THE CHEMISTRY OF POLONIUM

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Polonium, the heaviest member of the sulphur family (Group VIb of the Periodic Table), has hitherto been available only in less than microgram quantities derived from natural sources. This has limited the study of its chemistry to co-precipitation experiments from which little definite information could be gathered. Within the last few years, however, the situation has radically changed because the isotope ^{210}Po, once obtainable only as the penultimate member of the radium decay series, can now be made in milligram amounts by the neutron-irradiation of bismuth. The natural and the artificial routes are shown for comparison :

$$\begin{tikzcd}
{}^{210}_{82}\mathrm{Pb}(\mathrm{Ra}\text{-}D) \arrow[dr, "\beta", "22\ \mathrm{yr.}"'] & & & \\
& {}^{210}_{83}\mathrm{Bi}(\mathrm{Ra}\text{-}E) \arrow[r, "\beta", "5\ \mathrm{days}"'] & {}^{210}_{84}\mathrm{Po}(\mathrm{Ra}\text{-}F) \arrow[r, "\alpha", "138{\cdot}4\ \mathrm{days}"'] & {}^{206}_{82}\mathrm{Pb}(\mathrm{Ra}\text{-}G) \\
{}^{209}_{83}\mathrm{Bi} \arrow[ur, "n{,}\gamma"] & & &
\end{tikzcd}$$

By ordinary standards these quantities are small ; nevertheless, by applying suitable experimental methods, a quantitative study of compounds in visible amounts has been possible and, as it is hoped to show, great advances have been made in our knowledge of the element itself and of its reactions.

Natural Occurrence and Discovery.—Polonium (namely ^{210}Po) is in radioactive equilibrium with radium (^{226}Ra) in all uranium minerals, and pitchblende (U_3O_8) contains approximately 0·1 mg. per ton. It was in this material that Mme. Curie[1] discovered the element in 1898, being led to suspect the presence of a strongly radioactive substance from the fact that the activity of uranium minerals was always greater than would be expected of the uranium actually present. The story of the processing of a vast bulk of uranium ore on the lines of group analysis, remarkable for the time at which it was done, has been told and filmed. Here it is only necessary to mention that an extremely active material was precipitated with bismuth ; from this precipitate Mme. Curie was able to make a rough separation by fractional precipitation of the bismuth hydroxide or sublimation of the sulphides in a vacuum. Satisfied that it was a hitherto unknown element, she named it after her native Poland.[2]

Although clearly a new element, polonium was for a time known as " radioactivated bismuth ",[3] implying that it consisted of bismuth which

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[1] M. Curie, *Compt. rend.*, 1898, **126,** 1101.

[2] P. Curie and M. Curie, *ibid.*, 1898, **127,** 175.

[3] Giesel, *Ber.*, 1900, **33,** 1665.

had acquired radioactivity by contact with another radioelement, a view derived from the fact that bismuth became intensely α-active when immersed in solutions of radium salts. The activity was, of course, due to the electrochemical replacement of bismuth by polonium. As polonium could be separated from the crude bismuth fraction by addition of stannous chloride and as this precipitate carried down a good deal of tellurium (an impurity in the uranium ore), the element received another temporary name, " radiotellurium ".[4] The various preparations displayed markedly different half-lives in their decay through contamination with various proportions of other α-emitters. Measurements of the half-life of later preparations of greater radioactive purity showed that the α-emitting constituents were identical and, since the chemical properties of polonium, as far as they were then ascertained, resembled those of tellurium, it seemed probable that polonium was the missing higher homologue of tellurium, which it eventually proved to be.

Isotopes.—There are 21 known isotopes of polonium, of which the 138·4-day α-emitter of mass 210 is the one most commonly used. The longer-lived 3-year ^{208}Po and the 100-year ^{209}Po would be better for chemical work because of their much lower activity. They can be produced, but unfortunately only in relatively small quantities, by the bombardment of lead or bismuth with high-energy α-particles, protons, or deuterons.

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\begin{aligned}
{}^{207}\mathrm{Pb} + {}^{4}\mathrm{He} &\longrightarrow {}^{208}\mathrm{Po} + 3n \\
{}^{209}\mathrm{Bi} + {}^{1}\mathrm{H} &\longrightarrow {}^{208}\mathrm{Po} + 2n \\
{}^{209}\mathrm{Bi} + {}^{2}\mathrm{D} &\longrightarrow {}^{209}\mathrm{Po} + 2n
\end{aligned}
$$

The other isotopes are all short-lived.

Hevesy and Guenther [5] found no evidence of an inactive isotope, but Hulubei and his co-workers [6] claim to have detected an inactive or long-lived isotope in certain ores of tellurium ; it has not yet been assigned a mass number nor has its existence been confirmed.

The separation of polonium

The extraction of polonium from uranium is extremely tedious and the tracer amounts used in investigations before 1945 were usually obtained from aged radon ampoules ; after the radon (3·825-day ^{222}Rn) has decayed they contain a mixture of radium-*D*, -*E*, -*F*, and -*G* contaminated with some mercury and other impurities. Most of the early literature on the element is devoted to its separation from such a mixture and many of the methods then devised have since been applied to the purification of milligram amounts.

Methods of Dealing with Mixtures of Radium-*D*, -*E*, and -*F*.—These can be conveniently considered when divided into four different groups according to the operations involved. In the first, a large part of the lead,

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[4] Marckwald, *Ber.*, 1902, **35**, 4239.

[5] Hevesy and Guenther, *Nature*, 1930, **125**, 744.

[6] Hulubei and Cauchois, *Compt. rend.*, 1940, **210**, 761 ; 1947, **224**, 1265 ; Ripan, Paladi, and Hulubei, Geneva Conference 1955, paper A/Conf. 8/P/1096.

both radioactive (^{210}Pb) and stable, is removed by ordinary chemical means; in the second the polonium is precipitated from solution on a carrier; in the third it is separated by solvent extraction, ion exchange, or paper chromatography, methods which have, however, been applied to the recovery of tracer amounts only. The fourth group comprises the electrodeposition of the element on a suitable metal from which it can later be removed by chemical or physical means; such depositions provide the most commonly used ways of purifying both tracer and milligram amounts. The groups of methods are described below in detail commensurate with their importance and interest.

(i) Much of the lead in lead-rich polonium solutions is precipitated by the addition of concentrated nitric [7] or hydrochloric acid,[8] and this provides a useful preliminary concentration. From weakly acid or alkaline solution, lead can be removed by dialysis since it alone migrates from the solution; [9] unfortunately a good deal of the polonium is adsorbed meanwhile on the semipermeable membrane.[10] Neither of these methods takes the purification very far.

(ii) Various carriers have been used in the precipitation of traces of polonium: these include compounds of tellurium, antimony, bismuth, and the rare earths.

Tracer amounts are brought down with lead tellurate from dilute acid solution. The lead is eliminated by digestion with sulphuric acid: tellurium, after reduction to the quadrivalent state by boiling hydrochloric acid, is removed as the element by treatment with sulphur dioxide, leaving a relatively pure solution of polonium.[11] Polonium and active bismuth (Ra-*E*) are precipitated together by 0·5N-nitric acid on antimony or bismuth pyrogallate.[12]

The polonium formed in bismuth by neutron-irradiation can be separated from the latter by co-precipitation with elementary tellurium following reduction by stannous chloride.[13a, b] After removal of the tellurium it is often convenient to concentrate the polonium on a precipitate of lanthanum hydroxide brought down by making the solution alkaline. Further purification can then be achieved by dissolving the hydroxide in acid and precipitating the sulphides insoluble in acid with hydrogen sulphide. The mixed sulphides, when heated in a vacuum to 500°, give a sublimate of metallic polonium and leave, as a residue, lead and other stable, non-volatile sulphides.[13c]

(iii) (a) *Solvent extraction.* Over the last decade this mode of partition, employing a variety of organic materials, has been increasingly used.

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[7] I. Curie, *J. Chim. phys.*, 1925, **22,** 471.

[8] Debierne, *Compt. rend.*, 1904, **139,** 281; Broda and Wright, British report BR 641, 1946.

[9] Paneth, *Sitzungsber. Akad. Wiss. Wien, Abt.* II*a*, 1912, **121,** 2193.

[10] Haissinsky, *J. Chim. phys.*, 1932, **29,** 453.

[11] Karl, *Sitzungsber. Akad. Wiss. Wien, Abt.* II*a*, 1931, **140,** 199.

[12] Guillot and Haissinsky, *Bull. Soc. chim. France*, 1935, **2,** 239.

[13] (*a*) Meinke, American report AECD 2738, Sec. 84–1, 1949; (*b*) Rollier, *Gazzetta*, 1954, **84,** 658; (*c*) Bagnall and Robertson, *J.*, 1957, 1044.

Tributyl phosphate (TBP) extracts polonium from aqueous hydrochloric acid;[14] the amount taken up depends markedly on the acid concentration, reaching a maximum when it is between 7N and 9N. Solubility studies [14a] suggest that the complex formed is $PoCl_4,2TBP$. A little bismuth is extracted from even a 6N-solution, but most of this can be removed from the organic phase by backwashing with fresh 6N-hydrochloric acid.[14] The polonium itself can be recovered from the organic extract by means of concentrated nitric acid.[13a] The extraction of high-level polonium sources with tributyl phosphate has not given entirely reproducible results, probably because of radiolysis of the solvent.

Dithizone, dissolved in chloroform, removes [15] traces of polonium from both nitric and hydrochloric acid at pH 0·2—5. Milligram amounts are, however, readily hydrolysed at low acidities; further, the dithizone is rapidly decomposed by the α-radiation. It seems probable that the red complex extracted by hydrochloric [14a] or nitric acid [16] is $PoODz_2$ (Dz = dithizonate ion). The volatility of the complex [14a, 17] makes it difficult to determine the polonium content with accuracy.

"Thenoyl*t*rifluoroacetone" (2-$\gamma\gamma\gamma$-trifluoroacetoacetylthiophen) (TTA), in benzene, extracts the element from solutions at pH 0—2, and a reasonable separation from lead and bismuth is effected.[18] With polonium in milligram amounts, the high neutron emission from the α,n nuclear reaction with fluorine might make the use of the reagent a little hazardous.

It has been stated that tracer polonium can be extracted from aqueous solution with di*iso*propyl ketone [19] or mesityl oxide.[20]

Acetylacetone and *iso*butyl methyl ketone (hexone) remove milligram amounts of polonium from dilute hydrochloric acid almost quantitatively, the extraction probably depending on a condensation with the ketones analogous to that displayed by tellurium tetrachloride.

(iii) (b) *Ion exchange.* When dissolved in dilute hydrochloric acid, bismuth and polonium can be separated on Dowex 50 resin; the bismuth is removed by elution with 2N-nitric acid and the polonium with 2N-hydrochloric acid.[20a] With Dowex 1X-4 resin the three heavier elements of Group VIB in 12N-hydrochloric acid can be separated from one another; selenium is eluted by 6N-hydrochloric acid, tellurium by 2N-hydrochloric acid, and polonium by N-nitric acid. Sulphur, as sulphate, is not adsorbed by the resin under these conditions.[20b]

These methods have been restricted to tracer studies. The presence of milligram amounts might introduce difficulties from the effect of the

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[14] Karracker and Templeton, *Phys. Rev.*, 1951, **81**, 510.

[14a] Bagnall and Robertson, *J.*, 1957, 509.

[15] Bouissières and Ferradini, *Analyt. Chim. Acta*, 1950, **4**, 610.

[16] Ishimori, *Bull. Chem. Soc. Japan*, 1954, **27**, 520.

[17] Kimura and Mabuchi, *ibid.*, 1955, **28**, 535.

[18] Hagemann, *J. Amer. Chem. Soc.*, 1950, **72**, 768.

[19] Cairo, Geneva Conference 1955, Paper A/Conf. 8/P/1028.

[20] Marechal-Cornil and Picciotto, *Bull. Soc. chim. belges*, 1953, **62**, 372.

[20a] Radhakrishna, *J. Chim. phys.*, 1954, **51**, 354.

[20b] Sasaki, *Bull. Chem. Soc. Japan*, 1955, **28**, 89.

α-radiation on the resin and solvent; gas evolution from the latter would probably cause vapour-locks in the column. If this were the only difficulty, it could be overcome by passing the solutions up the column or using it in a horizontal position.

Paper chromatography does not appear to have been very much used as a means of separating the element; only one application of this technique to the separation of tracer polonium has been recorded.

(iv) (a) *Electrochemical replacement.* The most interesting procedures for the isolation of polonium utilise its spontaneous deposition on a less noble metal. The element, when present in dilute hydrochloric acid solution, is rapidly plated out on copper,[21] nickel,[22] and, under reducing conditions, on platinum [22] and palladium,[23] but in all instances there is some contamination by bismuth when it is also present. From the same acidic medium, polonium is deposited on gold by the intervention of thiourea, and this procedure is said to give a good separation from bismuth.[24]

The use of silver for the separation of polonium has the advantage of giving an almost complete separation from bismuth and massive amounts of bismuth do not interfere with the deposition.[25] The conditions necessary to attain this are somewhat critical and the literature on the subject is rather conflicting. The best results are obtained from 0·5—2·0N-hydrochloric acid at 70—80°; at this temperature the ozone, formed by the α-bombardment of water, is largely expelled from the solution before it can attack the silver surface.[25] The deposition of polonium is inhibited by gold, mercury, platinum, or tellurium and these impurities must first be removed by reduction with hydrazine. Even in the absence of impurities, the presence of a reducing agent is advantageous, particularly when dealing with milligram amounts of polonium. A little hydrocyanic acid is also beneficial when heavy deposits are being formed since it removes from the receiving surface much of the silver chloride which would be formed there by electrochemical replacement. By following the procedure described, multi-curie sources of a density about 2 curies per square centimetre of foil surface can readily be prepared.

These conditions of deposition do not prevent the formation of a black film, presumably of silver oxide, on the surface of the silver foil, even when very small amounts of polonium are involved. The extraction of the polonium from this film can be extremely difficult.[25a] Generally the polonium is sublimed from the silver in a vacuum and, if this is done immediately after the formation of the deposit, the recovery is good, but it falls off very markedly if the surface is allowed to remain in the plating solution or in air. The reason for this is unknown: possibly a comparatively stable silver compound is formed as the result of oxidation, or an oxide

[21] Bates and Rogers, *Proc. Roy. Soc.*, 1924, *A*, **105,** 360; Cook, *J. Chem. Educ.*, 1934, **11,** 313.

[22] Erbacher, *Z. phys. Chem.*, 1931, **156,** *A*, 142.

[23] Kanne, *Phys. Rev.*, 1937, **52,** 380.

[24] Erbacher, *Naturwiss.*, 1932, **20,** 390.

[25] Erbacher and Philipp, *Z. Physik*, 1928, **51,** 309.

[25a] Erbacher and Käding, *Z. phys. Chem.*, 1933, **165,** *A*, 421.

film grows over the surface of the polonium, or the element diffuses into the silver to some extent. Of course the polonium can always be recovered by dissolving the foil in nitric acid and precipitating the silver as chloride, and, provided the acidity is sufficient to prevent hydrolysis of the polonium chloride, very little of it is adsorbed on the surface of the silver chloride.

Metallic bismuth has afforded a very effective means of separating milligram amounts of polonium from quantities of irradiated bismuth. The irradiated material is converted into chlorides, and the polonium separated from the solution on a few grams of bismuth powder ; by repeating this process a number of times with decreasing volumes of acid and amounts of metal, the concentration of polonium relative to bismuth can be increased several thousandfold.[26]

(iv) (b) *Electrodeposition.* This obvious alternative has also been used. Thus milligram amounts of polonium can be easily electroplated on a platinum or gold electrode and the procedure is frequently used as a final stage in its purification.[26, 27] The pure metal is recovered from the cathodes by vacuum-sublimation.[27]

As a method of obtaining tracer quantities of the element from mixtures of radium-*D*, -*E*, and -*F* it has probably little value as a primary separation ; certainly the published data on the subject are rather conflicting.

Handling of polonium

Before describing the element and its chemistry in greater detail, it is necessary to give some idea of the problems involved in handling the material in the laboratory. The first thing to note is that, since polonium is almost a pure α-emitter, radiation shielding is not required. The real difficulty arises because the maximum permissible tolerance for ingested ^{210}Po is as low as 0·02 microcurie, that is $4{\cdot}5 \times 10^{-12}$ g., so that one curie, the amount normally used for preparative and analytical work at Harwell, represents no less than 5×10^{7} tolerances. In order to safeguard the chemist these experiments must be carried out under the most stringent control.

The chemical work is usually done in glove-boxes (also known as dry-boxes because they were earlier used for hygroscopic materials) which have Perspex windows, and are fitted with shoulder-length rubber gloves. Boxes typical of those used for polonium are shown in Plates 1 and 2 : they are constructed of Perspex sheet on a steel frame and are enclosed in an outer shell of similar construction. The box itself and the enclosed space about it are both maintained at a pressure less than that of the laboratory by means of air-ejectors. Thus, in the event of a leak, air flows from the laboratory into the box and prevents the exit therefrom of dangerous dust or vapour. The extracts from the box and shell are passed through a filter system to remove any contamination before being discharged into the extract ducts of the laboratory.

The normal glove-boxes contain a wide range of equipment and reagents and have the ordinary laboratory services such as gas, electricity, etc. ;

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[26] Burbage, *Record of Chem. Progr.*, 1953, **14,** 157.

[27] Bagnall, D'Eye, and Freeman, *J.*, 1955, 3959.

they are, in fact, miniature self-contained laboratories. Special services, which include vacuum-systems and counting-equipment, are available in separate glove-boxes connected to the working areas by trunking through which specimens or equipment can be conveyed on a trolley. Fresh reagents and equipment are introduced into the glove-box system through a double-transfer box which acts as an air-lock between the glove-box and the laboratory. Contaminated trash is brought out into a plastic bag attached to the box and this, when full, is sealed off by means of a radio-frequency heat-sealer.

The operator working in this laboratory must wear surgical gloves in order to guard himself against skin contamination since the natural-rubber gloves fitted to the boxes are rapidly penetrated by polonium. Neoprene gloves are more impervious but are generally more clumsy to work in, and tear more easily than those made of natural rubber. It goes without saying that the successful handling of small pieces of equipment such as, for example, X-ray capillaries, with the hands so protected requires a good deal of practice.

When milligram quantities of polonium are used the radiation effects are considerable in both a physical and a chemical sense. This is understandable, for the specific α-activity is 4·5 curies per milligram, that is, 10^{13} disintegrations per minute per milligram.

Glassware is attacked by the α-bombardment and becomes crazed within a few days (cf. Plate 3), the change being attended by the separation of visible amounts of silica and a marked increase in fragility. X-Ray capillaries containing anhydrous polonium compounds have a tendency to disintegrate round the areas in contact with the material. In some cases the capillaries explode owing to the formation of gas which may give rise to a pressure of six atmospheres in the course of a week. With hydrated compounds explosion usually occurs within a few hours of sealing; this makes it impossible to obtain powder photographs of them. There is risk of contamination from such explosions, though this can be considerably reduced by painting the capillaries with a suitable plastic immediately after sealing; the coating so formed is sometimes strong enough to withstand the explosion.[28]

An interesting effect is the degree of self-heating of the specimen resulting from the stoppage of the disintegration of α-particles within its boundaries. This is very considerable, amounting to 27·4 calories per hour per curie of ^{210}Po, or about 140 watts per gram. As a consequence, compounds cannot be accurately weighed and the polonium is assessed from the α-emission, for which purpose the half-life must be accurately known. The rise in temperature does, however, afford a useful method for the rapid determination of large polonium sources, and a simple calorimeter for this purpose has recently been described.[29]

Another physical effect is the glow which surrounds the element and its compounds arising from the excitation of the surrounding gas; this is quite bright with milligram amounts, as may be gathered from Plate 4 which

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[28] Bagnall and Freeman, *J.*, 1956, 4579. [29] White, *J. Sci. Instr.*, 1956, **33**, 230.

shows a specimen of the metal photographed in its own light. Incidentally the external temperature of the containing tube was 75°. As might be expected, such intense radiation induces a marked fluorescence in silica or glass.

Turning to specifically chemical effects we have to note both decomposition and synthesis. The radiation-induced decomposition of solid polonium compounds is often extremely rapid, so rapid indeed that it has not yet been possible to analyse the salts formed by organic acids, the cyanide, and similar compounds. In preparative experiments the effects may obscure the reactions taking place. Thus, for example, the radiolysis of the solvent in a 10^{-3}M-polonium solution (*i.e.*, 1 curie per millilitre) causes a visible, continuous evolution of gas [30, 31] (cf. Plate 5). Work with precipitates containing the element is complicated by scattering of the solid as a result of radiolysis of the trapped solvent. Further, the intensely oxidising conditions, resulting from the attack on water, make the study of the element in its lower valency states very far from easy. Another difficulty associated with high-level polonium work arises from the oxidation of nitrogen in the air ; this causes an exposed polonium compound to be rapidly converted into a white solid, probably a basic nitrate.[31] To avoid the trouble, milligram amounts of the element or its compounds are usually handled in sealed systems, generally under a vacuum.

Many authors have reported the appearance of widespread contamination about open polonium sources and, in the past, this has been attributed to an aggregate recoil mechanism.[32] Observations on curie sources suggest, however, that the effect is mainly due to the volatility of the compound itself. For instance, the difference in the spread of the contamination experienced after high-level spills of the involatile dioxide and volatile tetrachloride was particularly noticeable. With the former the activity showed no sign of spreading and air-monitoring gave no evidence of airborne activity, but with the latter contamination was widespread and appreciable amounts of the activity became airborne.

Metallic polonium

The metal is easily prepared by the vacuum-sublimation of the deposits obtained by electrodeposition on platinum [33a, b] and gold,[34] by spontaneous deposition on silver and nickel,[31] or by thermal decomposition of the sulphide or dioxide under a vacuum. Thick layers (~1 C/cm.^{2}) have a silvery metallic appearance, whereas thinner layers (~10 mC/cm.^{2}) appear as a smoked film. The metal exists in at least two allotropic modifications : α-polonium, the low-temperature form, with a simple cubic lattice, and β-polonium, the high-temperature form, with a simple rhombohedral lattice.[32, 33a, b] The α–β-transformation takes place at about 75°

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[30] Curie and Debierne, *Compt. rend.*, 1910, **150**, 386.

[31] Bagnall and D'Eye, *J.*, 1954, 4295.

[32] *E.g.*, Lawson, *Sitzungsber. Akad. Wiss. Wien, Abt.* IIa, 1915, **124**, 509, 637.

[33] (*a*) Beamer and Maxwell, *J. Chem. Phys.*, 1946, **14**, 569 ; (*b*) 1949, **17**, 1293.

[34] Bagnall, D'Eye, and Freeman, *J.*, 1955, 2320.

and is said to be accompanied by a small increase in volume ;[35] however, the *X*-ray data show that the β-form has a higher density. Freshly prepared specimens of the metal always consist of the β-form owing to the heating effects of the α-radiation. The sample cools as the polonium decays and, after a few days, the α-form appears. Lead, formed in the decay of the polonium, seems[33b] to form a solid solution with polonium up to about 50 atoms %. The physical properties of polonium metal, summarised in Table 1, resemble those of thallium, lead, and bismuth, its neighbours in the Periodic Table, rather than those of tellurium, its lower homologue.

TABLE 1

	α-Po		β-Po
Cell parameter[33b]	$a_0 = 3{\cdot}345$ Å		$a_0 = 3{\cdot}359$ Å $\alpha = 98° 13'$
Calc. density (g./c.c.)	9·32		9·51
Space group	O_h^1		D_{3d}^5
Resistivity (10^{-6} ohm cm. at 0°)[35]	42 ± 10		44 ± 10
Atomic diameter[33b]		3·288 Å	
M.p.[35]		254°	
B.p.[36]		962°	
ΔH_{vap} (kcal./mole)[36]		24·597	

V.p.[36] $\log p = -5377{\cdot}8/T + 7{\cdot}2345$ (at 438—745°)

The first studies of its electrochemistry were made on such extremely dilute solutions that it remained uncertain whether deductions based on the ordinary electrochemical laws could be made. The normal electrode potential at dilutions of 10^{-8}—10^{-9}M-polonium could be obtained only by an extrapolation of the critical decomposition potential, determined by measuring the rate of deposition of the element at different cathode potentials. The mean value[37] resulting from this approach was E_0^H Po,Po^{4+} = + 0·77 volt. Recently[38] the electrode potential has been measured directly, by using a gold wire coated with 0·2 mg. of polonium as the polonium electrode; the result, + 0·76 volt, is in good agreement with that from the tracer studies. The potentials of the polonium–polonium chloride electrode were also investigated, but the ionic species involved are uncertain. An attempt to measure directly the Po–Po^{2+} potential was unsuccessful owing to oxidation brought about by the high α-particle flux, amounting to 10^{11} α-particles per cm.^{2} per sec. across the electrode layer.

Chemistry of polonium

The account given below presents in some detail current knowledge of the chemistry of the element. As has been indicated, the earlier work, restricted to tracer quantities, has been greatly extended and amplified as the result of experiments made with milligram amounts. Since the later work, which afforded a sight of a number of compounds, is likely to be

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[35] Maxwell, *J. Chem. Phys.*, 1949, **17**, 1288.

[36] Brooks, *J. Amer. Chem. Soc.*, 1955, **77**, 3211.

[37] Haissinsky, Comité intern. Thermodynam. et Cinét. electrochim., Compt. rend. Réunion (1951), 1952, 214.

[38] Bagnall and Freeman, *J.*, 1956, 2770.

of special interest in this Review, it has been dealt with first instead of adopting a chronological order.

The upshot of all the investigations has been to show that polonium behaves chemically very much as might be expected from its position in the Periodic Table, although, as has been mentioned, its metallic properties are more akin to those of bismuth and lead. The "inert-pair" effect, likely to be more marked in polonium than tellurium, is very little in evidence, for there is but slight resemblance to the chemistry of lead which this would imply. By analogy with tellurium, the element should show valencies of 2, 4, and 6. The bivalent state has been well established by the characterisation of the halides, and the quadrivalent equally well by the characterisation of the dioxide, halides, and other compounds. The evidence for the sexavalent state rests partly on the behaviour of the anodic deposit of tracer polonium from acid solution.[39] This deposit is of unknown composition, but the fact that it dissolves in hydrogen peroxide [40] suggests it may be a higher oxide. Other evidence for sexavalency is based on observations of the co-precipitation of tracer polonium with tellurates,[41] but these could also be explained by the formation of a polonium tellurate. A stable, and probably volatile, hexafluoride is the most likely compound of this valency, but such a compound has not yet been prepared. There does not seem to be any conclusive evidence for the tervalent state (shown so markedly by bismuth), deduced by many authors from tracer electrochemical and co-precipitation experiments.

Group	IV		V		VI	
	C		N		O	
	Si		P		S	
		Ge		As		Se
		Sn		Sb		Te
		Pb		Bi		Po

The well-known acidic character of the sulphur sub-group is vestigially present in polonium (witness the formation of polonides and a hydride) but it is so weakened with increase in atomic weight that even tellurium exhibits feebly basic properties, forming a tartrate and some basic salts, such as a nitrate and sulphate. As would be expected, polonium dioxide and hydroxide are even less acidic than their tellurium analogues; this is demonstrated by the ease with which they react with weak acids such as acetic and oxalic.[41a] Polonium, in contradistinction to tellurium, also forms a well-defined disulphate, and its dihalides are much more stable than the corresponding tellurium compounds which disproportionate rather readily.

Studies of the solubilities of the sulphate,[28] nitrate,[42] acetate, and oxalate [41a] in their respective acids show extensive complex-formation in

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[39] Hevesy and Paneth, *Sitzungsber. Akad. Wiss. Wien, Abt.* II*a*, 1914, **123**, 1619; *Monatsh.*, 1915, **36**, 45.

[40] Haissinsky and Cottin, *Compt. rend.*, 1947, **224**, 467.

[41] Samartzewa, *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **33**, 498.

[41a] Bagnall and Freeman, unpublished results.

[42] Orban, American report MLM-973, 1954.

solution; indeed the chemistry of polonium has been described as a chemistry of complexes.

Polonides.—Lead and mercuric polonides [43] have recently been prepared from the elements at 325—350°; both are black and have a simple cubic (NaCl) lattice with cell edge 6·590 Å for PbPo and 6·250 Å for HgPo. The calculated densities are 9·6 and 11·1 g./c.c. respectively. No chemical properties have been recorded for either compound. Tracer experiments suggest that sodium polonide results from the reduction, by sodium dithionite, of polonium in alkaline solution under an atmosphere of hydrogen.[44a, b]

Hydride.—This has been prepared on a tracer scale in poor yield by the action of dilute hydrochloric acid on magnesium foil upon which polonium had been deposited chemically or electrolytically,[45] or by the addition of magnesium powder to a solution of tracer polonium in dilute hydrochloric acid.[46] It is not formed from the elements on a milligram scale.[26] Polonium hydride appears to be even less stable than bismuth hydride and is said to be rapidly decomposed by most drying agents.[45, 47] A number of its physical properties have been estimated by extrapolation; the probable melting and boiling points are 237·0° and 308·5° K respectively.[48]

Halides.—These, like the tellurium halides, are covalent, volatile, readily hydrolysed compounds of which the quadrivalent are rather less, and the bivalent much more, stable than their tellurium analogues. Complex salts of the form M_2PoX_6(IV) (X = Cl, Br, I) have been prepared from the quadrivalent halides, and closely resemble the corresponding tellurium derivatives with which they are isomorphous. Of the univalent metals, cæsium gives the least soluble complex salt in every instance.

(1) *Fluorides.* There is no record of the making of a fluoride on the milligram scale, though an unsuccessful attempt to prepare a volatile one has been reported.[26] Incidentally such compounds might be rather hazardous to handle because of the high neutron emission from the α–n reaction with fluorine.

(2) *Chlorides.* (i) The tetrachloride is a bright yellow, monoclinic or triclinic solid which melts in chlorine at about 300°.[34, 49] The molten salt is straw-coloured below 350° and scarlet at higher temperatures, possibly through decomposition to the dichloride. The liquid boils at 390°, giving a purple-brown vapour which becomes blue-green above 500°.[34] The compound is formed from the elements at 200° or when the dioxide is heated in the vapour of carbon tetrachloride, in hydrogen chloride, or in thionyl chloride, or with phosphorus pentachloride.[26, 34, 49] It is hygroscopic and

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[43] Wittemann, Giorgi, and Vier, American report LA-1890, 1955.

[44] (*a*) Chlopin and Samartzewa, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **4**, 433; (*b*) Samartzewa, *Trav. Inst. État Radium U.S.S.R.*, 1938, **4**, 253.

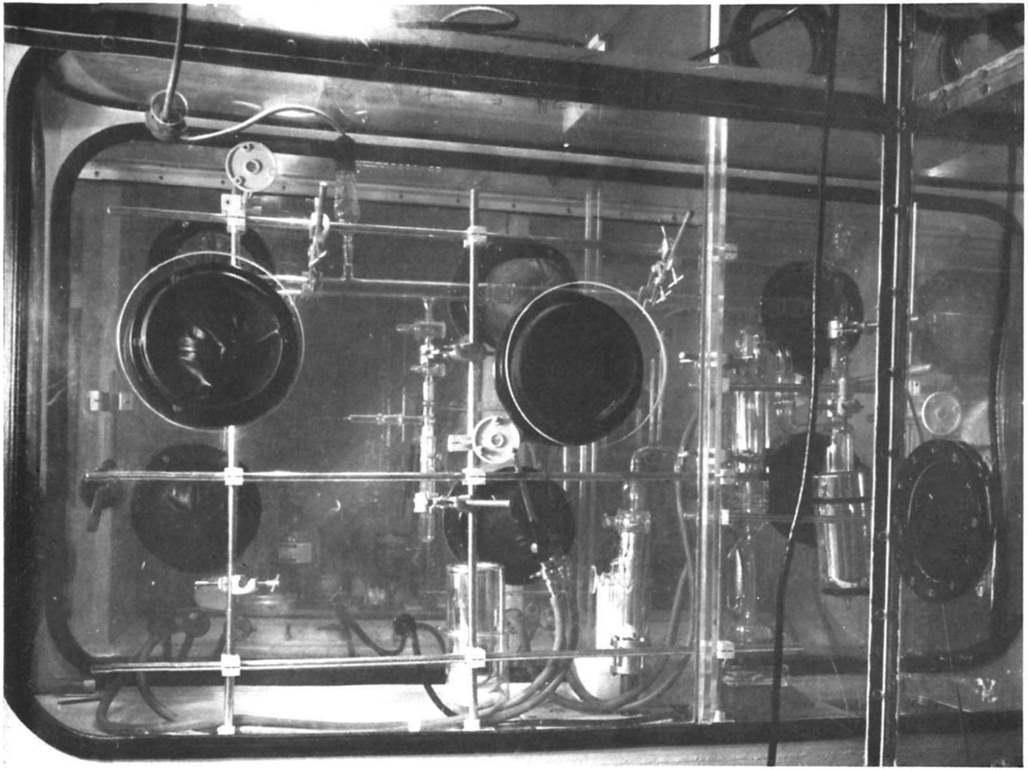
[45] *E.g.*, Paneth, *Sitzungsber. Akad. Wiss. Wien, Abt.* IIa, 1918, **127**, 1729.

[46] Paneth, Johannsen, and Matthies, *Ber.*, 1922, **55**, 769.

[47] Adler, *Sitzungsber. Akad. Wiss. Wien, Abt.* IIa, 1938, **147**, 197; Paneth and Rabinowitsch, *Ber.*, 1925, **58**, 1138.

[48] Pearson and Robinson, *J.*, 1934, 736.

[49] Joy, American report M-4123, 1947.



PLATES 1 & 2
Boxes used in handling polonium.

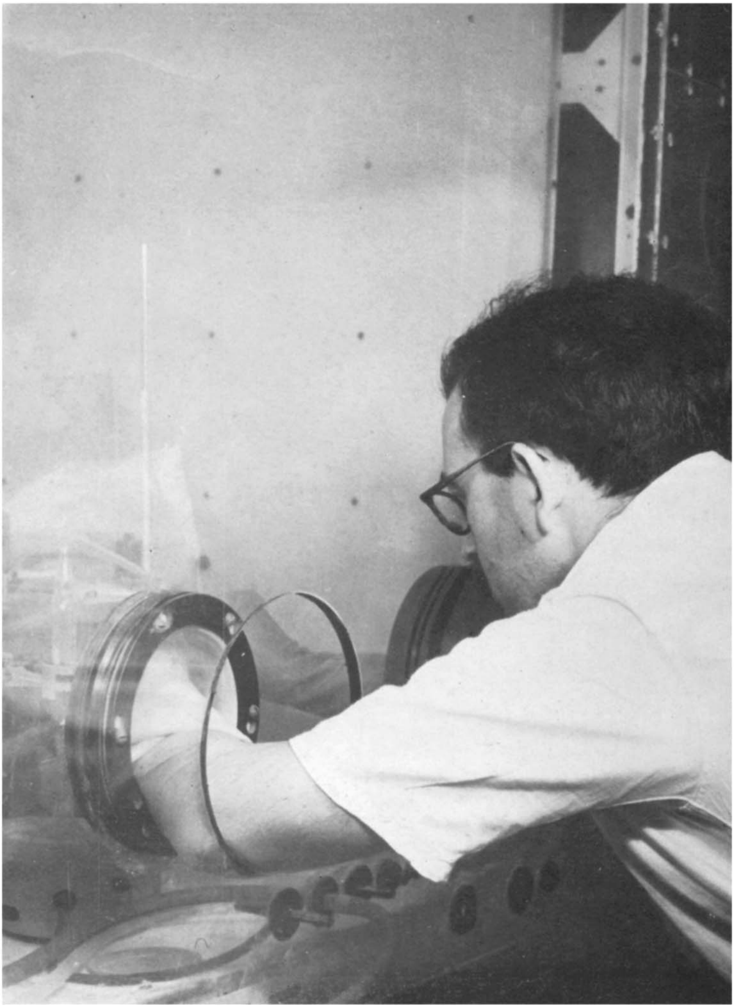


Plate 2

PLATE 3
Radiation attack on glass.

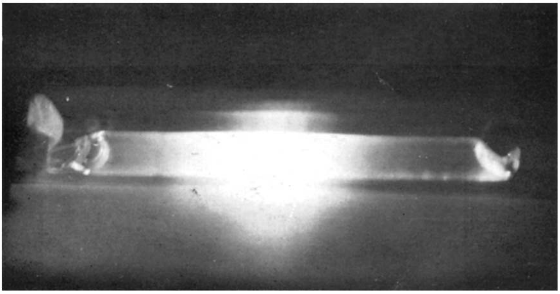


PLATE 4
^{210}Po *photographed by its own light emission.*

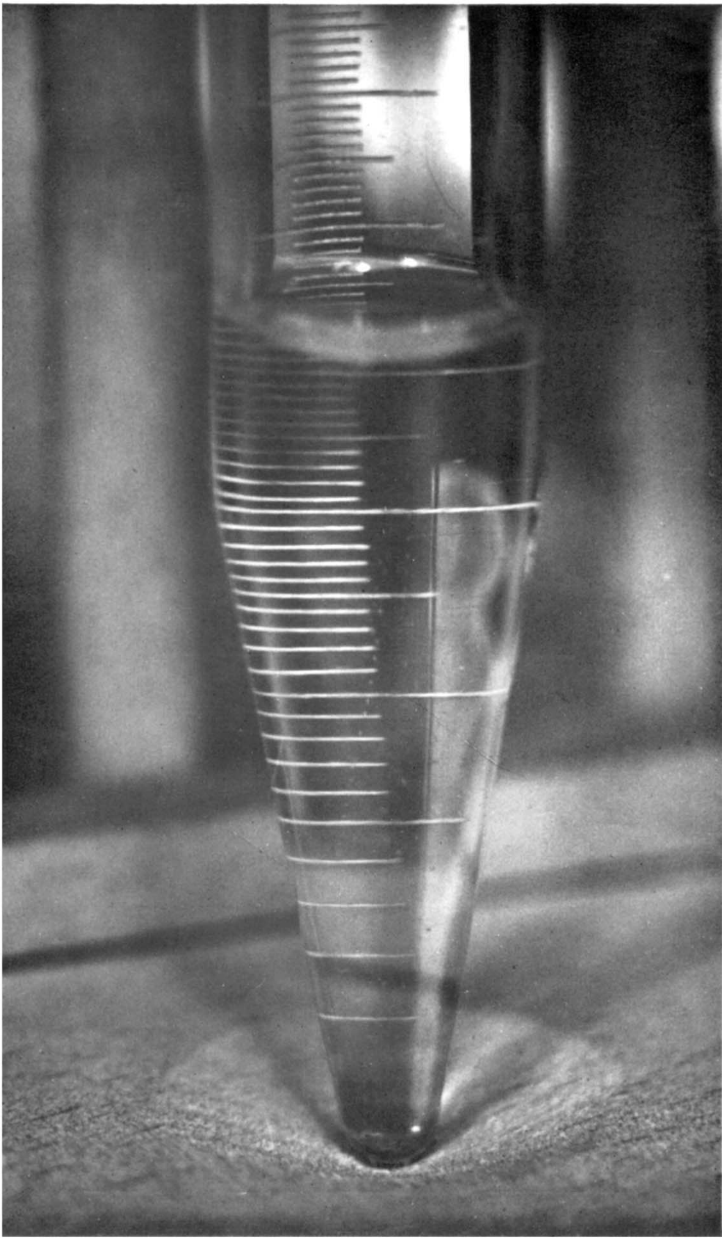


PLATE 5

Gas evolution from 10^{-3}M-*polonium tetrachloride solution* (*ca.* 1 C/*ml.*).

readily hydrolysed to a white solid of indefinite composition; there is no certain evidence for a basic chloride such as $PoOCl_2$.

The tetrachloride dissolves in hydrochloric acid, in thionyl chloride, and, with slow hydrolysis, in water. It is moderately soluble in ethyl alcohol, acetone, and some other ketones, the solubility in ketones being probably due to compound formation. Solutions in all these solvents are bright yellow, and the presence of complex ions in hydrochloric acid is shown by an immediate precipitation of greenish-yellow cæsium hexachloropolonite, Cs_2PoCl_6(IV),[34, 50] on addition of an alcoholic solution of cæsium chloride. The equilibrium constant for the reaction

$$Po^{4+} + 6Cl^- \rightleftharpoons PoCl_6^{2-}$$

has been calculated from electrochemical data [38] to be about 10^{14}.

The tetrachloride may form an ammine with gaseous ammonia at a low temperature, but decomposition with the formation of the metal occurs on storage in excess of the gas at the ordinary temperature; an ammine of the dichloride may also be formed.[34] These observations are probably best explained as reduction effects due to the atomic hydrogen resulting from irradiation of the ammonia.

(ii) The dichloride is a dark ruby-red solid which melts above 355° and sublimes at 190°,[49] and may be orthorhombic or possibly monoclinic or triclinic.[34] It is prepared by the thermal degradation of the tetrachloride in a vacuum at 200°,[34, 49] and by the reduction of that salt in hydrogen [49] at 200°, in hydrogen sulphide or carbon monoxide at 150°,[34] or in sulphur dioxide at room temperature. Continued heating in hydrogen or hydrogen sulphide takes reduction as far as the metal. Solutions of the dichloride are obtained by reducing the tetrachloride in hydrochloric acid with sulphur dioxide or hydrazine in the cold, or with arsenious oxide on warming. Neither hydroxylamine nor oxalic acid reduces a solution in this acid, possibly because of the stability of the chloride complex.[34]

The dichloride dissolves in dilute hydrochloric acid to give a pink solution which is oxidised to the quadrivalent state, rapidly by the products of the radiolysis and immediately by chlorine water or hydrogen peroxide.[34] The oxidation induced by its own radiation has been used to obtain a value for the redox potential. The trichloride may be formed in the course of this oxidation. Migration experiments indicate that the dichloride forms complexes in hydrochloric acid.[38] An ammine is formed by interaction of the dichloride and ammonia at 200°.

(3) *Bromides.* (i) The tetrabromide is a bright-red, probably face-centred, cubic solid which melts about 300°.[27, 51] The liquid boils [51] at 360°/200 mm. It can be obtained by heating the metal to 250° in bromine at 200 mm. pressure for 1 hour [26] and, more rapidly, by heating it in a stream of bromine vapour carried by nitrogen; by dissolving the metal or dioxide in hydrobromic acid and evaporating the solution to dryness; or by heating the dioxide in hydrogen bromide. Polonium does not react readily with bromine in the cold.[27]

[50] Staritzky, American report LA-1286, 1951.
[51] Joy, *Chem. Eng. News*, 1954, **32**, 3848.

This compound is hygroscopic and easily hydrolysed. It dissolves in hydrobromic acid giving a solution which is orange-red at 0·001M-$PoBr_4$ and carmine-red at 0·025M, and contains some complex ions since aqueous cæsium bromide precipitates dark-red cæsium hexabromopolonite, Cs_2PoBr_6(IV). When the hydrobromic acid solution itself is cooled to −30°, the complex acid separates as a blackish-brown solid. The tetrabromide is insoluble in benzene, chloroform, and carbon tetrachloride, sparingly soluble in bromine, and quite soluble in ethyl alcohol, acetone, and other ketones. With ammonia at room temperature it forms an unstable yellow ammine and gives some indications of a volatile colourless one.[27]

(ii) A dibromide is formed by thermal degradation of the tetrabromide in a vacuum at about 250° or by its reduction by hydrogen sulphide in the cold. This purple-brown solid sublimes, with slight decomposition, at $110°/30\mu$, and appears to disproportionate at 270—280°/1 atm. In hydrobromic acid and a number of ketones it gives purple solutions in which the polonium is rapidly oxidised to the quadrivalent state. Solutions of the dibromide in hydrobromic acid can be obtained by methods similar to those used for the corresponding chloride. There is no evidence, however, of an intermediate tribromide in the course of the autoxidation from bi- to quadri-valency.[27]

(4) *Tetraiodide.* The only iodide known, this is a black solid which sublimes, with partial decomposition to the metal, at 200° in nitrogen. It may be prepared by heating the elements to 40°/1 mm.; by allowing the "hydroxide" or dioxide to react with 0·1N-hydriodic acid; by precipitation from an acid solution of the tetrachloride with 0·1N-hydriodic acid; or by sublimation from the dioxide in a stream of hydrogen iodide at 200°. In the cold the dioxide and hydrogen iodide appear to form a black addition compound. The tetraiodide is insoluble in 2N-hydrochloric acid, N- and 2N-nitric acid, acetic acid, chloroform, and other organic solvents, and slightly soluble in acetone and ethyl alcohol. It is slowly hydrolysed by water and is oxidised by acidified potassium nitrite and other oxidising agents.

Studies of the solubility of the tetraiodide in aqueous hydriodic acid indicate the formation of the complex ions PoI_5^- and PoI_6^{2-}:

$$PoI_4 + I^- \rightleftharpoons PoI_5^-, \qquad K_c = 6{\cdot}7 \times 10^{-5} \text{ at } 22°$$
$$PoI_4 + 2I^- \rightleftharpoons PoI^2{}_6^-, \qquad K_c = 5{\cdot}9 \times 10^{-3} \text{ at } 22°$$

and black cæsium hexaiodopolonite is precipitated from solutions in 2N-hydriodic acid on the addition of cæsium iodide.

The tetraiodide does not seem to react with ammonia. It is reduced to the metal by hydrogen sulphide, without evidence of an intermediate di-iodide.[52]

(5) *Interhalogen compounds.* Polonium dichlorodibromide is formed as a salmon pink solid by the reaction of bromine with polonium dichloride.[27] Polonium dichloride and dibromide may form black unstable interhalogen compounds with iodine by reaction with solutions of iodine in carbon tetrachloride.[52]

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

(6) *Hexahalogenopolonites.* Tracer co-precipitation studies had indicated the presence of hexachloropolonite ion in hydrochloric solution,[53] but the valency of the polonium was uncertain. The preparation of the cæsium salt has already been described; the rubidium, potassium, ammonium, and tetramethylammonium compounds are formed by evaporating a hydrochloric acid solution of the two constituents.[50] The ammonium salt can be made by heating the two halides together. The tetramethylammonium salt is rapidly discoloured by autoirradiation. Cæsium hexabromo- and hexaiodo-polonite are prepared by precipitation, and ammonium hexabromopolonite by heating the two bromides together. All the compounds are brightly coloured; the chlorides are greenish-yellow, the bromides dark red, and the iodide black: they are isomorphous with their tellurium analogues. The cæsium salts decompose into their components when heated, but ammonium hexabromopolonite blackens and explodes at about 300°, possibly owing to the formation of an unstable nitride.

Oxides and Hydroxides.—*Trioxide.* This may be formed by the anodic deposition of tracer polonium from acid solution [39] but no analytical data are available; it has not been prepared on the milligram scale. If it exists it should be acidic.

Dioxide. The solid has two crystal forms,[31, 54] tetragonal (apparently red) and face-centred cubic (yellow). The latter is the low-temperature modification and is a UO_2-type oxide with variable oxygen content; the cell edge [31] varies from 5·626 to 5·687 Å. The radius of the Po^{4+} ion, deduced from the *X*-ray data, is 1·02 [54] or 1·04 Å,[31] and the calculated density about 9 g./c.c. It is formed from the elements at about 250° and becomes progressively darker when heated, having a chocolate colour at 885°, the sublimation temperature under 1 atmosphere. The colour changes are reversible. Polonium dioxide decomposes to the metal at 500° under a vacuum.[31] The corresponding hydroxide or hydrated oxide is obtained as a pale-yellow, flocculent precipitate on the addition of aqueous ammonia or alkali hydroxide to acid solutions of polonium salts; it is sparingly soluble in alkali,[34] and its composition is unknown. As with tellurium, these compounds should show some acidic character, but it is not well marked.

Monoxide. The black solid is produced in the spontaneous decomposition of polonium sulphotrioxide or selenotrioxide.[28] The corresponding hydrated oxide, or hydroxide, is formed as a dark-brown precipitate on addition of alkali to solutions of the dihalides in acid. It is rapidly autoxidised to the quadrivalent state.[34]

Sulphates and Selenate.—*Hydrated disulphate.* The white solid results from treating polonium tetrachloride or " hydroxide " with 0·5—5·0N-sulphuric acid. It suffers dehydration when kept or heated, becoming pink at 200° and deep purple at 380°, and can also be dehydrated by washing it with anhydrous ether. The purple anhydrous salt, stable up to over 400°, decomposes to the dioxide at about 550°. The disulphates are insoluble in acetone and ethyl alcohol, but may be hydrolysed by the latter.

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[53] Guillot, *J. Chim. phys.*, 1931, **28**, 107.
[54] Martin, *J. Phys. Chem.*, 1954, **58**, 911.

They are very soluble in dilute hydrochloric acid. On the other hand, the solubility in dilute sulphuric acid is remarkably low, only 420 μg. of the anhydrous salt per l. of 0·5N sulphuric acid ; an increase in solubility with acid concentration suggests complex-ion formation.[28]

Basic polonium(IV) *sulphate.* This is also a white solid, though yellow above 250°, and may be made in the same way as the disulphate by using more dilute (0·02—0·25N) sulphuric acid. The compound appears to be $2PoO_2,SO_3$, analogous to tellurium sulphate, and is stable up to over 400° ; decomposition takes place at about 550°. It is more soluble in dilute sulphuric acid than the disulphate ; solubility studies indicate that the basic sulphate is metastable.[28]

Polonium(II) *sulphate.* The reduction of suspensions of the disulphate in boiling N—2N-sulphuric acid with hydroxylamine [28] probably yields a solution of the bivalent sulphate. Earlier tracer observations had suggested that reduction occurred under these conditions.[55a, b] The polonium is re-oxidised to the quadrivalent state on cooling and the disulphate is reprecipitated even in the presence of an excess of hydroxylamine.[28]

Basic polonium(IV) *selenate.* The white solid made by treating polonium tetrachloride or hydroxide with 0·015—5·0N-selenic acid has the composition represented by $2PoO_2,SeO_3$. It becomes deep yellow above 250° and appears to be stable to temperatures over 400°. It is very soluble in dilute hydrochloric acid, and studies made of its solubility in selenic acid suggest complex formation. A diselenate has not been prepared.[28]

Other Compounds.—*Monosulphide.* This is formed as a black precipitate by the action of hydrogen sulphide on solutions of polonium dichloride or tetrachloride in dilute hydrochloric acid ; [13c] it decomposes to the metal when heated under a vacuum (cf. polonium dioxide) and slowly dissolves in hydrochloric acid, probably owing to the chlorine liberated by the α-bombardment. The solubility product is about 5×10^{-29}.

Workers using tracer amounts of polonium believed the compound to be the sesquisulphide,[53] a description which was also applied to the material formed by the slow decomposition of polonium *NN*-diethyldithiocarbamate in chloroform.[56, 57]

Nitrate. Polonium metal is vigorously attacked by concentrated nitric acid giving a solution, yellow when 10^{-5}M in respect of polonium and becoming colourless on dilution [31] ; evaporation of either solution yields a white solid of uncertain composition.

The solubility of a polonium nitrate in nitric acid has been determined over a wide range of concentration and temperature. The method used consisted in finding the polonium content of the solution in equilibrium with a deposit of the metal on platinum.[42] The nature of the nitrate formed in this way is uncertain, but since the observed solubilities were extremely low, of the same order as that of barium sulphate in water, it

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[55] (*a*) Guillot and Haissinsky, *Compt. rend.*, 1934, **198,** 1911 ; (*b*) Haissinsky and Guillot, *J. Phys. Radium,* 1934, **5,** 419.

[56] Guillot, *J. Chim. phys.*, 1931, **28,** 14.

[57] *Idem, Compt. rend.*, 1930, **190,** 127, 1553.

seems probable that a basic nitrate is involved. Complex ions such as $Po(NO_3)_5^-$ may be present but definite information is not yet available on this point.

Oxides of nitrogen, derived from the α-bombardment of air, react slowly with polonium and many of its compounds, coating them with what appears to be a white basic nitrate. A similar material is also formed by the action of dilute nitric acid on polonium halides.

Acetylacetone Complexes. A mixture of ter- and quadri-valent acetylacetone complexes is said to be formed by the action of acetylacetone on tracer quantities of polonium " hydroxide ".[58] The valencies were deduced from co-crystallisation studies with thorium, aluminium, and scandium acetylacetone complexes. The compound (or mixture) appeared to distil with partial decomposition at 230°/10 mm. By contrast, milligram amounts of the acetylacetone complexes seem to be much more volatile and two series of compounds have been obtained : one containing two atoms of halogen, the other none. It seems likely that the products of the reaction of acetylacetone with the polonium di- and tetra-halides are cyclic, formed by condensation of the polonium halide across the terminal methyl groups of the diketone in a way analogous to the behaviour of tellurium.[59] If this view of the structures is correct, then the co-crystallisation data are valueless. It is interesting that similar compounds are formed with monoketones and in every case there appears to be one form with two atoms of halogen per polonium atom and another without any halogen at all.[60]

Investigation of these compounds is hindered by rapid charring due to the α-bombardment ; determination of the carbon would be facilitated by labelling the acetylacetone with ^{14}C.

Camphorate. Alcoholic camphoric acid is said to react with alkaline suspensions of tracer polonium, and about half of the product is then extracted by benzene and is soluble in chloroform. Its composition is unknown.[61]

Dimethyl and dibenzyl derivatives. Tracer amounts of dimethylpolonium can be prepared in about 10% yield by the action of dimethyl sulphate on mixtures of the polonide and telluride of sodium in water saturated with hydrogen.[44b] It is possibly formed [62] in the decay of tetramethylradiolead (^{210}Pb). Dibenzylpolonium is stated to be produced when benzyldimethylphenylammonium chloride acts on a mixture of sodium polonide and telluride in water.[44a, b] These compounds have not been analysed.

NN-*Diethyldithiocarbamate.* Tracer polonium is precipitated from weakly alkaline solution in about 87% yield by sodium *NN*-diethyldithiocarbamate ; the product is soluble in chloroform and co-crystallisation studies are said to indicate that the polonium is here tervalent.[56, 57]

Dithizonate. Solvent-extraction work on tracer amounts of polonium in

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[58] Servigne, *Compt. rend.*, 1933, **196**, 264 ; *J. Chim. phys.*, 1934, **31**, 47.

[59] Morgan and Drew, *J.*, 1925, **127**, 531.

[60] Bagnall, Freeman, and Robertson, unpublished results.

[61] Servigne, *Compt. rend.*, 1934, **198**, 731.

[62] Mortensen and Leighton, *J. Amer. Chem. Soc.*, 1934, **56**, 2397.

nitric acid[16] and milligram amounts in hydrochloric acid[14a] point to the formation of a compound which is probably $PoODz_2$ (Dz = dithizonate ion). This sublimes[17] at 120°/1 atm.

Tracer Solution Chemistry.—There is an extensive literature on tracer experiments carried out with extremely dilute solutions of polonium but, largely owing to the unavoidable absence of analytical data, the inferences drawn from these are somewhat speculative. A good deal of the work seems to have been concerned with seeking what have proved to be very tenuous similarities between polonium and bismuth, its neighbour in the Periodic Table. The much closer relationship of its chemistry to that of its homologue tellurium was rather overlooked. A number of comprehensive reviews of the tracer work have been published,[63] and for the convenience of the reader the results obtained are summarised under the individual reagents studied.

Hydrochloric acid. The electrodeposition of polonium from hydrochloric acid is principally anodic even in an 0·2N-solution.[64] Diffusion and ion-mobility studies in more dilute acid indicate the presence of bivalent cations ;[65] the species involved is probably a partially ionised, or hydrolysed, form of polonium tetrachloride, $PoCl_2{}^{2+}$ or PoO^{2+}. Solvent-extraction data obtained with dithizone suggest the latter. A soluble basic chloride has been thought to be present in N—3N-hydrochloric acid,[53] and hydrolysis to the hydroxide in very dilute acid has been postulated. But this is not in agreement with results on a milligram scale which indicate some complex-ion formation even in N-acid.

Tracer co-precipitation work has shown that very little polonium is carried down on silver chloride at high concentrations of acid or chloride,[66] and that it is not co-precipitated with lead chloride[53] or mercurous chloride.[67]

Nitric, oxalic, and sulphuric acid. Studies of the diffusion of tracer polonium in these acids[68] and measurements of its deposition in neutral sodium nitrate or potassium sulphate solution[69] indicate the formation of complex ions. Results from co-crystallisation with lanthanum and other rare-earth oxalates are said to indicate tervalency.[58, 70] It was thought[71] that oxalic acid reduced solutions of polonium to a lower valency state, but the electrochemical data on which this idea was based might also be taken to indicate complex formation.[55b]

Reducing agents. Stannous chloride precipitates polonium from solution,

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[63] Gmelin, " Handbuch der anorganischen Chemie ", System nr. 12, Verlag Chemie, Berlin, 1941 ; Haissinsky, " Le Polonium ", Act. Sci. 517, Hermann et Cie., Paris, 1937 ; *idem,* " Electrochimie des Substances Radioactives ", Act. Sci. 1009, Hermann et Cie., Paris, 1946.

[64] Paneth and Benjamin, *Z. Electrochem.*, 1925, **31,** 572.

[65] Hevesy, *Phil. Mag.*, 1914, **27,** 586.

[66] Escher-Desrivières, *Ann. Chim.* (*France*), 1926, **5,** 251.

[67] Brennan, *ibid.*, 1925, **3,** 390.

[68] Servigne, *J. Chim phys.*, 1934, **31,** 147, 211.

[69] Guillot and Haissinsky, *Compt. rend.*, 1934, **198,** 1758 ; Haissinsky, *ibid.*, 1932, **195,** 131.

[70] Servigne, *ibid.*, p. 41.

[71] Joliot, *J. Chim. phys.*, 1930, **27,** 119.

probably as the metal.[4, 57] Sulphurous acid reduces it to the bivalent state,[34] but in the presence of selenium some precipitation of polonium may occur,[72, 73] possibly through its adsorption on the selenium.[74] Polonium selenide might also be formed under these conditions. Sulphur dioxide inhibits the electrodeposition of tracer polonium from sulphuric acid solution,[71] owing, probably, to a reduction of the sulphite to dithionite, which might well precipitate the polonium as metal.[12]

Hydrazine reduces solutions to the bivalent state,[34, 55b] but the further reduction to metal does not occur [72] even at 100°. In alkaline solution the metal is said to be precipitated in the cold,[12] but the precipitate may consist of the bivalent hydroxide. Although sodium nitrite has been described [55a] as precipitating tracer polonium from solution, this does not appear to occur with milligram amounts of polonium.[52] Ferrous sulphate,[75] formic acid, and formaldehyde do not effect its reduction in acid but formaldehyde is said to precipitate the metal from an alkaline solution.[12, 55a]

Hydrolysis in Aqueous Solution.—A large number of papers deal with the precipitation of tracer quantities from neutral or weakly acidic solutions, and the ease with which tracer polonium can be centrifuged from such solutions suggested that the polonium is present as a genuine suspension. But the solubility products of the compounds concerned are so small that this explanation seems rather unlikely; it is more probable that the impurities present act as centres of adsorption for the material.[76] Paneth [9] and Godlewski [77] have shown that solutions of tracer polonium under these conditions do exhibit colloidal properties, but it is uncertain whether the polonium is present as a genuine colloid or is adsorbed on another colloid also present. Further work using larger amounts will be necessary in order to clarify the position.

Uses

Polonium has been mainly used for the preparation of neutron sources which are virtually free from γ-radiation. These are made by mixing or alloying polonium with other elements, such as beryllium, possessing a high α,n cross-section.

Attempts have been made to use it in the manufacture of "static eliminators" for the removal of static charges which are troublesome in certain industries. These eliminators were found to be unsafe owing to the leakage of polonium from them; [78] but with improved design directed to overcoming this trouble such a use might very well become considerable.

The incorporation of polonium in alloys for the electrodes of sparking

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[72] Marckwald, *Ber.*, 1905, **38,** 591.

[73] Reymond and da Tchang Tcheng, *Compt. rend.*, 1931, **192,** 1723.

[74] Haissinsky, *J. Chim. phys.*, 1937, **34,** 94.

[75] Hevesy and Guenther, *Z. anorg. Chem.*, 1930, **194,** 162.

[76] Paneth, "Radioelements as Indicators", McGraw-Hill Book Co., Inc., New York, 1928, p. 55.

[77] Godlewski, *Kolloid. Z.*, 1914, **14,** 229.

[78] Bryan and Silverman, American report AECU-343 (UCLA-18), 1949; Silverman and Bryan, American report UCLA-84, 1951.

plugs in internal combustion engines has the effect of reducing the breakdown voltage across the gap. An engine fitted with such plugs is said to be more easily started from the cold than one with the usual variety. When, however, the engine reached its normal working temperature, the polonium would be rapidly vaporised from the points and would, in certain circumstances, introduce an undesirable hazard to health.

One of the most interesting applications of polonium is to analysis, though this requires comparatively large sources of about 160 millicuries. For example,[79] small amounts of fluorine can be determined by counting the positron emission from the 2·6-year ^{22}Na formed in the reaction ^{19}F$(\alpha,n)^{22}$Na.

[79] Odeblad, *Acta Radiol.*, 1954, **42**, 391.