

IONIZATION AND THERMAL E. M. F.
IN SELENIUM VAPOR

W. T. SPROULL and R. E. MARTIN, Hanover College

PART I.

It is well known that the electrical resistance of properly annealed metallic selenium is decreased by illumination with visible light. One of the leading theories of this action supposes that the light causes a change in the crystalline structure of the selenium.¹ Thus, F. C. Brown² suggested in 1911 that the observed phenomena could be explained by assuming that selenium has three crystalline forms, A, B, and C. A is non-conducting; B has a conductivity approaching that of the metals, and C has a very low conductivity. The A form has a tendency to pass over into the B form, and the B into the C form, and both of these changes are reversible. The action of the light is to affect the rates at which these transformations proceed, thus changing the relative quantities of the three types present, and so altering the conductivity.

The other leading theory³ of this light action supposes that the light acts directly on the electronic structure of the selenium, or in other words that the phenomenon is a modified photoelectric effect.⁴ The term "photoelectric effect" is here used in a broad sense, including any effect in which light or other electromagnetic radiation acts directly on the orbital electrons, ejecting them from the atom. By 1915, F. C. Brown⁵ had come to the conclusion that the annealed selenium may contain "electronic centers, possibly atomic, in an almost unstable condition," and that the light still further lowers the stability, freeing a few electrons temporarily.

For ordinary commercial selenium as obtained from the chemist, however, R. Hamer⁶ has found that the photoelectric threshold is 2670 \AA . It must be remembered that only the specially annealed form of selenium is light sensitive.

With these things in mind, it seemed that if the second theory of the light action in selenium were the correct one, it could be conjectured that the "electronic centers... in an almost unstable condition" might be found in gaseous or vaporized selenium where the great thermal agitation would tend to produce instability.

Consequently, this work was originally undertaken to see if ionization could be produced in selenium vapor by radiation of a longer wave-length than would be expected if selenium were only an ordinary substance without unusual light-sensitive properties. It is to be kept in mind that ionization of selenium vapor, and photoelectric emission from metallic selenium are basically identical processes.⁷

The first step was to see if ionization could be produced with ordinary visible light. A diagram of the apparatus used is shown in figure 1, with the

¹Berndt, *Phys. Zeits.* 5., pp. 121-124, 1904. Marc, *Zeits. Anorg. Chem.* 37, pp. 459-475, 1903; 48, pp. 393-426, 1906.

²*Phys. Rev.* (1), 33, 1, 1911.

³Ries, *Phys. Zeits.* 12, pp. 480-490, 1911.

⁴H. S. Allen "Photo-Electricity," p. 96.

⁵*Phys. Rev.*, (2), 5, p. 404, 1915.

⁶O. S. A., F., 9, pp. 251-257, 1924.

⁷Starling, "Electricity and Magnetism" (4th Edition), p. 582.

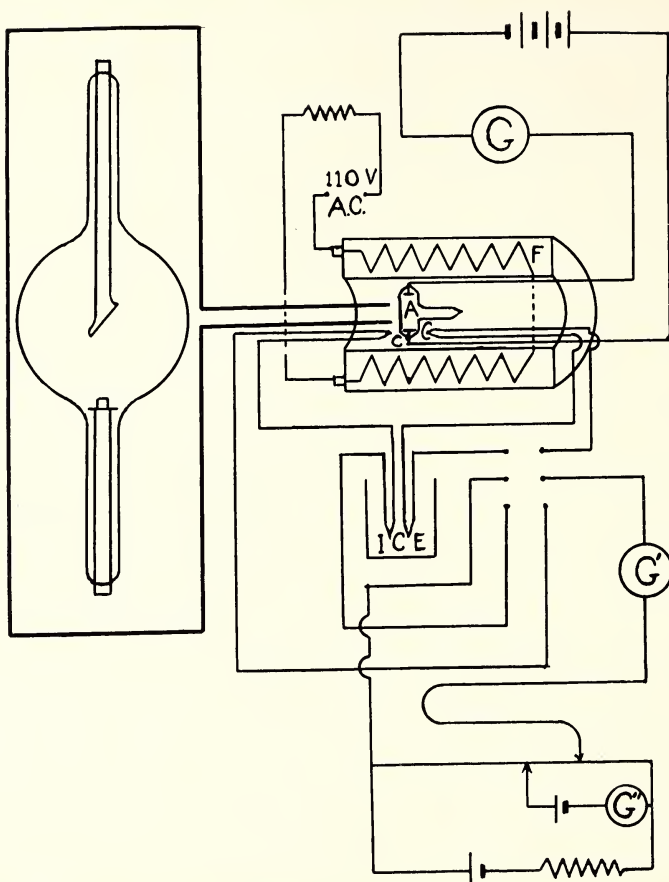


Fig. 1—Diagram of apparatus for producing and measuring ionization in selenium vapor.

exception that a large 1,000 watt incandescent light bulb replaces the X-ray tube shown. F is a cylindrical electric resistance furnace, a longitudinal section being shown in the figure. A is a cylindrical pyrex tube in which the selenium was vaporized. The length of the tube was about $4\frac{1}{2}$ cm., and its diameter about 2 cm. Circular tungsten disks brazed to tungsten lead-in wires formed the electrodes. Immediately outside the tube the tungsten wire was securely bolted to copper wire by means of small brass bolts. The copper wires were connected so as to put the tube in series with a D'Arsonval galvanometer and a storage battery, usually of 240 volts e.m.f. The temperature of the tube was measured by two copper-constantan thermo-couples having the hot junctions, C, C' almost against, and on opposite sides of the tube. The e.m.f.'s of the thermocouples were read with a Leeds & Northrup type K potentiometer.

In studying the problem of the proper quantity of selenium to vaporize in the tube, one must consider the fact that the number of atoms per molecule of vapor varies with pressure and temperature⁸ as shown in figure 2, which is due to

⁸Zeits. physical Chem. 1912, 81, p. 129. (G. Preuner and I. Brockmiller).

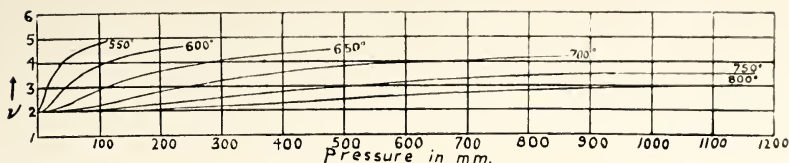


Fig. 2.—Curves obtained by Preuner and Brockmiller showing number of atoms per molecule in selenium vapor at various pressures and temperatures.

Preuner and Brockmüller. The proper amount of c.p. selenium was introduced through the side tube, after which the pyrex tube was exhausted of air and sealed off.

The intensity of illumination produced in the tube by the large lamp was measured with a Sharp-Millar portable photometer. The end of the furnace opposite the bulb was closed to prevent air currents, and the interior of the furnace was painted black to prevent reflection.

Trials were then made at various temperatures from 300 to 600°C, to see if any change in galvanometer deflection occurred as the lamp was turned on and off. The first trials showed a marked change in deflection which increased systematically as the lamp was brought nearer to the furnace. However, as a precautionary measure, the trials were repeated with the pyrex tube containing only air, and precisely the same results obtained. It was then obvious that most of the effect, at least, was due to the heating of the pyrex by the intense radiant heat from the huge lamp, the resulting change in the conductivity of the pyrex causing the spurious effect.

A water cell was then inserted between the lamp and the tube, and the experiments repeated. It was then found that no observable change in deflection resulted when the lamp was turned on and off, up to intensities of 3,500 foot-candles. Since the deflection was about 20 cm., and a change of .1 cm. could be easily noted, it was concluded that no ionization was produced sufficient to cause a $\frac{1}{2}$ per cent change in conductivity.

The large bulb and the water cell were then replaced by a Coolidge X-ray tube contained in a heavy lead box fitted with a thick walled lead pipe of about $\frac{1}{4}$ inch internal diameter. This served to produce a small beam of X-rays which was concentrated on the tube so as to miss the tungsten electrodes by a wide margin as shown in figure 1. The rays striking the tube had a minimum wavelength of about $\frac{1}{4}$ Å. and an intensity of about 1 erg/sec./sq. cm. They produced a marked ionization, causing changes in deflection as high as 40 per cent depending upon the quantity of selenium in the tube and the temperature.

The X-ray tube was then replaced by a quartz mercury arc, and the pyrex tube A, figure 1, by a quartz tube. This quartz tube was shaped like a test tube and the open end was fitted with an asbestos plug through which passed two tungsten wires as electrodes. Since this tube was not perfectly gas tight, sufficient selenium was introduced to keep the tube filled with saturated vapor. The results were the same as with visible light, that is, no change in conductivity as great as $\frac{1}{2}$ per cent was produced.

Due to the fact that the work function involved in the ionization of a gas is, in general, greater than the work function involved in photoelectric emission from the same substance in the solid state, one should not expect any ionization

in selenium vapor until radiations considerably below the 2670°A photoelectric threshold for commercial selenium are reached, *provided* the vapor has no special light sensitive property such as the specially annealed metallic form. One of the strong mercury lines has a wavelength of 2537°A . The fact that ultra violet light of this wave-length produced no ionization indicated that the vapor has no special light sensitive property.

Of course, if the theory that light action in selenium is due to crystalline changes is the correct one, it would be absurd to expect light action in the vapor.

PART II.

During the progress of these experiments, it was found that if the storage battery were removed from the circuit running to the tube, and the circuit now containing only the galvanometer and the tube, were closed, a deflection would result when the temperature of the tube was above about 450°C . Since the tube had been mounted crosswise in the furnace, as shown in figure 1, the opposite ends of the tube could not have varied in temperature by more than two or three hundredths of a degree Centigrade. When the galvanometer was replaced with a Leeds & Northrup type K potentiometer, the e.m.f. was found to be of the order of .01 volt, or 10,000 microvolts. An e.m.f. of this magnitude, in view of the very small temperature difference existing seemed impossible to explain as a thermal e.m.f. However, when the e.m.f. was measured with the tube at various temperatures, and with it containing different quantities of selenium, it was found that the e.m.f. varied quite erratically both in magnitude and direction. Since we were unable to explain it on any other basis, we had to assume that it must be an extraordinarily large thermal e.m.f.

Going on this assumption, we prepared some new pyrex tubes similar to the old ones, but very much longer, being about 15 inches in length. For electrodes, plain tungsten wire was used without any disk brazed to the ends of the wires. The tube was mounted lengthwise in two electric furnaces, one end being in one furnace and the other in the other, as shown in figure 3. The gap between the two furnaces was closed with an asbestos apron so as to keep the central part of the tube hot. The tube was filled, in most cases, with sufficient selenium to keep the interior filled with saturated vapor. The electrodes were connected by copper wires to a Leeds & Northrup type K potentiometer, as shown. The open ends of the furnaces were closed, and mercury thermometers inserted so that the bulbs were in contact with the opposite ends of the tube. One furnace was maintained at a constant temperature such that the thermometer read 350°C

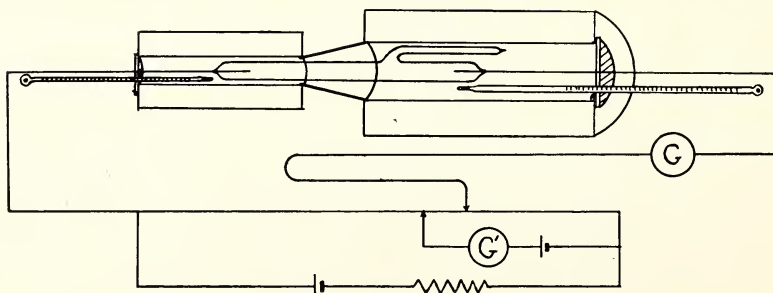


Fig. 3—Diagram of apparatus for measuring thermal e.m.f. in selenium vapor at various temperatures.

The temperature of the other furnace was varied from 470° to 620°C. Below 470°, the resistance of the vapor became so great that the balance point of the potentiometer could not be determined with satisfactory accuracy. At 620°, the pyrex began to melt, so that these two temperatures determined the range of temperature to be used. Since copper lead-in wires were used, the thermal e.m.f. resulting would be between the vapor and copper.

With such a tube filled with sufficient selenium to maintain a saturated vapor, the e.m.f. was carefully measured for various temperatures of the hotter furnace, both while rising and while falling. The values obtained on the first trial are shown in column 3 of the table, the corresponding curve being the one marked by the \oplus marks in figure 4. This experiment was then repeated after allowing a day or so to elapse, without in any way disturbing the apparatus. In this trial, the values shown in column 4 of the table were obtained, the cor-

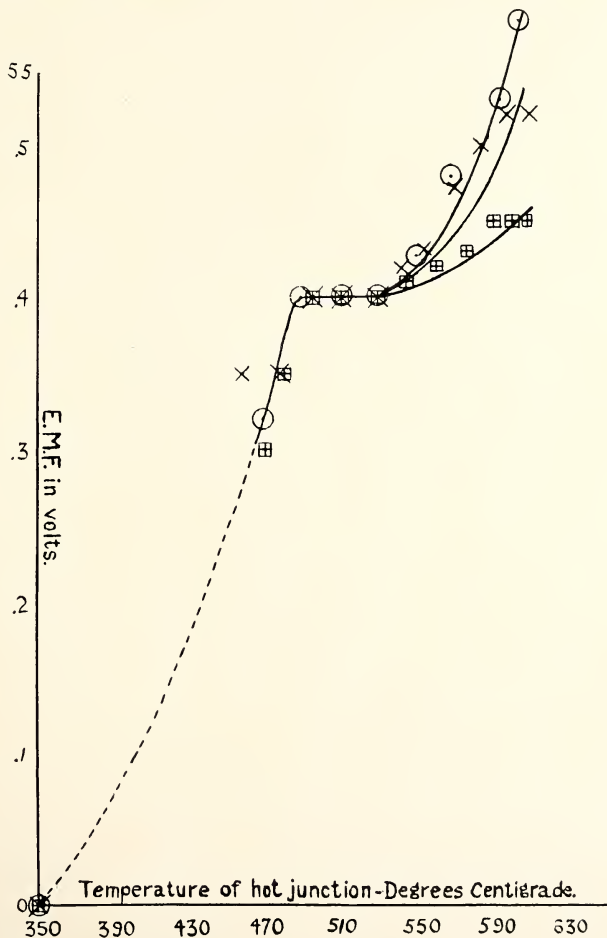
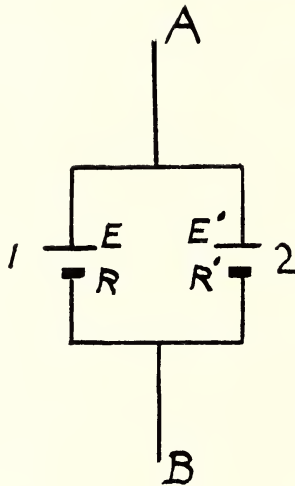


Fig. 4—Thermal e.m.f. curves for selenium vapor against copper showing effect of vapor action on tungsten electrodes.

responding curve being the one marked by X's. A day or so later, without disturbing the apparatus, a third trial was made, and this time the values shown in column 5 were obtained, the corresponding curve being marked with the circles.

Before attempting to explain these curves, it is well to show that these e.m.f.'s could not have been thermal e.m.f.'s in the pyrex of the tube. Considering the circuit, one sees that between the electrodes the current has the choice of two parallel routes: (1) Through the vapor, or (2) Through the pyrex. After the trials mentioned above were run, the tube was opened and the selenium entirely expelled by baking in a hot furnace. The trial was then repeated with the empty tube, and it was found to be impossible to accurately balance the potentiometer, for even when the balance was off by as much as $\frac{1}{2}$ volt, a scarcely perceptible galvanometer deflection was produced. This showed clearly that the resistance of the pyrex was at least 50 times that of the vapor.



Let us then consider (Fig. 5) two cells, 1 and 2, in parallel, connected to a potentiometer, which of course draws no current when balanced. Let No. 1 represent the vapor, and let E =its e.m.f. and R =its resistance. Let No. 2 represent the pyrex, and let E' =its e.m.f. and R' =its resistance. Consider the circuit from A to B (Fig. 5) open. Assume E greater than E' . Then the current flowing through the walls of the tube is given by

$$\frac{E - E'}{R + R'}$$

Thus the potential difference between the electrodes, or between A and B is

$$\frac{E - E'}{R + R'} R' + E'$$

Now if R' is very large compared to R , as was found to be the case, this p.d. reduces to $E - E' + E' = E$.

Or, assume E' larger than E . Then the current becomes $\frac{E' - E}{R + R'}$, and the p.d. be-

$$E' - E$$

comes — $R + E = E$ when R' is very large compared to R . Thus we see that $R + R'$

the potential difference measured between the electrodes by the potentiometer is, within 1 or 3 per cent the actual e.m.f. of the selenium vapor.

After dismantling the apparatus, it was discovered that the tungsten electrodes had entered into a chemical combination with the selenium forming a very heavy coating of a yellowish substance which must have been a selenide of tungsten. In fact, the electrodes had been completely disintegrated into the yellowish powder in some places. This gives a suggestive clue as to the probable explanation of the peculiar shape of the curves above 490°C .

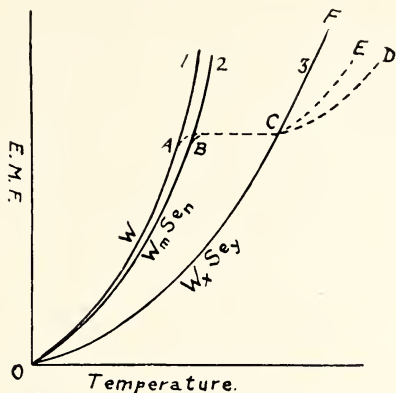


Fig. 6.

After considerable thought, it seemed as though the observed effects could be explained as follows. In figure 6, suppose curve 1 is the e.m.f.-temperature curve with pure tungsten electrodes, and that No. 2 is the curve for some tungsten selenide, $W_m\text{Se}_n$, and that No. 3 is for some other tungsten selenide, $W_x\text{Se}_y$.

In the first trial run, the curve obtained was of a form similar to OACD. It seems likely that at the point A, the tungsten began to combine with the selenium, forming the compound $W_x\text{Se}_y$, and that at the point C, the entire surface had become coated with the selenide, so that the curve CD resulted. As the furnace cooled, it seems that some change began when C was reached again. We can assume that the $W_x\text{Se}_y$ began to change into another selenide $W_m\text{Se}_n$, the change being complete when the point B was reached. The curve BO was then followed as the cooling continued. During the second trial, the e.m.f. retraced the curve OB, until at B, the $W_m\text{Se}_n$ began to change again into $W_x\text{Se}_y$. However, when C was reached this time, more of the tungsten beneath the surface had combined forming $W_x\text{Se}_y$, so that the e.m.f. was not exactly the same as before, but followed the curve CE. On cooling, the path ECBO was retraced similarly to the first trial. On the third trial, practically the entire electrode had changed to $W_x\text{Se}_y$, giving the curve CF, which is the curve for that compound.

This hypothesis supposes that the curve OA for pure tungsten, and the curve OB for $W_m\text{Se}_n$ lie so close together that they appeared as the same curve from the data. It cannot be assumed that the $W_x\text{Se}_y$ compound decomposed back

into tungsten and selenium on cooling, for after the tube was cold, it was found that the electrodes had changed completely into the yellow selenide called W_mSe_n in this hypothesis. This theory is the only one which has occurred to us which will explain all of the observed facts.

An attempt was made to see what effect would be produced in the curves by using tubes containing unsaturated selenium vapor. It was found, however, that as soon as a run was attempted with only enough selenium in the tube to form an unsaturated vapor, that the formation of the selenide absorbed so much vapor that the resistance of that vapor remaining became about the same as that of the pyrex walls in the tube so that e.m.f. measurements of any accuracy were impossible. This trouble might be eliminated if some other metal like, say, platinum were used for the electrodes, but since tungsten lead-in wires would have to be sealed in the pyrex, these wires would be attacked by the vapor, and it is not likely that satisfactory results could be obtained.

A trial was also made using saturated mercury vapor in the tube, but even though the furnace was heated until the mercury vapor swelled the tube out of shape, the resistance of the vapor was still so high that no satisfactory measurements could be made.

The results of the experiments on ionization thus lead us to conclude that vaporized selenium has no unusual light sensitive properties such as are found in the specially annealed metallic form. This shows that either (1) light action in the annealed selenium is due to crystalline transformations as suggested by Berndt and Marc, or (2) if the light action is a modified photoelectric effect, no "electronic centers. . . . in an almost unstable condition" are present in the vapor such as those suggested by Brown as existing in the annealed selenium.

The experiments on the thermal e.n.f. of selenium vapor show that the vapor has an unusually high thermoelectric power against tungsten, but that chemical combination between the vapor and the tungsten makes it impossible to obtain the true e.m.f. curve above about 485°C.

TABLE I

Temperatures in degrees C.		E. M. F. in Volts		
Hot Furnace	Cold Furnace	Trial 1	Trial 2	Trial 3
460	358	..	.35	..
470	35332
471	340	.30
480	352	..	.35	..
482	347	.35
491	35040
496	350	.40
498	350	..	.40	..
511	351	.40
512	35140
512	349	..	.40	..
531	351	.40
531	347	..	.40	..
531	35340
544	349	..	.42	..
546	351	.41
552	34743
556	348	..	.43	..
562	350	.42
570	34748
571	347	..	.47	..
577	347	.43
585	354	..	.50	..
592	344	.45
596	35053
600	350	..	.52	..
602	349	.45
610	352	.45
611	350	..	.52	..
616	35058