

results have been correlated with the equilibrium data of the Haber and Fixed Nitrogen Laboratories and have been used further to compute

equilibrium constants for the Ostwald reaction in which ammonia is oxidized to nitric oxide.

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[CONTRIBUTION FROM THE UTAH AGRICULTURAL EXPERIMENT STATION]

Evidence Favoring the Existence of the Compound Hydrogen Perselenide¹

BY JOHN P. NIELSEN,² SHERWIN MAESER AND D. S. JENNINGS

While attempting to develop a method for the determination of selenium, the authors encountered what appears to be a previously undescribed compound of selenium. Mellor in his treatise on "Inorganic and Theoretical Chemistry" does not describe hydrogen perselenide, although he does discuss some of the salts of this acid. Fresenius, Fischback and Frommes³ mention that when selenium is treated with reducing agents such as zinc-hydrochloric acid mixtures, there is a compound carried over with the hydrogen. When this compound is allowed to bubble through lead acetate, a black precipitate is formed, which the authors assumed to be lead selenide. However, they do not give any quantitative results.

Experimental Part

A known solution of selenious acid was made up and standardized by reducing the selenium to the elemental state with hydroxylamine, filtering, drying and weighing. The solution was also standardized by adding potassium iodide and sulfuric acid and titrating the released iodine with standardized sodium thiosulfate.

Known quantities of the selenious acid solution were introduced into a generating flask which was connected by glass tubing to the bottom of an absorbing tube containing lead acetate solution. Five grams of 20-mesh aluminum and enough water to make about 20 ml. of solution were placed in the generator; about 3 ml. of concentrated hydrochloric acid was then added through the funnel. When the reaction was well started, the acid concentration was adjusted in such a manner that 2 or 3 bubbles passed through the absorber per second. The absorber contained 25 ml. of the following lead acetate solution: 10 g. of $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ + 3 ml. of glacial acetic acid + 100 ml. of 1 *N* NH_4Ac in a total volume of 1 liter. The type of absorber used worked efficiently. A second absorber was connected to the first in several runs but there was never any precipitate formed in it. The efficient absorption is probably due to two factors: 1, the insolubility of lead diselenide; 2, the high solubility of the perselenide gas.

(1) Authorized for publication, July 15, 1938.

(2) Present address: National Cannery Association, San Francisco, Calif.

(3) Fresenius, Fischback and Frommes, *Z. anal. Chem.*, **96**, 447 (1934).

The selenium in the generator appeared to be reduced to elemental selenium and then the reduction proceeded further. A black precipitate was obtained in the absorber. This precipitate was filtered with suction through No. 00 Munktell filter paper in a Gooch crucible. At this point several different procedures were tried. In one of them the precipitate was dried and weighed. The composition was calculated on the assumption that all of the selenium in the generator had been converted into the lead-selenium compound. The data in Table I show that the percentage composition corresponded to PbSe_2 .

The time necessary for complete removal of the selenium from the generator varied with the amount added. Fifteen to twenty minutes was long enough for quantities around 1 mg. but one and one-half hours were necessary for 10-mg. quantities. This was shown by changing absorbers during the reaction period until a precipitate was no longer formed in the lead acetate solution. If solid material such as soil was present in the generator, much longer periods of time were necessary for complete removal of the selenium. For instance, about one hour was necessary to remove 1 mg. of selenium from 20 g. of soil.

TABLE I

RECOVERIES OF SELENIUM FROM AQUEOUS SOLUTIONS				
Se added (H_2SeO_3), mg.	PbSe_2 , mg.	Calculated wt. PbSe_2 , mg.	PbSO_4 , mg.	Calcd. wt. PbSO_4 , mg.
10.00	23.20	23.05		
10.00	22.40	23.05		
10.00	23.00	23.05	19.00	19.10
10.00	22.50	23.05	18.50	19.10

In a second procedure the lead-selenium precipitate was filtered, dried and weighed, then decomposed with nitric acid, evaporated to fumes with sulfuric acid and then diluted with alcohol and water so that the final mixture contained 10% sulfuric acid and 30% ethyl alcohol. The lead sulfate so obtained was filtered, ignited at 400°, cooled and weighed. The weight of lead sulfate obtained was compared with the theoretical yield, assuming the composition of the lead-selenium precipitate to be PbSe_2 (see Table I).

In a third procedure the lead-selenium precipitate was filtered, washed with hot, saturated ammonium acetate solution and decomposed with 1 ml. of concentrated nitric acid. The acid was neutralized with ammonia and the lead determined by the well-known Dithizone procedure of Winter, Robinson, Lamb, and Miller.⁴ Knowing the

(4) Winter, Robinson, Lamb and Miller, *Ind. Eng. Chem., Anal. Ed.*, **7**, 265 (1935).

amount of lead and assuming the composition of the precipitate to be $PbSe_2$, the recovery of selenium was compared with the known amounts added. Sample results are given in Table II.

TABLE II
RECOVERIES OF SELENIUM BY DITHIZONE METHOD ASSUMING FORMULA $PbSe_2$

Se added, mg.	1.00	0.50	0.10	0.10	0.10	0.10
Pb precip., mg.	1.29	.65	.12	.12	.14	.13
Se recovered, mg.	0.99	.50	.09	.09	.11	.10

Because of the possibility that the lead-selenium precipitate could have the formula $Pb(HSe)_2$, the gas was run into sodium plumbite solution and the precipitate filtered, dried, and weighed. Results similar to those of the precipitation in acid solution were obtained.

When the lead-selenium precipitate is treated with hydrochloric acid, red selenium is formed, a gas is released and a black precipitate remains. This is what one would expect if the compound were $PbSe_2$, because the selenium would oxidize and reduce itself and elemental selenium and hydrogen monoselenide would be formed. Probably some of the hydrogen monoselenide is precipitated as $PbSe$.

When the hydrogen-selenium gas is passed over calcium chloride, red selenium is deposited and the gas which comes over forms a precipitate with lead acetate having a composition between $PbSe$ and $PbSe_2$. Hydrogen persulfide exhibits the same properties.

A titration procedure was tried to determine the valence of the selenium in the gas formed by its reduction with aluminum-hydrochloric acid mixture. The previously described generator was used, but instead of placing lead acetate in the absorber sodium hydroxide was used. Known quantities of selenium were again used and the gas absorbed. When the reaction was complete, standardized ferric ammonium sulfate was added to the absorbing solution and the mixture acidified with sulfuric acid. Red selenium appearing in a colloidal state was coagulated by allowing carbon dioxide to pass through the solution. The reduced iron was titrated with potassium permanganate and, knowing the amount of selenium added, its average valence was calculated.

Table III shows that the valence is minus one. Care must be taken in order to obtain complete coagulation of the selenium, as any selenium remaining in the colloidal state would be oxidized by the permanganate. Since this observation was made, Coleman and McCrosky⁵ have

(5) Coleman and McCrosky, *THIS JOURNAL*, **59**, 1458 (1937).

TABLE III
TITRATION OF $NaSe$ WITH THE $Fe_2(SO_4)_3$, $KMnO_4$ SYSTEM

Se added, mg.	Calcd. milliequiv. assuming valence of minus one	No. of milliequiv. from titration
5.00	0.0632	0.0632
5.00	.0632	.0625
5.00	.0632	.0610

published a method of determining selenium by titrating it in the colloidal state with different oxidizing agents.

When the gas is passed into sodium hydroxide a yellow solution results, which on acidification forms red selenium and a gas.

A number of determinations of the selenium content of a sample of wheat were made using the method described in this paper for the removal of the selenium from the plant ash. In several of the determinations known quantities of selenium were added to the wheat before ashing. Good recoveries were obtained indicating a complete removal of the selenium from the generator and the adequacy of the absorber (see Table IV).

TABLE IV
RECOVERY OF SELENIUM FROM ASHED PLANT MATERIAL

Sample	Wt., g.	Se added, mg.	Total Se recovered, mg.	Net Se recovered blank subtracted, mg.
Wheat grain	25.0	0.00	0.10	
Wheat grain	25.0	.00	.09	
Wheat grain	25.0	1.00	1.00	0.90
Wheat grain	25.0	0.50	0.54	.44
Wheat grain	25.0	.30	.38	.28
Wheat grain	25.0	.20	.28	.18
Wheat grain	25.0	.10	.20	.10

The authors made an unsuccessful attempt to liquefy the hydrogen perselenide. The failure was probably due to lack of proper equipment.

Summary

1. Selenious acid is reduced to a gaseous compound by aluminum-hydrochloric acid mixtures.
2. Selenium can be recovered from ashed plant material by reduction to a gaseous compound which is absorbed in lead acetate solution.
3. On the basis of quantitative data obtained in a number of reactions involving this gas, it is concluded that its empirical formula is HSe .