opinions or conclusions contained in this report are those of the author. They are not to be construed as necessarily reflecting the views or endorsement of the Navy Department. Not copyrighted.

(3) Dudley, *et al.*, *J. Pharm. & Expt. Therap.*, **95**, 482, 487 (1949); **96**, 135, 224 (1949).

(4) Dudley and Garzoli, THIS JOURNAL, **70**, 3942 (1948).

(5) Neogi and Nandi, *J. Indian Chem. Society*, **13**, 399 (1936), **14**, 492 (1937).

further purification contained 25 to 26% gallium, was completely water soluble, was stable at pH 7–8, and was suitable as a water solution (pH 7.4) for subcutaneous or intramuscular injection at concentrations of 20 mg. Ga/cc. From 50 g. of the metal there was obtained 122 g. of the citrate (yield 66%), an amorphous white powder, slightly hygroscopic. The product does not melt, caramelization begins at 200°. Solubility at 20°, in water is 92.4 g./100 cc., in 95% ethanol is 0.12 g./100 cc., in absolute ethanol is 0.07 g./100 cc. Gallium citrate is insoluble in benzene, acetone and ether. Further purification was accomplished by repeated precipitation from cold absolute ethanol. Analytical results after three purifications indicate a somewhat unstable basic citrate which loses water easily.

Anal. Calcd. for $Ga(C_6H_6O_7)(OH)$: Ga, 25.18; C, 26.03; H, 2.55. Found: (sample dried at 100° over $CaCl_2$): Ga, 26.49; C, 23.29; H, 2.73.

On continued heating there is a reversible loss of 1 molecule of H_2O at 130°, and a second molecule at 200°. Heating above 200° produces irreversible dehydration, so that the third and fourth molecule of H_2O are lost at 250° and 280°.

As a concentrated solution of the citrate cools, no crystallization takes place. On evaporation the solution concentrates to a viscous mass, which on cooling solidifies into an amorphous transparent solid. No means of crystallizing gallium citrate has been found.

When gallium citrate is dissolved in water (75 mg./ml.) the resulting solution has a pH of 2.5. A solution suitable for physiological studies is prepared by bringing a solution of this concentration to pH 7–7.4 with 0.1 N NaOH. Such a solution is suitable for intramuscular or subcutaneous injection if some local anesthetic is used. Procaine hydrochloride is compatible with the gallium citrate at pH 7.4 and thus may be administered simultaneously with the gallium if so desired. These solutions do not cause precipitation of fresh horse serum or egg albumin.

Radiogallium Citrate.—Commercially available metal (98.6%, Eagle–Picher) was used to obtain a purified gallium nitrate which would have no long life radioactive contaminants following neutron bombardment. The metal was dissolved in mixed hydrochloric and nitric acids and precipitated as a hydroxide, using ammonia in slight excess. This suspension was heated to boiling, then filtered and the resulting flocculent gallium hydroxide was heated at 1000°, cooled and stored in a desiccator. Using this oxide as standard Ga_2O_3 sufficient of the material was dissolved in nitric acid and diluted so that the final solution contained 15 mg. Ga/cc. Solution of this refractory oxide is slow but may be accomplished by dissolving in a rather large volume of nitric acid and concentrating the solution by evaporation on a steam-bath. When dissolving metallic gallium, discard the residue which resists solution in the acids as this mass contains the majority of the impurities. Spectroscopic analysis by the National Bureau of Standards of Ga_2O_3 prepared as described, indicated the following (in p. p. m.): Ag, 0.1; Al, 2; Cu, 8; Fe, 0.5; In, 0.5; Mg, 1; Pb, 3; Si, 1; Mn, trace; not detected, As, Au, Be, Bi, Cd, Co, Cu, Ge, Hg, Mo, Na, Ni, P, Sb, Sn, Ti, Tl, V, Zn.

Five cc. of the standard $Ga(NO_3)_3$ solution was placed in quartz ampoules, dried at 140°, sealed and forwarded to the Atomic Energy Commission for neutron bombardment. These ampoules must have an outside diameter of not more than 18 mm., and an over-all length not to exceed 80 mm., the wall thickness of 1 mm. has withstood all shocks of handling and such pressures as may be built up therein. After irradiation, the ampoules were returned by air freight and used immediately. The quartz ampoule when removed from the shipping container was placed in lead shields, the end crushed and 1 cc. of the 20% HCl added. The ampoule was heated gently to near boiling to facilitate the solution of the gallium complex. The mixture was transferred quantitatively to a 50-cc. graduated cylinder. After adding 1 cc. of brom cresol purple (pH 5.6–6.5) indicator, 2 cc. of 20% citric acid were added. The solution was neutralized with sodium hy-