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Some Structural Features of Selenium Deposited by Condensation from the Vapor State in the Neighborhood of the Melting Point

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SOME STRUCTURAL FEATURES OF SELENIUM DEPOSITED BY CONDENSATION FROM THE VAPOR STATE IN THE NEIGHBORHOOD OF THE MELTING POINT[1]

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The primary object of this paper is to record some experimental observations. During work[2] on the vapor tension of the element selenium, above and below the melting point, where the Knudsen method of molecular flow was used, the condensed material deposited itself on the cooling tube of the apparatus in a noteworthy manner. Some numerical data on it in addition to that necessary for the vapor pressure measurements were obtained incidentally at the time of the experiments. A description of the behavior of the deposit, from run to run of the pressure measurements, is here given, partly by means of the accompanying tables, including the numerical data mentioned. The type of tube upon which the material condensed is described in the paper already referred to, on the sublimation curve. Dimensions of tubes E and F, used in two series respectively of pressure measurements, are stated in connection with figure 124.

Table I has reference to a series of eleven measurements on the hexagonal crystalline form of selenium as first produced by Major F. C. Brown,[3] and by him furnished to the writer, for the vapor tension work.

Table II presents the same kind of data for a similar series of thirty measurements on the vapor pressure above the melting point. The material evaporated in this second series was amorphous selenium obtained in stick form from Eimer and Amend.

There are at least two points of interest regarding the deposit, first, deposition in zones of the selenium as it condenses, and sec-

[1]The original title of this report as read by proxy before the Academy at its spring meeting, 1918, did not refer to the selenium deposits condensed from vapor on both sides of the melting point, but only above it. At the present writing (Sept., 1919), however, the data for a series of experiments below the melting point, as well as above it, are at hand, and the scope of the paper has been extended by insertion of Table I, while the discussion of an unusually heavy deposit, mentioned at that time, obtained by a special evaporation not belonging to either of the E and F series of pressure measurements, has been omitted.

[2]See paper on sublimation curve for the hexagonal crystals of selenium, this number of the Proceedings.

[3]With regard to the method of production of selenium crystals of large size see Brown's paper, Physical Review, 5, pp. 236-237, March, 1915.

ond, the existence of two general characters of the deposit in the E series.

The three zones can be readily distinguished in the photograph, figure 125, although they are actually much more sharply differentiated as to appearance than in the photograph. Figure 126 shows

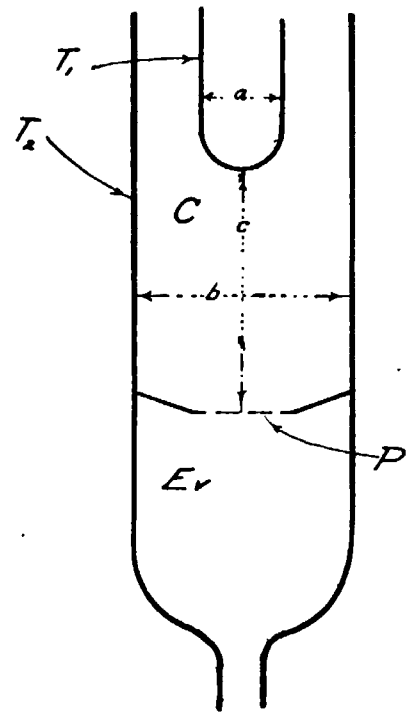

FIG. 124. See legend below.

Tube	Lengths in cms.		
	a	b	c
E	1.45	2.3	6.1
F	1.2	2.5*	4.3

*Outside measurement.

T_1=condensation tube
T_2=outside tube
C =condensation chamber
Ev=evaporation chamber
P =platinum partition

how the lengths of the zones are indicated in the tables. The zone nearest the end, or rather at the end and spreading up the sides of the tube for two or three centimeters, which will be referred to as zone 1, contains by far the greater weight of the condensed selenium, and is opaque over the major part of its length, with a dull lustrous appearance by reflected light. Zone 3 lies farthest up the tube, and farthest away from the apertures in the platinum partition where the molecules enter the condensation chamber. This upper zone has a dark, dirty color, and is fairly opaque by transmitted light. There is a possibility that this consists of impurity in the selenum, although this zone was present in some runs of the F series, where crystals supplied the vapor. Whatever the explanation, there must have been a separation from the others of the molecules making up this

zone, by a process incidental to the condensation. It would seem that these molecules had been crowded out from below. The transparent middle zone may possibly be a continuation of the first zone, which becomes red, a characteristic selenium color, by transmitted light when opacity ceases. But since a thin layer of red material

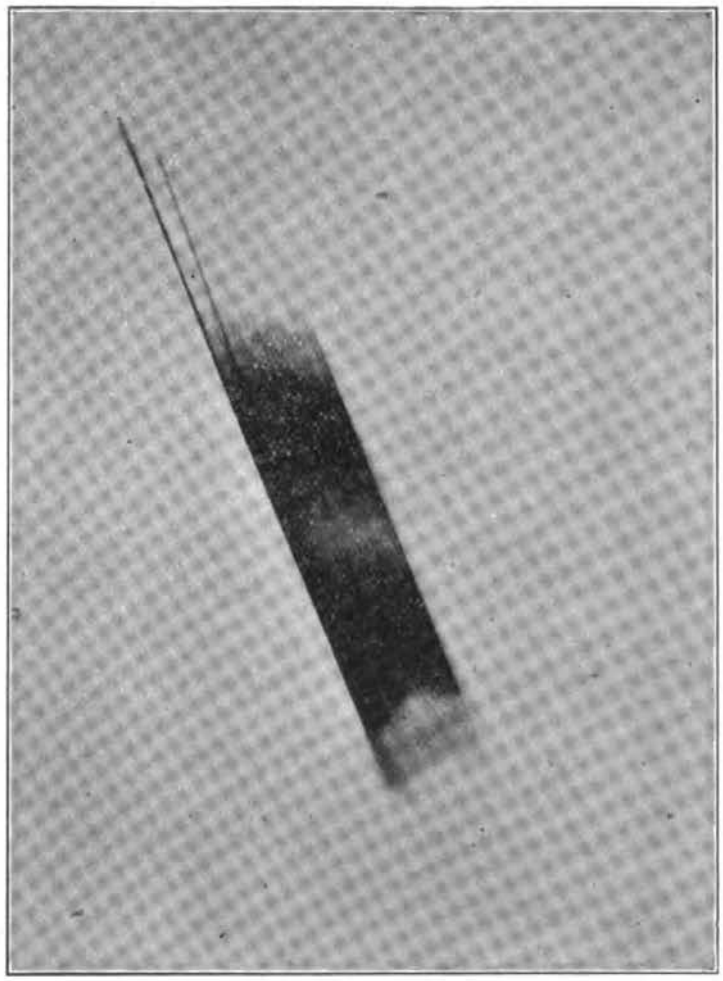

FIGURE 125

was frequently noted beneath the material of zone 1 and next the glass, there is some reason for doubting this. Conceivably both this red substratum and zone 2 are made up of substance deposited in the brief interval required for the vacuum to reach the required stage.

Egerton,[4] in describing similar work on the vapor tension of zinc and cadmium, using the same method of molecular flow, speaks of zones of different thicknesses on the condensation tube. But he makes no mention of differences in color, and suggests that mole-

[4]Phil. Mag., V. 33, 193, p. 33, Jan., 1917.

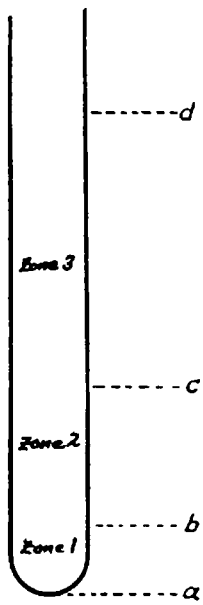

FIGURE 126

cules of different ranges are present in the vapor. It may be supposed that atoms in different states of aggregation in the molecules account for two or more different molecular types, and that these different types are re-evaporated from the condensation surface, according to Langmuir's view, before they finally settle permanently in position, such re-evaporation taking place with different degrees of ease for the various types, so that a kind of sifting of the molecules is effected. At any rate it would appear that molecular flow as applied in the vapor pressure work mentioned might be used for a separation of molecules of different types, mixed in the vapor state, whether these types belong to the same element, or substance, in different states of atomic aggregation in the molecules, or whether they are of different elements, or substances.[5] If such separation in reality occurs for the vapor molecules of different elements, then the method of molecular flow, with condensation at one end of the flow, ought to be available as a method of purification.

With special reference to the two general characters of series E, the runs not indicated in the tables as of character either "a" or "b," are probably in all cases "a," which was the usual form of the deposit. In fact, it was not until the sixth run that a new character, that subsequently designated "b," appeared. A note made at the time of this run, when the changed appearance of the condensed selenium could not escape notice, reads: "Character of zone 1 has changed somewhat. Instead of rather sharp margin this zone gradually shades off into zone 2, with the addition of an intermediate zone between the region of dull luster of zone 1 and the transparent zone 2, which appears black and glossy. This intermediate zone is translucent over much of its length. Nodules, small but distinct, and with fortuitous distribution, on end of tube, extending up over bend to sides." A similar note with reference to the eighth run of this series states: "Many nodules on end and sides in zone 1. Deposit more like that of E6 than of E7. Zone 3 noted to be opposite deposit on outside tube; but in E9, while zone 3 is about

[5] In this event an interesting question for experimental study would be, how susceptible to such a separating effect are molecules of mixed vapors of different elements, where the molecules all have the same number of atoms.

opposite lower part of deposit on outside tube, it extends farther down than the latter (less than ½ cm.) and not nearly so far up. Deposit on outside tube is [by this time] some 8 or 9 cms. long [much longer than usual]."[6] Still another note, referring to the tenth run, reads: "Zone 1 scrapes off harder than when deposit is of character 'a,' and in the transparent region of zone 2 the deposit has appreciable thickness and resists the knife. Zone 3 [which in this case appears to have been on the condensation tube itself] is fairly below the [previous] deposit on the walls of the outside tube. Zone 1 has nodules, on end and sides."[7]

Examination of the material in the two tables shows no marked effect of time on the character of the deposit, except of course to deepen it. There seems to be some increase in the total length with rising temperature. The two characters of the deposit in the E series appear to be unrelated to both time and temperature, and it is noticeable that the total length of the deposit does not depend markedly upon which one of the two characters is present. Also, the apparent transfer of zone 3 from the inside to the outside tube, observed in a few cases, is unexplained, although it was noted to occur, particularly in run E8, when the second character, b, was present. Whether it occurred only when this character was present is unknown.

Since the vacuum for by far the greater part of the time of each run was in all cases what may be termed "good," that is, a vacuum high enough to insure molecular flow, it is to be supposed that any variations of the vacuum over the small range of low pressures present had no effect on the nature of the deposit. Whether the relatively poor vacuum over a short part of each run before pressure conditions permitting molecular flow were established, had anything to do with determining which of the two general characters should prevail in a run of the E series, is undetermined. The cause of these two general characters does not appear to be cleared up by the present data on the basis either of varied temperature, of changing time of run, or of poor vacuum. They remain for the time being unexplained.[8]

[6]The point corresponding to this run has been found to lie a little low on the vapor pressure curve, perhaps because the material condensed on the outside was not weighed. Condensation on the outside tube occurred in some of the runs, but the amount so deposited was usually small.

[7]Considerable light is thrown on this nodule structure appearing on the outside surface of zone 1, by a study of the special thick deposit, discussion of which has been omitted from the present paper, as already stated.

TABLE I

Run	ab	bc	cd	ad	Temp (°C.)	Time (secs.)	Vacuum (mm.)	Remarks
F 1					193.6	3000	n. r.* before end of run	Condensation tube discolored to about 10 cms. Three zones not noticed. Practically all of deposit within 2.2 cms. from end of condensation tube, or point "a", Fig. 126.
2					197.6	2760	n.r.– 9†	Condensation tube discolored to more than 9 1/2 cms. from point a. Deposit opaque to 2.5 cms. from a. Practically all of deposit in this region.
3					200.3	2205	good– 5	Deposit symmetrical, and opaque to 1.3 cms. from a. Discoloration of tube to 12 cms.
4	3.2 1.8‡	3.3	5.5	12.0	203.2	2370	fair– 4 good–13	Upper zone [zone 3] first makes appearance. Zone 1 lustrous [by reflected light] to 3.2 cms., and opaque to 1.8 cms. Zone 2 translucent.
5	2.5 1.8‡	4.5	4.0	11.0	204.4	2610	good–13	A little deposit on outside tube, 12 cms. from point a.
6	3.8 2.2‡	5.7	3.5	13.0	206.5	2445	good–14	
7	3.0 1.5‡	4.5	4.5	12.0	208.9	2130	good– 7	
8	3.5 2.3‡	5.0	4.5	13.0	210.6	2025	good–10	
9	5.0 4.0‡				212.5	1020	good– 8	Zone 3 not evident [due to its transfer to walls of outside tube (?)]. Discoloration to unknown point rather high up on condensation tube. Nodules appearing in zone 1.
10	4.0 3.0‡	7.0			214.0	1830	good–12 good–12 good–28	Zone 3 not evident on inside tube, but deposit [opposite its former position on condensation tube(?)] on outside tube, with lower margin 8 cms. from point a.
11	4.2	5.8			215.5	2070	fair–10 0.0008–20 0.0008–27	Nodules in zone 1. Zone 3 missing from condensation tube [probably again transferred to outside tube]. Poorer vacuum here than in preceding runs, but not preventing molecular flow.

*"n. r." means "not readable on MacLeod gauge."

†The dash and numeral in this column indicate the time in minutes from the beginning of the run, when the vacuum reading was taken.

‡The first of the two numbers in column ab for a given run gives the length of the zone determined by its characteristic lustrous appearance by reflected light, while the second number indicates the opaque length.

TABLE II

Run	ab	bc	cd	ad	Temp (°C.)	Time (secs.)	Vacuum (mm.)	Char. of Dep.	Remarks
E1	2.5	5.5	2.5	10.5	221.0	2055	0.0002– 7* .00016–14 .00016–27		
2	3.0	4.0	3.5	10.5	219.0	2950	not good–2 <0.0001–16 n.r.–22 n.r.–41		Zone 3 follows wiping marks other zones do not. Narrow ring around outside wall within 1 cm. of point a; cause(?), two resistance lamps of auxiliary heating circuit had been off during this run.
3	3.2	5.3	2.5	11.0	228.0	2520	0.0002– 6 n.r.–17 good–35		
4	3.2	4.8	3.0	11.0	226.8	2400	n.r.– 7 n.r.–30		
5	3.5	5.0	3.5	12.0	233.7	2430	n.r.– 7 n.r.–30		
6	1.8	6.7	4.0	12.5	238.0	2355	<0.0001– 5 <0.0001–12 better–23 good–35	b	(For note on this run see discussion.)
7	3.5	5.5	3.5	12.5	231.7	2210	<0.0001– 8 n.r.–28	a	Nodules on end of condensation tube.
8	2.0†	7.5	3.5	13.0	231.2	2520	n.r.– 9 good–29	b(?)	(See discussion.)
9	4.0	4.5	2.0	10.5	232.0	2400	0.0002–6 n.r.–21 good–35	a	See discussion, where note is given for E8.
10	1.5†	5.5	2.0	10.0	229.6	2400	n.r.– 9 good–26	b	(See discussion.)
11	3.0	3.5	3.5	10.0	222.7	2355	0.0001–10 n.r.–26	a	
12	3.0	5.0	2.5	10.5	222.2	2470	0.0001– 9 n.r.–21 good–30	a	Individual nodules in zone 1 not noticeable.
13	3.3	4.7	2.5	10.5	224.8	2400	0.00004– 7 good–24	a	Selenium below must have solidified very soon after removal of tube from oven.
E14	3.5	4.5	2.0	10.0	224.0	2460	0.0002– 7 n.r.–18	a	Fine nodules, zone 1.
15	1.5†	6.5	2.0	10.0	223.4	2400	0.0002–11 n.r.–21 good–30	b	Nodules, zone 1.
16					227.7	2400	n.r. –8 good–20 good–34	b(?)	No measurements on zones. Margins not defined (?). Deposit scrapes off like character b.
17	1.0†	6.5	2.0	9.5	227.5	2370	0.0002– 8 n.r.–17 good–30	b	Small nodules, zone 1.
18	3.5	3.5	2.5	9.5	225.5	2400	n.r.– 9 good–20 good–34	a	Small nodules, zone 1, a little larger than in E17

TABLE II—Continued

Run	ab	bc	cd	ad	Temp (°C.)	Time (secs.)	Vacuum (mm.)	Char. of Dep.	Remarks
19	3.5	3.5	2.0	9.0	225.8	1930	n.r.– 9 good–21	a	
20	3.5	3.5	2.5	9.5	224.8	2910	0.0001–10‡ good–22	a	Run interrupted after 8 1/2 mins., then resumed. Nodules, zone 1.
21	not taken		1.5	9.5	223.8	2430	good– 9 good–31	b	Deposit translucent, in spite of considerable thickness, nearly to end a
22	3.0	4.0	2.0	9.0	226.6	2460	good– 7 good–20 good–31	b	
23	3.0	3.5	2.5	9.0	224.1	1830	good– 8	a	
24	3.0	4.0	2.0	9.0	223.2	2385	<0.0002–8 n.r.–25	a	
25	3.0	4.0	2.0	9.0	221.3	2400	n.r.– 6 good–23 good–33	a	
26	3.0 to 3.5	4.0 to 3.5	2.0	9.0	222.0	2400	n.r.– 7 good–17 good–31	a	
E27	3.0	4.0	2.0	9.0	224.5	2430	0.00004– 9 good–24	a	
28	3.0	4.0	2.0	9.0	223.9	2400	n.r.– 7 good–23 good–36	a	
29	3.0	5.0	2.0	10.0	226.2	2430	n.r.– 8 good–25	a	
30	3.0	5.0	2.0	10.0	228.2	2400	good– 9 good–28	a	Excess heat from fan?

*See second note, Table I.
†Length of zone 1 to point where opacity ceases.
‡After second start.