Summary

The value of directly measured heat data as a supplement to vapor-pressure data is pointed out.

The heat of vaporization of mercury is determined calorimetrically to be 14,670 ± 50 cal. at 298.1° K.

The heat of vaporization of cadmium is found to be 25,350 ± 100 cal. at 594.1° K.

The generalizations regarding the entropies of monatomic gases and relating vapor pressures to heats of vaporization are confirmed for zinc, cadmium and mercury.

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THE ACTION OF SELENIUM OXYCHLORIDE ON VARIOUS METALS AND METALLIC OXIDES[1]

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In his studies of selenium oxychloride, Lenher[2] has shown that this inorganic solvent reacts with most of the metals to give the chloride of the metal and selenium monochloride; also that many of the metallic oxides are dissolved by selenium oxychloride.

The object of this research was to study these actions in greater detail and to extend the study, in certain cases, to the action of selenium oxychloride on some closely related substances such as the selenides and the selenites.

The temperatures at which the reactions take place have been varied between room temperature, that of a steam-bath (about 90°), and in some cases the boiling point of selenium oxychoride (175°). A few reactions were studied at even higher temperatures.

Manipulation

About 10 cc. of selenium oxychloride, prepared by the interaction of selenium dioxide and selenium tetrachloride and purified by vacuum distillation,[3] and from 0.2 to 0.5 g. of the metal or oxide were placed in tubes and sealed, to avoid the access of moisture and the consequent hydrolysis. These sealed tubes were allowed to stand at room temperature or were heated on the steam-bath until reaction was complete, or had progressed sufficiently far for our purposes. In some cases a day was required, in others a year.

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[1] Abstract of a part of the thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Lenher, THIS JOURNAL, **43**, 29 (1921).

[3] Lenher, *ibid.*, **42**, 2498 (1920).

In the experiments at the boiling point of the selenium oxychloride, the reactants were gently boiled either in small Erlenmeyer flasks or in glass tubes closed with watch glasses, and heated on a sand-bath or an electric hot-plate.

Analytical Procedure

In analyzing the precipitates formed in the various reactions it was necessary to use a non-aqueous solvent to wash out the excess of selenium oxychloride, and selenium monochloride when any was formed. The solvents found most satisfactory were carbon tetrachloride and chloroform.

The general method used to prepare the precipitates for analysis was to pour the selenium oxychloride containing the precipitate into a large excess of chloroform. The precipitate was washed several times by decantation, given a final washing on a filter paper or Gooch crucible, and dried in an air oven at 115° or in a special electrical drying apparatus in a current of dry air, depending upon whether it was easily hydrolyzed by the moisture of the air.

Selenium.—Selenium was determined gravimetrically as elementary selenium. It was precipitated from a hot, 15% hydrochloric acid solution, with a saturated solution of sulfur dioxide.

Selenium Monochloride.—Selenium monochloride reacts with water according to the following equation.

$$2Se_2Cl_2 + 3H_2O = 4HCl + H_2SeO_3 + 3Se \qquad (1)$$

The weight of the selenium precipitated is used to calculate the amount of monochloride that may be dissolved in selenium oxychloride, as the action of water on the selenium oxychloride gives selenious and hydrochloric acids.

Chlorine.—Chlorine was determined gravimetrically as silver chloride, sufficient nitric acid being used to prevent the precipitation of silver selenite.

Metals.—The general method of analyzing the residues obtained from the action of selenium oxychloride on the various metals and their oxides was to use one sample for the determination of chlorine and another for the determination of selenium. The filtrate from the selenium determination was evaporated to dryness and the metal in this residue determined by the most convenient method.

Experimental Part

Copper.—When selenium oxychloride is added to sheet copper at room temperature, the metal gradually becomes covered with a black substance which analysis indicates to be a mixture of cuprous and cupric selenides, Cu_2Se and CuSe. This black coating is gradually changed into anhydrous cupric chloride. Selenium dioxide and selenium monochloride are formed at the same time. The completed reaction might be expressed as follows.

$$3Cu + 4SeOCl_2 = 3CuCl_2 + 2SeO_2 + Se_2Cl_2 \qquad (2)$$

The determination of the amount of selenium monochloride formed when a definite amount of copper is acted on by selenium oxychloride substantiates Equation 2.

Cuprous selenide, prepared by heating copper and selenium to 600°, reacts with selenium oxychloride to give cupric chloride, selenium monochloride and selenium dioxide.

A New Selenite of Copper.—When selenium oxychloride and anhydrous cupric chloride are heated together in contact with the air, a green crystalline salt is formed. Analysis shows this salt to be an acid selenite of copper, $CuSeO_3.SeO_2$, which has not hitherto been reported. Various experiments indicate that the formation of the salt is as follows.

$$CuCl_2 + 3SeO_2 = CuSeO_3.SeO_2 + SeOCl_2 \qquad (3)$$

The selenium oxychloride simply acts as a solvent for cupric chloride and selenium dioxide. Selenium dioxide formed by the hydrolysis of some of the selenium oxychloride by moisture of the air is dissolved in the excess of selenium oxychloride, and when a certain concentration of selenium dioxide is reached the copper selenite is formed. The reaction may be made to go from right to left by adding selenium oxychloride that is not saturated with selenium dioxide.

Anhydrous cupric chloride and selenium dioxide heated together give selenium oxychloride and a selenite of copper.

Oxides of Copper.—Selenium oxychloride slowly reacts with cupric oxide to form cupric chloride and selenium dioxide according to the following equation.

$$CuO + SeOCl_2 = CuCl_2 + SeO_2 \qquad (4)$$

Cuprous oxide heated with selenium oxychloride is oxidized to cupric chloride, while a part of the selenium oxychloride is reduced to selenium monochloride.

$CuSeO_3.2H_2O$.—Selenium oxychloride reacts at once with cupric selenite $CuSeO_3.2H_2O$ to give anhydrous cupric chloride. Many other copper salts were treated with selenium oxychloride, and in every case anhydrous cupric chloride was formed. The reaction may be expressed as follows.

$$CuSeO_3.2H_2O + 3SeOCl_2 = CuCl_2 + 4SeO_2 + 4HCl \qquad (5)$$

Silver.—Selenium oxychloride acts very slowly on sheet silver, yet the reaction is similar to that between selenium oxychloride and copper. Black silver selenide, Ag_2Se, which is later changed into silver chloride, is first formed, or at least is formed in such quantities as to mask the silver chloride that may be formed simultaneously. Both the silver selenide and the silver chloride form a coherent film on the silver, and this retards further action. Silver selenide, prepared by heating precipitated silver with an excess of selenium at red heat for 20 minutes, reacts slowly with selenium oxychloride to give silver chloride.

Precipitated silver is rapidly changed into silver chloride when carefully added to cold selenium oxychloride. Silver leaf added to cold selenium oxychloride turns black at once, and in less than a minute is changed into a sheet of gelatinous silver chloride that floats on top of the selenium oxychloride. If the selenium oxychloride be hot, the reaction is similar, except that the film of silver chloride is thicker.

Silver Oxide.—Selenium oxychloride and silver oxide react with the evolution of light and heat to give selenium dioxide and silver chloride. The heat of the reaction decomposes a part of the silver oxide.

Lead.—Selenium oxychloride reacts more rapidly with lead than with either copper or silver. There is no indication that lead selenide is formed as an intermediate compound. The lead chloride that is formed is granular and drops away from the metal, thus exposing fresh surfaces to the action of the selenium oxychloride.

The Oxides of Lead.—When selenium oxychloride in small amounts is added to lead oxide, red lead and lead dioxide, the reaction is accompanied by the evolution of heat and light. With the last two oxides chlorine is evolved. The following equation represents the action of selenium oxychloride on lead dioxide.

$$PbO_2 + 2SeOCl_2 = PbCl_2 + 2SeO_2 + Cl_2 \qquad (6)$$

Nickel and Cobalt.—Nickel and cobalt are very slowly attacked by selenium oxychloride. These metals in sheet form were placed with selenium oxychloride in sealed tubes and allowed to remain at room temperature for over a year. The selenium oxychloride was slightly darkened by selenium monochloride, while a small amount of the metallic chloride was in the bottom of each tube. The reaction between selenium oxychloride and the finely divided metals is more rapid.

The oxides of these metals slowly react with selenium oxychloride to give the metallic chloride and selenium dioxide.

Iron.—The chlorides of the metals so far discussed are either insoluble, or only slightly soluble, in selenium oxychloride. Thus, when the metal is added to a large excess of selenium oxychloride, the selenium monochloride and the selenium dioxide formed during the reaction are dissolved in the excess of selenium oxychloride, while the metallic chloride separates. A number of other metallic chlorides are more soluble in selenium oxychloride.

Iron dissolves rapidly in hot selenium oxychloride. The ferric chloride formed during the reaction remains in solution, but some of it is precipitated when the solution is repeatedly heated and cooled. In the cold, the reaction is slow and most of the ferric chloride separates from solution as fast as formed.

Ferric oxide is only slowly affected by selenium oxychloride at room temperature, but when selenium oxychloride in the vapor state is passed over ferric oxide heated to 400°, the reaction is rapid. Ferric chloride and selenium dioxide collect on the cooler portions of the tube.

Antimony and Bismuth.—These metals treated with a large excess of selenium oxychloride dissolve completely. A study of the amount of selenium monochloride formed during the reactions shows that bismuth is oxidized to the trichloride. The amount of selenium monochloride formed when antimony is dissolved in selenium oxychloride is more than would be formed to oxidize the antimony to the trichloride, but not enough to oxidize it to the pentachloride.

Tin.—When tin is added to cold selenium oxychloride, action begins at once. The selenium oxychloride becomes dark red from the selenium monochloride formed during the reaction. No precipitate is formed. When sufficient tin is present, the reaction continues until the solution becomes so viscous that it will not run from one end of the tube to the other. The tin is oxidized to stannic chloride.

It was not possible to prepare Weber's[4] compound, $SnCl_4.2SeOCl_2$, from the action of selenium oxychloride on tin. The presence of selenium dioxide and selenium monochloride dissolved in selenium oxychloride evidently prevents the reaction between the latter and stannic chloride to form $SnCl_4.2SeOCl_2$.

The author wishes to acknowledge his appreciation of the inspiration and helpful suggestions received from Professor Victor Lenher, under whose direction this work was carried out.

Summary

1. A detailed study has been made of the action of selenium oxychloride on 9 metals, 9 metallic oxides, and 2 selenides.

2. A new selenite of copper has been prepared.

MADISON, WISCONSIN

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[4] Weber, *Pogg. Ann.*, **125**, 135 (1865).