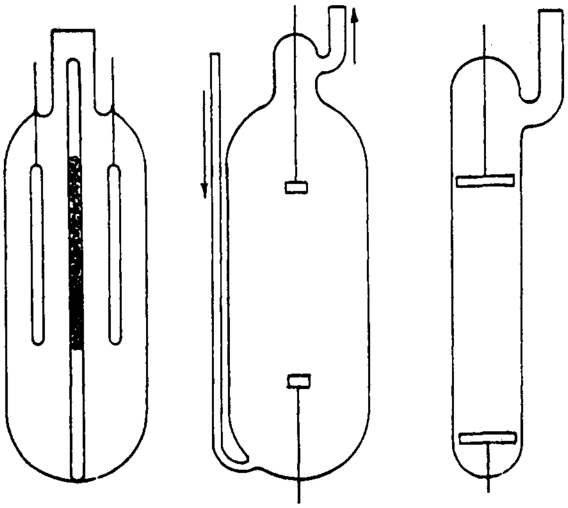
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Oxidation of Selenium in the Glow Discharge. II. A Study of Variables and Further Characterization of Product[1]

BY EARL OLSON AND V. W. MELOCHE

In a previous study of the oxidation of selenium in the glow discharge,[2] it was found that a mixture of selenium dioxide and selenium trioxide was produced. Since very little was known concerning the mechanism of the reaction, it was thought that the study could be extended profitably. The present paper includes a description of the effect of variables, pressure, current, electrode distance, shape of tube, and distance of selenium from the electrodes on the production of selenium trioxide, and also gives some general facts concerning chemical action in the glow discharge.



Tube I Tube II Tube III

Fig. 1.

Apparatus.—The apparatus was essentially the same as that used by Kramer and Meloche.[3] A 25,000-volt transformer served as the source of alternating current. For direct current, a single phase full wave rectifier circuit (two RCA-866 tubes) was used. Three types of discharge tubes were used in this investigation.

Materials and Analysis.—The preparation of materials and the methods of analysis are the same as the ones described by Kramer and Meloche. Ordinary analytical methods were later augmented by X-ray examination of the product.

Procedure.—In general, the procedure used was the same as that described by Kramer and Meloche, *viz.*, elementary selenium was supported between the two electrodes of a tube and subjected to the glow discharge at a definite oxygen pressure, the walls of the tube being at the temperature of liquid air. In order to provide a constant pressure for a given experiment, pure dry oxygen was allowed to enter the apparatus through a Hoke micro-valve at such a rate that the inflow of oxygen was balanced by its removal with the pumps. It should be noted that it was possible to pass a current of oxygen into the bottom of tube II by sealing the small side-arm to the micro-valve and sealing the large exit to the pump line of the apparatus. In this manner a current of oxygen passed over the sample whereas in tubes I and III the oxygen reached the sample by diffusion. Other details of procedure will be given in connection with the individual experiments.

Effect of Pressure.—Using tube I, a 25,000-volt transformer and a constant alternating current of 44 m. a., elementary selenium was melted on a rod which was supported in a vertical position between the electrodes and subjected to the action of oxygen at a definite pressure. The curves shown in Fig. 2 represent the analyses of various products which were obtained at various pressures of oxygen.

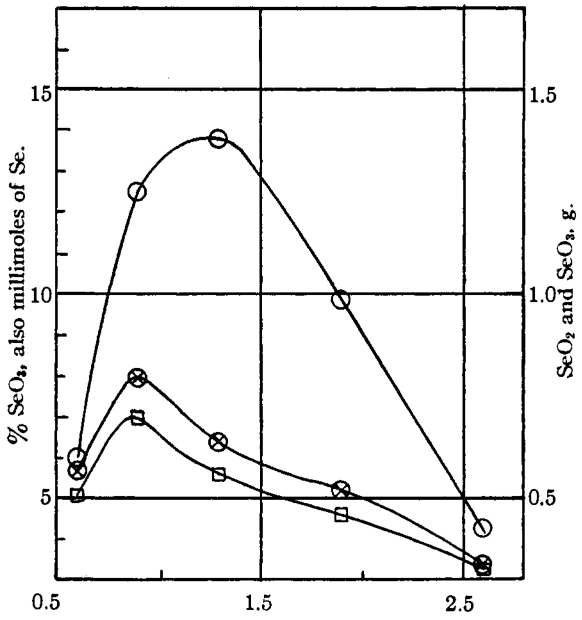


Fig. 2.—○, % SeO_3; ⊗, SeO_2 and SeO_3, g.; □, millimoles of Se.

Kramer and Meloche have reported a maximum in selenium trioxide concentration at a pressure of 1.2 mm. This maximum is shown in Fig. 2 at 1.1 mm. Curves 2 and 3 show the variation of weight of product and the variation of millimoles of selenium in the product with the change in pressure. For these two curves, maxima are found at 0.9 mm. pressure. A difference in the maxima for

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[2] Kramer and Meloche, THIS JOURNAL, **56**, 1081 (1934).

curves 2 and 3 as contrasted to curve 1 is to be expected since the weight of product depends primarily upon the vaporization of selenium while the percentage of selenium trioxide depends upon both vaporization and activation of selenium.

Two factors affect the vaporization of selenium, thermal radiation from the cathode and electron bombardment. The percentage of selenium trioxide depends to a large extent upon activation by electron bombardment after vaporization. Using tube I, thermal vaporization of selenium is greatest at 0.9 mm. Maximum activation of the selenium is obtained at 1.1 mm. pressure.

Maxima may also be noted in Fig. 3. In this case tube II was used and selenium was suspended on a glass holder midway between the electrodes. The maximum concentration of selenium trioxide was produced at 0.8 mm. pressure. Since the electrodes were farther apart than in tube I, a lower pressure was required to keep the selenium vapor in the negative glow, which is the most reactive region of the discharge.

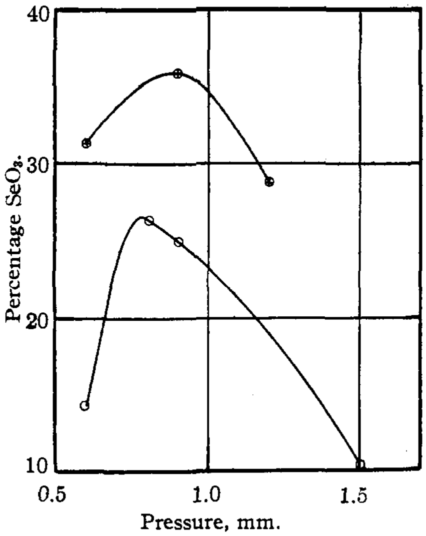

Fig. 3.

Shape of the Tube.—The curves of Fig. 2 using tube I and of Fig. 3 using tube II show that a higher concentration of selenium trioxide was obtained in tube II, identical conditions of current and temperature having been maintained. This was probably due to the fact that the electrodes in tube II were smaller than those in tube I and since the discharge column in tube II was smaller, the current density was higher.

When tube III was used, large amounts of selenium were found mixed with the oxides of selenium. In this tube, the walls were very close to the discharge column. It is therefore likely that some of the deposited product was decomposed or that some elementary selenium condensed on the walls before combination with oxygen could occur.

Still another factor exists other than the proximity of the walls to the region of glow. As has been noted, the small side-arm of tube II could be connected to the Hoke microvalve and the large opening of the tube could be connected to the pump side of the apparatus, thereby making it possible to have a positive flow of oxygen through the tube in the direction of the pumps. It was also possible to seal off the small side-arm and when the large outlet of the reaction tube was sealed to the system, the oxygen reached the sample by diffusion. In Fig. 2, the upper curve shows that a steady flow of oxygen through tube II caused a marked increase in the percentage of selenium trioxide. The lower curve represents results obtained when the oxygen diffused into the tube. If it may be assumed that the flow of oxygen through the tube provides an excess of unactivated oxygen, whereas, in the second case, the oxygen diffuses into the tube and is largely activated, the above results probably indicate that selenium combines more readily with unactivated oxygen than with activated oxygen to form selenium trioxide.

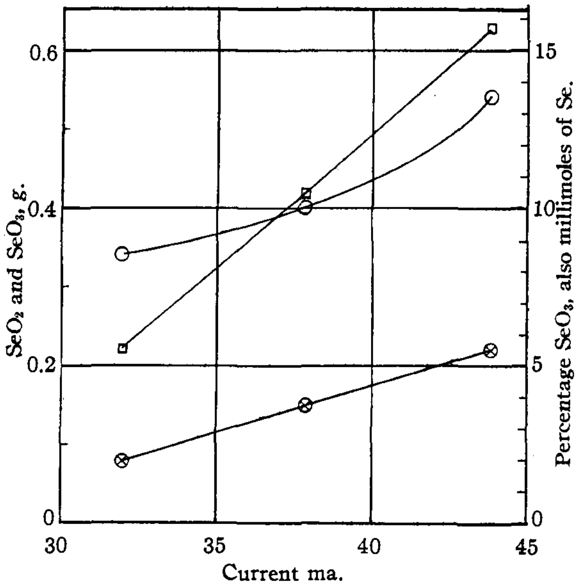

Fig. 4.—○, Percentage SeO_3; ⊗, millimoles of Se; □, SeO_2 and SeO_3, g.

Electrode Distance.—It is well known that the extent of the negative glow is independent of the distance between the electrodes and is dependent on the nature of the gas and the pressure. In tube I a relatively large selenium surface is exposed and the region of negative glow represents a relatively large volume. In contrast the electrodes in tube II are smaller and, therefore, for the same power, the region of negative glow is smaller in volume but more concentrated in electrons for the same current. Results obtained under identical conditions of pressure and current show consistently a larger amount of product for tube I than for tube II and a higher percentage of selenium trioxide for tube II than for tube I. As might be expected, the change of distance between the electrodes of tube II does not affect the percentage of selenium trioxide in the product, pressure and current being the same.

Distance of Selenium from the Electrodes.—It was found that no perceptible reaction took place unless the selenium was in the region of the negative glow. Using direct current, excessive volatilization of selenium took place when the selenium was too near the cathode and selenium was found in the product.

Effect of Current.—The curves of Fig. 3 show distinctly that the percentage of selenium trioxide, the weight of

TABLE I

Pressure, mm.	Current, ma.	Electrode distance, cm.	Distance ot Se from cathode, cm.	Wt. of product, g., behind		% SeO_3, behind	
				Anode	Cathode	Anode	Cathode
				Tube I			
1.5	45 d. c.	2	1	0.1169	0.1736	4.66	11.15
1.5	45 d. c.	2	1	.1663	.2996	3.35	7.69
				Tube II			
				Between electrodes	Behind cathode	Between electrodes	Behind cathode
1.0	44 a. c.	6.5	1.2	0.0151	0.1633	16.16	19.9
0.9	45 d. c.	4	1	.0317	.0302	8.15	13.23
1.2	45 d. c.	4	1	.0381	.0700	4.47	14.58

product, and millimoles of selenium increase with an increase of current. In these experiments special care was taken to maintain identical conditions, varying only the amperage and voltage. Using the same tube, the voltage must be increased to produce a higher current. Brewer,[3] in his studies of various reactions, also has reported a larger rate with an increase of current. Particularly significant is the relation between percentage of selenium trioxide and current. Evidently the percentage of selenium trioxide is dependent on the power factor, which would lead one to believe that the activation of selenium is an important factor in the production of selenium trioxide. Calculations of m/N ratios have not been attempted because of the complications introduced by the solid reactant and the heterogeneous product.

Deposition of Product.—Using tube I, Kramer and Meloche[2] have reported a higher percentage of selenium trioxide in the product behind the electrodes. Using direct current instead of alternating current, as was the case in the above experiments, a higher percentage of selenium trioxide and a larger weight of product was found behind the cathode. Some typical results, using tubes I and II, as shown in Table I, show conclusively that the product concentrates behind the cathode.

Using tube II, the deposit, in many cases, formed in diffuse rings. The majority of the product was usually concentrated in a ring just below the cathode.

Characterization of the Product.—In the earlier work with alternating current, the products of the oxidation of selenium in the glow discharge were analyzed chemically and reported to be a mixture of selenium dioxide and selenium trioxide. In the present study using direct current the same type of product was obtained. However, since it was realized that chemical analyses could not alone establish the character of the product, X-ray powder photographs were taken of typical samples. A characteristic which interfered with chemical analyses also made the X-ray examination difficult, namely, the strong affinity of the product for water. In the solution of samples for chemical analysis it was necessary to place the weighed dry sample in a weighing bottle and place a drop of water on the wall of the bottle, allowing the sample to stand long enough for the water vapor to reach the product and thus provide slow hydration. When this occurred the sample could be moistened and diluted to the desired volume. If this precaution was not taken and water was added directly to the fresh sample, the reaction was so violent that some sample would be lost.

When samples were prepared for the X-ray examination, the usual thin-walled tubes were filled in a desiccator box to avoid contamination of the sample with water. It was necessary to prepare a standard photograph of selenium dioxide, as there is no X-ray data on this oxide in the literature. A molybdenum target tube was used with a zirconium oxide filter, thereby producing monochromatic light of 0.70997 Å. wave length. An unusually long exposure was required, discernible lines appearing after twenty-four hours.

The data in Table II give the actual diameters of diffraction rings and the calculated interplanar distances of the planes producing these rings.

TABLE II

SeO_2		Discharge product	
Distance between lines, cm.	Interplanar distance, Å.	Distance between lines, cm.	Interplanar distance, Å.
..	....	6.24	1.1560
5.92	1.2164	..	....
5.66	1.2710	5.66	1.2710
5.44	1.3213	5.44	1.3213
5.18	1.3865	5.18	1.3865
4.58	1.5643	4.54	1.5780
..	....	4.00	1.7865
..	....	3.64	1.9602
3.22	2.2163	3.26	2.1889
2.76	2.5773	2.82	2.5247
2.38	2.9909	2.38	2.9909
2.20	3.2350	2.20	3.2350
1.90	3.7375	1.90	3.7375
1.74	4.0864	1.74	4.0864

The above table shows that selenium dioxide crystals are produced by the oxidation of selenium in the glow discharge since selenium dioxide lines are found in the photograph of the glow discharge product. It is doubtful that a double oxide forms, since the selenium dioxide lines on the two photographs were of practically equal intensity (a double oxide would decrease the selenium dioxide percentage). It is more reasonable to suppose that, since there are three additional lines in the selenium dioxide and selenium trioxide photograph, selenium trioxide exists as crystals.

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[3] Brewer, *et al.*, *J. Phys. Chem.*, **36**, 2133 (1932); and earlier papers.

Acknowledgment

The authors with to express their indebtedness to Dr. A. T. Lincoln for the use of the X-ray diffraction apparatus at Carleton College.

Summary

In the reaction between selenium and oxygen in the glow discharge, the effects of the variables, pressure, current, electrode distance, shape of tubes, were studied. From these studies, optimum conditions for the production of selenium dioxide and trioxide were ascertained. The characterization of these products, by means of chemical analysis, was supplemented by X-ray diffraction studies.

The reaction is best initiated in the negative glow and is completed by the deposition of product on the cold tube walls.

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The Oxidation of Selenium in the Glow Discharge. III. Striated Deposits and Possible Mechanism[1]

BY EARL OLSON AND V. W. MELOCHE

Although the glow discharge may be said to comprise a rather complex field for chemical reaction, the use of solid selenium as one of the reactants and the cooling of the walls of the tube in liquid air greatly reduce the complexity of the system. In a homogeneous system, it is difficult to determine the nature of the reaction in the various parts of the discharge column. Since the products of the oxidation of selenium are solids, it has been possible to study the deposits which formed as striations *in the column* and to study the effect of the change of pressure and power on these striations. We propose to describe the results of this study and use these data together with results published in a previous paper in support of a proposed mechanism for the oxidation of selenium in the glow discharge.

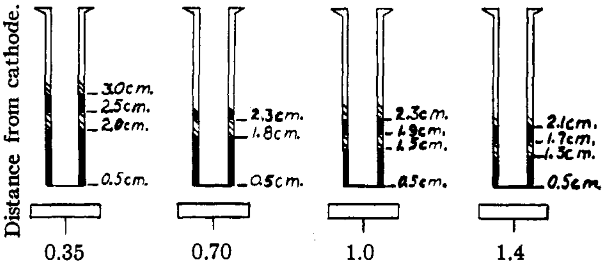

Fig. 1.—▨, Oxides of selenium; ▮, elementary selenium.

Apparatus.—The apparatus used in this research was the same as that described in previous papers.[2,3] The data to be presented were obtained with the discharge tube III, illustrated in the second paper, having a distance of 10 cm. between the electrodes. Direct current was used.

Striated Deposits in the Discharge

Selenium was fused on the bottom of a glass suspension 0.5 cm. from the cathode as shown in Fig. 1. The basket was suspended in the center of the discharge column. After subjecting the selenium to the glow discharge for an hour and a half, it was found that oxides and elementary selenium deposited not only on the walls of the tube but also on the vertical glass supports directly in the path of the discharge. Distinct striations of white selenium oxide and elementary selenium were sharply defined if the pressure were held constant during the run. The striation dimensions of four constant pressure runs are given in Fig. 1. The lined areas represent deposits of oxides, while the solid black areas represent deposits of elementary selenium. For example, the striations occurring at 0.35 mm. pressure consisted of a 1.5-cm. deposit of black elementary selenium, then 0.5 cm. of white oxide of selenium, 0.5 cm. of red elementary selenium, and above this another selenium oxide deposit of 0.4 cm. No deposit was detectable higher on the glass support. It is well known that red selenium is transformed to the black variety byheat. In agreement with this is the fact that the black selenium deposited close to the cathode where the temperature was relatively high and the red selenium deposited farther away from the cathode where the temperature was undoubtedly lower.

It is believed that this is the first report of striated depositions occurring directly in the discharge column. Brewer[4] has reported a well defined band of deposit on the wall of the tube in the region of the negative glow; also, under special conditions, striated deposits on the wall in the positive column region. The above figure represents striated deposits in the head of the positive column. The lower black area is in the region of the negative glow and Faraday's dark space. The two oxide deposits (lined areas) and the upper black area are in the region of the head of the

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[1] This investigation was supported in part by the Wisconsin Alumni Research Foundation. This paper is presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kramer and Meloche, THIS JOURNAL, **56**, 1081 (1934).

[3] Olson and Meloche, *ibid.*, **58**, 2511 (1936).

[4] Brewer, *et al.*, *J. Phys. Chem.*, **34**, 153, 2343 (1930); **35**, 1281, 1293 (1931).