# ART. XLIII.—*The Reduction of Selenic Acid by Hydrochloric Acid;* by F. A. GOOCH and P. S. EVANS, JR.

[Contributions from the Kent Chemical Laboratory of Yale College—XLV.]

IT has long been known that selenic acid is reducible by hydrochloric acid with evolution of chlorine, but the reaction was regarded as more or less uncertain until Petterson showed* that conditions of action may be secured under which the reduction proceeds so regularly that the chlorine evolved may be estimated iodometrically and taken as the measure of the selenic acid originally present, or of the selenious acid produced. According to this method of determination, it is only necessary to boil a solution of selenic acid in hydrochloric acid of moderate concentration, and if the solution is not too dilute the reduction is obtained in a few moments. Petterson did not, however, fix with exactness the limits of dilution within which a successful determination of the selenic acid may be expected. The object of this paper is to record the results which we have obtained in studying more closely the conditions necessary to an accurate and rapid reduction. We have used in our experiments solutions of selenic acid prepared by oxidizing pure, white, resublimed selenium dioxide according to the method laid down in a previous paper from this laboratory† for the quantitative determination of that substance. A portion of the crystalline oxide, approximately two grams, was carefully weighed, dissolved in 120 $cm^3$ of water containing one-twelfth of its volume of sulphuric acid, and treated with a strong solution of potassium permanganate until the color characteristic of a distinct excess of that reagent prevailed distinctly over that of the brown oxide of manganese thrown down in the oxidation. The liquid was warmed to about 50° C., bleached by oxalic acid, and the excess of this reagent was destroyed by more permanganate. On account of the tendency of manganous salts, when present in considerable amount in warm solutions containing but little free acid, to react upon any considerable excess of permanganate with the deposition of higher oxides of manganese, it is generally necessary to repeat the bleaching and oxidizing process two or three times before the final color of a slight excess of the permanganate remains in clear solution and indicates the completion of the oxidation of the selenium. Finally, the liquid was filtered, diluted carefully to the volume of one liter, and used as a standard solution.

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* Zeitschr. Anal. Chem., xii, 287.

† Gooch and Clemons: this Journal, l, 51.

To determine in a general way the point of dilution at which mixtures of selenic and hydrochloric acids yield chlorine, we submitted various mixtures to distillation in a retort arranged with an inverted condenser (so that the aqueous distillate might be constantly returned to the retort) which was joined to an absorbtion apparatus charged with a solution of potassium iodide. A current of carbon dioxide was passed through the apparatus during the distillation, to carry forward whatever chlorine might be evolved in the process. The iodine liberated in the absorbtion apparatus was determined by titration with standard sodium thiosulphate. The results of these experiments are given in the accompanying table.

| $SeO_3$ present. grm. | Total volume. $cm^3$ | Per cent of HCl, sp. gr. 1·20, by volume. | Time in minutes. | Chlorine in terms of the theoretical total. |
|---|---|---|---|---|
| 0·1144 | 100 | 5 | 5 | None |
| " | " | 10 | " | None |
| " | " | 15 | " | About 1% |
| " | " | 20 | " | " 7% |
| " | " | 25 | " | " 30% |
| " | " | 30 | " | " 70% |

It is plain that so long as the volume of the hydrochloric acid, sp. gr. 1·20, does not amount to more than ten per cent of the entire liquid no chlorine whatever is evolved, and that only when the percentage of this acid rises as high as thirty does the chlorine evolved during boiling for five minutes approach the theoretical yield. In the ordinary process of distillation, in which the inverted condenser is not used, the liquid must gradually concentrate and the acid become stronger, so that under such conditions the yield of chlorine in a definite period of time must generally be greater than that obtained in the corresponding experiments of the table. Obviously it is advantageous, in attempting the practical reduction of selenic acid, to begin the distillation with acid of strength sufficient to insure the evolution of chlorine in quantity at the outset, and we have found it best to start with a mixture one-third of which is the strongest aqueous hydrochloric acid, sp. gr. 1·20. With solutions so constituted the reduction goes on rapidly. We have found, however, that care must be taken not to prolong the boiling after the solution reaches a concentration corresponding to hydrochloric acid of half-strength; for under such conditions—attained in our experiments either by boiling down mixtures of selenious acid and hydrochloric acid, or by making mixtures of selenious acid containing hydrochloric acid of half-strength—we have found that selenium appears visibly in the distillate, while iodine is set free from the iodide in the receiver. Good results may be expected when the mixture, containing one-third of its volume of the strongest aqueous hydrochloric acid at the beginning, is boiled until all chlorine is expelled, care being taken that the volume of the liquid shall not become less than two-thirds of the original volume.

These are conditions which are easily kept; and we have found that from solutions having a total volume of 75 cm$^3$ and containing 25 cm$^3$ of the strongest aqueous hydrochloric acid (sp. gr. 1·20), the entire amount of chlorine corresponding to the reduction of 0·2 grm. of selenic acid to selenious acid is liberated in ten minutes. The details of these experiments are given in the accompanying table.

Se = 79·1, O = 16.

| $SeO_3$ taken. grm. | Total volume at the outset. | HCl, sp. gr. 1·20, present. | Time in minutes. | $SeO_3$ found. grm. | Error. |
|---|---|---|---|---|---|
| 0·0572 | 75 cm$^3$ | 25 cm$^3$ | 10 | 0·0568 | 0·0004 — |
| 0·0572 | " | " | " | 0·0569 | 0·0003 — |
| 0·1144 | " | " | " | 0·1143 | 0·0001 — |
| 0·1144 | " | " | " | 0·1137 | 0·0007 — |
| 0·1144 | " | " | " | 0·1147 | 0·0003 + |
| 0·2288 | " | " | " | 0·2233 | 0·0005 — |
| 0·2288 | " | " | " | 0·2279 | 0·0009 — |