

are produced from the mixed hydrochloric acid-selenic acid solution by treatment with the corresponding carbonate, when the mixed selenate and chloride is formed. Inasmuch as the chlorides of these metals are soluble in alcohol or acetone, the mixed salts can be extracted with either of these solvents and finally obtained in fairly pure condition. The selenates can then be dissolved in water, reprecipitated by alcohol or acetone and obtained in a high degree of purity.

Summary

A new procedure is given for the preparation of selenic acid and of certain selenates.

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SELENIC ACID AND THE SELENATES

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That certain tellurites absorb oxygen and form tellurates when heated in the air to 400–500° has been shown by one of us.¹ It has now been found that many of the selenites take up oxygen from the air when heated to high temperatures and yield selenates.

From a number of these selenates, selenic acid can be economically produced.

Selenates of the Alkali Metals

Potassium Selenate.—Potassium selenite is a colorless hygroscopic salt most readily formed by bringing together in aqueous solution molecular quantities of potassium carbonate and selenium dioxide. The dried salt when heated to 875° is converted to selenate. With a few tenths of a gram of salt the complete oxidation requires only a few minutes, while with larger quantities the time required for complete oxidation is proportional to the surface of the selenite exposed to the air.

Instead of starting with pure potassium selenite, molecular quantities of potassium selenite and selenium dioxide can be heated to a temperature just below that of the melting point of potassium carbonate (896°). Under these conditions, the mixture must be heated slowly or selenium dioxide volatilizes before it reacts with the potassium carbonate. The system can be alkaline with excess of potassium carbonate, or it can be acid with excess of selenium dioxide, or it can have equimolecular ratios of potassium carbonate and selenium dioxide, and when heated to 875° the conversion of selenite to selenate is complete.

¹ Lenher and Wolesensky, *THIS JOURNAL*, **35**, 718 (1913).

A simpler procedure is to roast a mixture of molecular quantities of potassium carbonate with elementary selenium, beginning at a low temperature, when the selenium oxidizes to the dioxide which in turn liberates carbon dioxide from potassium carbonate forming the selenite, and this takes up oxygen from the air to form the selenate.

Sodium Selenate.—Sodium selenite when heated to $700\text{--}725^\circ$ in the air is converted into selenate. Dry sodium carbonate and selenium dioxide as well as a mixture of sodium carbonate and elementary selenium when heated, also form the selenate.

Lithium, Rubidium and Cesium Selenates.—The selenites of these rarer alkalies, as well as the mixtures of the carbonates with selenium dioxide or elementary selenium, when heated in the air yield selenates. The temperature of oxidation of the lithium salt is 720° , rubidium selenite is transformed to selenate at 400° , while cesium selenite changes to selenate at 450° .

Barium Selenate.—Barium selenite when heated in the air is oxidized to selenate at a temperature of $700\text{--}750^\circ$. In small quantities, the reaction proceeds rapidly, but when large amounts are used the material must be repeatedly stirred, inasmuch as the selenate forms a protecting layer around the selenite, which greatly delays the oxidation. When a mixture of barium carbonate and selenium dioxide or elementary selenium is roasted in the air, barium selenate is formed.

Strontium selenite as well as the carbonate mixed with either selenium dioxide or elementary selenium gives selenate at 800° , while calcium selenite is only incompletely oxidized at any temperature.

The selenites of magnesium, manganese, nickel, cadmium, silver, copper, zirconium, aluminum, zinc, iron, mercury, stannic tin and lead give either no selenate or a very low yield of selenate.

Preparation of Selenic Acid from the Selenates

Barium selenate, when suspended in water and treated with dil. sulfuric acid, gives selenic acid and insoluble barium sulfate. Since potassium selenate can be produced with great ease, it is conveniently used in the preparation of selenic acid. Perchloric acid forms the insoluble salt, which is then filtered off through an asbestos filter, after which evaporation under diminished pressure removes the excess of perchloric acid. Selenic acid of a high degree of purity can be obtained in this manner.

Summary

1. It has been shown that certain of the selenites when roasted in the air are converted into selenates.
2. A number of the carbonates of the metals mixed with selenium dioxide or elementary selenium will, when roasted, give selenates.
3. From the selenates thus prepared selenic acid is readily produced by precipitation methods.