The Preparation of Polonium Metal and Polonium Dioxide.

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Milligram amounts of very pure metallic ^{210}Po (Ra*F*) have been prepared by vacuum-sublimation of polonium deposited on silver, nickel, and platinum. A similar procedure using polonium deposited on copper yielded a mixture of metallic polonium and cuprous chloride. An oxide has been prepared, which, from its chemical behaviour, is considered to be PoO_2. The crystal structures of the two modifications of this oxide have been determined.

The spontaneous deposition of tracer amounts of polonium from solution on to the less noble metals is well known. Russell and Chadwick (*Phil. Mag.*, 1914, **27**, 112) and others have described the deposition of polonium on to copper, Tammann and Wilson (*Z. anorg. Chem.*, 1928, **173**, 137) the deposition on to nickel, and Marckwald (*Ber.*, 1902, **35**, 2285; 1903, **36**, 2662) and many others the deposition on to silver. The preparation of tracer sources on platinum by electrodeposition has been described by Paneth and Johannsen (*Ber.*, 1922, **55**, 2622) and by I. Curie (*J. Chim. phys.*, 1925, **22**, 471), the results being somewhat variable, and this procedure has been successfully used on the milligram scale by Beamer and Maxwell (*J. Chem. Phys.*, 1946, **14**, 569; 1949, **17**, 1293). Vacuum-sublimation of the polonium from tracer sources has been described by Bonet-Maury (*Ann. Physique*, 1929, **11**, 253) and many others, but the chemical nature of the sublimates so obtained was uncertain, owing to the very small amounts (10^{-6} to 10^{-8} g.) of polonium used.

There is very little published research carried out with " weighable " amounts of polonium. Beamer *et al.* (*loc. cit.*) have reported the crystal structure of metallic polonium prepared by vacuum-sublimation from a source electrodeposited on platinum. The results of their *X*-ray diffraction studies indicate that the metal exists in two crystalline modifications, α-polonium (the low-temperature form) with a simple cubic lattice, and β-polonium (the high-temperature form) with a simple rhombohedral lattice, the phase transformation occurring at about 75°.

It was found that at room temperature the sample maintained itself in the β-form owing to the energy released in the stoppage of the disintegration α-particles within the sample [calculated to be 27·4 cal. per hr. per curie of ^{210}Po (Beamer and Easton, *J. Chem. Phys.*, 1949, **17**, 1298)]. As the sample decayed, a slow transformation of the β- into the α-form was observed, owing to the decrease in the amount of heat evolved. The publication of the detailed powder pattern of β-polonium by these authors simplified the problem of identification of the products obtained by vacuum-sublimation from various supporting metals.

Martin (American report MLM 855, 1953) described PoO_2 prepared by direct oxidation of the metal, the composition being determined by measuring the decrease in pressure of oxygen in contact with metallic polonium. The product was described as a pale yellow solid.

Experimental

Preparation of Polonium Stock Solution.—A multi-curie polonium source, prepared by pile-irradiation of bismuth ($^{209}\mathrm{Bi} \xrightarrow{n,\,\gamma} {}^{210}\mathrm{Bi} \xrightarrow[5\mathrm{d}]{\beta} {}^{210}\mathrm{Po}$), was available as a deposit of polonium on nickel sheet, and the polonium was separated from the nickel by vacuum-sublimation in a quartz tube. The sublimate was dissolved in N-hydrochloric acid and, after α-counting to determine the polonium concentration, the solution was diluted with 0·5N-acid to a polonium concentration of 2 curies/ml. (2×10^{-3}M), the final hydrochloric acid concentration being about 0·8N. This solution was bright yellow and suffered extensive radiation decomposition, made evident by the steady evolution of gas.

Handling of High-level Sources.—Owing to the high specific activity of ^{210}Po (4·5 curies/mg., *i.e.*, 10^{13} disintegrations per min. per mg.) the hazard due to contamination is high. The tolerance dose of ingested ^{210}Po is only 0·02 μc ($4{\cdot}5 \times 10^{-12}$ g.) and all work with this element must be carried out in glove-boxes (see, *e.g.*, AERE C/R 958, SO-70-674-0-75, Figs. 2 and 3 and pp. 2—11). Work with the element in solution is complicated by radiation decomposition of the solvent, and in the solid state by disruption and scattering of the solid preparations by the high α-emission, leading to gross contamination of the surrounding objects (Lawson, *Sitzungsber. Akad. Wiss., Vienna*, IIa, 1919, **128**, 795, and many other authors).

By carrying out most of the operations in a sealed system, the contamination can be kept to a minimum, but continuous monitoring of the laboratory is essential. Since polonium rapidly penetrates the rubber gloves fitted to the glove boxes, a pair of surgical gloves must also be worn as a secondary protection, and both sets of gloves must be monitored regularly. The mechanism of this penetration is uncertain and attempts to measure the rate of diffusion of polonium and its compounds through rubber were unsuccessful. It is probable that penetration occurs *via* pores or pinholes which are only opened when the rubber is stretched in use.

Preparation of the Deposits.—(a) *On nickel.* Pellets of nickel wool prepared from pure nickel wire 0·001 in. in diameter were degreased by 30 minutes' refluxing with trichloroethylene and washed in turn with benzene, absolute alcohol, concentrated hydrochloric acid, and distilled water. They were then placed in a 10-ml. centrifuge tube and 0·5 ml. of the stock solution was added. The solution was agitated gently by means of a small Pyrex dropper for 5 min., the yellow colour being discharged, and the pellets then appeared uniformly black. The spent solution was removed in the Pyrex dropper, and the pellets were rinsed with distilled water (5 × 1 ml.) and transferred to a quartz sublimation tube. This tube consisted of a B.14 socket sealed at *A* to a tube *B* of 6-mm. internal diameter, which was sealed at its other end *C* to a thin-walled tube *D* of 0·5-mm. internal diameter.

(b) *On silver.* Precipitated silver (100 mg.; from Messrs. Johnson Matthey) was treated in a 2-ml. centrifuge cone with the polonium stock solution (0·5 ml.). In *ca.* 2 min. the colour was discharged and the silver powder had become coated with a black deposit. The solution was centrifuged, the spent solution removed, and the powder washed with N-hydrochloric acid (3 × 1 ml.), followed by distilled water (3 × 1 ml.). The top half of the centrifuge tube was then cut off and the resulting cone placed in the sublimation tube. In later work pellets of fine silver wool were used as described for nickel.

(c) *On copper.* Both copper powder and copper wool were used as described for silver and nickel. The colour of the solution changed rapidly from yellow to pink, probably owing to reduction of the polonium to the bivalent state. This is being further investigated. The copper powder finally became dull purple (similar to cuprous oxide) and it is not yet known whether this is due to compound formation with polonium or whether cuprous oxide is formed. Procedure was then as for silver.

(d) *Electrodeposition on platinum.* A solution of polonium in N-nitric acid containing 50 mc/ml. was prepared as follows. Lanthanum nitrate (50 mg.) was added to the polonium stock solution (1 ml.) followed by an excess of aqueous ammonia (*d* 0·88). The precipitated hydroxide was centrifuged and washed several times with 1% ammonia solution and then dissolved in N-nitric acid (40 ml.). 20 ml. of this solution were transferred to a simple deposition cell, and the polonium was deposited at a current density of 1 milliamp./cm.^{2} and 2·2 v, argon being bubbled through the solution continuously to provide stirring. About 80% of the polonium was deposited in 1 hr. The deposits were uniform and grey. The platinum foil was then well washed with distilled water and transferred to the sublimation tube.

Sublimation of the Deposits.—The source was placed in the quartz sublimation tube at *B*, and the collar at *A* was thickened preparatory to sealing off under vacuum. The tube was evacuated to 1 μ and the source at *B* heated at 150—200° for 10 min. to degas it, after which the tube was sealed under vacuum at *A*, and the section *A*-*B*-*C*-*D* was heated in an electric furnace at 400° with the capillary *C*-*D* projecting from the furnace. A bright metallic-silver mirror appeared on the collar of the tube at *C* and was sublimed along the capillary by heating it with a gas micro-burner. The tube was sealed off at *C* and the process repeated until the metal had been driven up to the end of the capillary which was sealed and transferred to the *X*-ray camera.

Preparation of the Oxide.—Since the oxide does not sublime appreciably below 900° in oxygen and decomposes to the metal when heated in a vacuum (see below), some difficulty was experienced in preparing capillaries of the oxide for *X*-ray diffraction analysis. Two methods were used, neither of which was very satisfactory.

In the first a capillary containing metal was prepared as described above and this was opened in oxygen and heated to 250—300° for some hours to ensure complete oxidation since it took some time for the oxygen to diffuse into the capillary. At a higher temperature metallic poltonium was ejected from the capillary and rapidly oxidised. In the second method, the metal was sublimed as far as the collar at *C* under vacuum and the tube was opened to oxygen at *D* by breaking off the tip of the capillary. The sublimed metal was oxidised at 700° in an electric furnace, and the oxide was sublimed into the capillary by heating it carefully with an oxy-gas flame. Generally not more than 50% of the oxide could be driven into the capillary, the remainder fusing into the silica between *C* and *D*.

Spectroscopic Analysis of the Samples.—After photography, a number of the *X*-ray capillaries were taken and each was crushed with concentrated nitric acid (0·1 ml.). The solutions so obtained were subjected to spectroscopic analysis by the Emission Spectroscopy group. Polonium is not readily soluble in dilute nitric acid, a white microcrystalline solid of unknown composition being formed, which is soluble in concentrated nitric and hydrochloric acid.

X-*Ray Analysis.*—Powder-diffraction photographs were taken with a 9-cm. Unicam camera and filtered Cu-$K\alpha$ radiation. The intensities of the lines were estimated visually.

RESULTS

Metal.—The spectrochemical analyses, when compared with the blank for the acid used to dissolve the sample, indicate that the metal sublimed from platinum, silver, and nickel contained no more impurity than was contained in the acid. The metal sublimed from copper, however, contained cuprous chloride, identified by *X*-ray powder photography; its presence is due to the difficulty of freeing the copper–polonium powder or wool from traces of the copper chloride formed in the reduction of the polonium solution. One early sample distilled from nickel contained nearly 50% w/w of nickel and this was traced to adventitious nickel chloride. Very thorough washing of the deposits is essential, but no pure polonium could be obtained by sublimation from copper. With this exception, all the metal sublimates formed bright silvery mirrors in thick layers, thinner layers having a smoky brown appearance.

In air or oxygen at room temperature the metal slowly becomes covered with a thin film of pale yellow oxide, oxidation being very rapid at 250—300°. (If the metal is kept in air in a closed vessel for some time oxides of nitrogen become visible and the yellow surface oxide becomes white, perhaps owing to formation of a nitrate.)

The metal is rapidly dissolved by 2N-hydrochloric acid (see Staritzky, American report LA 1286, 1951), giving first a pale pink solution believed to contain polonium dichloride (Bagnall and Freeman, unpublished work). This solution gradually becomes yellow and on evaporation then yields polonium tetrachloride (*idem, loc. cit.*). Addition of hydrogen peroxide or chlorine water to this pink solution accelerated the colour change (pink to yellow). The yellow solutions containing tetrachloride are reduced to the pink chloride by sulphur dioxide, arsenious oxide, or hydrazine in hydrochloric acid.

The metal reacts vigorously with concentrated nitric acid, giving a yellow solution (when concentrated, *e.g.*, 10 curies of ^{210}Po/ml.) but this becomes colourless on dilution. It is probable that the concentrated solution contains the quadrivalent nitrate.

Oxide.—The oxide is readily soluble in dilute hydrochloric or hydrobromic acid, giving yellow and orange-red solutions respectively, which yield yellow polonium tetrachloride and carmine-red tetrabromide on evaporation to dryness. These two compounds have also been prepared by passing the dry halogen acid gas over the dry freshly prepared oxide and it is therefore inferred that this oxide is PoO_2. A solution of aqueous iodine-free hydriodic acid reacts with the oxide to give a black, insoluble, very volatile solid which is believed to be polonium tetraiodide. These polonium halides will be described fully in subsequent papers.

In thin layers (less than 0·1 mg./cm.^{2}) the oxide is a pale yellow solid, but thicker preparations are orange-red to brick-red. When heated as a thin source in oxygen the pale yellow oxide begins to darken at 300°, appearing orange at 335—415°. On further heating it becomes much darker—orange-red (500—600°), brick red (650°), dark brownish-red (780°)—and finally sublimes at 885°/1 atm.

Cooling in oxygen to room temperature reverses the colour changes, although a tinge of orange persists in the sample for some days. Since the colour appeared to be a function of temperature, a thick sample, initially dark red, was cooled in liquid air for 6 hr. The sample then became pale yellow, but at room temperature it gradually returned to its original red. These colour changes have been correlated with the crystal structure of the two modifications (see below).

The assignment of colour to polonium compounds is complicated by the blue glow surrounding them and by the fluorescence induced in the silica containing tube under the α-bombardment.

When heated at 1 μ the oxide becomes very dark at about 500° and then decomposes, a sublimate of metallic polonium appearing in the cool parts of the apparatus.

X-*Ray Determinations.*—The diffraction patterns of both the metal and oxide were of rather poor quality owing to the sample's being only *ca.* 0·2 mg. and to the background caused by the γ-radiation. Thus a high degree of accuracy in the $\sin^2 \theta$ values cannot be expected. Further it is probable that diffraction lines having a weak intensity might well be lost in the high background. This would tend to make the number of absences in the observed indices of reflections appear rather high. However from the diffraction photographs both α- and β-polonium were unambiguously identified and also an oxide.

(a) *Polonium metal.* The data obtained from diffraction patterns of metal, taken immediately after sublimation from platinum, silver, or nickel, were identical with those given by Beamer and Maxwell (*J. Chem. Phys.*, 1949, **17**, 1293) for β-polonium. However, photographs of polonium sublimed from copper showed appreciable amounts of cuprous chloride as impurity. After a few days X-ray photographs of the metal showed a further phase. This could be indexed in terms of a simple cubic cell and is, according to Beamer and Maxwell (*loc. cit.*), the low-temperature (α-) modification of polonium.

(b) *Polonium–oxygen system.* Diffraction patterns of the oxide taken immediately after preparation showed apparently two phases, one being f.c.c. with $a = 5\cdot687 \pm 0\cdot005\ kX$. The lines due to the other phase could be indexed in terms of a tetragonal cell with $a = 5\cdot44 \pm 0\cdot01\ kX$, $c = 8\cdot34 \pm 0\cdot01\ kX$. As the diffraction pattern faded out at $\theta = \sim 27°$ and was also very weak, the tetragonal indexing could not necessarily be completely unambiguous and thus the proposed cell might in fact be a pseudo-cell.

After the sample had been kept for 7 days in oxygen the diffraction pattern still showed two phases but the cell constant of the f.c.c. phase had decreased to $a = 5\cdot676 \pm 0\cdot005\ kX$. A further photograph of the sample after it had been cooled in liquid air for 6 hr., again in oxygen, showed primarily the f.c.c. phase with a much decreased cell constant $a = 5\cdot626 \pm 0\cdot005\ kX$. A trace of the tetragonal phase was still present.

On warming of this sample to 400° for 24 hr. the photograph showed two distinct phases: the f.c.c. phase having $a = 5\cdot681 \pm 0\cdot005\ kX$ which is close to the original value, and the tetragonal phase.

This variation of phase with temperature suggests that the f.c.c. form is yellow whereas the tetragonal form is red.

From a consideration of other f.c.c. oxides with the fluorite-type structure it appears that the polonium oxide has a composition close to PoO_2. The cell constant, however, as seen above, contracts reversibly from 5·687 to 5·626 kX on cooling. It is known that absorption and desorption of oxygen by a fluorite-type oxide, *e.g.*, UO_2, give rise to variability of cell constant. The variations in cell constant in the present case can therefore be accounted for in an analogous manner. Thus, at 80°, the temperature of the sample immediately after preparation, the oxide could exist in either the stoicheiometric form PoO_2 or the non-stoicheiometric form PoO_{2-x}. As the oxide cools, oxygen could be taken up, giving in the former case PoO_{2+x}, and in the latter case PoO_2. The oxide has been found to have a high dissociation pressure, losing oxygen readily when heated *in vacuo* and even being degraded as far as the metal. Thus it seems more probable that the non-stoicheiometric form PoO_{2-x} exists at 80°. On this assumption the photographs taken after strong cooling represent near-stoicheiometric PoO_2, giving $a = 5\cdot626 \pm 0\cdot005\ kX$ and a cell volume of $178\cdot1\ kX^3$. It has the fluorite-type structure space group O_h^5 – Fm 3m with the polonium atoms on the 4(a) and oxygen atoms on the 8(c) special positions. Since the isotope used is ^{210}Po the calculated density is $f_c = 8\cdot96$ g./c.c. The interatomic distance Po–O is 2·44 kX, giving a radius for the Po^{4+} ion of 1·04 kX if the radius of oxygen is 1·40 kX (Pauling, Internationale Tabellen, Vol. II).

As stated above, the phase occurring with the f.c.c. phase at 80° can be indexed from a consideration of the $\sin^2 \theta$ values by Hesse's methods (*Acta Cryst.*, 1948, **1**, 200) in terms of a pseudo-tetragonal cell with $a = 5\cdot44$ and $c = 8\cdot34$. The agreement of the observed with the calculated values of $\sin^2 \theta$ is seen from the Table to be fair.

Intensity	$\sin^3 \theta_{obs.}$	$\sin^2 \theta_{calc.}$	*hkl*
m	0·0397	0·0400	110
s	0·0551 *	0·0540	102
m-	0·0773 *	0·0740	112
vw	0·0801	0·0800	200
vvw	0·1557	0·1560	104
		0·1565	203
vvw	0·1762	0·1760	114
		0·1765	213
vvw	0·1888	0·1885	301
vvw	0·2153	0·2140	302
		0·2160	204

* Probably overlap with the f.c.c. lines.

The number of absences in the observed indices of the reflections is very high but this might be caused by the weaker lines' being lost in the heavy background.

As with the f.c.c. phase we have, at the moment, no chemical results to indicate the composition of this phase. There would, however, appear to be two possibilities : (i) the phase is a high-temperature modification of the f.c.c. PoO_2 with a transition point at about 80°, analogous to the phase change in metallic polonium; (ii) the phase is a suboxide. Volume calculations throw little light, as the cell can hold, for example, six PoO_2, four Po_2O_3, or one Po_6O_{11}. That the oxide has a high dissociation pressure makes the hypothesis of a sub-oxide the more feasible alternative.

It is stated in an American Report (Martin, MLM 855, 1953) that PoO_2 exists in a tetragonal form which after a few days passes into the fluorite structure with $a = 5{\cdot}60$ and $f_c = 9{\cdot}18$, the radius of the Po^{4+} ion being 1·02 Å. Our results are in fair agreement with this statement, although we have further shown that the f.c.c. oxide probably exists over a solid-solution range and that the f.c.c. $\rightarrow$ tetragonal phase change is temperature-dependent and reversible.

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