THE CHEMISTRY OF POLONIUM

K. W. Bagnall

United Kingdom Atomic Energy Research Establishment, Harwell, Didcot, Berkshire, England

I. Introduction

The heaviest elements in every group of the Periodic Table have a special interest because of the marked change in properties which occurs in passing down a group; thus, in the heaviest member, the maximum group valency is achieved with difficulty, if at all. In the sulfur family (group 6B), of which polonium is the heaviest member, there is the added interest of a gradation from nonmetallic to metallic properties.

Unlike its lower homologues, sulfur, selenium, and tellurium, polonium has no long-lived or stable isotopes. It has, in fact, one of the most unstable nuclei of naturally occurring elements, the only readily accessible isotope being that of mass 210; this decays by alpha emission with a half-life of 138.4 days and occurs in nature as the penultimate member of the radium decay series, the last three stages being

$$\underset{\text{RaD}}{{}^{210}_{82}\text{Pb}} \xrightarrow[22\text{yr}]{\beta} \underset{\text{RaE}}{{}^{210}_{83}\text{Bi}} \xrightarrow[5\text{d}]{\beta} \underset{\text{RaF}}{{}^{210}_{84}\text{Po}} \xrightarrow[138.4\text{d}]{\alpha} \underset{\text{RaG}}{{}^{206}_{82}\text{Pb}}$$

The rarity of polonium is evident from a calculation (*1*) which shows that the outermost mile of the earth's crust contains only 4000 tons of the element, whereas radium, usually classed as rare, is present to the extent of 1.8×10^7 tons. The abundance of polonium in uranium ores is only about 100 μg per ton and hence separation of the element from such mineral sources cannot seriously be considered. However, radium, at equilibrium with its daughters, contains 0.02 wt % of polonium and, until recently, most of the element was obtained either from radium itself or, more usually, from expended radon ampoules which, after the radon decay is complete, contain radium-D and its daughters. Fortunately, however, the parent of polonium in these sources, bismuth-210, can be synthesized by neutron bombardment of natural bismuth [Bi^{209} (n,γ) Bi^{210}] and with the advent of the nuclear reactor it has become practicable to prepare milligram amounts of polonium. Almost all of the chemistry of the element recorded in the recent literature has been the result of studies carried out with polonium-210 prepared in this way.

In the last decade, most of the contributions to the chemistry of polonium have, rather naturally, been made by workers employed in the Atomic Energy Establishments of the United Kingdom and the United States, where milligram amounts of the element have been extracted from irradiated bismuth. Before this, all the experimental work on the element had been on the trace scale, in which quantities from 10^{-10} to 10^{-6} g were used, apart from one large source, of about 100 μg of polonium mixed with

2–3 mg of impurity, which had been prepared by Mme. Curie and Debierne (*34*) for spectroscopic examination.

The trace scale work has been frequently described and discussed (*4, 45, 57*). Here it is sufficient to say that many of the data obtained in this way have been confirmed by subsequent work on weighable amounts of the element.

Since the last reviews appeared in 1956 (*104*) and 1957 (*3, 4*), more information has become available and over fifty compounds of the element have now been identified.

The discovery of the element by Mme. Curie (*32*) in 1898 resulted from her observation that the radioactivity of uranium minerals was always greater than could be accounted for from the uranium content. Suspecting the presence of a strongly radioactive substance, she undertook, with primitive equipment and laboratory facilities, the processing of a vast quantity of uranium ore residues, based on the conventional lines of group analysis, and finally succeeded in isolating an extremely radioactive fraction which was precipitated along with bismuth. A rough separation from bismuth was secured by a fractional precipitation of the hydroxides and by a vacuum sublimation of the sulfides. The new element, the first to be discovered solely on the evidence of its radioactivity, was named polonium in honor of Mme. Curie's native Poland (*35*). The discovery and isolation of the element in almost invisible quantities under such adverse conditions was a remarkable feat of experimental chemistry by any standard. Mme. Curie's doctoral thesis (*33*), one of the most remarkable of this century, is worth reading even to this day.

II. Isotopes

Twenty-seven isotopes of polonium, ranging in mass from 192 to 218, are now known (Table I). Of these, the 138.4 day alpha emitter, polonium-210, is usually used in chemical work; the longer lived isotopes of masses 208 (half-life 2.9 yr) and 209 (half-life 103 yr), produced by alpha, proton, or deuteron bombardment of lead or bismuth [Pb^{207} (α,3n) Po^{208}; Bi^{209} (p,2n) Po^{208}; Bi^{209} (d,3n) Po^{208}; (*66, 79, 128*) and Bi^{209} (d,2n) Po^{209}], would be much more convenient for handling because of their much lower specific activity, but, owing to the difficulty of producing them in sufficient quantity, only one instance of their use for purely chemical work has been reported (*132*).

Stable or long-lived isotopes of polonium in nature have been frequently sought. Von Hevesy (*61, 62*) failed to find indications of a stable isotope, but Hulubei (*67, 68, 116*) claimed from X-ray studies evidence for the presence of such an isotope in petzite and in altaïtes, both of which are telluriferous minerals. Although Meitner (*97*) considered that there might be a stable

isotope in the region of mass 218, present views on nuclear stability render this rather unlikely. Since all the isotopes from mass 192 to 218 are known,

TABLE I
THE ISOTOPES OF POLONIUM

Mass number	Half-life	Mode of decay	α energy (mev)
192	0.5 sec	α	6.58
193	4 sec	α	6.47
194	13 sec	α	6.38
195	30 sec	α	6.26
196	1.9 min	α	6.14
197	~4 min	α	6.04
198	~6 min	α	5.935
199	~11 min	α	5.846
200	11 min	EC, α	5.770
201	18 min	EC, α	5.70
202	51 min	EC(98%), α(2%)	5.57
203	42 min	EC	—
204	3.8 hr	EC(~99%), α(~1%)	5.37
205	1.8 hr	EC(>99%), α(0.074%)	5.2
206	8.8 days	EC(95%), α(5%), γ	5.218
207	5.7 hr	EC(>99%), α(0.01%), γ	5.10
208	2.93 yr	EC, α, γ	5.108
209	103 yr	EC(~0.5%), α(>99%), γ	4.877
210 (RaF)	138.40 days	α, γ (1.22×10^{-3}%)	5.305
211^m	25 sec	α	7.14
211 (AcC′)	0.52 sec	α	7.442
212 (ThC′)	3.04×10^{-7} sec	α	8.780
213	4.2×10^{-6} sec	α	8.35
214 (RaC′)	1.64×10^{-4} sec	α	7.680
215 (AcA)	1.83×10^{-3} sec	α(>99%), β^-(5×10^{-4}%)	7.36
216 (ThA)	0.158 sec	α(>99%), β^-(0.014%)	6.775
217	<10 sec	α	6.54
218 (RaA)	3.05 min	α(>99%), β^-(0.02%)	5.998

Hulubei's reported stable or long-lived isotope, if actually polonium, might be a nuclear isomer of a species which is already known.

III. Separation of Polonium

The extraction of polonium from uranium ores is now only of historical interest. The trace level amounts used in the earlier work were usually obtained either from the lead residues of uranium ore processing, which contained lead-210, or, more commonly, from aged radon ampoules which, after the complete decay of the radon, contained Pb^{210}, Bi^{210}, Po^{210}, and

Pb^{206}, but were often contaminated with mercury from the pumps used to convey the radon from its radium parent.

Much of the early literature of polonium describes methods for separating it from these mixtures; many of these have subsequently been adapted to the separation of milligram amounts of polonium from irradiated bismuth and to its purification. The methods range from a simple chemical separation of the element with a tellurium carrier to its electrodeposition on to a more noble metal or its spontaneous electrochemical replacement on the surface of a less noble metal.

For the chemical separation, the irradiated bismuth is dissolved in acid, tellurium carrier is added, and metallic polonium and bismuth are precipitated from solution with stannous chloride (*96*, *117*). The metals are dissolved in acid and the tellurium reprecipitated with sulfur dioxide (*76*), leaving polonium in solution in the bipositive state.

It has long been known that the spontaneous deposition of trace polonium on to silver from hydrochloric acid is much more quantitative at high temperatures; under these conditions a good separation from massive amounts of bismuth (*39*) is attained. On the milligram scale, a further improvement in the deposition is brought about by reducing agents, such as hydrazine or sulfur dioxide, the optimum temperature being about 50°C (*12*, *111*). However, when polonium deposited on silver in this way is sublimed from the collecting surface, it always contains some silver chloride, but the amount of silver chloride is much reduced when the deposition has been made in the presence of cyanide (*12*). For reasons not understood, the polonium deposit on silver becomes involatile when it has stood for a few hours in air or in the depositing solution. This may be due to oxidation, for a part of the polonium can be recovered from the plated foil, after it has been heated in hydrogen or hydrogen sulfide, by vacuum sublimation. Heating the deposit on silver in carbon monoxide at 500°C leads to sublimation and condensation of some of the polonium as metal, while about 10% of it remains in the gas stream, from which it can only be recovered by burning the gas and condensing the polonium dioxide; about 50% of the polonium remains on the foil (*12*). These observations with carbon monoxide exactly parallel the trace level experience of Lecoin (*86*). Reaction between milligram amounts of polonium metal and carbon monoxide does not occur, so that the high volatility of polonium recorded above may be due to the formation of a polonium carbonyl in the presence of a silver catalyst (*12*).

Polonium, however, can be readily recovered from aged silver foils by dissolving them in nitric acid and precipitating the silver with hydrochloric acid; little or no polonium is lost by adsorption on the precipitated chloride provided the acidity is high. An insoluble black residue, left after the bulk

of the silver has dissolved, is apparently silver chloride mixed with some finely divided silver (*111*).

The deposition of polonium on to copper does not give a good separation of the element from bismuth (*83*, *111*), but bismuth powder itself provides a quite successful process (*25*). In practice, the irradiated bismuth is dissolved in a mixture of hydrochloric and nitric acids, and after elimination of the latter, the solution is stirred with a few grams of powdered bismuth; the polonium is deposited completely on to the bismuth. The product is dissolved in acid and the whole process repeated with decreasing amounts of metallic bismuth, until the proportion of polonium to bismuth is high enough for the former to be precipitated as the metal with stannous chloride.

In the final purification, polonium is either dissolved in nitric acid and electrodeposited onto platinum, or, better, gold (*6*, *25*); the polonium is sublimed in a vacuum from the support metal or dissolved off the latter in dilute hydrochloric acid and precipitated as the monosulfide. Either hydrogen sulfide itself or the sulfide ion produced by the hydrolysis of thioacetamide may be used. The monosulfide is decomposed by heating under vacuum and the pure metal sublimed (*14*).

An interesting method (*88*) for the separation of trace amounts of polonium makes use of the volatility of some, as yet unidentified, organic compounds. Polonium complexes with diphenylcarbazone, diphenylcarbazide and diphenylthiocarbazone sublime below 100°C under atmospheric pressure and those with thiourea, 8-hydroxyquinoline, *s*-diphenylthiourea, thiosemicarbazide and other related compounds sublime below 160°C under the same conditions. Thus trace polonium has been separated from dilute nitric acid in the presence of diphenyl carbazide by steam distillation.

The electrochemical separation of polonium from irradiated bismuth has not been investigated to any extent; it appears, however, that electrodeposition from hydrofluoric acid solution offers a practical means of separation (*131*).

Solvent extraction by tributyl phosphate (TBP) (*13*, *96*), dithizone (*20*, *71*, *72*), cupferron (*89*), thenoyl trifluoroacetone (TTA) (*55*), di*iso*propyl ketone (*26*), mesityl oxide (*92*), tri-*n*-benzylamine and methyl di-*n*-octylamine (*99*), di*iso*propyl and di*iso*butyl carbinol (*100*) have all found some application on the trace scale. Acetylacetone and methyl isobutyl ketone extract milligram amounts of polonium almost quantitatively from hydrochloric acid, but the stable polonium-organic compounds which are formed make it difficult to recover the polonium in a useful form from solutions in these ketones (*7*). Ion exchange (*22*, *115*, *119*) and paper chromatography (*44*, *87*) have also been used for trace scale separations of polonium, but the effects of the intense alpha-radiation on organic com-

pounds make the methods employing these materials unattractive when an appreciable amount of polonium is present.

IV. Handling Problems and Preparative Techniques

Reactions used for the preparation of polonium compounds are straightforward, but the experimental techniques are strictly determined by the small amount of the commonly used polonium-210 which is available and by the exceptionally high specific activity of the isotope (4.5 curies/mg, i.e., 10^{13} disintegrations/min/mg). Apart from the major effects of the alpha bombardment to be described, the separation of polonium-210 from its lead daughter, which grows in at a rate of 0.5%/day, constitutes a major chemical problem. It calls for rapid and efficient methods of purifying the polonium stock before each experiment; the best of these is the sulfide process described in Section III.

The main and ever present problem with polonium is the health hazard. Alpha emitters such as polonium-210 do not emit penetrating radiation, but may be lethal when ingested owing to the complete absorption of the alpha particle energy by the organ, or organs, in which the radioactive material is retained. For polonium, the critical organs are the spleen and kidneys. The maximum permissible body burden for ingested polonium is only 0.03 μcuries; this represents a particle weighing 6.8×10^{-12} g, or about 2×10^{10} atoms. Thus 200 μg of polonium-210, the amount normally used for a single preparation, represents no less than 3×10^{7} tolerances. The high toxicity of the isotope becomes even more manifest when the maximum permissible concentrations in air of the better known poisons are compared with that for polonium. The safe limit for carbon monoxide is 100 mg/meter^3, for hydrocyanic acid, 10 mg/meter^3 and for polonium-210, only 4×10^{-11} mg/meter^3 (*123*), which makes it, weight for weight, 4×10^{12} times as toxic as hydrocyanic acid.

Obviously work with polonium must be done under very strictly controlled conditions. Fortunately, shielding by lead is unnecessary, since the gamma activity associated with the decay of polonium-210 is slight. It is, however, absolutely necessary to prevent any trace of the isotope being ingested by the worker and thus all work must be carried out in a glove-box. This is really a well-ventilated, miniature laboratory bench, totally enclosed and suitably maintained under slightly reduced pressure relative to the air in the laboratory; this ensures that any movement of air is *from* the laboratory *into* the glove-box and entirely prevents dangerous dust or vapor from leaving the box. The air extracted from the box passes through a filter system to remove radioactive material before its discharge into the main laboratory extract system.

The conventional glove-box used on polonium work at Harwell is con-

structed of Perspex sheet mounted on a steel frame and enclosed in an outer shell of similar construction which, like the glove-box proper, is also maintained at a slightly reduced pressure as a safeguard against leakage of radioactive material through the gloves. Natural rubber is rapidly penetrated by polonium and it is necessary to wear surgical gloves when working in the box-gloves in order to guard against skin contamination. As may be imagined, the successful handling of small, fragile pieces of equipment, such as X-ray capillaries, through two thicknesses of rubber requires patience and a good deal of practice. Box-gloves made of neoprene are somewhat less permeable to polonium than those of natural rubber, but the precautions above still apply.

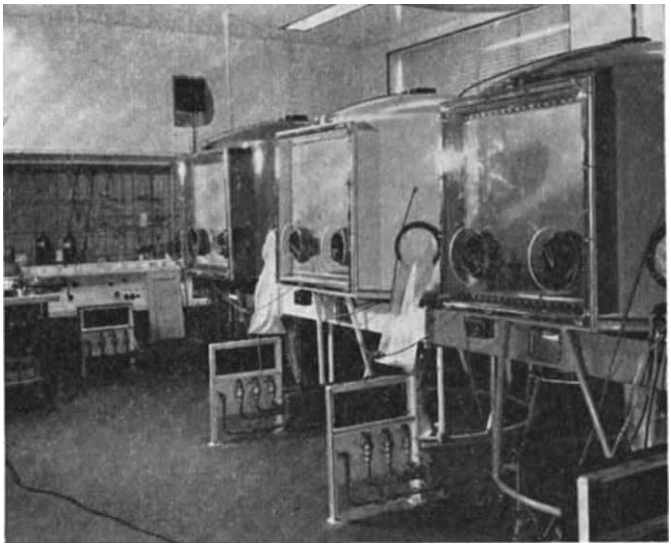


FIG. 1. Suite of three rotating-table glove-boxes.

A more recent rotating-table glove-box is shown in Figs. 1 and 2; this was designed for work with high levels of alpha activity (*15*). A suite of three of these boxes, connected together to permit the transfer of active material from one box to another by means of a trolley, is shown in Fig. 1. Figure 2 shows the interior of one of these boxes, the radius of which is 27 in., the normal reach of the average man. By rotating the turntable, the whole of the floor space becomes available and gives a working area of about 14 ft^2.

A major problem in glove-box work is the corrosion within the box of metal parts and equipment, due to unavoidable concentrations of acid fumes which occur even when the box is swept by a high air-flow. This can

be largely avoided by the use of noncorrodible materials, such as fiberglass or plastic, in the construction of the box and its equipment. There does not seem to be a lacquer or varnish which will effectively protect for very long a metal surface subjected to these severe conditions; at present, epoxy resin paints appear to be the most promising materials.

The alpha radiation chemical effects at the curie level are severe, leading to the self-decomposition of most polonium compounds; thus solid polonium salts of organic acids char rapidly and polonium iodate evolves free iodine.

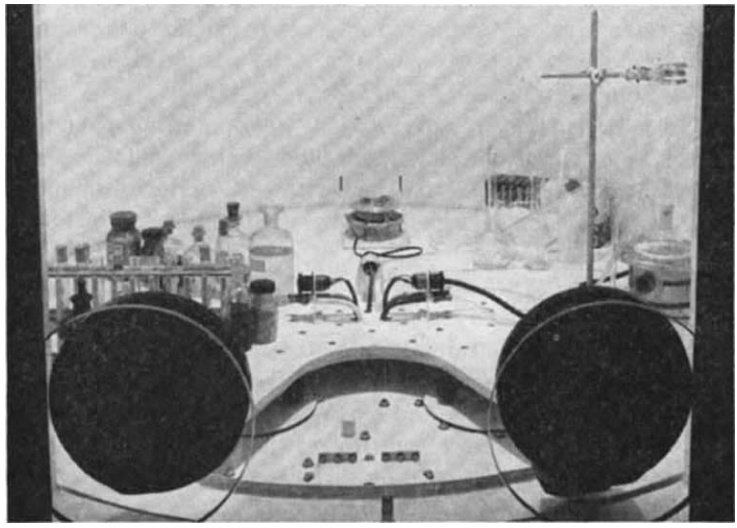


FIG. 2. Interior of glove-box.

It has been shown (*37*) that the alpha radiation displaces every atom in the lattice of a simple crystalline compound, such as polonium tetrabromide, at least once a day. It is therefore not surprising that X-ray powder photographs of polonium compounds are generally poor.

Self-heating, due to the stoppage of the alpha particles within the solid, is a well known phenomenon and calculation shows that the energy release from one gram of polonium metal would be about 140 watts. This high energy output affords a useful and absolute method for the rapid determination of polonium in large sources by calorimetry.

Glassware suffers from the alpha bombardment and crazing appears after a few days, particularly where solid polonium compounds are in contact with the glass. The change causes the glass to become markedly more fragile and this, coupled with pressure increases arising from gaseous decomposition products from the anion, hydration water or organic ligand, and even from helium from the alpha particles, often leads to the bursting

of X-ray capillaries containing polonium compounds, the free internal volume being extremely small.

The most spectacular radiation effect is the glow emitted by polonium and its compounds arising from excitation of the surrounding gas (see ref. *3*, plate 4; ref. *4*, *frontispiece*); a marked fluorescence is also induced in the glass or quartz of the container.

The radiation decomposition in 10^{-3} *M* polonium solution (~1 curie/ml) causes a visible evolution of gas (*5*, *34*). The radiolysis products are strongly oxidizing, which adds difficulty to the study of the element in its lower, bipositive, state. Peroxide formation appears to be the factor which prevents a study of solutions of the element in the sexapositive state (*12*), at any rate on the milligram scale.

There have been many reports of the "wandering" of polonium from open sources, behavior at one time attributed to an aggregate recoil mechanism (*84*), but more recent observations with curie quantities indicate that contamination only spreads when volatile compounds, for instance polonium tetrachloride, are involved.

The trace level work with polonium was bedeviled by its radiocolloidal behavior in neutral or weakly acid solution. This led to the deposition of polonium on the wall of containing vessels, a behavior which is much less evident with macroscopic amounts. The conflicting views as to the cause of this phenomenon are outside the scope of this article and further information may be obtained from recent reviews and papers (*4*, *41*, *57*, *127*).

Most of the published work dealing with weighable amounts of polonium has consisted of studies of its solid compounds, X-ray powder crystallography being used to extend and complement the chemical work. The preparative methods are rendered relatively simple by the ease with which the pure metal can be prepared and by its volatility. In a generally applicable procedure, the pure metal is sublimed under a vacuum into an X-ray capillary in which it is allowed to react with the selected reagent, usually in the gaseous form. A microfilter stick can be used in the preparation of insoluble compounds which require separation from the mother liquor (*6*). Centrifugation in a microcone is not usually very successful because of the rapid disruption of the precipitate by the gases arising from the radiolysis of the solvent trapped in it. The handling problems and preparative techniques are more fully described in the reviews (*3*, *4*).

V. Polonium Metal

A. Preparation and Properties

The usual methods of obtaining the metal are the electrodeposition from acid solution (usually nitric, sometimes hydrofluoric) on to platinum

(*18*, *19*) or gold (*6*), or the spontaneous deposition on to silver or nickel (e.g., *6*), followed by vacuum sublimation of the polonium from the support metal. The metal is also readily produced by the thermal decomposition of the sulfide (*14*) or, less easily, of the dioxide (*5*) under a vacuum, and by the action of ammonia, either anhydrous liquid or concentrated aqueous solution, on polonium hydroxide and some other polonium compounds. It is also obtained by the action of hydrazine, hydroxylamine, or sodium dithionite on alkaline suspensions of the hydroxide, or of stannous chloride, titanous chloride or sodium dithionite on acid solutions of polonium tetrachloride (*17*), in agreement with the earlier trace scale observations of the action of hydrazine, titanous chloride (*54*), and stannous chloride (*91*). Reduction by ammonia appears to be ascribable to atomic hydrogen liberated by the alpha bombardment, since primary and secondary amines also reduce polonium hydroxide, although more slowly than ammonia, and little reduction occurs with triethylamine or tetraethyl ammonium hydroxide (*17*).

The precipitated metal is a grey-black powder, but when sublimed, polonium is silvery in thick layers [$\sim$0.2 mg (1 curie)/cm^2] and a transparent smoked film in thin ones. When the thicker metal mirrors, obtained by vacuum sublimation onto a glass surface, are treated with a little 8 *N* nitric acid, a part of the metal can be detached from the glass as a thin foil.

The metal, which is soft (*104*, p. 18), has at least two allotropic modifications, the low temperature form, α-polonium, which is simple cubic, and the high temperature form, β-polonium, which is simple rhombohedral; the two forms were identified by X-ray powder photography (*18*, *19*). It is difficult to locate the transition temperature with any accuracy owing to radioactive heating effects, and the best figures, obtained from X-ray diffraction data, are 18°C for the $\beta \rightarrow \alpha$ and 54°C for the $\alpha \rightarrow \beta$ transitions. The two phases coexist between 18°C and 54°C (*49*). When freshly sublimed, the metal is always in the β form owing to the heating effect but as the polonium decays, the specimen cools and the α-form appears. The finely divided metal prepared by reduction from aqueous solution is largely ($\sim$70%) in the α-form (*17*). Lead, the decay product, seems to form a solid solution with polonium up to about 50 atoms per cent (*19*).

The physical properties of the metal (Table II) resemble those of thallium, lead and bismuth, its neighbors in the Periodic Table, rather than those of tellurium, its lower homologue. The low melting and boiling points are particularly noteworthy; an attempted study of the Hall effect in polonium metal has also been reported (*90*). In chemical properties the metal is very similar to tellurium, the most striking resemblance being in its reactions with concentrated sulfuric acid (or sulfur trioxide) and with concentrated selenic acid. The products are the bright red solids, $PoSO_3$ and

TABLE II
PHYSICAL PROPERTIES OF POLONIUM METAL

Property	Specification	Reference
Melting point	254°C	*95*
Boiling point	962°C	*23*
ΔH_{vap}, kcal/mole	24.597	*23*
Vapor pressure (438°–745°C)	Log $p_{mm} = -5377.8/T + 7.2345$	*23*
Atomic radius, Å	1.644	*19*
Linear coefficient expansion (−196° − +30°C)	2.3×10^{-5} cm/cm/deg	*21, 46*
Calculated density, α Po, gm/cc	9.196 (36°C)	*48*
Calculated density, β Po, gm/cc	9.398 (39°C)	*48*
Observed density, β Po, gm/cc	9.4	*95*
Cell parameter, α Po, Å	3.359	*48*
Cell parameter, β Po, Å	3.366, $\alpha = 98°5'$	*48*
Space group, α Po	O_h^1	*19*
Space group, β Po	D_{3d}^5	*19*
Resistivity, α Po, 10^{-6} ohm	42 ± 10 (0°C)	*95*
Resistivity, β Po, 10^{-6} ohm	44 ± 10 (0°C)	*95*

$PoSeO_3$, both of which decompose rapidly at room temperature to the unstable black monoxide (*10*).

B. SPECTRA

1. X-ray Spectra

Earlier observations of some of the L lines of polonium (*69, 124*), obtained with trace amounts of the element, have been confirmed by more recent work on its K and L spectra, in which a copper target was coated with 2–3 mg of the element (*112*).

2. Optical Spectra

The earlier trace level work (*34, 36, 77*) has also been substantiated by the observations of Charles *et al.* (*30, 31*) and of Vernyi *et al.* (*130*). The ionization potential for the neutral polonium atom is 8.43 ev (*30*), in good agreement with theory. Measurement of spectrograms of electrodeless discharges in pure polonium vapor has yielded over 450 red-shaded band heads for polonium-210 and more than 500 heads for mixtures of polonium-208 and 209. About 350 of these have been classified in the principal system of Po-Po; the dissociation energy of the lower state is calculated to be 1.895 volts (*30*). Other spectroscopic data, including the vibrational energy levels of diatomic polonium-210, are given by Moyer (*104*).

C. Diffusion of Polonium in Metals

The rather variable results of half-life determinations made by direct alpha-counting of samples mounted on metallic supports may be due to

TABLE III
Diffusion of Polonium in Metals

Metal	Temperature (°C)	Diffusion coefficient	Reference
Aluminium	Ambient	3×10^{-13} cm²/sec	*43*
Aluminum	500	5×10^{-11} cm²/sec	*43*
Armco 18-8 steel	300	1×10^{-22} cm²/sec	*43*
Armco 18-8 steel	750	5×10^{-22} cm²/sec	*43*
Bismuth	150	5×10^{-11} cm²/sec	*43*
Bismuth	200	5×10^{-10} cm²/sec	*43*
Gold	470	$\sim 10^{-9}$ cm²/day	*133*
Lead	150	10^{-9} cm²/day	*113*
Lead	200	10^{-7} cm²/day	*113*
Lead	310	1.3×10^{-5} cm²/day	*63*
Nickel	Ambient	10^{-13} cm²/day	*113*
Platinum	470	$\sim 10^{-9}$ cm²/day	*133*

diffusion into the support (*78*); a good deal of work on the diffusion of polonium in metals, from this and other aspects, has been reported (Table III).

D. Polonium Hydride

Paneth (*108, 109, 110*) has shown that a volatile species, probably a polonium hydride, can be prepared in poor yield on the trace scale by the action of dilute hydrochloric acid on magnesium foil plated with polonium and the diffusion of trace polonium in hydrogen saturated platinum or palladium may be due to migration of a hydride (*85*). More recent trace level experiments (*135*) indicate that a hydride may be formed by the action of nascent hydrogen on polonium. Work with milligram amounts of polonium has shown that a hydride is not formed from the elements on heating (*25*), or by treating polonium tetrachloride with ethereal lithium aluminium hydride, which gives polonium metal only, or by the action of dilute hydrochloric acid on magnesium polonide (*12*). These negative results may, however, be caused by decomposition of the hydride, as it is formed, by high levels of alpha radiation.

E. Polonides

A number of polonides have been prepared by heating the elements together at relatively low temperatures (300°–400°C); all are grey or grey-

black solids, and have been identified by X-ray powder crystallography (Table IV). Unlike the other polonides, magnesium and mercuric polonides are not isomorphous with their tellurium analogues. Mercuric polonide is very volatile and readily formed from the elements at 200°C or below, so that care must be taken when polonium is handled on vacuum lines incorporating mercury diffusion pumps (*134*). The deposition of trace polonium on mercury from acid or ketone solutions may also lead to the formation

TABLE IV
CRYSTALLOGRAPHY OF THE POLONIDES

Compound	Structure	Cell parameters (Å)	Calculated density (gm/cc)	Reference
AgPo(?)	orthorhombic (monoclinic?)	a 7.384, b 5.565, c 7.813	—	*47*
BaPo	fcc (NaCl)	a 7.119	6.3	*134*
BePo	fcc (ZnS)	a 5.838	7.3	*134*
CaPo	fcc (NaCl)	a 6.514	6.0	*134*
CdPo	fcc (ZnS)	a 6.665	7.2	*134*
HgPo	fcc (NaCl)	a 6.250	11.1	*134*
MgPo	hexagonal (NiAs)	a 4.345, c 7.077	6.7	*134*
Na_2Po	fcc (CaF_2)	a 7.473	4.08	*47*, *104* p. 91
NiPo	hexagonal (NiAs)[a]	a 3.973, c 5.661	11.53	*47*, *104* p. 91
PbPo	fcc (NaCl)	a 6.590	9.6	*134*
$PtPo_2$	hexagonal ($Cd(OH)_2$)	a 4.104, c 5.606	12.47	*47*, *104* p. 91
SrPo	fcc (NaCl)	a 6.796	6.3	*134*
ZnPo	fcc (ZnS)	a 6.309	7.2	*134*

[a] The nickel-polonium system resembles the analogous tellurium system in that compounds of composition varying continuously between NiPo and $NiPo_2$ are formed, with structures between the NiAs and $Cd(OH)_2$ types (*134*).

of this compound (*27*, *28*, *29*, *42*). Metallic gold dissolves polonium without reaction but aluminium, carbon, iron, molybdenum, tantalum, and tungsten do not react with the metal (*47*). Polonium seems to alloy with bismuth and the two metals are miscible in all proportions (*47*). Zinc polonide sublimes at 400°C and the silver, lead, and platinum compounds decompose at about 600°C (*47*). Copper polonide is unstable and sublimes near 400°C (*134*).

F. ELECTROCHEMISTRY

Work with trace amounts clearly indicates a value of +0.77 volts for the electrode potential of the metal, $E_0{}^H Po/Po^{4+}$ (*56*). Subsequent work with milligram amounts (*9*) gave a value of +0.76 volts for this potential,

in good agreement considering experimental difficulties arising from alpha radiation. Thus polonium lies between tellurium and silver in the electrochemical series, in conformity with its known behavior towards reducing agents (*54*). There are a number of useful surveys of the electrochemistry of polonium, both on the trace and on the milligram scale work, which describe the experimentation in considerable detail (*4*, *58*, *104*).

VI. Polonium Oxides and Sulfide

A. Polonium Trioxide

This compound is said to be formed on the trace scale by the anodic deposition of polonium from an acid solution (*64*, *65*) and, although there is no direct experimental evidence for the composition of the anodic deposit or the presence of a peroxide linkage, the dissolution of the deposit by hydrogen peroxide (*59*) is certainly suggestive of a higher charge number. On the milligram scale, the attempted oxidation of polonium(IV) hydroxide with aqueous chromium trioxide initially yields polonium(IV) chromates (Section VIII,C), but on long standing in an excess of chromium trioxide solution (*12*), all the polonium passes into solution as an alkali-soluble form which may be a complex acid of polonium(VI) and chromium(VI) [cf. tellurichromic acid (*98*, page 97)] since precipitation of polonium(IV) hydroxide from the alkaline solution by hydrogen peroxide is indicative of the presence of a higher valency state (*12*).

The treatment of polonium(IV) with nitric acid/potassium permanganate under reflux yields a sludge of manganese dioxide which contains all the polonium originally present; the valency state is uncertain. Polonium(IV) in weighable amounts is not oxidized by persulfate, ceric salts or chlorine in alkaline solution (*12*), although trace scale work indicates that both ceric salts and dichromate do oxidize polonium to polonium(VI) (*94*).

Fusion of polonium dioxide with a potassium chlorate/hydroxide mixture gives a bluish solid (colorless when hot) which is more soluble in water than the corresponding polonite (PoO_3^{2-}); this presumably contains some potassium polonate. The trioxide may possibly be formed by strongly heating polonium dioxide and chromium trioxide in air (*12*).

The difficulty of obtaining polonium trioxide and the corresponding polonates by the direct oxidation of quadrivalent polonium may be largely due to the high levels of radiation associated with the polonium-210 used. Similar work with curium showed that the higher oxidation state is almost impossible to achieve with 163-day curium-242, although this is relatively easily achieved with 18-yr curium-244. It is suggested that work in this field with the longer-lived polonium isotopes would be more fruitful.

B. Polonium Dioxide

This oxide is formed from the elements at 250°C, its composition being established by measuring the oxygen taken up by the metal (*93*, *103*). It exists in two crystal modifications, a yellow low temperature form (face-centered cubic) and a red high temperature form (tetragonal) (*5*, *93*). The former, density about 9 gm/cc, is a UO_2-type oxide with variable oxygen content, the cell edge varying from 5.626 to 5.687 kX (*5*). The tetragonal modification has cell parameters $a = 5.44$ kX and $c = 8.34$ kX.

The radius of the Po^{4+} ion calculated from the X-ray data is 1.02 Å (*93*) or 1.04 Å (*5*); the ratio of the ionic radii Po^{4+}/O^{2-} is thus about 0.73, the lower limit of stability for cubic coordination, explaining the existence of the two modifications (*93*).

Freshly prepared polonium dioxide is always in the tetragonal form, the face-centered cubic modification appearing on standing (*5*, *93*) or on strong cooling (*5*). The dioxide darkens on heating, becoming chocolate at the sublimation temperature (885°C in oxygen at 1 atm) and decomposes into the elements at 500°C under vacuum (*5*). It is slowly reduced to the metal at 200°C in hydrogen (*103*) or at 250°C in ammonia or hydrogen sulfide (*12*). It does not react with liquid sulfur dioxide, but a white compound is formed on heating the dioxide in sulfur dioxide at 250°C and this may be a polonium sulfite (*12*). In all its chemical reactions with acids, polonium dioxide behaves very much like its tellurium analogue, giving the corresponding polonium(IV) salts.

The corresponding hydroxide is obtained as a pale yellow flocculent precipitate on the addition of aqueous ammonia or dilute alkali to solutions of freshly prepared polonium salts (aged preparations, containing much decay lead, give a brownish precipitate). Like tellurous acid, polonium hydroxide is much less soluble in aqueous ammonia than in aqueous alkali. The well known acidic character of the oxides of the sulfur group is much weakened with increasing atomic weight, and polonium dioxide and the corresponding hydroxide are much less acidic than their lower homologues. This is shown particularly by the ease with which polonium salts are formed by reaction with weak acids such as acetic, hydrocyanic, and oxalic (*11*) and by a study of the solubility of polonium hydroxide in aqueous potassium hydroxide, from which the equilibrium constant $K_c = [PoO_3^{--}]/[OH^-]^2$ for the reaction

$$PoO(OH)_2 + 2OH^- \rightleftharpoons PoO_3^{--} + 2H_2O$$

has been found to be 8.2×10^{-5} at 22°C. The solubility in alkali increased from 1.04 mg (of Po^{210})/liter in 0.26 *N* potassium hydroxide to 53.3 mg/liter in 1.73 *N* potassium hydroxide (*11*). Recent publications quote a figure of

about 7.8 mg (of Po^{210})/liter for the solubility of the hydroxide at pH 6 (*136*, *137*). However, the hydroxide was described as forming a white, voluminous precipitate, which suggests either the presence of impurities such as bismuth or that the product was a basic salt rather than the hydroxide. The latter is the more likely.

Fusion of polonium dioxide with potassium hydroxide in air, or with potassium nitrate, gives a colorless melt; the solubility of the polonium after this treatment corresponds with the solubility data for potassium polonite (*12*).

C. Polonium Monoxide

The black monoxide appears to be formed by the spontaneous decomposition of polonium sulfotrioxide and selenotrioxide (*10*). The corresponding hydroxide (or hydrated oxide) is obtained as a dark brown precipitate when alkali is added to a freshly prepared solution of bipositive polonium (*6*). Both are rapidly oxidized to polonium(IV) in air or in contact with water.

D. Polonium Monosulfide

It has long been known that trace polonium could be precipitated from acid solution by hydrogen sulfide, the precipitate being insoluble in yellow ammonium sulfide. It was also observed that the precipitated polonium was more volatile than bismuth sulfide, from which it could be separated by vacuum sublimation at 700°C (*35*). However, recent work with weighable amounts has shown that the metal and sulfur do not react (*25*). The black precipitate produced by hydrogen sulfide (either the gas itself or generated *in situ* by the hydrolysis of thioacetamide at 80°C) on dilute acid solutions of quadripositive or bipositive polonium is the monosulfide (*14*). It is immediately insoluble in dilute hydrochloric acid or yellow ammonium sulfide, but dissolves in the former on long standing, probably through oxidation by the chlorine liberated from the acid by alpha-bombardment. The solubility product is about 5.5×10^{-29}. The monosulfide can also be prepared by the action of yellow ammonium sulfide on polonium hydroxide.

It is readily decomposed by aqueous bromine, aqua regia or by hypochlorite and is comparatively soluble in concentrated hydrochloric acid; it decomposes to the elements at 275°C under vacuum, a property utilized for the preparation of pure polonium metal (*14*).

VII. Polonium Halides

The chemistry of the polonium halides is, as would be expected, very similar to that of tellurium, but with the bipositive halides much more

stable, and the quadripositive halides rather less stable, than their tellurium analogues. All the identified polonium halides are covalent, volatile, readily hydrolyzed compounds; the quadripositive complex halides are of the type $M_2^IPoX_6$ (X = Cl, Br, I) and are isomorphous with their tellurium analogues, cesium giving the least soluble alkali metal salt in every case. There is little evidence for the formation of polonium(III) compounds, although a study of the auto-oxidation of polonium(II) in acid solution indicates that polonium(III) may have a transient existence in dilute hydrochloric acid (*6*) but not in dilute hydrobromic acid (*7*).

A. Fluorides

A white solid, possibly polonium tetrafluoride, is obtained by treating polonium hydroxide or tetrachloride with dilute aqueous hydrofluoric acid; treatment of this solid, in suspension in dilute hydrofluoric acid, with sulfur dioxide yields a bluish grey product (possibly PoF_2) which rapidly reverts to the original white solid on standing, presumably owing to radiolytic oxidation (*12*). The solubility of polonium(IV) in aqueous hydrofluoric acid increases rapidly with acid concentration, indicating complex ion formation (*104*, p. 48).

There have been some unsuccessful attempts to prepare a volatile hexafluoride from fluorine and polonium-210 (*25*, *104*), but recently such a fluoride has been prepared in this way from polonium-208 plated on platinum (*132*). The product appears to be stable while in the vapor phase, but on cooling a nonvolatile compound is formed, probably polonium tetrafluoride resulting from radiation decomposition of the hexafluoride. Analytical data are not recorded for any polonium fluoride, largely owing to the difficulty of determining fluoride ion accurately at the microgram level.

B. Chlorides

Polonium tetrachloride is a bright yellow solid; it melts in chlorine at about 300°C (*6*, *74*) to a straw-colored liquid which becomes scarlet at 350°C, possibly through decomposition to the dichloride. It boils at 390°C to give a purple-brown vapor which becomes blue-green above 500°C (*6*). The reason for this reversible color change is unknown.

The compound is produced by evaporating hydrochloric acid solutions of polonium(IV) (*6*, *25*, *74*), by heating the dioxide in carbon tetrachloride vapor (*74*), in hydrogen chloride, thionyl chloride or with phosphorus pentachloride (*6*) and by heating the metal in dry chlorine at 200°C (*6*, *25*, *74*). It is hygroscopic and hydrolyzes in moist air to a white solid, possibly a basic chloride (*74*). The tetrachloride is soluble in thionyl chloride and in water with hydrolysis, and is moderately soluble in ethanol, acetone, and

some other ketones (*6*). It is slightly soluble in liquid sulfur dioxide, with which it does not react (*12*). Its solutions in hydrochloric acid are bright yellow, the color being perceptible even in 5×10^{-5} *M* solution. There is some evidence (*6*) for the formation of ammines with gaseous ammonia and the complex with nitrosyl chloride may have the composition $PoCl_4 \cdot 4NOCl$ (*12*). The tetrachloride is converted to polonium dioxide on heating in air or oxygen at 300°C (*6*).

Complexes with organic compounds have been reported. Solubility studies with tributyl phosphate (TBP) indicate the formation of a complex $PoCl_4 \cdot 2TBP$ (*13*). Weighable amounts of polonium tetrachloride in dilute hydrochloric acid can be titrated to a colorless end point with ethylenediamine tetra-acetic acid (EDTA); the results suggest a complex with two molecules of EDTA, but solubility studies favor a 1:1 complex. The EDTA complex is soluble in alkali and is more stable in alkaline than in acid media, but the ligand is rapidly destroyed by the radiation and solvent radiolysis products (*12*). However, EDTA can apparently be used to complex trace polonium in the separation of radium D-E-F mixtures (*129*).

Polonium dichloride is a dark ruby red solid which sublimes in nitrogen at 190°C with some decomposition. It is obtained by thermal degradation of the tetrachloride under vacuum at 200°C (*6*, *25*, *74*), by reduction of the tetrachloride in hydrogen at 200°C (*25*, *74*), in hydrogen sulfide or carbon monoxide at 150°C or in sulfur dioxide in the cold (*6*). Reduction to the metal occurs on continued heating in hydrogen or hydrogen sulfide. A brown ammine (possibly $PoCl_2 \cdot 2NH_3$) appears to be formed in dry ammonia gas at 200°C (*6*).

Bipositive polonium in hydrochloric acid solution (pink) is oxidized to polonium(IV) by hydrogen peroxide, by hypochlorous acid or by the radiolysis products of the alpha bombardment of the solvent. Solutions of polonium(II) in acid are obtained by the reduction of polonium(IV) with sulfur dioxide or hydrazine in the cold, or with arsenious oxide on warming. Polonium(IV) is not reduced in hydrochloric acid by either hydroxylamine or oxalic acid, even on boiling (*6*).

X-ray crystallographic data on the dichloride and some other polonium halides are presented in Table V.

C. Bromides

Polonium tetrabromide is a bright red solid which melts, in bromine vapor, at about 330°C (*7*, *75*), and boils at 360°C/200 mm (*75*). It is prepared by heating polonium metal in bromine vapor at 200 mm pressure for 1 hour at 250°C (*7*, *75*) or, more rapidly, in a stream of nitrogen saturated with bromine vapor at 200°–250°C, and by heating polonium dioxide in hydrogen bromide or by evaporating a solution of polonium(IV) in hydro-

TABLE V
X-RAY CRYSTALLOGRAPHIC DATA FOR THE HALIDES

Compound	Symmetry	Space group	Lattice constants (kX)	Molecules/ unit cell	Calculated density (gm/cc)	Reference
$PoCl_4$	monoclinic?	—	—	—	—	*74*
$PoCl_2$	orthorhombic[a]	—	$a = 3.66$, $b = 4.34$, $c = 4.49$	1	6.50	*6*
$PoBr_4$	fcc	O_h^5-Fm3m	$a = 5.60$	1	—	*7*
$(NH_4)_2PoCl_6$	fcc	O_h^5-Fm3m	$a = 10.33$	4	2.76	*6*
Cs_2PoCl_6	fcc	O_h^5-Fm3m	$a = 10.59$	4	3.82	*126*
$(NH_4)_2PoBr_6$	fcc	O_h^5-Fm3m	$a = 10.82$	4	3.78	*7*
Cs_2PoBr_6	fcc	O_h^5-Fm3m	$a = 10.99$	4	4.75	*7*
Cs_2PoI_6	fcc	O_h^5-Fm3m	$a = 11.77$	4	5.0	*8*

[a] The observed cell may be a pseudocell and the symmetry might be monoclinic or triclinic with the cell angle or angles near 90° (*6*). The X-ray data have also been indexed as orthorhombic with $a = 4.331$, $b = 8.944$ and $c = 7.292$; the calculated density, assuming 4 molecules per unit cell, is then 6.55 gm/cc (*74*).

bromic acid to dryness (*7*). Polonium metal does not react with liquid or gaseous bromine in the cold.

Its solutions in dilute hydrobromic acid are a carmine-red (0.025 *M* $PoBr_4$) and in more dilute solution (10^{-3} *M*), orange red. The tetrabromide is soluble in ethanol, acetone and some other ketones, and is sparingly soluble in liquid bromine. It is hygroscopic and is easily hydrolyzed to a white, basic bromide of variable composition. It forms a yellow ammine in ammonia gas and this yields polonium dibromide and polonium metal on standing, presumably because of radiation decomposition of the ammonia and subsequent hydrogen reduction of the tetrabromide (*7*).

Polonium dibromide is a purple-brown solid which sublimes with slight decomposition at 110°C/30 μ and appears to disproportionate on melting in nitrogen at 270°–280°C (*7*). It is prepared by vacuum thermal degradation of the tetrabromide at 200°C and also by reduction of the tetrabromide in hydrogen sulfide in the cold. Sulfur dioxide does not reduce the tetrabromide completely, even on heating. Its solutions in hydrobromic acid are purple and are obtained in the same way as solutions of the chloride. The dibromide is soluble in ketones to give purple solutions which are rapidly oxidized to polonium(IV). The solid dibromide is rapidly reduced to the metal on heating in ammonia (*7*).

D. Iodides

Polonium tetraiodide (*8*) is a black solid which sublimes in nitrogen at 200°C with partial decomposition to the metal. It is formed from the elements at 40°C/1 mm, by treating polonium dioxide or hydroxide with 0.1 *N* hydriodic acid, and is precipitated from solutions of polonium(IV) in dilute hydrochloric acid on the addition of 0.1 *N* hydriodic acid. It is also obtained as a black sublimate by heating polonium dioxide in hydrogen iodide at 200°C; a black addition compound ($PoO_2 \cdot xHI$) is formed in the cold. Polonium metal does not react with iodine dissolved in carbon tetrachloride, but with iodine dissolved in benzene it does react to some extent.

The tetraiodide is slightly soluble in acetone and in ethanol (about 1 gm PoI_4/liter) but is insoluble in dilute mineral acids and in ethers, aliphatic acids and hydrocarbons. It is slowly hydrolyzed by water and by concentrated alkali, the white product presumably being a basic iodide, and is decomposed by chlorine, hypochlorite, nitrite, and hot concentrated nitric acid. It does not react with ammonia gas but is reduced to the metal on heating in hydrogen sulfide. Suspensions of the tetraiodide in 0.1 *N* hydriodic acid are unaffected by hydrazine or sulfur dioxide, even on boiling, and there is no evidence for a diiodide.

A study (*8*) of the solubility of polonium tetraiodide in dilute hydriodic

acid shows that the PoI_5^- ion ([HI] < 0.02 *N*) and PoI_6^{--} ion ([HI] > 0.02 *N*) are formed, the equilibrium constants for

$$PoI_4 + I^- \rightleftharpoons PoI_5^-$$

and

$$PoI_4 + 2I^- \rightleftharpoons PoI_6^{--}$$

being 6.7×10^{-5} and 5.9×10^{-3} respectively at 22°C. The temperature/solubility curve goes through a minimum at 30°C and solutions of the tetraiodide in dilute hydriodic acid are green at 0°C and red-brown above 20°C; the changes are presumably due to a change in the hydration of the anionic species.

E. Interhalogen Compounds

Polonium dichloride reacts with bromine vapor at room temperature to give salmon pink $PoCl_2Br_2$. Neither polonium dichloride nor the dibromide reacts with iodine vapor on heating, but both may form unstable interhalogen compounds on treatment with iodine in carbon tetrachloride (*7*, *8*).

F. Complex Halides

Early trace level work (*52*) with polonium suggested the presence of the hexachloropolonite ($PoCl_6^{--}$) ion in hydrochloric acid solution; more recent work (*9*) with weighable amounts of polonium indicates that the equilibrium constant for $Po^{4+} + 6Cl^- \rightleftharpoons PoCl_6^{--}$ is about 10^{14}. The molar absorbancy index (*70*) of the complex ion present in 12.2 *M* hydrochloric acid is 1.058×10^{-4} (418 mμ).

Addition of the appropriate cesium halide to solutions of polonium(IV) in halogen acid yields a precipitate of the cesium hexahalogenopolonite. The chloride is greenish yellow (*6*, *126*); the rubidium, potassium, ammonium, and tetramethylammonium salts are more soluble in acid, but can be prepared by evaporating solutions of the components (*126*) or, in the case of the ammonium salt, by heating the solid components together (*6*). All are face-centered cubic (Table V) and are isomorphous with their tellurium analogues. The corresponding cesium bromopolonite is dark red (*7*) and the iodide derivative is black (*2*, *8*).

Solutions of polonium(IV) in hydrobromic acid deposit a blackish brown solid on cooling to −30°C; this is unstable at room temperature and appears to be the hydrated acid, H_2PoBr_6. The ammonium bromopolonite is obtained in small yield by heating polonium tetrabromide in ammonia gas at 100°C; on heating more strongly in a sealed tube, this salt blackens and detonates, possibly owing to the formation of an explosive nitride (*7*).

All the cesium complex halides are easily hydrolyzed and decompose on heating under vacuum.

VIII. Polonium Salts of Oxy-acids

A. Polonium Bromate

Metallic polonium is not affected by 15% bromic acid, even at 70°C, and polonium dioxide or polonium(IV) hydroxide are only slightly soluble (2.5 mg PoO_2/liter) in 10% bromic acid. Polonium tetrachloride is converted to a white solid of unknown composition by 15% bromic acid; this could be a basic chloride (*12*).

B. Polonium Carbonate

Long treatment of polonium(IV) hydroxide with water saturated with carbon dioxide yields an unstable white solid, apparently a carbonate (*12*).

The solubility of "oxidized" polonium—probably the dioxide—in aqueous sodium carbonate is about 0.3 mg (of Po^{210})/liter and does not change appreciably with the carbonate concentration. However, the solubility in aqueous ammonium carbonate increases from 0.089 mg (of Po^{210})/liter in 0.25 *M* solution to 5.2 mg/liter in 0.75 *M* solution (*104*, p. 53).

C. Polonium Chromates

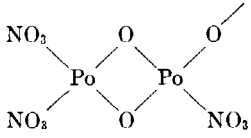
Aqueous 1 *M* chromium trioxide (*12*) does not react with metallic polonium, but with polonium(IV) hydroxide or tetrachloride yields an orange-yellow solid, thought to be $Po(CrO_4)_2$. This is insoluble in an excess of the reagent and is easily hydrolyzed by water or wet acetone to a dark brown basic chromate with a composition close to $2PoO_2 \cdot CrO_3$ (cf., the basic sulfate and selenate). On long standing in an excess of aqueous chromium trioxide, oxidation to polonium(VI) may occur (Section VI,A).

D. Polonium Iodate

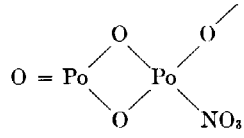
Although polonium hydroxide does not react with 0.2 *N* iodic acid, the white quadripositive iodate, probably $Po(IO_3)_4$, is readily precipitated from solutions of polonium(IV) in nitric acid by adding iodic acid in the same medium (cf. thorium iodate; the Po^{4+} and Th^{4+} ions have almost the same ionic radii. However, polonium, unlike thorium, is not precipitated from nitric acid solution by periodic acid). Polonium iodate decomposes slowly on standing, liberating iodine presumably because of the intense alpha bombardment, and decomposition is rapid above 350°C. The salt is soluble in 2 *N* hydrochloric acid; its solubility decreases markedly with increasing iodic acid concentration, falling from 9.55 mg (of Po^{210})/liter in 0.045 *N* HIO_3/2 *N* HNO_3 to 1.72 mg/liter in 0.167 *N* HIO_3/2 *N* HNO_3 (*12*).

E. Polonium Nitrates

Treatment of polonium(IV) hydroxide or chloride with dilute (0.1–2 *N*) nitric acid gives white, unstable addition compounds ($PoO_2 \cdot x\ HNO_3$). However, a moderately stable, white crystalline basic nitrate, with the ratio NO_3^-; Po = 3:2, is obtained by allowing polonium(IV) hydroxide or chloride to stand under 0.5 *N* nitric acid for 12 hr. and vacuum-drying the product at room temperature. This compound is also obtained by treating polonium metal with a mixture of oxygen and gaseous nitrogen dioxide or by keeping the metal in air for 3 days. In the latter instance the oxides of nitrogen are formed by the fixation of atmospheric nitrogen by alpha bombardment. This basic nitrate decomposes at about 100°C to a yellowish white compound in which the ratio NO_3^-:Po = 1:2 (cf., tellurium nitrate, thought to be $2TeO_2 \cdot HNO_3$ (*98*, p. 119). It is also obtained by evaporating nitric acid solutions of polonium(IV) to small volume and vacuum drying the product. The compound decomposes to polonium dioxide at 130°C and both basic nitrates decompose to the metal by way of the dioxide on long standing under a vacuum or in dry nitrogen. These basic nitrates probably have a dimeric oxygen-bridge structure (I and II)



(I)



(II)

derived from the unknown basic nitrate, $PoO(NO_3)_2$ (*16*). This would accord with the low solubility of polonium dioxide in nitric acid; the increased solubility at higher acid concentrations is presumably due to complex ion formation (*107*), the cation exchange behavior of polonium in nitric acid media showing a marked increase in the anionic species at high acid concentrations (*16*).

Polonium tetranitrate, with at least one molecule of dinitrogen tetroxide of crystallization, is formed as a white crystalline solid by the action of liquid dinitrogen tetroxide on polonium dioxide or tetrachloride; polonium metal does not react with this reagent or with its solution in ethyl acetate. The dinitrogen tetroxide is rapidly lost on standing and the resulting tetranitrate decomposes to the basic salt (I) in 1½–2 hr. under vacuum (*16*).

F. Polonium Phosphate

This is a white, gelatinous solid of composition close to $2PoO_2 \cdot H_3PO_4$, made by the action of 1 *M* diammonium phosphate on solid polonium tetrachloride or of 2 *M* phosphoric acid on polonium hydroxide. It appears

to be unaffected by washing with water or aqueous ammonia but is decomposed by 0.1 N potassium hydroxide and by dilute mineral acid (*12*). Its solubility in 0.5 M phosphoric acid is about 6.7 mg (of Po^{210})/liter, equivalent to about 3×10^{-5} M solution (*104*, p. 53). The solubility in ammonium, sodium, and potassium phosphate solutions is much lower.

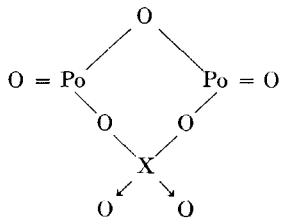
G. Polonium Selenate

The white basic selenate, $2PoO_2 \cdot SeO_3$, is obtained by treating polonium(IV) hydroxide or chloride with selenic acid (0.015 N–5.0 N); the salt is yellow above 250°C and is stable to over 400°C. It is rather less soluble than the basic sulfate, but the solubility increases a hundredfold in passing from 0.05 N to 5 N selenic acid (*10*), indicating complex ion formation.

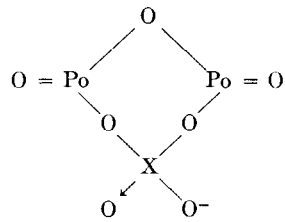
H. Polonium Sulfates

The white basic sulfate, $2PoO_2 \cdot SO_3$, results when polonium(IV) hydroxide or chloride is treated with 0.02 N–0.25 N sulfuric acid. Like the selenate, it is yellow above 250°C and decomposes to the dioxide at 550°C. Solubility studies indicate that it is metastable in contact with 0.1 N–0.5 N sulfuric acid (*10*).

The ready formation of basic salts of the form $2PoO_2 \cdot XO_3$ (X = S, Se, Cr), and of a phosphate of rather similar composition, suggests that these compounds may have oxygen-bridge structures (III), the phosphate (IV) being analogous (*12*).



(III)



(IV)

The white hydrated disulfate $Po(SO_4)_2$ is obtained in the same way as the basic salt, but with more concentrated acid (>0.5 N). The compound is less soluble than the basic salt and solubility studies indicate complex ion formation when the acid concentration is increased. The deep purple anhydrous salt is obtained by heating the hydrate above 100°C or by washing it with anhydrous ether. It decomposes to the dioxide at 550°C.

Suspensions of the disulfate in N–2 N sulfuric acid dissolve on boiling with hydroxylamine to give a pink solution, characteristic of polonium(II), but the disulfate hydrate is reprecipitated on cooling, even in the presence of an excess of hydroxylamine (*10*), in accord with earlier trace level

observations (*53*, *60*). It should thus be possible to determine the redox potential for the system Po^{4+}/Po^{2+} in sulfuric acid by determining accurately the temperature at which reduction takes place and then obtaining the corresponding potential for the reducing agent in a similar, but nonradioactive system.

IX. Other Polonium Compounds

A. Organic Salts

1. Polonium Acetate

This salt is a white crystalline solid made by treating polonium(IV) hydroxide or chloride with dilute acetic acid. Its solubility in the latter increased from 0.2 mg (of Po^{210})/liter in 0.1 *N* acid to 82.5 mg/liter in 2 *N* acid, indicating complex ion formation. The acetato complex is colorless in solution and appears to be more stable than the hexachloro complex (*11*).

2. Polonium Camphorate

Alcoholic camphoric acid reacts with alkaline suspensions of trace polonium giving a product soluble in benzene or chloroform (*122*).

3. Polonium Citrate

The solubility of polonium dioxide in 1 *M* citric acid is about 10.2 mg (of Po^{210})/liter (*104*, p. 53).

4. Polonium Cyanide

This is a white crystalline solid made by treating polonium(IV) hydroxide or chloride with aqueous hydrocyanic acid. It blackens rapidly on standing owing to radiation decomposition. Its solubility in aqueous potassium cyanide is low, increasing from 0.089 mg (of Po^{210})/liter in 0.05 *M* solution to 1.19 mg/liter in 1.5 *M* solution, so that cyanide complex ions may be formed (*11*).

5. Polonium Diethyldithiocarbamate

Some trace level studies (*50*, *51*, *81*) of the extraction of this compound from weakly alkaline solution have been reported. It appears to be soluble in chloroform (*50*, *51*), amyl alcohol and carbon tetrachloride (*81*).

Ion exchange and solvent extraction data indicate that the compound contains one diethyldithiocarbamate ion attached to each polonium atom. It sublimes at about 110°C (*81*).

6. Polonium Formate

The treatment of polonium hydroxide with 2 *N* formic acid yields a black solid of uncertain composition and low solubility (*11*).

7. Polonium Oxalate

This is a white crystalline solid obtained by treating polonium(IV) hydroxide or chloride with aqueous oxalic acid; solubility studies indicate complex ion formation (*11*).

8. Polonium Tartrate

Polonium tetrachloride is very soluble in 2 *N* tartaric acid, giving a colorless solution which slowly darkens owing to radiation decomposition. Electrolysis leads to deposition of about 12% of the polonium on the cathode and 65% on the anode (*11*).

B. Organic Complexes and Organometallic Compounds

1. Polonium Acetylacetonate

Cocrystallization studies of the distribution of trace polonium in aluminum, scandium and thorium acetylacetonates indicated that the action of acetylacetone on polonium hydroxide might give a mixture of terpositive and quadripositive acetylacetonates. The product sublimed at 230°C/10 mm and was slightly soluble in water and very soluble in warm chloroform, benzene, ethanol, acetone, and acetylacetone (*120*, *121*). More recently (*12*), work on the solvent extraction of milligram amounts of polonium(IV) from hydrochloric acid solution has shown that certain mono- and diketones (for instance methyl*iso*butyl ketone, acetylacetone) extract the polonium completely from the aqueous phase over a wide range of acid concentration. Other ketones (di*iso*propyl ketone, diphenyl ketone/chloroform), however, extracted little polonium. Evaporation of the acetylacetone or methyl*iso*butyl ketone extracts yielded a yellow oil from which a pale yellow crystalline solid was obtained on recrystallization from 60°/80° petroleum ether. Both of these ketones react with solid polonium tetrachloride or tetrabromide with the evolution of 2 moles of halogen acid to give yellow (chloro) or orange (bromo) compounds. From these the halogen is removed by shaking with aqueous potassium hydroxide, to yield in both cases a volatile, purple violet solid which is also obtained by treating polonium dichloride or dibromide with the appropriate ketone. At least one carbonyl group in these compounds is free to react, for the red 2:4 dinitrophenyl hydrazine derivative is readily produced. This behavior is com-

pletely analogous to that of the tellurium halides, which form cyclic derivatives with acetylacetone by condensation of the tellurium halide across the two terminal methyl groups of the diketone (*101*); the halogenated product (V) gives (VI) on treatment with alkali

2,4 dioxo *cyclo* pentylene polonium (tellurium) dichloride

(V) (VI)

Both polonium derivatives are chemically very stable, requiring hot fuming nitric acid for their decomposition. However, they char rapidly under the intense alpha bombardment and attempted analyses with acetylacetone labeled with carbon-14 in the 1 and 3 positions were unsuccessful. It is interesting that the corresponding yellow oxide, prepared by treating (VI) with aqueous hydrogen peroxide, reverts to (VI) on treatment with aqueous alkali (*12*).

2. Polonium Dithizonate

Solvent extraction studies on both the trace (*71*) and milligram (*13*) scale indicate the formation of a compound with two molecules of dithizone, probably $PoODz_2$ (*71*). The compound is red (*13*) and sublimes at about 120°C in air (*82*).

3. Other Complexes

Trace polonium is extracted from aqueous acetate solution by 8-hydroxyquinoline in chloroform, probably forming a 1:1 compound; this sublimes at 140°C (*81*). The thionalide complex appears to have 2 molecules of ligand to each polonium atom; volatile complexes with thiourea, thiosemicarbazide, diphenylcarbazide, and analogous reagents have also been reported (*81*).

4. Organometallic Compounds

These compounds have only been studied on the trace scale. An ether soluble polonium dibenzyl is reported (*80, 118*) to be formed by the action of dimethylphenylbenzyl-ammonium chloride on sodium polonide/telluride mixtures in water saturated with hydrogen. The dimethyl was prepared in the same way, but with dimethyl sulfate (*118*) and may also be formed in

the decay of lead-210 tetramethyl (*102*). A more recent study (*105*) of the products of the decay of bismuth-210 triphenyl and triphenyl dichloride indicates the formation of polonium diphenyl and diphenyl dichloride. These were separated by ascending paper chromatography and identified by comparison with the positions of the peaks of the corresponding tellurium compounds.

X. The Uses of Polonium

Polonium is used mainly for the production of neutron sources of low gamma-emission; for this purpose it is alloyed with elements which have isotopes of high α,n cross section, such as beryllium (e.g., *104*). These sources can be used for neutron activation analysis and for indirect analysis such as the determination of boron in glass; for this last, the neutron source is immersed in a water moderator and the absorption of thermal neutrons by the glass is measured by neutron counting (*114*). Polonium sources have also been used for alpha activation analysis of elements which cannot easily be determined by neutron activation; for example, submilligram amounts of fluorine can be determined by counting the sodium-22 formed by the reaction $F^{19}(\alpha,n)Na^{22}$ (*106*). The main chemical application of polonium is in studies of the effects of alpha radiation on solids or liquids, and there is a considerable literature on this subject.

Polonium has also found some use in industry; alpha particle transmission gauges, in which the energy loss of the alpha particle is an index of the thickness of the absorbing material, have been used in paper research and its use in static eliminators has also been reported. These, however, can be very dangerous if the sealing of the radioactive material is inadequate (*24*, *125*).

One of the earliest reported uses was for the improvement of the cold starting properties of internal combustion engines, the polonium being incorporated into the sparking plug electrode alloy (*38*), but its effectiveness for this purpose has been disputed (*40*) and a health hazard would certainly arise from the burning off of the polonium from the electrode and its discharge into the air.

XI. Summary

By analogy with tellurium, polonium should show valencies of +2, +4, and +6; although the evidence for polonium(VI) is still rather slight, the other states are well established. The acidic character of the sulfur subgroup remains evident in a minor way in polonium, as is shown by the formation of polonides and the slightly acidic character of polonium(IV) hydroxide (polonous acid). This is, however, more basic than its tellurium analogue and compounds such as the disulfate and tetranitrate, for which there are

no tellurium analogues, demonstrate the increased metallic character of the element. A further difference lies in the stability of the halides, the polonium dihalides being far more stable than the corresponding tellurium compounds, which disproportionate readily.

The basic salts of quadrivalent polonium, such as the sulfate and selenate, show a marked resemblance to those of tellurium and further resemblances appear in the quadrivalent halides, particularly in their complexing with halide ions in solution, while complexing of polonium(IV) with weak acids, such as acetic, oxalic and tartaric, seems to be more marked than is the case with tellurium.

In the past 15 years a large number of polonium compounds have been prepared in visible quantities for the first time and as a result of these investigations it has been shown that polonium behaves chemically very much as would be expected from its position in the Periodic Table, with the "inert-pair" effect, likely to be more marked in polonium than in tellurium, still little in evidence.

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