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Thermal Reactions of Polonium

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Published information on the interaction of polonium with the chemical elements has been surveyed and systematised. Attention is paid to specific features of experimental methods for investigating the properties of polonium compounds. Conditions for the direct synthesis of binary polonium compounds and their thermal properties are given. The applicability of the Samsonov classification of chalcogenides to polonium compounds is shown.
Bibliography of 43 references.

CONTENTS

I. Introduction 622
II. Methods of investigation 622
III. Chemical and physical properties of polonium 623
IV. Interaction of polonium with the chemical elements 624
V. Conclusion 628

I. INTRODUCTION

The first papers containing communications about phenomena connected with thermal reactions between polonium and chemical elements[1,2] appeared in 1932.

Rona[1] studied the influence of the material of the substrate on which polonium had been deposited electrochemically on the vaporisation of the polonium; vaporisation starts at 280 °C from a gold substrate, at 300 °C from a platinum substrate, and at 550 °C from a palladium one. After a specimen of polonium on a gold substrate had been stored for five months the temperature for the start of the vaporisation of the polonium had increased to 400 °C. Tamman and Löwis of Menar[2] investigated the behaviour of poloniun during the crystallisation of metals by melting filings of silver, copper, lead, bismuth, tin, antimony, cadmium, zinc, or tellurium on which trace amounts of polonium had been deposited electrochemically. Radiographic study of sections of the ingots showed that the polonium is located at the grain boundaries of the metals; it was concluded that polonium differs from other metals in its insignificant tendency to form solid solutions.

The systematic investigation of the thermal reactions between polonium and the chemical elements was begun after milligramme amounts of it had been obtained by irradiating bismuth in atomic reactors.

Detailed information about polonium and its compounds (discovery, distribution, methods of production, physical and chemical properties, state and behaviour in solutions, electrochemistry, analytical chemistry, applications, and safety techniques) has been given in monographs[3-8]. Early American work was surveyed in a review paper[9].

The present review deals with thermal reactions between polonium and the chemical elements which proceed in the interaction of polonium vapour with the liquid or solid elements or the interaction of the gaseous elements with metallic polonium. This information is scattered in the earlier literature. Special attention is paid to works which have appeared in the last decade (after the reviews mentioned above were written). Many experimental investigations have shown that in accordance with its position in the Mendeleev Periodic Table polonium and its compounds exhibit properties close to those of the other chalcogens (especially to tellurium) and their compounds; consequently the material is presented mainly in accordance with the scientific classification of the chalcogenides proposed by Samsonov[10].

II. METHODS OF INVESTIGATION

The use of many contemporary methods of investigation is restricted in working with milligramme amounts of polonium-210 because of the high toxicity of polonium, its ability to form radioactive aerosols, and its tendency to migrate along surfaces; it is also necessary to allow for its high energy release (144 W g^{-1}), the destructive power of the nuclear recoil during radioactive decay (166 TBk g^{-1}) [sic. The energy of the recoiling nucleus is 100 keV (Ed.of Translation)], and the constant accumulation of the radiogenic lead-206 in the specimens (0.5% per 24 h). In addition, the strong α-emission of the polonium brings about ozonisation of the atmospheric oxygen, leading to intense oxidation of the specimens. In working with gramme amounts of polonium the radiogenic heating of the specimens is so great that forced cooling of them is necessary. Safety control of the investigations imposes limitations on the choice of methods (the possibility of carrying out the experiment in glove-boxes, simplicity of the equipment, hermetic sealing of the specimens, and remoteness of the quantitative and qualitative determinations).

Direct vacuum-thermal synthesis[11] in the various versions used industrially was employed in most studies of the interaction of polonium vapour with the chemical elements. In some papers[12] it is called the differential-thermal or ampoule method.

X-Ray powder diffraction, metallographic (determination of the microhardness of layers and their dimensions), and tensimetric (various versions) methods were used for studying some of the properties of the polonium compounds obtained. The composition of the vapour during the heating of the specimens was usually determined by the simplest method—from the sublimation temperature of the condensed vapour. In some investigations the atomic ratio of a component of the vapour was found by using radioactive nucleides and determining their amounts with a γ-spectrometer or the mass characteristics of the vapour found with a mass spectrometer. The melting points of the lanthanide polonides were determined with an optical pyrometer from the change in the emissivity of tungsten when the powder of the compound being studied was deposited on it. The amount of polonium in the specimens was determined calorimetrically or radiometrically.

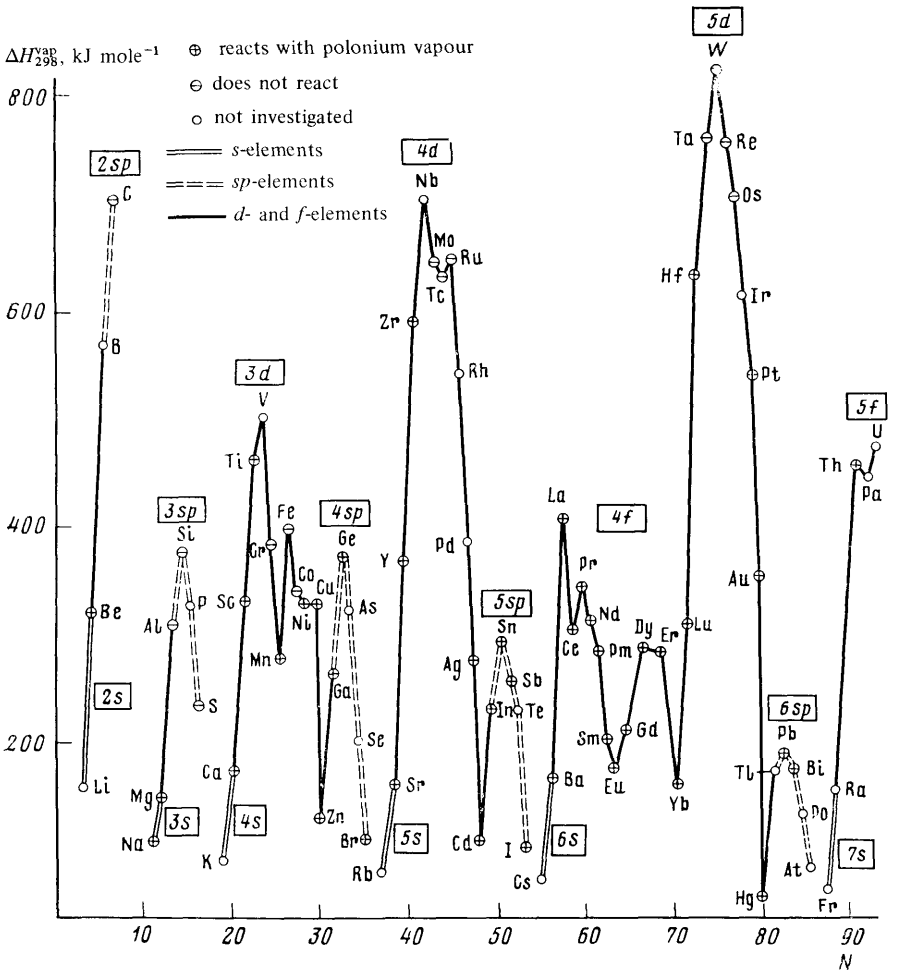


Figure 1. Periodic change in the heats of vaporisation of the chemical elements as a function of their atomic number.

III. CHEMICAL AND PHYSICAL PROPERTIES OF POLONIUM

According to its position in Group VI of the Periodic Table and its electronic structure $\ldots 5s^2 5p^6 5d^{10} 6s^2 6p^4$, polonium has a valence shell of six electrons; consequently it (like all the chalcogens—the representatives of this group) can have the following valence states: −2, +2, +4, +6. In accordance with the general rule, the stability of the +6 state becomes weaker with increase in the atomic number of the element along the series of chalcogens. Polonium(IV) is formed under extreme conditions (high concentrations or pressures of the oxidants) and is unstable under ordinary conditions. The existence of polonium exhibiting a valency of −2 (hydride, dimethylpolonium, alkali and alkaline earth metal polonides), +2 (halides), or +4 (dioxide, halides) has been proved in many investigations. The +4 valence state is most characteristic of polonium.

The appearance of the great "metallicity" of polonium in comparison with the other, lighter chalcogens is connected with the decrease in the energetic stability of the s^2p^4-configuration of the outer electrons as the number of the element is increased. This is shown by the periodicity of the change in the enthalpy of vaporisation of the elements (as a measure of the energetic stability of the solid substance in relation to its passage into the gaseous state) as a function of the atomic number of the element (Fig.1). As Fig.1 shows, the enthalpy of vaporisation of polonium is considerably less than those of sulphur, selenium, and tellurium, which corresponds to the general rule for *s*- and *sp*-elements. However, for the *d*- and *f*-elements an increase in the enthalpy of vaporisation with the atomic number is observed. The similarity of the energetic stabilities of the outer electron shells of the 6*sp*-elements is responsible for the similarity in their physical properties.

The temperature dependence of the vapour pressure of polonium was determined by direct (with a Bourdon manometer)[13] and indirect-static (from the radiometrically determinable amount of vapour in a known volume, assuming that polonium vapour is monatomic)[14] methods and is expressed by the equation

$$\lg p[\text{Pa}] = A - B/T, \qquad (1)$$

with the following coefficients:

t, °C	A	B
438—745	9.3545±0.0068	5377±6.7
368—604	9.46±0.05	5440±60

The heats of vaporisation of polonium calculated from equations with these coefficients are 103 and 104 kJ mole^{-1} respectively. The slight difference between the vapour pressures calculated from the results of these methods shows there is a small proportion of diatomic molecules in polonium vapour. The existence of Po_2 molecules has been established spectroscopically[15].

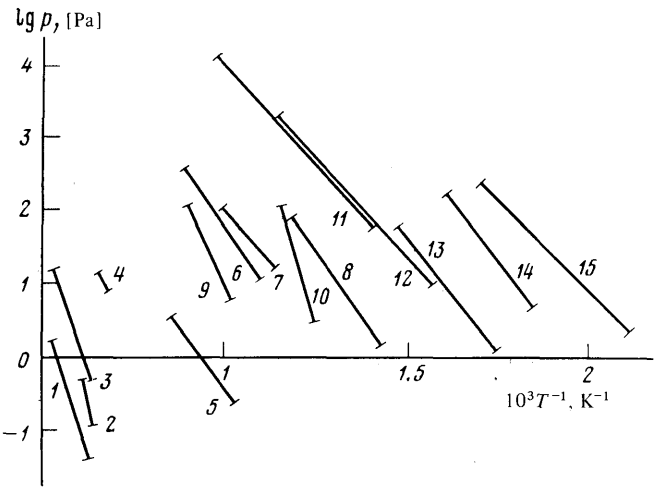


Figure 2. Vapour pressure of polonium above the polonides: *1*) yttrium; *2*) holmium; *3*) dysprosium; *4*) scandium; *5*) hafnium; *6*) lead; *7*) gallium; *8*) indium. Vapour pressure of polonium dioxide during vaporisation (*9*) and its dissociation (*10*); vapour pressure of polonium according to Brooks[13] (*11*) and Abakumov and Ershova[14] (*12*); vapour pressure of polonium hexa-, tetra-, and di-iodides (*13*, *14*, and *15*).

IV. INTERACTION OF POLONIUM WITH THE CHEMICAL ELEMENTS

From a consideration of the peculiarities of the electronic structure, bond type, and properties Samsonov[10] proposed a principle for the classification of the chalcogenides, in which they are divided into three main groups: (1) chalcogenides of metals having outer *s*-electrons in a completed shell, or more deeply lying incomplete electron shells with an ionic–covalent type of bond; (2) chalcogen compounds of elements having outer *sp*-electrons with a covalent–ionic type of bond; (3) chalcogenides of the transition metals having completed *d*- and *f*-electron shells, with a covalent-metallic type of bond in the superposition of a definite fraction of ionic bond.

For convenience in finding general rules the information on the interaction of polonium with the chemical elements and the properties of its compounds are grouped in the present review in accordance with Samsonov's classification. Special attention is paid to polonium compounds with hydrogen and helium.

Hydrogen does not react with polonium when heated. A volatile polonium hydride is formed in insignificant amounts by the action of 0.2 *N* HCl on magnesium foil on which polonium had been deposited and is released from solution when nitrogen, hydrogen, or oxygen is bubbled through. Polonium hydride is formed in lower yield (0.2%) when magnesium powder is added to an acid solution containing trace amounts of polonium. An even lower yield of hydride is obtained by the action of acid on zinc on which trace amounts of polonium had been deposited. Polonium hydride is condensed at −84 °C, its melting point is −36 °C, and boiling point +35.5 °C; it is an unstable compound and belong to the group of covalent hydrides with weak molecular bonds.

Helium forms a volatile compound with polonium under the action of an electric discharge at reduced pressure (0.4–1 kPa). A high temperature favours the occurrence of this reaction[3]. The existence of such a compound is questionable. Probably, we are speaking about the reaction of polonium with He^+ ions, isoelectronic to hydrogen, which can arise in the electric discharge.

1. Polonides of the *s*-Metals

The thermodynamic characteristics of the polonides of the alkali and alkaline earth metals, calculated by Krestov[16], are given below:

Polonide	Na_2Po	K_2Po	Rb_2Po	Cs_2Po	MgPo	CaPo	SrPo	BaPo	RaPo
$-\Delta H^\circ$, kJ mole^{-1}	347	368	335	343	54	255	268	305	284
$-\Delta G^\circ$, kJ mole^{-1}	343	364	335	339	54	255	268	305	284
S°, J mole^{-1}K^{-1}	138	163	186	202	83	95	110	119	127

Sodium polonide Na_2Po (f.c.c. lattice of CaF_2 type, a = 7.473 Å, density 4.08 g cm^{-3}) is observed in specimens of polonium which have been stored in Pyrex capillaries[15]. When an alkaline solution of sodium dithionite containing polonium acts on elemental tellurium at 80 °C and is then crystallised at 0 °C, 40% of the polonium passes into the sodium telluride crystals from the solution. The distribution of polonium in the crystal is constant, which shows isomorphous cocrystallisation and confirms the formation of sodium polonide[17].

Beryllium polonide BePo (a black substance, f.c.c. lattice of ZnS type, a = 5.838 Å, density 7.3 g cm^{-3}) is formed when beryllium is heated (600 °C) in polonium vapour. It is volatile at temperatures above 600 °C.[12]

Magnesium polonide MgPo (a black substance, hexagonal lattice of NiAs type, a = 4.345 Å, c = 7.077 Å, density 6.7 g cm^{-3} [12]) is formed when magnesium is heated (350–450 °C) in polonium vapour. It is volatile at 650 °C and is condensed as magnesium polonide[1].

Calcium polonide CaPo (a grey nonmetallic substance, f.c.c. lattice of NaCl type, a = 6.514 Å, density 6.04 g cm^{-3}) is formed when calcium is heated (550 °C) in polonium vapour. It is volatile at temperatures above 600 °C.[12]

Strontium polonide SrPo (grey metallic substance, f.c.c. lattice of NaCl type, a = 6.796 Å, density 6.3 g cm^{-3}) is formed when strontium is heated (500 °C) in polonium vapour. It is volatile at temperatures above 650 °C.[12]

Barium polonide BaPo (grey metallic substance, f.c.c. lattice of NaCl type, a = 7.119 Å, density 6.3 g cm^{-3}) is formed when barium is heated (525 °C) in polonium vapour. It is volatile at temperatures above 650 °C.[12]

Copper polonide is formed by the condensation of polonium vapour on copper. At 400 °C it is unstable and volatilises[12].

Silver polonide Ag_2PO? (orthorhombic, a = 1.327, b = 5.565, c = 1.404 Å) was obtained in 1950 when silver was heated (400 °C) in polonium vapour. It decomposes at

559 °C.[9] Reliable X-ray diffraction results have not been obtained[12].

Gold dissolves polonium vapour at a temperature above 650 °C; the solubility depends on the temperature of the gold and the vapour pressure of the polonium[12].

Zinc polonide ZnPo (f.c.c. lattice of ZnS type, $a = 6.309$ Å, density 7.2 g cm^{-3}) is formed when zinc is heated (550 °C) in polonium vapour. It sublimes at 400 °C. The saturated vapour pressure of zinc polonide at 500 °C is ~13 Pa.[12] It was first obtained in 1947.[15]

Cadmium polonide CdPo (f.c.c. lattice of ZnS type, $a = 6.665$ Å, density 7.2 g cm^{-3}) is formed when cadmium is heated (550 °C) in polonium vapour. It sublimes at 525 °C. The saturated vapour pressure of cadmium polonide at 500 °C is ~13 Pa.[12]

Mercury polonide HgPo (black crystalline substance, f.c.c. lattice of NaCl type, $a = 6.25$ Å, density 11.1 g cm^{-3}) is formed when polonium is heated (200–325 °C) in mercury vapour. It sublimes at 400 °C. The saturated vapour pressure of mercury polonide at 300 °C is ~13 Pa. An amalgam of mercury polonide is formed in the presence of an excess of mercury[12].

2. Compounds of Polonium with the *sp*-Elements

Aluminium in the solid state does not react with polonium vapour[18].

Gallium polonide GaPo (orange metallic substance) is formed when liquid gallium is heated (340–470 °C) in polonium vapour. Under these conditions a stationary concentration of polonium in gallium is reached, 51–52 at.% (the system can be regarded as a solution of polonium in gallium monopolonide, from which volatilisation of polonium starts at 420 °C). The temperature dependence of the dissociation pressure of gallium monopolonide at 605–735 °C and polonium concentrations of 50–39 at.% is described by Eqn.(1) with the coefficients: $A = 7.39 \pm 0.72$ and $B = 5410 \pm 670$. The enthalpy of the process is 103 ± 13 kJ mole^{-1}. At polonium concentrations <39 at.% the vaporisation of polonium depends on its concentration in the melt, which shows the formation of a solution[19].

Indium polonide InPo (bluish metallic substance) is formed when liquid indium is heated (340–490 °C) in polonium vapour. Under these conditions a constant concentration of polonium in indium (50 at.%) is achieved and is retained, but a loss of indium (and polonium correspondingly) from the specimen is noted. After equilibrium had been reached in the ampoule between the polonium condensate and the specimen it was found that the polonium condensate contained ~40 at.% of indium, which corresponds to the composition of indium sesquipolonide In_2Po_3; the latter seems to be volatile at 490 °C. The temperature dependence of the dissociation pressure of indium monopolonide at 425–575 °C and polonium concentrations of 47–41 at.% is described by Eqn.(1): $A = 9.87 \pm 0.16$, $B = 6740 \pm 120$. The enthalpy of the process is 129 ± 3 kJ mole^{-1}. At polonium concentrations <41 at.% the vapour pressure depends on its concentration in the melt, showing the formation of a solution[19].

Carbon does not react with polonium vapour during heating to 700 °C.[12]

Silicon does not react with polonium vapour during heating to 850 °C.[20]

Germanium starts to absorb polonium vapour when it reaches the melting point (940 °C). The amount of polonium absorbed by the germanium depends on the pressure of the polonium vapour. Raising the temperature of the melt to 980 °C leads to release of the polonium. It is assumed that polonium dissolves in the molten germanium[11].

Tin polonide is formed during the heating of molten tin (370–455 °C) in polonium vapour. After a layer of tin polonide (30 μg mm^{-2}) has formed on the surface the reaction rate is reduced by a factor of ~100, despite the temperature being raised to 590 °C, showing the low solubility of tin polonide in tin. Release of polonium from the resulting specimen on heating starts at 670 °C.[20]

Lead polonide PbPo (f.c.c. lattice of NaCl type, $a = 6.59$ Å, density 9.6 g cm^{-3}) is formed when lead is heated (350 °C) in polonium vapour and also appears in the condensate of metallic polonium during its α-decay[12]. The temperature dependence of the vapour pressure of lead polonide at 640–850 °C is described by Eqn.(1) with $A = 9.06 \pm 0.07$, $B = 7270 \pm 80$. The enthalpy of vaporisation is 139 ± 2 kJ mole^{-1}. When more than 3% radiogenic lead has accumulated in polonium the vapour pressure of the latter falls, negative departures from the vapour pressures calculated by Raoult's law being observed[14].

Nitrogen does not react with polonium during heating to 850 °C, since the polonium sublimes in an atmosphere of nitrogen without undergoing any changes[21]. An explosive polonium nitride is probably formed when ammonium hexabromopolonate(IV) is heated (200 °C).[22].

Antimony in the solid state starts to absorb polonium vapour at 340 °C; the process takes place more vigorously at 470–600 °C. When heated in a vacuum, antimony containing 7.5 at.% polonium starts to lose polonium at 420 °C. During vacuum distillation (600 °C) separation of the polonium and antimony is observed as distinct condensation rings, which shows that an alloy is formed[11].

Bismuth starts to absorb polonium vapour at 350 °C; the Bi–Po phase is assigned two structures: rhombohedral ($a = 4.456$–4.503, $c = 3.602$ Å) and f.c.c. ($a = 3.602$ Å), but there are no definite results for this system[18]. Analysis, by pyrochemical and distillation methods, of the polonium isolated from irradiated bismuth shows that a high degree of separation could be achieved but the polonium could not be completely freed from bismuth[7].

Polonium dioxide is formed slowly from the elements without additional heating, but this reaction is most vigorous at 250 °C. The composition of the oxide was determined from the change in oyxgen pressure during the oxidation of polonium[23]. When polonium dioxide is heated its colour changes gradually from pale yellow to reddish brown owing to a change in the structural modifications (yellow: f.c.c. lattice of UO_2 type, $a = 5.626$–5.687 Å; red: tetragonal, $a = 5.44$, $c = 8.34$ Å [23,24]). Polonium dioxide dissociates in a vacuum at 500 °C. The temperature dependence of the saturated vapour pressure of polonium during the dissociation of polonium dioxide (530–595 °C) is described by Eqn.(1) with $A = 21.57 \pm 0.71$, $B = 16\,920 \pm 500$. The enthalpy of the process is 324 ± 10 kJ mole^{-1}.[25]

Polonium dioxide starts to vaporise in oxygen at 690 °C. The temperature dependence of its saturated vapour pressure in oxygen (700–835 °C) is described by Eqn.(1) with $A = 11.13 \pm 0.11$, $B = 10\,070 \pm 150$. The enthalpy of vaporisation is 192 ± 3 kJ mole^{-1}. An oxygen pressure of 8.7 Pa is required to suppress the thermal dissociation of polonium dioxide at 500 °C, but 13 kPa is needed at 790 °C.[26] The coefficients of the temperature dependence of the polonium dioxide vapour pressure in the interval 718–932 °C were determined by a transpiration method: $A = 14.69 \pm 0.46$, $B = 14\,270 \pm 510$. The enthalpy of the process at 825 °C is 273 ± 10 kJ mole^{-1}.[27]

However, perhaps Steinmeyer and Kershner[27] were not observing the dissociation of polonium dioxide, as is shown by the similarity between the enthalpy of vaporisation they obtained[27] and the enthalpy of vaporisation of polonium dioxide with simultaneous flow dissociation (264 kJ mole^{-1}).[26]

Sulphur does not react with polonium. Polonium sulphide PoS is precipitated by hydrogen sulphide from acidic solutions of polonium and decomposes when heated (275 °C) in a vacuum[3].

Fluorine. Volatile polonium hexafluoride could not be obtained by the fluorination of polonium[9]. Metallic polonium is readily soluble in hydrofluoric acid, probably with the formation of fluoro-complexes. A white solid substance (probably polonium tetrafluoride) is formed by the action of dilute hydrofluorice acid on polonium hydroxide or tetrachloride[3,15].

Polonium dichloride and tetrachloride are obtained as a mixture by direct synthesis from the elements at 125–200 °C. At low chlorine pressures and temperatures polonium dichloride is formed preferentially (ruby-red substance, orthorhombic); at high chlorine pressures and temperatures polonium tetrachloride (lemon-yellow substance, monoclinic or triclinic) is formed. Polonium dichloride is more volatile than the tetrachloride therefore they can be separated by sublimation[9]. Polonium tetrachloride in a medium of chlorine melts at 300 °C with the formation of a pale yellow melt; the melt becomes ruby-red at 350 °C, possibly as a result of decomposition to the dichloride, and at 390 °C it boils with the release of purple-brown vapours, which become bluish green above 500 °C, probably owing to a change in the degree of association. In a vacuum, polonium tetrachloride decomposes at 200 °C to the dichloride, which sublimes in an atmosphere of nitrogen at 190 °C with slight decomposition. Polonium dichloride is reduced to the metal during prolonged heating in hydrogen or hydrogen sulphide[28].

Polonium tetrabromide (bright red) is obtained when metallic polonium is heated (250 °C) in bromine vapour (27 kPa) and melts in a medium of bromine at 330 °C with the formation of a dark liquid, which broils at 360 °C. Polonium tetrabromide decomposes to the dibromide in a vacuum at 200 °C and is reduced to the dibromide by hydrogen sulphide (without heating) and sulphur dioxide (on heating). Polonium dibromide (purple-brown) sublimes in a vacuum at 110 °C and melts at 270–280 °C in a sealed volume (nitrogen atmosphere), probably with disproportionation[22].

Polonium tetraiodide (black) is formed when metallic polonium is heated (40 °C) in iodine vapour (133 Pa) and sublimes in an atmosphere of nitrogen at 200 °C with partial decomposition to the metal. Polonium tetraiodide is reduced to the metal when heated in hydrogen sulphide and does not react with ammonia[29]. When heated, polonium tetraiodide dissociates into polonium di-iodide and iodine. The temperature dependence of the vapour pressure of polonium di-iodide at 200–315 °C is described by Eqn.(1): $A = 10.7 \pm 0.71$, $B = 4905 \pm 362$. The enthalpy of the process is 93.7 kJ mole^{-1}.

At an iodine pressure of 4–9 kPa polonium hexaiodide is formed in the condensed phase; it dissociates into polonium tetraiodide and iodine when heated. The temperature dependence of the vapour pressure of polonium tetraiodide at 270–350 °C is described by Eqn.(1) with $A = 12.75 \pm 0.52$, $B = 6533 \pm 300$. The enthalpy of the process is 125 kJ mole^{-1}. At an iodine pressure of 101–147 kPa the temperature dependence of the vapour pressure (probably of polonium hexaiodide) at 300–540 °C is described by Eqn.(1) with $A = 10.94 \pm 0.48$, $B = 6200 \pm 300$. The enthalpy of the process is 119 kJ mole^{-1}.[30]

3. Polonides of the *d*- and *f*-Metals

Lanthanide polonides are obtained by heating these metals in polonium vapour. Table 1 shows that the sesquipolonides Ln_2Po_3 are obtained after 1–10.5 h at 1000 °C; the monopolonides LnPo are formed after 0.75–2 h at lower temperatures.

Table 1. Synthesis temperatures (t) and melting points (M.p.) of the lanthanide polonides (n = atomic radio Po/Ln).

Ln	t, °C	n	M.p., °C	n	M.p., °C
	According to Refs.31 and 32			According to Ref.33, t = 1000 °C	
Sc	—	—	—	1.59	⩾1840
Y	1000	1.03	1700	1.67	⩾1700
La	600	1.0	1457	1.60	1620
Ce	600	1.08	1430	1.57	1540
Pr	600	1.16	1235	1.56 *	1442
Nd	600	1.05	1423	1.62	1460
Pm	850	1.0	1292	—	—
Sm	600	0.87	1474	1.55	1495
Eu	800	0.81	1488	1.55	1670
Gd	600	1.07	1675	1.55	1635
Tb	700	0.82	2000	1.59	⩾1370
Dy	800	1.02	2048	1.57	2330
Ho	700	0.80	1760	1.58	⩾1460
Er	700	0.73	2081	1.59	⩾1435
Tm	800	1.09	2200	1.59	>2040
Yb	800	0.82	2212	1.57	>2400
Lu	1000	1.02	1898	1.56	1898

*t = 900 (Ref.33).

After reaction with polonium the lanthanide powders have become black and finely dispersed[31] and their specific volume is either retained (lanthanum, gadolinium) or doubled (praseodymium, samarium, dysprosium, holmium). The compounds of polonium with cerium or erbium give a dark red luminescence; those with gadolinium or lanthanum give red; with yttrium, orange; with erbium or scandium, yellow; with thulium, pale yellow; and with lutetium, light green; the compounds with terbium, neodymium, and yttrium do not emit light[33]. All the lanthanide polonides melt incongruently with a great loss of polonium. The promethium[32], samarium, terbium, dysprosium, holmium, thulium, ytterbium, lutetium[31], and yttrium[34] monopolonides have NaCl-type f.c.c. lattices, scandium monopolonide an NiAs-type hexagonal lattice[35].

The start of the reaction between polonium vapour and certain lanthanides is observed at lower temperatures (praseodymium 400 °C, gadolinium 500 °C,[11] scandium 850 °C,[36] yttrium 350 °C [37]). The mean reaction rate of polonium

vapour with yttrium at 700 °C is 6.2×10^{-3}, that at 900 °C is 0.13 μg mm^{-2} h^{-1},[38] but the rate is higher (0.34 μg mm^{-2} h^{-1}) during the most vigorous part of the process[39]. The interacetion of the polonium takes place frontally both at the yttrium grain boundaries and within the grains. After metallographic examination a quantitative estimate of the layers of yttrium polonide for yttrium shows the formation of the monopolonide—a black, crumbling and fragmenting substance with a lower microhardness (84–93 kgf mm^{-2}) than yttrium (103–137 kgf mm^{-2}).[38] The temperature dependence of the polonium vapour pressure during the dissociation of yttrium monopolonide (1300–1600 °C) is described by Eqn.(1) with $A = 8.52 \pm 0.13$ and $B = 15\,600 \pm 190$. The heat of dissociation is 298 kJ $mole^{-1}$. The radiogenic lead which accumulates and the care in setting up the experiment [sic] have no significant influence on the results in the determination of the dissociation pressure of yttrium polonide[37]. The temperature dependences of the vapour pressure above scandium, dysprosium, and holmium polonides are described by Eqn.(1) with the coefficients:

Polonide	Sc	Dy	Ho
t, °C	1200—1250	1300—1600	1300—1350
A	6.83	8.90	17.88
B	8695	14509	29543
ΔH kJ $mole^{-1}$	166	277	565

During the vaporisation of polonium from these polonides, the lanthanide is vaporised simultaneously[36]. The great differences in the enthalpies of the processes (ΔH) show that they are different (vaporisation, dissociation, and probably association, respectively).

Mass-spectrometric investigations of the thermal stability and of the vaporisation of lanthanum, neodymium, gadolinium, and dysprosium monopolonides showed that their vaporisation is incongruent, with decomposition into the elements. Appearance of polonium vapour starts to be observed at 1300 °C for lanthanum polonide, at 1100 °C for gadolinium polonide, at 1040 °C for dysprosium polonide, and 850 °C for neodymium polonide[40].

Thorium polonide is formed when thorium is heated (700 °C) in polonium vapour, the mean reaction rate at 700 °C being 3.1×10^{-3} mg mm^{-2} h^{-1}. The interaction takes place at centres[38].

Titanium monopolonide (NiAs-type hexagonal lattice) is formed when titanium is heated (540–550 °C) in polonium vapour; it dissociates at ~700 °C.[41] The loss of polonium from titanium polonide starts at 650 °C; it is almost complete after 8 h at 710 °C.[42]

Zirconium monopolonide (NiAs-type hexagonal lattice) is formed when zirconium is heated (460 °C) in polonium vapour; it dissociates at ~700 °C.[41]

Hafnium monopolonide (NiAs-type hexagonal lattice) is formed when hafnium is heated (380–400 °C) in polonium vapour; it dissociates at ~700 °C.[41] The temperature dependence of the polonium vapour pressure in the dissociation of hafnium polonide (700–900 °C) is described by Eqn.(1) with $A = 5.91 \pm 0.05$ and $B = 6335 \pm 704$. The enthalpy of the process is 121 kJ $mole^{-1}$.[43]

Table 2. Interaction of polonium vapour with the chemical elements.

Li	Be+ 600 >600 1						H— ind	He+					B	C— to 700	N— to 850 ind	O+ 250 500 *d* 0.5	F ind	Ne
Na+ 0.5	Mg+ 350 650 *v* 1												Al— to 700	Si— to 850	P	S— Ind	Cl+ >125 190 0.5; 0.25	Ar
K	Ca+ 550 >600 1	Sc+ 850 1040 *v* 1	Ti+ 540 700 *d* 0.9	V	Cr— to 1000	Mn+ 350 660 *d*	Fe— to 700	Co— to 900	Ni+ 350 >500 *v* 1—2	Cu+ — 400 *d* —	Zn+ 550 400 *v* 1	Ga+ 340 420 *d* 1	Ge+ 940 980 *d* —	As	Se	Br+ 250 200 *d* 0.25	Kr
Rb	Sr+ 500 >650 1	Y+ 350 1300 *d* 1	Zr+ 460 700 *d* 0.95	Nb	Mo— to 1600	Tc— to 1000	Ru— to 1050	Rh	Pd	Ag+ 400 559 *d* 0.5	Cd+ 550 525 *v* 1	In+ 340 420 *d* 1	Sn+ 370 670 *d* —	Sb+ 340 420 *d* —	Te	I+ 40 200 *d* 0.25	Xe
Cs	Ba+ 525 >650 1	La+ 600 1300 *d* 1	Hf+ 380 700 *d* 0.92	Ta— to 1600	W— to 1600	Re— to 1040	Os— to 1050	Ir	Pt+ — >450 *d* 2	Au+ >650 — —	Hg+ 200 400 *v* 1	Tl	Pb+ 350 700 1	Bi+ 350 — —	Po	At	Rn
Fr	Ra	Ac	Ce+ 600 — 1	Pr+ 400 >1050 1	Nd+ 600 850 *d* 1	Pm+ 850 — 1	Sm+ 600 — 1	Eu+ 800 — 1	Gd+ 500 1100 *d* 1	Tb+ 700 — 1	Dy+ 800 1040 *v* 1	Ho+ 700 1300 *v* 1	Er+ 700 — 1	Tm+ 800 — 1	Yb+ 800 — 1	Lu+ 1000 — 1	
Lanthanides																	
Actinides			Th+ 700 — —	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Notes: "+" = reacts with polonium vapour; "–" = does not react; investigated up to t, °C; "ind." = synthesised by an indirect route. In the first row is shown the temperature for the start of synthesis; in the second row, the vaporisation (v) or dissociation (d) temperature; in the third row, the atomic ratio of polonium to the element.

Manganese polonide is formed when manganese is heated (350 °C) in polonium vapour; it dissociates at 660 °C.[11] It was found earlier[9] that a large number of phases is probably formed in the manganese–polonium system, but a single hexagonal lattice is observed.

Nickel polonide is formed when nickel is heated (300 to 600 °C) in polonium vapour. The polonium : nickel atomic ratio in the compound varies between 1 and 2 and the lattice (NiAs-type hexagonal) parameters are variable. Nickel polonide is extremely volatile, it condenses at 500 °C, and its melting point is ~625 °C.[12]

Platinum polonide $PtPo_2$, obtained in 1949, probably has a hexagonal lattice of $Cd(OH)_2$ type and decomposes at 450 to 600 °C.[9]

Tantalum, molybdenum, tungsten (up to 700 °C), *chromium* (up to 1000 °C),[39] *rhenium* (up to 1040 °C),[11] *cobalt* (up to 900 °C), *technetium* (up to 1000 °C), *ruthenium, osmium* (up to 1050 C),[19] and *iron*[3] do not react with polonium vapour when heated to the temperatures stated in parentheses.

Tantalum, molybdenum[36,37] and tungsten[31,33] are used as materials of construction for supporting polonium preparations in high-temperature investigations, therefore it can be considered that these metals do not react with polonium, at least up to 1600 °C.

V. CONCLUSION

The interaction of polonium with most of the chemical elements has now been studied (cf. Table 2). All the alkali and alkaline earth metals investigated, which comprise the *s*-group elements, and the elements of the copper and zinc subgroup react with polonium to form the corresponding polonides.

The *sp*-elements investigated, when in liquid or gaseous state, react with polonium. The exceptions are nitrogen and sulphur probably because of the strong molecular bonds in these elements. The *sp*-metals and semimetals form unstable compounds which decompose rapidly. Beyond the limits of existence of these compounds, solutions are formed. Gaseous oxygen and the gaseous halogens react with metallic polonium to form the corresponding dioxide or halides of various compositions.

The *d*- and *f*-transition metals behave variously in their interaction with polonium vapour. The lanthanides form the most stable compounds. The metals of the IVB subgroup also form compounds, but their thermal stability is lower. The other metals investigated do not react with polonium. Because of the peculiar electronic structures of manganese, nickel, and platinum they are exceptions and do form compounds with polonium.

In most of the investigations the properties of the polonium compounds are compared with the properties of the tellurium compounds and their similarity is reported in accordance with the position of polonium in the Periodic Table.

Despite the considerable number of papers on the thermal reactions of polonium which have now been published there have been relatively few studies of its binary compounds and these are limited by the specific features of this element and the experimental difficulties in carrying out such investigations.

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