chloric acid solution by sulfur dioxide. The temperature of the precipitating solutions should not exceed 30°.

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THE PREPARATION OF SELENIUM MONOCHLORIDE AND MONOBROMIDE

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Selenium Monochloride.—The earliest record we have of this compound is its preparation by Berzelius[1] from selenium and chlorine. Divers and Shimose[2] prepared the compound by the action of hydrogen chloride gas on a solution of selenium in fuming sulfuric acid. A number of others have used various procedures, as Baudrimont[3] who caused phosphorus chloride to act on selenium, and on the selenide of phosphorus and antimony, Michaelis[4] who formed it from selenium dioxide and phosphorus pentachloride, Rathke[5] who replaced the sulfur in sulfur monochloride by selenium, Ramsay[6] who brought the tetrachloride together with elementary selenium, and Lenher[7] who showed the monochloride to be produced when the metals in general react with selenium oxychloride.

One of the outstanding properties of selenium monochloride, which is a common property of the chlorides of the non-metals, is its decomposition by water, to form, in this case, selenium, selenious and hydrochloric acids. It has hitherto been thought that in the formation of such substances water should not be present. On the contrary, both the monochloride and monobromide of selenium can be formed in the presence of as high amounts of water as 70%.

1. When a solution of selenium dioxide in concd. hydrochloric acid (36–37%) is treated with sulfur dioxide gas a yellow color is produced when a relatively small amount of selenium dioxide is used, but when a high concentration of selenium dioxide is used, the red, oily liquid, Se_2Cl_2, separates.

2. When selenium dioxide is dissolved in concd. hydrochloric acid and elementary selenium is added large quantities of the monochloride are formed and separate as the red-brown oil.

3. When selenium dioxide and selenium are suspended in either carbon tetrachloride or carbon disulfide and treated with hydrogen chloride,

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[1] Berzelius, *Ann. chim. phys.*, **9**, 225 (1818).

[2] Divers and Shimose, *Ber.*, **17**, 866 (1884).

[3] Baudrimont, *Ann. chim. phys.*, [4] **2**, 5 (1864).

[4] Michaelis, *Jena. Z.*, **6**, 93 (1870).

[5] Rathke, *Ann.*, **152**, 181 (1869).

[6] Ramsay, *Bull. soc. chim.*, [3] **3**, 783 (1890).

[7] Lenher, THIS JOURNAL, **43**, 29 (1921).

selenium monochloride is produced and passes into solution in the carbon tetrachloride or disulfide.

4. When a solution of selenium in selenium oxychloride is treated with hydrogen chloride, selenium monochloride separates.

5. When a mixture of selenium and selenium dioxide is added to concd. sulfuric acid and concd. hydrochloric acid is added the monochloride is produced.

6. The addition of sulfuric acid to a solution of selenium dioxide in hydrochloric acid precipitates white selenium tetrachloride which will react with elementary selenium if added to the mixture, forming the monochloride.

7. When a saturated solution of selenium dioxide in concd. hydrochloric acid (36–37%) is treated with sulfur dioxide, a small quantity of the monochloride is formed, but when this mixture is treated with concd. sulfuric acid, a large quantity of the monochloride appears.

8. The use of phosphorus pentoxide as a dehydrating agent is also possible, but phosphorus pentoxide in this reaction possesses no advantages over sulfuric acid nor do such dehydrating agents as calcium chloride and zinc chloride.

A typical procedure for the preparation of large quantities of the monochloride is as follows.

To a solution of 115 g. of freshly sublimed selenium dioxide in 500 cc. of concd. hydrochloric acid (36–37%) is added 235 g. of elementary selenium. Concd. sulfuric acid is introduced drop by drop from a dropping funnel. The reaction begins at once. The addition of the sulfuric acid is continued until there is no further liberation of hydrochloric acid. The mixture is then allowed to cool, when the red layer of monochloride can be separated from the mixture by means of a separatory funnel. In order to purify the product, it may be washed several times with concd. sulfuric acid, or it may be dissolved in fuming sulfuric acid and reprecipitated by hydrogen chloride. Since selenium monochloride has such a low solubility in concd. sulfuric acid, the yield is about 90%. The resulting product is a red-brown, oily liquid boiling at 130° and possessing great chemical activity.

Selenium Monobromide.—This substance is produced in the same general way as the monochloride. Hydrobromic acid is ordinarily not so common a reagent as hydrochloric acid. The acid can, however, be prepared by the action of a sulfur dioxide solution on bromine and then used in this mixture to form the monobromide.

Bromine (135 cc.) is gradually added by means of a separatory funnel to a solution of sulfur dioxide in ice water, sulfur dioxide being continuously passed into the solution. When the solution, which is a mixture of sulfuric and hydrobromic acids, is colorless it can be used directly for the preparation of the monobromide. Now, when 115 g. of selenium dioxide is added, followed by 235 g. of elementary selenium, the reaction starts at once with the production of the monobromide. About a liter of concd. sulfuric acid is added and as the mixture cools the monobromide separates as a dark red oil, which may be further purified, if desired, by washing with concd. sulfuric acid. The yield is about 90%.

Summary

A number of new methods for the preparation of selenium monochloride and selenium monobromide are given in this paper.

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THE SEPARATION AND DETERMINATION OF THE ALKALI METALS USING PERCHLORIC ACID. II. THE PRECISE ESTIMATION OF THE INSOLUBLE ALKALI METAL PERCHLORATES

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The separation of potassium, rubidium and cesium from sodium and lithium by the perchloric acid method is dependent upon the extraction of the latter two perchlorates from the former by means of an organic solvent. The choice of the most suitable solvent was the subject of the first paper of this series. The present paper has for its object the establishment of a correct procedure governing the separation and weighing of the insoluble perchlorates of this group. The procedures previously described are shown to have appeared exact as the result of a fortuitous compensation of errors.

The Dehydration Temperature of Potassium Perchlorate

Four weighed samples of potassium chloride (a foreign stock guaranteed to be 100.00%) were dissolved in hot water in weighed platinum crucibles. One cc. of pure 72.5% perchloric acid was then added to each, the resulting solutions were evaporated to fumes and heated until the large excess of acid was completely removed. The potassium perchlorate thus obtained was dissolved by the addition of hot water and again precipitated by evaporation to dryness on the hot-plate, then baked for two hours at approximately 140°. The crucible and contents were then dried for three hours at 140–150°, cooled in a desiccator and weighed.

The samples were next dried for one hour at 250° in a muffle, cooled as before and weighed. They were then dried for 15 minutes at 350°, cooled and reweighed. Finally the samples thus treated were dried to constant weight at 350°. The results of the experiments are listed in Table I.

The potassium chloride used for the determinations of Table I had been previously ground and ignited for several hours at 500°. The samples were weighed from a very small weighing bottle directly into the platinum crucibles previously cleaned and ignited. All weighings were made using a No. 10 Troemner balance and weights calibrated at the Bureau of Standards. The conversion factor of potassium perchlorate to potassium