[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PREPARATION OF SELENIC ACID AND OF CERTAIN SELENATES

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The methods which have been proposed for the preparation of selenic acid are either very complicated or the final product has been variously criticized[1] from the standpoint of purity.

The use of chlorine or bromine as oxidizing agent in many of the methods for the production of selenic acid either directly or incidentally adds halogen acid to the final selenic acid. Since hydrochloric or hydrobromic acid reduces selenic to selenious acid, they must be removed. This can be accomplished by the addition of either silver carbonate or silver selenate.

Metzner,[2] in studying the reaction of Rose[3] between selenious acid and chlorine, showed that the reaction is exothermic and, as well, that it takes place best in a 10% solution at the ordinary temperature. The hydrochloric acid formed cannot be removed by heat without reduction of the selenic acid. A simple procedure is to add silver carbonate in quantity just sufficient to precipitate the halogen. This is experimentally difficult to accomplish; hence, a slight excess is used, which in turn yields silver selenate which is soluble in the selenic acid. The silver is subsequently removed by hydrogen sulfide. Pure silver selenate itself can be used to remove hydrochloric acid from the mixed acids. The excess of silver is removed by hydrogen sulfide. Silver selenate is prepared by the double decomposition of calcium selenate and silver nitrate. It is sparingly soluble in water, its solubility at 20° being 1.182 g. per liter.

Concentration of the acid is accomplished on the water-bath to about 80%. A higher concentration can be effected under diminished pressure.

Preparation of Certain Selenates.—From the mixed acid obtained by the direct chlorination of selenious acid a number of the selenates can be prepared by neutralization with the carbonate of a metal. With lead, barium, strontium or calcium the resulting selenates, being sparingly soluble in water, are obtained as precipitates.

From the calcium salt the selenates of the alkalies and ammonia are obtained by double decomposition.

The selenates of copper, cadmium, zinc, cobalt, nickel and manganese

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[1] Mitscherlich, *Pogg. Ann.*, **9**, 623 (1827). Morris, *Trans. Wisconsin Acad. Sci.*, **19**, 1, 389 (1918). Dennis and Koller, THIS JOURNAL, **41**, 949 (1919). Stone, *ibid.*, **45**, 29 (1923). Diemer and Lenher, *J. Phys. Chem.*, **13**, 505 (1909). Benger, THIS JOURNAL, **39**, 2171 (1917).

[2] Metzner, *Compt. rend.*, **127**, 54 (1898).

[3] Rose, *Pogg. Ann.*, **45**, 337 (1838).

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.

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[1] Lenher and Wolesensky, This Journal, **35**, 718 (1913).