

413. *Solubility of Some Polonium Compounds.*

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The dependence of the solubility of polonium hydroxide on hydroxyl-ion concentration indicates that this compound is only feebly acidic; the solubilities of polonium acetate and cyanide have been determined for a wide concentration range of acetic acid and potassium cyanide respectively and some observations made on a formate, oxalate, and tartrate.

Polonium Hydroxide.—Papers on the tracer solution chemistry of polonium have indicated that this compound was acidic and analogous to tellurous acid.¹ Since our reported² value of 75 $\mu\text{g.}$ (of ^{210}Po)/litre for the solubility of this compound in water or excess of alkali appeared to be much larger than the values suggested by the tracer work, we have investigated the dependence of the solubility in potassium hydroxide solution in the concentration range 0.26—1.73N.

¹ Haissinsky, *J. Chim. phys.*, 1932, **29**, 453; Paneth and Benjamin, *Z. Elektrochem.*, 1925, **31**, 572; Haissinsky, *Compt. rend.*, 1932, **194**, 275, 1917; Blau and Rona, *Sitzungsber. Akad. Wiss. Wien, Abt. IIa*, 1930, **139**, 275; Guillot, *Compt. rend.*, 1930, **190**, 1553.

² Bagnall, D'Eye, and Freeman, *J.*, 1955, 2320.

The solubility in alkali slowly increases for 24 hr. and then remains constant, even for 5 days. The addition of hydrogen peroxide does not affect the solubility.

In our determinations, the equilibrium was approached from both higher and lower concentrations of alkali; the results were consistent to $\pm 1\%$. The plot of $\log [\text{KOH}]$ against $\log [\text{solubility}]$ is linear and of slope close to 2; activity corrections were not applied. The reaction involved is probably $\text{PoO}(\text{OH})_2 + 2\text{KOH} \rightleftharpoons \text{K}_2\text{PoO}_3 + 2\text{H}_2\text{O}$ for which the equilibrium constant

$$K_c = [\text{K}_2\text{PoO}_3]/[\text{KOH}]^2 = (8.2 \pm 0.4) \times 10^{-5}$$

However, one would not expect the reaction to be slow, and it is probable that other factors are involved.

Polonium hydroxide is therefore much less acidic than tellurous acid and, like the latter, its solubility in aqueous ammonia (d 0.88) is little different from its solubility in water (0.06 curie/l.).

Polonium Salts of Weak Acids.—These solubility determinations were part of a search for a suitable solvent for electrodeposition of polonium; nitric acid is normally used but polonium has a low solubility in this medium.

The salts described are formed as white crystals from solid polonium tetrachloride or hydroxide and an aqueous solution of the appropriate acid. Analyses were not possible owing to the rapid radiation decomposition of the solid phase after its removal from the acid solution.

Polonium acetate. The solubility in acetic acid increases from 0.88 curie/l. in 0.1N-acid to 375 curies/l. in 2N-acid, indicating complex-ion formation. The plot of $\log [\text{CH}_3\cdot\text{CO}_2\text{H}]$ against $\log [\text{solubility}]$ is approximately linear and of slope close to 2; the plot of $\log [\text{CH}_3\cdot\text{CO}_2^-]$ against $\log [\text{solubility}]$ has slope close to 4. The nature of the ion concerned is unknown, but the acetate complex appears to be more stable than the hexachloropolonite ion since the yellow colour characteristic of the latter does not appear when solutions of the acetate complex are acidified with hydrochloric acid.

The electrodeposits of polonium on gold prepared from solutions in acetic acid are bright and metallic and the deposition efficiency compares favourably with that from N-nitric acid. Unfortunately, comparatively large amounts of the polonium disappeared during the plating process in spite of careful trapping of the vapours emerging from the solution. Since the solution rapidly discoloured during the deposition, the losses of polonium may result from the formation of a volatile methylpolonium formed by the reaction of the elementary polonium on the electrode with free-radicals liberated in the solution, or at the electrode, by the intense α -bombardment.

Similarly, use of trichloroacetic acid is objectionable since free chlorine appears to be liberated by the α -bombardment when curie amounts of ^{210}Po are involved.

Acetic acid, might, however, be useful as a solvent for the preparation of milligram sources of the longer-lived polonium isotopes (^{208}Po and ^{209}Po), where the radiation intensity would be much less.

Polonium cyanide. The solid discolours within a few hours, even in contact with excess of potassium cyanide solution, and the salt becomes black on exposure to air. The solubility in potassium cyanide solution is low, increasing from 0.39 curie/l. in 0.05M-solution to 5.4 curies/l. in 1.5M-solution; some formation of complex ions may occur.

Polonium "formate." A black precipitate of uncertain composition and low solubility is formed by treating polonium "hydroxide" with 2N-formic acid.

Polonium "oxalate." Solubility studies with a wide concentration range of oxalic acid gave completely irreproducible results; the curve may be similar in form to the solubility curve of the polonium sulphates.³

Polonium "tartrate." Polonium tetrachloride is very soluble in 2N-tartaric acid,

³ Bagnall and Freeman, *J.*, 1956, 4579.

giving a colourless solution which slowly becomes grey. Electrolysis of this solution between gold electrodes led to the deposition of 12% of the polonium on the cathode and 65% on the anode; the remainder was not deposited; both electrodes became covered with a layer of carbon, presumably from the radiation decomposition of the tartaric acid.

Experimental.—All the work was carried out in glove-boxes in order to minimise the hazards associated with the handling of high levels of α -activity.

The techniques used for the solubility determinations have been described.^{3,4}

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⁴ Bagnall, D'Eye, and Freeman, *J.*, 1956, 3385.
