THE PREPARATION OF SELENIC ACID

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Selenic acid was first prepared by Mitscherlich in 1827. He decomposed lead selenate suspended in water, by hydrogen sulfide. In 1830 Berzelius suggested the oxidation of an alkali selenite by means of chlorine, for the preparation of selenic acid. In 1834 Ballard used hypochlorous acid for the oxidation. In 1840, Rose suspended selenium in water and passed in chlorine which oxidized it to selenic acid. Wohlwill in 1860 used potassium dichromate, lead dioxide, and manganese dioxide as oxidizing agents in the preparation of the acid. In the same year von Hauer prepared selenic acid by the decomposition of cadmium selenate with hydrogen sulfide. Nine years later Thomsen made what was claimed to be very pure selenic acid by treatment of silver selenite with bromine.

Thomsen took no steps to remove any selenious acid which might be present, and from the present work it seems that his preparation could not have been quite pure.

Von Gerichten, working in 1873, used a method very similar to that of Mitscherlich. In 1899 Cammeron and Macallan published their work on the concentration of selenic acid and showed that it could be obtained in the anhydrous condition. They constructed tables of the specific gravity and percentage strength of the acid, which were very good for the range covered, but which were later made complete by the work of Lember and Diemer.

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1 Ann Ph Ch Pogg 9, 623.
2 Berzelius Lehrbuch Ed III, s 16 der 4ten deutschen Auflage.
3 Ann Ph Ch Pogg 57, 225.
4 Ann Ph Ch Pogg, 45, 337.
5 Ann Chem Pharm Lieb 114, 169.
6 Sitz Akad Wein 59, 329.
7 Ber 2, 598.
10 Jr Phsic Chem 13, 505.

24—S. A. L.
In 1882, Mulpert\(^1\) made selenic acid by the oxidation of selenium with ozone. Metzner\(^2\) in 1898, showed that the reaction of chlorine on selenious acid is exothermic. The chlorine works best with about a ten percent solution of the dioxide. When chlorine is in excess the oxidation is complete, but if bromine is substituted in the reaction more heat is given off, and it requires somewhat of an excess of bromine to complete the reaction. The theoretical amount of bromine shows a red color in the solution, but all the selenium dioxide is not oxidized. Metzner further proposed a method of oxidation by permanganic acid, which he states gives good selenic acid. Another method of his depends on the electrolytic decomposition of copper selenate.

Other methods that have appeared depend either on the oxidation of selenious acid \(^3\)\(^4\), a selenite\(^5\), or selenate\(^6\) by means of the electric current, or the oxidation of selenious acid with hydrogen peroxide.\(^7\)

From the foregoing it appears that many methods for the preparation of selenic acid have been described; several of which seem to be fairly simple. Actually, however, many of the essential details are lacking, even though upon them depends the success of the method.

The method of J. Thomsen will yield excellent selenic acid under correct conditions, but it was only through repeated failures to obtain a stable preparation of the acid that these conditions were recognized and the causes of failure eliminated.

The main points to be observed are as follows: The preparation of silver selenite requires pure selenium dioxide. The bromine used to convert the silver selenite into selenic acid must be free from reducing substances. All dust must be rigorously excluded throughout the preparation.

\(^1\) C. R. 94, 1186.
\(^2\) C. R. 127, 54.
\(^3\) Chem Ztg 31, 360.
\(^5\) Ber 36, 4252.
\(^6\) Jr Am Chem Soc 30, 1374.
\(^7\) Ber 48, 1154.
Selenium dioxide of excellent quality is prepared in the following manner: Selenium is dissolved in nitric acid, specific gravity 1.2, and the solution evaporated to dryness. The impure dioxide resulting is heated to a temperature just below that at which it will sublimate in order to remove the excess of nitric acid. After the dioxide is dissolved in water, barium hydroxide is added until no further precipitate of barium sulfate forms. This is filtered off, and the solution again evaporated to dryness.

Selenium dioxide does not melt under atmospheric pressure, but may be sublimed as pure white needle shaped crystals, which are commonly several inches long.

During the sublimation very small amounts of impurities such as dust from the air, or lint from the towels used in cleaning the apparatus will reduce the selenium to its red form, thus contaminating the sublimate. Frequently the crystals are half red and half white so that a separation is impossible.

In case the quantity of impurities is such that a white sublimate can not be obtained easily, the selenium should be further purified in the following manner. The solution of the dioxide in water is acidified with hydrochloric acid, warmed, and treated with sulphur dioxide. The precipitated selenium is filtered on an asbestos felt, washed with water, dissolved in nitric acid, and treated as previously described. When free from reducing materials the selenium dioxide sublimes white.

A convenient apparatus for sublimation consists of an evaporating dish in which are placed three funnels fitting one inside the other. Slow sublimation is most efficient. Sublimation in a current of oxygen has been recommended, but this is not necessary.

The bromine on the American market was found to contain impurities of a reducing character which make it absolutely unfit for use in the preparation of selenic acid without careful purification. Bromine is such an unusual source of reducing materials that its quality may easily escape question. The stability of the selenic acid, however, is largely dependent on the purity of the bromine.

The interfering substances are removed from the bromine by treatment with a mixture of chromic and sulfuric acids and by subsequent distillation. The bromine, after standing with the acids for several days or until the evolution of carbon di-
oxide has ceased, is separated from the green residue that forms, and is distilled with fresh portions of the chromic and sulfuric acids. Only small amounts of the acids should be present during the distillation, as large quantities cause dangerous bumping. The still must be so arranged that no material but glass comes in contact with the bromine. Only the middle portion of the distillate is collected for use, and must be free from chromium and sulfuric acid. The presence may be detected by dissolving a few cubic centimeters of the bromine in dilute ammonia, boiling to precipitate any chromium present in the reduced condition, which would appear as hydrated chromic oxide, making acid with acetic acid, and adding barium chloride to show the presence of sulfuric acid or chromium as chromate.

Having obtained pure selenium dioxide and pure bromine, the next step is the formation of silver selenite. All glass coming in contact with the preparation is cleaned with a mixture of chromic and sulfuric acids, and the water used is distilled from potassium permanganate and sodium hydroxide.

A ten percent aqueous solution of the dioxide is treated with a slight excess of silver nitrate solution. Silver selenite precipitates as a white crystalline salt. This is washed by decantation until it is absolutely free from silver nitrate and nitric acid. If nitric acid is allowed to remain in the silver selenite, it decomposes the hydrogen sulfide used later thus contaminating the selenic acid.

The silver selenite is suspended in water, and bromine added in small portions with vigorous shaking after each addition, until the red color of the solution indicates that an excess of bromine has been added. The solution is then placed on a steam bath for at least twelve hours to complete the oxidation and coagulate the precipitate. During all these operations care must be taken to exclude dust. The silver bromide is filtered off on well cleaned glass wool.

The filtrate is concentrated by distilling off the bromine and water under reduced pressure. The distillation apparatus is so arranged that no corks, or rubber stoppers, come in contact with the acid. A Jena glass retort, sealed to a water jacketed condenser which in turn is connected to a suction flask and pump, serves the purpose very well. A few glass beads placed in the retort prevent bumping.
The concentrated acid is drawn from the retort into a large wash bottle, care being taken to avoid drawing air through the solution. Well washed hydrogen sulfide is next passed through the acid until precipitation is complete, and the precipitate has become flocculent. The excess of hydrogen sulfide is then blown out by a stream of air from which all dust has been removed by bubbling through concentrated sulfuric acid.

The hydrogen sulfide serves to remove any selenious acid which may be present, decomposing it with the precipitation of sulphur and selenium. This precipitate is removed by filtering through an asbestos felt.

It is frequently stated that selenic acid is not acted upon by hydrogen sulfide, but after each concentration of the acid, hydrogen sulfide produces a light precipitate. That this is not due to the decomposition of selenic acid by heat is shown in the following manner: Selenic acid free from selenious acid and giving no precipitate with hydrogen sulfide is concentrated at room temperature in a vacuum desiccator over sulfuric acid or sodium hydroxide. This acid as it becomes more concentrated will give a precipitate with hydrogen sulfide.

By these experiments it is shown that the method of J. Thomsen will give excellent selenic acid if particular attention is given to certain details of the process.