ART. XVIII.—*A method for the Separation of Selenium from Tellurium based upon the difference in volatility of the Bromides*; by F. A. GOOCH and A. W. PEIRCE.

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

It has been shown in previous articles from this laboratory* upon the reducibility of selenic acid by the action of the halogen acids, that when small amounts of selenic acid are boiled in aqueous solution with potassium iodide and hydrochloric acid, selenium is precipitated, while the iodine set free simultaneously may be collected in the distillate, estimated, and taken as the measure of the selenic acid originally present; that if the iodide is omitted from the mixture, so that the hydrochloric acid alone shall be the reducer, the reduction proceeds only to the point of formation of selenious acid, provided the boiling is not continued after the hydrochloric acid has reached the condition of half-strength at which it boils unchanged under normal atmospheric pressure; and that a solution of selenic acid, potassium bromide, and sulphuric acid of regulated dilution and proportions also yields under defined conditions selenious acid as the product of reduction. When, however, the ebullition of a solution of selenious acid in hydrochloric acid is continued after the acid has reached the condition of half-strength, traces of selenium appear in the receiver and connecting tubes, the distillate sets free iodine from potassium iodide, and it is evident that the selenious acid is undergoing further reduction. So also when the boiling of the mixture of sulphuric acid, potassium bromide, and selenious acid is pressed beyond the point at which the solution begins to be colored, selenium appears in traces in the tube leading to the receiver and the distillate liberates iodine from an iodide. Obviously the conditions have been at this time reached in the processes of concentration when selenium tetrachloride and selenium tetrabromide, respectively, are forming from the acid, and that the appearance of the elementary selenium is due to partial decomposition of the halogen salts. We have observed more recently phenomena of a similar nature (as would naturally be expected under the conditions), when aqueous solutions of selenious acid, phosphoric acid, and sodium chloride are submitted to distillation: that is to say, there comes a time in the process of boiling such mixtures when the appearance of elementary selenium and the action of the distillate upon potassium iodide make evident the volatilization and partial decomposition of the selenium compounds of the

* This Journal, 1, 254, 400, 402.

halogens, and the further continuance of the treatment results in the more or less complete removal of the selenium compounds to the distillate. From the mixture containing the phosphoric acid, selenious acid, and sodium chloride we have been able to secure only a partial volatilization of the selenium chloride. The transfer of the selenium bromide, however, from the mixture of the acids and potassium bromide is rapid and complete, and this fact points out a possible method for the separation of selenium from substances which do not form volatile products under similar conditions of treatment. Tellurium proves to be such a substance, and the work to be detailed has to do with a process for the separation of selenium from tellurium, based upon the volatility of selenium tetrabromide and the non-volatility of tellurium tetrabromide under definite conditions.

The selenious acid which we used was made by dissolving in water a known weight of the white, crystalline, anhydrous dioxide prepared from pure selenium by oxidation with nitric acid, treatment in solution with barium hydroxide to remove selenic acid, and repeated sublimation in a current of oxygen. The tellurium was obtained in solution in its lower condition of oxidation by dissolving in potassium hydroxide a known weight of tellurium dioxide (made by oxidizing presumably pure tellurium by nitric acid and igniting the product at a low red heat), neutralizing with phosphoric acid, and redissolving in a sufficient excess of that acid the precipitate formed in the process of neutralization.

In our preliminary experiments we made use of a form of apparatus previously employed for similar purposes and described in former articles from the laboratory, viz: a Voit flask, serving as the retort, sealed to the inlet tube of a Drexel wash-bottle, used as a receiver, the outlet tube of which was trapped by sealing on Will and Varrentrapp absorption bulbs. Later the apparatus was changed to the form shown in the accompanying figure by introducing a second Voit flask, in order that the selenium might be estimated in the distillate more conveniently.

Into the first Voit flask, V^1 , were put measured amounts of the solution of selenious acid with 20 cm³ of syrupy phosphoric acid (sp. gr. 1.70), 1 gm. of potassium bromide, and water enough to make the entire volume of liquid 50 cm³. The second flask, V^2 , contained about 15 cm³ of water, and was kept cool by immersion in water.

The Drexel bottle and bulbs contained a solution of potassium iodide. A current of carbon dioxide was passed slowly through the apparatus to secure quiet ebullition and to aid in the transfer of the distillate to the receiver. Upon applying heat to the first flask, V^1 , the solution boiled quietly and without change until the volume of liquid had decreased to about 30 cm³, when traces of red selenium began to deposit in the tube joining the first and second flasks. When the volume had further diminished to about 25 cm³ the liquid began to take on color, darkened rapidly, and evolved bromine, which at once attacked the selenium previously deposited. The greater part of the bromine was absorbed in the second flask, V^2 , but a trace found its way to the Drexel bottle, in which it set free a slight amount of iodine from the iodide, as was afterward proved by the effect upon starch. As the operation progressed, an orange-yellow crystalline solid, presumably selenium tetrabromide for the most part, appeared in the tube where the selenium had been, while a dark oily liquid, consisting largely, no doubt, of the monobromide, condensed in drops upon the walls of the flask and returned to form a floating layer upon the hot liquid. Finally, when the volume had diminished to 15 cm³, the liquid had become perfectly clear and colorless, white fumes of hydrobromic acid were evolved, and the tube between the two flasks had been cleared. At this point the operation was stopped and the apparatus allowed to cool. The addition of potassium iodide to the contents of the first flask neither liberated iodine nor precipitated selenium, and so proved that no reducible compound of selenium still remained in that flask. The amount of selenium which had been volatilized we determined directly by means of a method worked out in this laboratory and to which reference has already been made.* We introduced into the second flask, V^2 , which now contained (beside a trace of selenium corresponding to the slight amount of bromine which had escaped to the Drexel bottle) the colorless selenious acid regenerated by the action of the water and free bromine upon the mixed bromides which had distilled, 1 gram of potassium iodide and 5 cm³ of hydrochloric acid and, after removing the first flask, V^1 , and connecting the carbon dioxide generator with the inlet tube of V^2 , boiled the solution ten minutes while a current of carbon dioxide passed through this apparatus. At the end of this time the iodine set free by the action of the iodide had been almost completely removed to the Drexel bottle, leaving a nearly colorless solution containing particles of dense, crystalline selenium. The iodine in the receiver, including of course the small amount set free by the bromine which reached the

* Gooch and Reynolds, this Journal, 1, 254.

receiver in the first stage of the process, together with the small amount remaining in the flask, was titrated with sodium thiosulphate and taken as the measure of the selenium dioxide acted upon originally. In this way we obtained the following results :

SeO ₂ taken. gram.	SeO ₂ corresponding to iodine found in the distillate. gram.	Error. gram.
0.0366	0.0372	0.0006 +
0.0366	0.0377	0.0011 +
0.1098	0.1090	0.0008 —
0.1098	0.1101	0.0003 +

It is obvious from these results that the iodine finally found in the receiver is actually an accurate measure within reasonable limits of the selenium dioxide originally put into V¹ and volatilized therefrom by the action of phosphoric acid and potassium bromide.

When tellurium dioxide is subjected to similar treatment the phenomena are different. The solution containing the tellurous acid, potassium bromide, and phosphoric acid, in the proportions used in the experiments with selenious acid, colors at about the same degree of concentration at which the solution containing the selenious acid began to darken. As the concentration progresses the color deepens, ruby red crystals (probably hydrated tellurium tetrabromide) form, which accumulate upon the walls of the flask and turn yellow, and when the volume of the solution is diminished to 15 cm³ a green vapor begins to distil. During the process no iodine is set free in the Drexel bottle, and upon stopping the boiling we found that the addition of potassium iodide to V² liberated no iodine, even when the boiling had gone so far that a trace of the green vapor had condensed and run into the water in the flask. In view of these facts it seemed probable that the process of treatment which we have described might be applied to the determination of selenium associated with tellurium. In the following experiments, made to test the point, tellurium dioxide was weighed out and dissolved in strong potassium hydroxide, the alkali was neutralized and the precipitate thus formed was redissolved by phosphoric acid, and 20 cm³ of the acid of sp. gr. 1.70 were added in excess. To the solution were added definite amounts of selenium dioxide taken in a standardized solution and 1 gram. of potassium bromide, and the whole was introduced into the first flask, V¹, with enough water to make the entire volume of the solution 50 cm³. The second flask, V², contained 10 cm³ of water, and the Drexel bottle and trap were charged with a solution of potassium iodide. Carbon

dioxide was passed through, and the solution in V^1 was boiled. The phenomena of each individual set of experiments with the selenious and tellurous acids occurred now together—the coloring of the liquid, the evolution of bromine, the distillation of the selenium bromides, the crystallization of the tellurium tetrabromide, the disappearance of the selenium compounds from the connecting tube, and the final stopping of the distillation when the volume of the residue has diminished to 15 cm³. After cooling, the first flask V^1 was removed, 1 gm. of potassium iodide and 5 cm³ of hydrochloric acid were added to the contents of the second flask, V^2 , the current of carbon dioxide was again started through the apparatus, the mixture was boiled ten minutes, and the iodine in the flask, receiver and trap was determined by titration with sodium thiosulphate and taken as the measure of the selenium dioxide. In some preliminary experiments trouble was experienced in removing the last traces of the selenium bromides held back mechanically by the oily tellurium compound which collected upon the walls of the distillation flask and in the connecting tube; but the difficulty was satisfactorily overcome by cloaking the flask with a mantle of asbestos board and flaming the connecting tube gently toward the close of the process of distillation. The results obtained are gathered in the following table:

TeO ₂ taken. gram.	KBr taken. gram.	H ₃ PO ₄ (Sp. gr. 1.70) taken. cm ³ .	Final volume. cm ³ .	SeO ₂ taken. gram.	SeO ₂ found. gram.	Error. gram.
0.1	1	20	15	0.0733	0.0735	0.0002 +
"	"	"	"	0.0997	0.0995	0.0002 —
"	"	"	"	0.1004	0.1003	0.0001 —
"	"	"	"	0.0916	0.0914	0.0002 —
"	"	"	"	0.0997	0.0995	0.0002 —
"	"	"	"	0.1010	0.1014	0.0004 +
"	"	"	"	0.1015	0.1008	0.0007 —
"	"	"	"	0.1019	0.1022	0.0003 +
"	"	"	"	0.1010	0.1012	0.0002 +
"	"	"	"	0.1002	0.1000	0.0002 —
"	"	"	"	0.1006	0.1004	0.0002 —
"	"	"	"	0.1006	0.1001	0.0005 —

Obviously the error of the process, when carefully conducted and applied to the amounts of material which we have employed, is very small.