remain solid. Previous results indicating such solution may probably be explained by lack of careful temperature control, and by possible adsorption of nitrogen in solid cupric oxide giving high initial pressures. Results below the eutectic point are in agreement with those of Foote and Smith.[1]

2. The pressure-temperature equilibrium curves for the system CuO, Cu_2O,O_2 have been established over the range (1), in which the oxides remain solid, below the eutectic point, and (2) above the eutectic point where cupric oxide remains the solid phase, up to 1233°.

3. The pressure and temperature of the quadruple (eutectic) point for the system have been established from the intersection of these 2 curves. The quadruple point lies at 1080.2° and 390 mm. pressure.

4. The general direction of the equilibrium curve has been indicated for the system when cuprous oxide remains the only solid phase, and it has been proved that, in accordance with theory, the equilibrium pressure drops in this case with rise in temperature.

5. It has been shown that pure cupric oxide does not melt without dissociation below 1233°.

The foregoing investigation was begun by one of us at the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology. The work was interrupted at the declaration of war and has been continued in this Laboratory.

WASHINGTON, D. C.

THE DIELECTRIC CONSTANT OF SELENIUM OXYCHLORIDE.

BY JAMES E. WILDISH.

Received October 16, 1920.

Selenium oxychloride was prepared by bringing together molecular proportions of selenium dioxide and selenium tetrachloride. The dioxide was prepared according to Lenher.[2] The selenium tetrachloride was prepared in the usual manner by treating selenium with an excess of dry chlorine. This was accomplished by allowing finely powdered selenium[3] to fall through an atmosphere of dry chlorine. The operation was carried out in the apparatus shown in Fig. 1. A glass tube, A, about 45 cm. long and 38 mm. in diameter, was tightly fitted into a 4-liter flask, B. A glass tube, C, about 25 mm. in diameter and 91 cm. long, was tightly fitted into Tube A. The whole apparatus was made perpendicular by suspending a small weight from the center of the top of the tube. The dry chlorine was passed in at D, until the whole apparatus was filled with

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[1] *Loc. cit.*

[2] Lenher, THIS JOURNAL, **20**, 555 (1898).

[3] The selenium used in this work was obtained through the courtesy of the Baltimore Copper Smelting and Refining Company.

chlorine. The selenium was then slowly and at short intervals dropped into the top of the tube through a Gooch crucible. Between the intervals, the tube was covered with a crucible lid. At first, the main part of the reaction takes place near the top of the tube, but the selenium was added at such a rate that most of the reaction took place in A and the lower part of C.

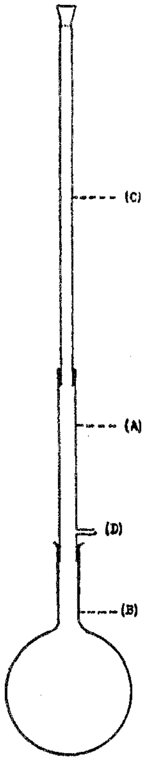

Fig. 1.

The major portion of the selenium tetrachloride falls directly into the flask. If formed too high in the tube some of it is driven out by the heat of the reaction and the larger part is always mixed with diselenium dichloride. If the main part of the reaction occurs in Tube A some of the material will sublime on the sides of the tube. This may be pushed down into the flask. If the main part of the reaction is allowed to take place in the large flask there is insufficient chlorine for the reaction and the dichloride is formed.

When sufficient tetrachloride had been formed, the chlorine supply was shut off and the small tube, C, which contains a small amount of tetrachloride, mixed with the dichloride, is removed. Any tetrachloride formed in Tube A could then be forced down into the flask. Tube A was thereupon removed and the tetrachloride corked up tightly.

By knowing the weight of the flask, the weight of the tetrachloride is easily calculated. Selenium dioxide is then added in molecular proportions and the flask gently heated to form selenium oxychloride. This, when distilled 3 times, had a constant boiling point of 179.4° (at 745.44 mm.), and a conductivity of about $^1/_{10}$ that of conductivity water.

The apparatus used for the determination of the dielectric constant was that of Drude as modified by Schmidt.[1]

Three cells of somewhat different electric capacities were used. These were standardized with acetone distilled over fused calcium chloride and 4 solutions of this purified acetone and water, 2 of which had dielectric constants below that of selenium oxychloride and the other 2 had dielectric constants above it. The data for these solutions were taken from Drude.[2] The water used was that prepared for conductivity work.

Ten readings were taken for each cell for each solution; of these, 5 were taken by each of 2 observers. By plotting the scale readings against the dielectric constants a curve was thus obtained for each cell, and the value of the dielectric constant for selenium oxychloride was deduced from

[1] W. Schmidt, *Ann. Phys.*, **9**, 919 (1902).

[2] Drude, *ibid.*, **8**, 336(1902).

the scale. The unusally high value of the dielectric constant thus obtained is of interest.

The following results were obtained.

TABLE I.—DIELECTRIC CONSTANT OF SELENIUM OXYCHLORIDE.

	At 20°.	At 10°.	Solid at 0°.
Cell 1	46.50	.....	.....
Cell 2	47.10	51.30	13.80
Cell 3	44.20	50.70	18.80

Liquid selenium oxychloride has a dielectric constant of 46.2 ± 1 at 20°, 51.00 ± 0.5 at 10° and a temperature coefficient of 1.04%.

Solid selenium oxychloride has a dielectric constant of 16.8 ± 2 at 0°.

This work was suggested by Dr. Herman Schlundt of the Department of Chemistry. His valuable assistance, in every way, is hereby acknowledged.

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VOLATILIZATION LOSSES OF PHOSPHORUS DURING EVAPORATIONS OF PHOSPHATES WITH SULFURIC ACID OR FUSIONS WITH PYROSULFATE.[1]

BY W. F. HILLEBRAND AND G. E. F. LUNDELL.

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I. Introduction.

Little has been written as to the possibility of volatilization losses of phosphoric acid during operations involving evaporation of phosphates with sulfuric acid or fusion with pyrosulfate, although these questions are of prime importance in the determination of phosphorus in rocks, ores, metallurgical products and many other materials. The experiments to be described were therefore undertaken with a view to determining whether any appreciable volatilization takes place, and in case of evidence of volatilization, to discovering contributing causes and preventive measures.

Rose[2] says in speaking of the treatment of phosphates with sulfuric acid, "Erhitzt man bis zum Verdampfen der Schwefelsäure so kann sich eine Spur Phosphorsäure verflüchtigen."

One of us[3] has repeatedly called attention to the fact that the possibility of loss of phosphorus pentoxide by volatilization during a pyrosulfate fusion or evaporation with sulfuric acid must be borne in mind.

Fresenius-Cohn[4] discuss losses of phosphorus pentoxide by volatiliza-

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[1] Published by permission of the Director of the Bureau of Standards.

[2] H. Rose, "Handbook of Quantitative Analysis," Finkener Ed., **2,** 575 (1871).

[3] W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* **700,** p. 116; and earlier editions.

[4] Fresenius-Cohn, "Quantitative Chemical Analysis," J. Wiley and Sons, **1,** pp. 444–445 (1904).