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THE SOLUTION CHEMISTRY OF POLONIUM

(Ad Interim Report)

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Date: March 22, 1949

Prepared by: R. G. Yalman

Distributed: JUL 12 1949

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INTRODUCTION

A consideration of the valences of the elements of Group VI-A would indicate that the oxidation states of -2, 2, 4, and 6 might be expected for polonium. From the decrease in stability of the hydrides of the VI-A elements with increase in atomic number, one would be led to predict that the compound H_2Po would be very unstable and that the oxidation state of -2 would not occur in solution. (The gas H_2Po has not been observed although conditions favorable for its formation have been obtained during purification of polonium by reduction of the oxide with hydrogen.) Furthermore, the stability of the oxidation state +6 as well as the stability of the highest oxidation state of a given element decreases as the atomic number increases in Group VI-A and Period VI respectively. For these reasons the oxidation state +6 for polonium would be expected to occur only in a strongly oxidizing medium.

The oxidation state of +4 would be expected to be stable. This follows from Sidgwick's rule that the elements of Period VI belonging to the "A" Groups have a stable valence state which is two less than the maximum expected valence state. According to Sidgwick the stability of the electron pair in the 6s orbital accounts for the formation of dimeric-mercurous mercury as well as the occurrence of Tl^+ , Pb^{++} , Bi^{+++} (and Po^{++++}).

The work discussed below indicates that polonium exists as PoO^{++} in a nonoxidizing (other than oxygen) or reducing medium. In a reducing system such as Hg, Hg_2Cl_2 , and As, As^{+++} polonium probably exists as the ion Po^{++} .

It should be kept in mind that the determination of the valence of polonium in a well defined system is exceedingly difficult. Most physical-chemical methods used to study the chemistry of an element require a sufficiently large amount of polonium (10^{-4} molar) that secondary chemical reactions produced by the interaction of the alpha particles with the solvent may obscure the chemical properties of polonium itself. When small quantities of polonium (10^{-10} molar) are used, adsorption on the walls of the container and the formation of radiocolloids on dust or other slightly soluble particles or at liquid interphases may again obscure the chemistry of the ion.

Valence Studies

1. Polarographic Method - This method, which can be used as the general term for the determination of deposition potential on an electrode by noting the change in current as a function of the applied voltage, was first applied to the determination of the valence of polonium in 1944 by Haring. In a supplementary report in July, 1945,²⁸ Haring felt that the results of his experiments indicated that in 1.5 N nitric acid 2 was the most probable oxidation state and that there were no oxy-ions present (migration experiments) also indicate that there

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are no oxy-ions present in this strength acid). On the other hand, Haring preferred the valence of 4 in 1.5 N sodium hydroxide and hydrochloric acid. It was realized, however, that the formation of ozone, hydrogen peroxide and chlorine in the various solutions may have obscured the actual deposition potential of polonium. Haring's experiments were not able to be reproduced with satisfactory precision either by himself or following workers. At the present time, W. Power of the General Chemistry Research Group is using an ionization chamber to detect the deposition potential of polonium.

2. Migration Experiments - This work, originally begun by Fainberg under Haring's direction, has been carried on by Barth and Staniforth.² Most of the work has concentrated upon the determination of the charge of the polonium ions in various solutions. The results indicate that polonium forms a complex with nitrate and sulfate anions as well as with chloride, citrate, etc. ions at as low an acidity as 0.05 molar. This is in agreement with the ease of formation of chloro complexes to be expected from the work of the Production Research Group³ on the formation of the silver, copper, and bismuth chloro complexes. It is surprising, however, to find the formation of the nitrate complex to occur so readily. Few nitrate complexes are known and they are always associated with ions of high charge such as cerium, bismuth, uranium, etc. This would indicate that polonium has an oxidation state of three or higher.

Barth⁴ has also carried out experiments to show the effect of increasing chloride ion concentration at constant H^+ concentration. Conversely, these experiments show that the formation of the chloro complex of polonium is a function of H^+ concentration. This indicates that polonium does exist as an oxy-ion in a noncomplexing medium.

3. Equilibrium Studies - Kirby⁵ indicated a method for determining the valence of polonium by studying its equilibrium concentration in two reducing systems whose oxidation-reduction potentials were known or could be determined. Later Kirby calculated⁶ a valence of 1.85 (2) using the two systems Hg , Hg_2Cl_2 and As , As^{+++} in hydrochloric acid. Fernelius⁷ showed that Hg_2Cl_2 will reduce polonium even in 12 N hydrochloric acid. An independent study of the reducing effect of arsenious ion has not been made. Kirby finds that the potential of the arsenic system is not well defined and that no two samples of arsenic give the same oxidation-reduction potentials. His latest data for the arsenic-arsenious ion potentials would give polonium the valence of 1.

These experiments do indicate that in hydrochloric acid solution in the presence of certain reducing agents, polonium can exist in an oxidation state of either 1 or 2.

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4. Other Experiments - Martin^{8,9} has shown that the very stable yellow oxide, PoO_2 , exists in the dry state. Joy,¹⁰ in the same group, obtained a yellow tetrachloride of polonium and a red-orange dichloride in the dry state. Joy has also prepared polonium tetrabromide.³⁰

Solutions of polonium in hydrochloric acid are known to be yellow precipitates of polonium and are obtained by neutralizing nitric acid solutions with ammonium hydroxide. A sulfuric acid solution, however, gave a pink residue on repeated evaporation to dryness²⁶ and Wehrmann¹¹ observed a pink precipitate while trying to determine the solubility of polonium in sulfuric acid. Payne reported¹² that during the reduction of polonium in hydrochloric acid by slowly adding stannous chloride a transient violet color was obtained.

These observations indicate that there are two different valences of polonium in solution, but they give no definite information as to what the oxidation states are.

During the early part of this project many experiments were carried out with preformed scavengers as well as with scavengers in situ. None of these experiments were carried out with the view of determining whether or not isomorphous crystals were obtained with the host compound. Information was obtained on the relative solubility of some of the polonium compounds (see below) but nothing can be said about the oxidation state of polonium from these experiments.

Complex Compounds

A great deal of information has been obtained about the formation of complexes of polonium. Many of the experiments, such as those carried out by studying the extraction of polonium by nonaqueous solvents in the presence of a complexing agent, can be regarded as being very incomplete. Definite information is listed below:

1. Fluoro Complexes - In view of the low solubility of thorium tetrafluoride and bismuth trifluoride, the high solubility of polonium in hydrofluoric acid solutions as reported by both the Neutron Source Group¹³ and the Electrodeposition Group¹⁴ indicates that polonium forms a very strong fluoro complex.

2. Chloro Complexes - The existence of chloro complexes was early recognized from the change in deposition rate of polonium as a function of hydrochloric acid concentration.¹⁵ Migration experiments¹⁶ also proved that the chloro complex occurs and that it is negatively charged. Scavenging experiments¹⁷ with LaF_3 as a function of hydrochloric acid concentration also indicate that polonium forms a chloro complex.

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3. Nitrato Complex - The migration experiments of Barth¹ prove that polonium forms a negatively charged nitrato complex.

4. Oxalato Complex - Experiments carried out by the Bismuth-Tellurium Process Group in April, 1945³² indicate that polonium may form an oxalato complex. The data are not conclusive nor were the experiments very exhaustive. Data of the Electrochemical Deposition Group in May, 1945³¹ indicate that oxalic and tartaric acid both form very strong complexes with polonium.

5. Citrate Complex - Fainberg's migration experiments² carried out at a pH of 2-6 using a citrate buffer indicate that citrate forms a strong complex with polonium. The data are still not conclusive.

6. Phthalate Complex - Fainberg² also used phthalate buffers and said that in the region pH 3-6 phthalate partially complexes. At the same time he observed that all phthalate solutions turn yellow and that the intensity of the color is a function of the polonium concentration.

7. Sulfato Complex - Barth's¹⁸ experiments indicate that negatively charged sulfato complexes also form.

8. 8-OH Quinoline - The Bismuth-Tellurium Process Group²⁵ reported that polonium adsorbed on a column of 8-OH quinoline could only be removed by completely dissolving the 8-OH quinoline. This is a disagreement with extraction experiments of Marchi²¹ which indicate that no complexing is obtained with this substance.

9. Dithizonate Complexes - Reports of the Bismuth Research Group¹⁹ indicate that polonium can be extracted from 6 N hydrochloric acid by shaking with carbon tetrachloride in the presence of dithizone. Experiments by E. Power in the Production Research Group at the present time indicate that only partial complexing occurs. Summary of the above ions appear in Table I.

Soluble Compounds

There is very little information about soluble polonium compounds. No group has yet devoted its time to this subject. Experiments by Joy of the Gamma Scale Research Group at the present time with polonium bromide formed in the dry state indicate that the bromide is completely hydrolyzed in neutral solutions to give what is probably a hydrous oxide.

Solubility of Polonium Compounds

Because no investigation has yet been made to determine the constitution of solid phases in polonium solutions, the solubility data indicate only the

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Table I

<u>TYPE OF ION</u>	<u>TYPE OF EVIDENCE</u>	<u>VALIDITY OF EVIDENCE</u>	<u>REFERENCE</u>
Fluoro Complex	Solubility	Suggestive	3
Chloro Complex	Electrodeposition	Suggestive	15
	Migration	Conclusive	16
Nitrato Complex	Migration	Conclusive	1
Oxalato Complex	Electrodeposition	Suggestive	
Citrate Complex	Migration	Suggestive	2
Phthalate Complex	Migration	Suggestive	2
Sulfato	Migration	Suggestive	18
8-OH Quinoline Complex or p.p.t.	Extraction	Negative	27
	Absorption	Suggestive	25
Dithizonate Complex	Extraction from HCl solutions	Suggestive	19
Oxy-ions	Migration	Conclusive	4
<u>COMPOUND</u>			
PoO ₂	Preparation	Conclusive	8,9
PoCl ₄	Preparation	Conclusive	10
PoCl ₂	Preparation	Conclusive	10
PoBr ₄	Preparation	Conclusive	30

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relative solubility of polonium. Aside from the problem of the formation of the least soluble solid phase, all solubility experiments are subject to the difficulties inherent in the radioactive nature of polonium itself. The formation of alpha particles may: (1) produce secondary chemical reactions which may change the nature of the solution during the period necessary to make the solubility measurement; (2) cause the solution to heat, and (3) cause bubbling which makes analysis of the solutions difficult.

Some preliminary experiments have been carried out¹³ which indicate a high solubility in hydrofluoric and hydrobromic acids and a very slight solubility in liquid ammonia (April, 1948). Experiments by the Electrodeposition Group in March, 1948 indicate that polonium fluoride is much more soluble than bismuth fluoride in strong hydrofluoric acid solutions. This is indicative again of the formation of fluoro complexes since in moderately acid solutions LaF_3 is a good scavenger.

Barth (present work reported in General Chemistry Reports) and Fainberg² show from diffusion experiments that polonium is very slightly soluble in solutions of pH 4-10. In solutions less than pH 3 or greater than pH 10 the solubility increases.

Haring²⁰ found that the solubility of polonium in 1.5 N sodium hydroxide is 3×10^{-4} molar. This of the same order of magnitude as the solubility of polonium in nitric acid solutions reported by Staniforth²¹ and Orban.²²

The set of solubility experiments carried out by Staniforth was the only attempt made to allow the experiments to extend over a sufficiently long period of time for equilibrium with the least soluble solid phase to be established. These solutions were allowed to stand for three months. He reports a solubility of $\approx 1 \times 10^{-4}$ moles/liter at 28.0°C . The results of Orban's experiments²² using the same acid strength and the same temperature are nearly three times as great. Furthermore, Orban observed that the solubility in his strong acid solutions decreased with time and he extrapolated his values to zero time. If he had extrapolated his values to infinite time, his results would have been similar to those of Staniforth's. Orban suggests²³ that the observed change in solubility with time may have corresponded to the slow transformation of a slightly soluble hydrous oxide to a less soluble basic nitrate.

Insoluble Compounds

Except for the oxide or hydrous oxide there is very little known about other slightly soluble compounds of polonium. According to the Fundamental Research Progress Report for April, 1946, the solubility of the sulfide is of the order of 10^{-6} moles/liter. An insoluble phosphate is probably formed when a solution of polonium in phosphoric acid is diluted, and a basic carbonate is

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probably formed when nitric acid solutions of polonium are neutralized with sodium carbonate. Scavenging experiments indicate that the sulfide, fluoride, dichromate, tellurate, and basic chloride form slightly soluble compounds. (Fajan's adsorption rule states that the adsorption of an ion will be greater the less soluble ^{is} the compound formed between that ion and the ion of opposite sign of the host compound.) The very effective scavenging of polonium by lead dioxide²⁴ in lead nitrate solutions may be due to an isomorphous crystal structure of lead dioxide and polonium dioxide.

Action of Reducing Agents

The following refers to 3-6 N hydrochloric acid solutions containing a maximum of 10^{-3} molar polonium.

1. Metals - Much work has been done in determining the nobility of polonium by electrochemical deposition on less noble metals. Thus, bismuth and silver have been used as scrubbers to concentrate polonium (this is in agreement with the electrodeposition potential of polonium which is more positive than bismuth and nearly the same as that of silver). All metals higher in the electromotive series than bismuth are capable of reducing polonium to the metal. Tellurium does not reduce polonium.

2. Reducing Agents

<u>Reagent</u>	<u>Intermediate Oxidation State</u>	<u>Formation of Metal</u>
Sn^{++}	Transient Violet	+
SO_2	- ?	-
$\text{H}_2\text{S}_2\text{O}_4$	- ?	+
H_3PO_2	- ?	+
Hg_2Cl_2	+	
As^{+++}	+	
H_2N_2	- ?	-
Ti^{+++}	- ?	+
HCHO	- ?	-
HCOOH	- ?	-

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Oxidation

At present the only information as to the oxidation of polonium compounds or ions is that of the metal itself. Due to the ionizing effect of alpha particles in the presence of other substances, polonium metal is readily oxidized to apparently a higher oxidation state in the presence of oxygen, water, etc., even at room temperature. Moisture apparently catalyzes the air oxidation at room temperature.²⁵ In solution the presence of solvents such as hydrochloric acid and sodium hydroxide increases the rate of oxidation by solution of the surface film. The presence of hydrogen peroxide, nitric acid, and other oxidizing agents also increases the rate of oxidation of the metal. In all cases the metal is apparently oxidized to a valence of 4.

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