878. *The Sulphates and Selenate of Polonium.*

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A basic sulphate and selenate, $2PoO_2,SO_3$ and $2PoO_2,SeO_3$, and a disulphate, $Po(SO_4)_2$, have been prepared; the disulphate probably forms a series of hydrates. The solubilities of these compounds in sulphuric and selenic acid have been investigated. Unstable compounds analogous to the tellurium and selenium derivatives are formed from polonium metal and sulphur trioxide or selenium trioxide.

Studies of the diffusion,[1] electrochemical,[2,3] and solvent-extraction [4] behaviour of polonium as tracer in sulphuric acid solution appear to indicate the formation of complex ions in solution, but there are no data on the composition of the species involved. We have therefore attempted to fill certain gaps in our knowledge of these compounds.

Polonium Disulphate.—The hydrated disulphate is obtained as a white solid by treating solid polonium tetrachloride or " hydroxide " with sulphuric acid (0·5—5·0N); removal of the supernatant liquid leads to a series of irreversible colour changes at room temperature; these are also observed on heating (pink at 200°, deep purple at 380°) and are probably due to progressive dehydration. The hydrate (or hydrates) can also be efficiently dehydrated by washing with anhydrous ether. It was not possible to obtain *X*-ray powder photographs of the hydrates owing to the spontaneous dehydration; the capillaries usually

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[1] Servigne, *J. Chim. phys.*, 1934, **31**, 147, 211.
[2] Guillot and Haissinsky, *Compt. rend.*, 1934, **198**, 1758.
[3] Haissinsky, *ibid.*, 1932, **195**, 131.
[4] Cairo, Geneva Conference 1955, Paper A/Conf.8/P/1028.

exploded within a few hours of preparation, probably owing to the pressure of radiolytic gas formed within the capillary. The powder photographs of the anhydrous compound were complex and have not been indexed.

The anhydrous salt is stable to above 400° and decomposes to the dioxide at about 550°. The disulphates are insoluble in acetone or ethyl alcohol and may be hydrolysed by the latter; they are very soluble in dilute hydrochloric acid.

The disulphate is of particular interest since no tellurium analogue is known and the formation of this compound is evidence for the increased basicity of quadrivalent polonium which is to be expected from its position in the Periodic Table.

Basic Polonium Sulphate.—Analyses of this compound gave a value of 2·06 ± 0·05 for the ratio Po : SO_3. The *compound* is presumably $2PoO_2,SO_3$, analogous to the only known tellurium sulphate, $2TeO_2,SO_3$. Like tellurium sulphate, it gave very poor *X*-ray powder photographs. It is formed as a white solid (yellow above 250°) in the same way as the disulphate but with more dilute sulphuric acid (0·02—0·25N). It may also be formed by the hydrolysis of the disulphate. It is stable to above 400° and decomposes to the dioxide at about 550°. Specimens which were dried at 380° in *X*-ray capillaries were quantitatively converted into the disulphate; this is apparently due to the relatively high concentration of sulphuric acid vapour in the capillary as compared with the 1-cm. diameter filter sticks used for the analytical preparations. Samples for *X*-ray powder photography were therefore prepared as for analysis and transferred to the capillary by means of a microglass spatula.

The basic sulphate is more soluble in dilute sulphuric acid than the disulphate and is readily soluble in dilute hydrochloric acid.

Basic Polonium Selenate.—Analyses gave a value of 1·96 ± 0·16 for the ratio Po : SeO_3 and the *compound* is presumably $2PoO_2,SeO_3$. It is a white solid (deep yellow above 250°) and appears to be stable to above 400°. It is formed by treating polonium tetrachloride or " hydroxide " with selenic acid (0·015—5·0N) and is very soluble in dilute hydrochloric acid.

Bivalent Polonium Sulphate.—Polonium as tracer in sulphuric acid solution is reported to be reduced by hydroxylamine at the boiling point.[7, 8] Work with milligram amounts of polonium confirms these observations, since suspensions of the disulphate in sulphuric acid (1—2N) dissolve when boiled with hydroxylamine, yielding a pink solution; this colour appears to be characteristic of bivalent polonium. The quadrivalent sulphate is reprecipitated on cooling after some minutes, even in the presence of excess of hydroxylamine.

A knowledge of the reducing reaction involved and its redox potential would be of value since the potential could be equated to the Po(IV)–Po(II) redox potential.

Solubility Data.—The dependence of the solubilities of the sulphates and selenate upon the respective acid concentrations are expressed graphically in the Figure. The basic sulphate appears to be metastable since the solubility curve of the disulphate (*D*) can be extended to regions of lower acid concentration by diluting the acid in contact with solid polonium disulphate to concentrations at which the basic sulphate is normally formed (*A'*); further, seeding the aqueous phase in contact with the basic sulphate with small crystals of the disulphate decreases the solubility to a marked degree. Determinations made at sulphuric acid concentrations between 0·3 and 0·5N gave erratic results. The increase in solubility with acid concentration appears to indicate complex-ion formation, but no simple relationship could be deduced.

The solubility curve for the basic selenate in selenic acid does not show the discontinuity found for the sulphates; it is possible that the diselenate is formed at high acidities, but attempts to prepare the compound by evaporation of solutions of the basic selenate in concentrated selenic acid were unsuccessful.

Polonium Sulphotrioxide and Selenotrioxide.—Polonium metal reacts immediately with

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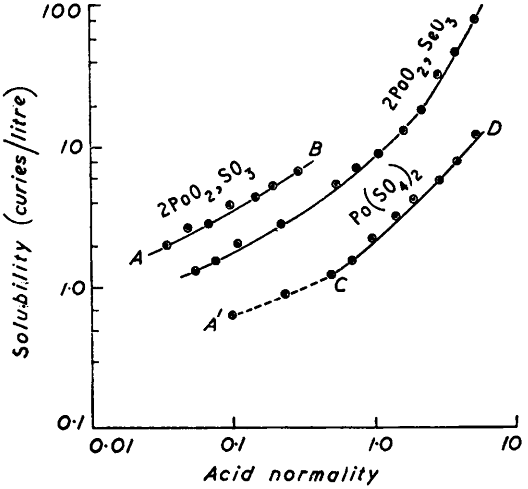
[5] Archer, *Analyst*, 1956, **81**, 181.

[6] Bagnall, D'Eye, and Freeman, *J.*, 1956, 3385.

[7] Guillot and Haissinsky, *Compt. rend.*, 1934, **198**, 1911.

[8] Haissinsky and Guillot, *J. Phys. Radium*, 1934, **5**, 419.

fuming sulphuric or concentrated selenic acids, or with the corresponding trioxides, forming extremely unstable dark red solids which are probably $PoSO_3$ and $PoSeO_3$ respectively, analogous to the corresponding reactions of elementary tellurium or selenium. Both compounds decompose within a few minutes to black solids (probably PoO) which are rapidly converted into the quadrivalent sulphate or selenate in the presence of excess of acid or acid trioxide. The sulphur compound is soluble in concentrated sulphuric acid, giving a red solution and gives a pink solution in water which may contain bivalent polonium; both solutions oxidise rapidly on standing. The selenium compound is insoluble in excess of selenic acid.



EXPERIMENTAL

All the experimental work was carried out in dry-boxes in order to minimise the hazards associated with the high levels of α-activity.

Analysis.—The principal difficulty in the analysis of sub-milligram amounts of these compounds lies in the removal of the excess of sulphuric or selenic acid from the preparation. For example, one curie of polonium as the disulphate contains only 67 μg. of combined sulphur, whereas 1 ml. of 2N-sulphuric acid, used for some preparations of this compound, contains 32 mg. of combined sulphur; in order to obtain a realistic analysis it was therefore necessary to ensure that less than 10^{-4} ml. of the acid used in the preparation remained with the solid. Washing the solid with alcohol or acetone gave unsatisfactory results, but the sulphates and selenate were stable to above 400° in air or nitrogen, so that the excess of acid could be largely removed by heating to 380° for 10 min. (sulphates) or 30 min. (selenate). Heating under a vacuum gave rather erratic results, possibly owing to decomposition. Neither the sulphates nor the selenate is volatile and the losses at 380° in 30 min. were less than 0·01%, as determined from the polonium collected on a cooled plate above the specimen.

The analytical method recently described by Archer[5] for the micro-determination of sulphur was found to be applicable with equal precision to the determination of selenate. The method involves the reduction of the sulphate to hydrogen sulphide by a mixture of hypophosphorous, hydriodic, and hydrochloric acids; the hydrogen sulphide is collected in an aqueous sodium hydroxide–acetone trap and is estimated by titration with N/1000-mercuric acetate, dithizone being used as indicator. Experiment showed that the method was reproducible to about 1% in the range 16—128 μg. of combined sulphur or its selenium equivalent. Tellurium and polonium compounds were reduced to the metal under these conditions, and since it would be difficult to estimate the polonium as a suspension in the reducing mixture, and since the α-bombardment from polonium produces a powerful oxidising effect on the reducing agent, the following separation was adopted.

The polonium sulphate or selenate (0·25—2 curies of ^{210}Po) in a slurry of the appropriate acid (1 ml.) was filtered by centrifugation through a 1-cm. No. 4 filter pad mounted in a 10-ml. centrifuge tube. The solid on the filter, after being dried at 380°, was dissolved in 4N-hydrochloric acid (2 × 0·25 ml.), and the solution centrifuged after each addition. The filtrate was added to ammonia solution (0·25 ml.; *d* 0·880) in a second filter-stick, and the precipitated polonium " hydroxide " was separated by centrifugation and washed with redistilled water (2 × 0·1 ml.); the combined filtrates were analysed for sulphate or selenate and the polonium " hydroxide " was dissolved in 4N-hydrochloric acid, the volume made up to 10 ml., and the polonium content determined by α-counting. This separation is almost quantitative; less than 0·5% of the sulphate or selenate appeared in the polonium solution and only 0·2% of the polonium was found in the ammoniacal sulphate or selenate solution. Less than 0·05% of the polonium was adsorbed on the filter-pads.

This analytical procedure requires either sulphur(or selenium)-free reagents or a knowledge of their sulphur or selenium content. All the reagents used, even when prepared by the methods used for work with dithizone, contained detectable traces of sulphur, and hence, for simplicity, the total reagent blank was determined by carrying out the above sequence of operations in the absence of polonium and estimating the sulphur content of the final ammoniacal solution. The results were sensibly constant for each of the pairs of filter-sticks used, but the blank represented a large fraction of the total sulphate or selenate found; some results obtained with one pair of filter-sticks are tabulated.

Reagent blank = $1{\cdot}9 \times 10^{-7}$ g.-mol. of sulphate.

		^{210}Po	SO_3 (moles $\times 10^6$):		
Compound	µg.	(g.-atoms $\times 10^6$)	found	corrected for blank	SO_3 (g.-mol.)/Po (g.-atoms)
$2PoO_2,SO_3$	190	0·907	0·640	0·450	0·497
	143	0·683	0·525	0·335	0·490
$Po(SO_4)_2$	161	0·768	1·710	1·52	1·98
	52·7	0·251	0·710	0·52	2·07

Solubility Determinations.—The solubility data were obtained by keeping polonium tetrachloride or " hydroxide " in contact with acid of known concentration; equilibrium was attained after 3 days. The aqueous phase cannot be sampled directly for the polonium content since it contains small, and, owing to the radiolysis, extremely mobile particles of the polonium compound. These can be removed by centrifugation through a sintered-glass disc, but the radiation attack on the glass leads to the disintegration of the disc after a few centrifugations. An alternative procedure, which gave results identical with those obtained by centrifugal filtration, involved coating the inside of a small centrifuge tube with a thin film of Vaseline; the suspension was placed in the greased tube and centrifuged for a few minutes so that the small crystals stuck to the grease. The polonium was easily recovered by washing with dilute hydrochloric acid. All the determinations were carried out in quadruplicate.

X-Ray Powder Photography.—In order to protect them against accidental breakage, the capillaries were coated with a thin film of a plastic solution consisting of 1 part of " Bostikote 9956 " diluted with 3 parts of " Bostikote " thinner. The transparent film did not affect the *X*-ray powder photographs.

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