

substituted for absolute alcohol with but small decrease in accuracy. Mixtures of *n*-butyl alcohol and ethyl acetate give the lowest solubilities and could probably be used in all proportions.

The data of the present paper are thus seen to be a practical guide to the selection of the most probably favorable conditions for any of the separations involved. Exact choices depend upon a more thorough study of each case.

Summary

1. The solubility of the alkali perchlorates in various mixtures of methyl, ethyl and *n*-butyl alcohols with ethyl acetate have been determined.
2. The solubility data thus obtained were shown to represent conditions advantageous in the separation and determination of the alkali metals by the extraction process.
3. An attempt was made to interpret the abnormal solubility results and to point out their analytical significance.
4. Solubility determinations were shown to be of value in establishing the purity of the solvents employed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE SEPARATION OF SELENIUM AND TELLURIUM BY SULFUR DIOXIDE IN HYDROCHLORIC ACID SOLUTION

BY VICTOR LENHER AND C. H. KAO

RECEIVED JANUARY 3, 1925

PUBLISHED MARCH 5, 1925

Although the use of sulfur dioxide as a precipitating agent for selenium and tellurium was known to Berzelius, the possibility of its utility in the presence of concd. hydrochloric acid as a means of separating these elements was first suggested by Divers and Shimose.¹ The method has come into the copper industry under the name of Keller² who has contributed certain details to the procedure. Lenher³ has suggested that when large amounts of tellurium are present, selenium and tellurium are coprecipitated and Keller has confirmed this observation and has recommended that the quantity of hydrochloric acid should be a hundred times that of the tellurium. This suggestion is, however, only part of the case. We have had in this Laboratory, where the method has had extended use, such widely varying results that the method has been carefully studied and important details have been suggested.

The concentration of the hydrochloric acid is a very important factor. The specific gravity of the acid used by Keller was 1.175. In our experi-

¹ Divers and Shimose, *Chem. News*, 49, 26 (1884).

² Keller, *THIS JOURNAL*, 19, 771 (1897); 22, 241 (1900).

³ Lenher, *ibid.*, 21, 347 (1899).

ments, it has been shown that the amount and concentration of the hydrochloric acid are very important. With hydrochloric acid having d. 1.143 (28.25%), tellurium does not precipitate in the presence of sulfur dioxide in 24 hours. This is the minimum concentration of acid which can be used. Higher concentration of acid is perfectly satisfactory, if the amount of selenium is small. With hydrochloric acid having a lower concentration than 28%, tellurium slowly separates. A solution of 150 cc. is used in the analysis and not more than 0.25 g. of tellurium should be present. It is equally important that the amount of selenium should be kept down to 0.25 g. When concd. hydrochloric acid (36 to 37%) is added to a highly concentrated solution of selenium dioxide and sulfur dioxide gas is passed into the solution, elementary selenium does not precipitate but the solution turns red due to the formation of selenium monochloride. When such a solution is warmed, selenium monochloride is so volatile that all of the selenium may be distilled as the monochloride and subsequently lost. Indeed, when the concentration of the acid is greater than 1.143 (28.25%) or approximately 1.2 (39%), a yellow or red color appears depending on the amount of selenium present but little or no precipitate is formed. Dilution with more acid of d. 1.2 in the presence of a large excess of sulfur dioxide is necessary so that the monochloride may be hydrolyzed with complete precipitation of elementary selenium. A very great excess of sulfur dioxide is essential in order to cause complete precipitation of elementary selenium from this strongly acid solution.

The temperature of precipitation is another point of great importance. When selenium is precipitated by means of sulfur dioxide, it appears as a red precipitate of the amorphous variety of selenium. This red selenium when warmed changes into the gray-black, crystalline variety and, during this transformation, there will be mechanically enclosed whatever happens to be present in the solution, whether it be a metallic salt, tellurium, or only the hydrochloric, sulfurous and sulfuric acids of the reaction. Once occluded, such substances cannot be removed by washing. A second factor is that when the red selenium is converted into the black selenium in the solution in which these various materials are contained, water is occluded in the black selenium, which cannot be driven off below a temperature that will also volatilize selenium. In other words, freshly precipitated red selenium cannot be transformed into the black variety in the solution in which it is precipitated without giving high results. For example, when 0.2501 g. of selenium was taken for analysis, 0.2532, 0.2519, 0.2502, 0.2527 g. were found, to give a few values out of many.

The procedure recommended is as follows. The oxides of the two elements, which should not contain more than 0.25 g. of either selenium or tellurium, are dissolved in 100 cc. of cold concd. hydrochloric acid; 50

cc. of concd. hydrochloric acid saturated at ordinary temperature with sulfur dioxide (this is sufficient to prevent the formation of the monochloride) is added during constant stirring. When concd. hydrochloric acid is used with a large excess of sulfur dioxide, selenium monochloride is not formed in the cold. The solution is then allowed to stand until the red selenium subsides, is filtered through an asbestos filter into a filtering flask, and the precipitate thoroughly washed with cold, concd. hydrochloric acid, then with cold water until it gives no test for chlorine, and finally with alcohol to displace the water, and ether to displace the alcohol. This is necessary, as water must not be allowed to remain in the red selenium, or later it cannot be removed. The red selenium is dried for three to four hours at 30–40° to remove the last traces of ether, after which it is heated to 120–130° for one to two hours to render the selenium perfectly dry. Whenever any moisture is allowed to remain in the red selenium when it is transformed to the black variety, high results due to oxidation inevitably result. The filtrate from the selenium is then concentrated to 50 cc. to remove the excess of acid. This is done on the steam-bath below 100°; otherwise the tellurium may be boiled off as chloride in this strongly acid solution. The tellurium is then precipitated by the Lenher-Homberger⁴ method; 15 cc. of a saturated solution of sulfur dioxide is added, then 10 cc. of a 15% solution of hydrazine hydrochloride followed by an additional 25 cc. of a saturated solution of sulfur dioxide, and the solution is boiled. Complete precipitation of the tellurium is almost instantaneous.

The precipitate is washed with hot water on a Gooch filter until all of the chlorine is removed, after which the water is displaced by alcohol as quickly as possible to prevent oxidation of the tellurium, and the crucible and contents are dried at 105°. Under these conditions of precipitation, tellurium does not oxidize, and the analysis gives more accurate results than by any other method.

TABLE I
SEPARATION OF SELENIUM AND TELLURIUM

No. of analyses	Selenium				Tellurium			
	Taken G.	Found mean G.	Error of mean G.	Av. dev. from mean =G.	Taken G.	Found mean G.	Error of mean G.	Av. dev. from mean =G.
7	0.2423	0.2424	+0.0001	0.0002	0.2106	0.2104	-0.0002	0.0002
4	.0231	.0234	+ .0003	.0001	.2106	.2103	- .0003	.0001
4	.2423	.2425	+ .0002	.0001	.0215	.0213	- .0002	.0001
4	.2423	.2423	.0000	.0001	.0211	.0211	.0000	.0001
		Av.	+0.0002	.0001		Av.	-0.0002	.0001

Summary

Details are given for the separation of selenium and tellurium in hydro-

⁴ Lenher and Homberger, *THIS JOURNAL*, 30, 387 (1908).

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

MADISON, WISCONSIN

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

THE PREPARATION OF SELENIUM MONOCHLORIDE AND MONOBROMIDE

BY VICTOR LENHER AND C. H. KAO

RECEIVED JANUARY 3, 1925

PUBLISHED MARCH 5, 1925

Selenium Monochloride.—The earliest record we have of this compound is its preparation by Berzelius¹ from selenium and chlorine. Divers and Shimose² 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 Baudrimont³ who caused phosphorus chloride to act on selenium, and on the selenide of phosphorus and antimony, Michaelis⁴ who formed it from selenium dioxide and phosphorus pentachloride, Rathke⁵ who replaced the sulfur in sulfur monochloride by selenium, Ramsay⁶ who brought the tetrachloride together with elementary selenium, and Lenher⁷ 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,

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**, 733 (1890).

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