

## THERMIONIC AND PHOTO-ELECTRIC PHENOMENA AT THE LOWEST ATTAINABLE PRESSURE.

BY C. F. HAGENOW.

SYNOPSIS.—The object of these investigations was fourfold:

1. To study the photo-electric effect of tungsten at the lowest possible pressures, especially after the illuminated plate had been denuded of occluded gases by continued electronic bombardment of such energy as to maintain it at a white hot temperature.

The pressures attained were as low as  $3.5 \times 10^{-7}$  mm. of mercury. Upon denuding a tungsten plate of its occluded gases by raising it to a bright yellow heat by electronic bombardment, the photo-current rose to many times the value obtained before such denuding and further heating produced no further change.

2. To find, by direct observation, the short wave-length limit for tungsten and to observe how this changes, if at all, with the removal of occluded gases.

The upper wave-length limit of tungsten was located in the region between 2100 and 2300 Å. According to Einstein's equation, the corresponding values of the work necessary to free an electron from the metal would then be between 5.7 and 6.3 volts. These are larger than the corresponding values in the case of thermionic emission.

3. To observe, with the aid of the electric vacuum gauge, recently devised by O. E. Buckley, the progress of the clean-up effect, particularly at extremely low pressures.

Under the conditions employed it was not found possible to reduce the pressure by means of the clean-up alone lower than  $10^{-5}$  mm., which was not as low as could be attained with the pump itself.

4. To study pressure and other changes accompanying the appearance of the "blue haze."

A gradually increasing potential difference was applied between the tungsten plate and a glowing filament until the blue haze appeared. *No pressure change whatever was observable at the moment of its appearance.* Certain current and voltage discontinuities, which occur under the experimental condition just described, were found to have characteristics similar to those observed by O. W. Richardson and Charles B. Bazzoni in the case of mercury vapor. The clean-up of the blue haze is very rapid and shows a striking increase in its rate of absorption as the pressure approaches the final minimum. This behavior is in marked contrast to the clean-up with a lighted filament, but without a field, and is quite similar to that observed by S. Brodetsky and B. Hodgson in their experiments with a vacuum tube discharge under the condition of abnormal cathode fall. At the pressures employed in these trials, about .01 mm. of mercury, this final pressure remained unchanged in the presence of the field, and did not change further even in those cases in which a trace of the blue glow remained in the tube.

### I. EFFECTS OF ELECTRONIC BOMBARDMENT UPON PHOTO-CURRENTS FROM TUNGSTEN.

THE question of the part played by occluded gases in photo-electric phenomena has received the attention of many observers. Among those who have contended that the photo-electric effect is essentially dependent upon the presence of occluded gases may be mentioned Paech,<sup>1</sup> Fredenhagen,<sup>2</sup> Küstner<sup>3</sup> and Wiedemann and Hallwachs.<sup>4</sup> In particular, Küstner finds a total absence of the effect in the case of zinc when gases were removed. The zinc was scraped in vacuo and all "reacting" gases were removed by a spark discharge over potassium.

These conclusions are contradicted by experiments made by Pohl and Pringsheim,<sup>5</sup> Hennings,<sup>6</sup> Piersol,<sup>7</sup> Dushman,<sup>8</sup> Millikan and Souder,<sup>9</sup> and Welo.<sup>10</sup> For example, Piersol finds an increased sensitiveness in a number of metals when the occluded gases are removed by heating the electrode with an electric current. He also observed a superposed maximum effect "dependent on the activity of the gaseous surface," which disappeared after the highest temperature was reached.

This author states that a vacuum of .0002 cm. of mercury was used

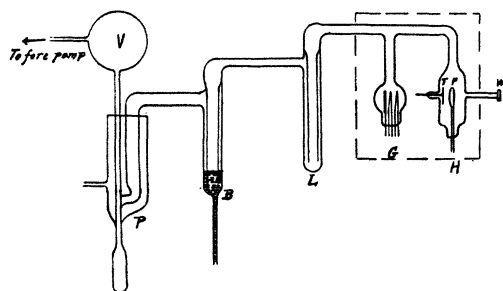


Fig. 1.

and does not mention the use of liquid air, so that the degree of exhaustion which he attained was not of the order aimed at in this experiment.

As the technique for the removal of the occluded gases and production of higher vacua has been improved, the evidence has become more and

<sup>1</sup> G. Paech, *Ann. der Phys.*, 43, 135, 1913.

<sup>2</sup> K. Fredenhagen, *Phys. Zeit.*, 15, 65, 1914.

<sup>3</sup> H. Küstner, *Phys. Zeit.*, 15, 68, 1914.

<sup>4</sup> G. Wiedemann and W. Hallwachs, *Ber. d. D. Phys. Ges.*, 16, 107, 1914.

<sup>5</sup> R. Pohl and P. Pringsheim, *Ver. d. D. Phys. Ges.*, 16, 336, 1914.

<sup>6</sup> A. E. Hennings, *PHYS. REV.*, 4, 228, 1914.

<sup>7</sup> R. J. Piersol, *PHYS. REV.*, 8, 238, 1916.

<sup>8</sup> See I. Langmuir, *Phys. Zeit.*, 15, 524, 1914.

<sup>9</sup> R. A. Millikan and W. H. Souder, *Proc. Nat. Acad. Sci.*, 2, 19, 1916.

<sup>10</sup> L. A. Welo, *PHYS. REV.*, 4, 251, 1918.

more conclusive for the contention that the photo-electric effect is an intrinsic property of the pure metal. This paper furnishes further convincing support of this point of view.

The apparatus (Fig. 1) was exhausted by the mercury diffusion pump *P* (kindly furnished by the Western Electric Company), working against a fore-vacuum of .01 mm. of mercury, or less, produced by a Töpler pump. Once established, no further pumping was necessary, as the volume, *V*, was quite large compared with that of the rest of the apparatus. A barometer tube, *B*, served as a valve to shut off the part to the right of it. *L* is the liquid air trap, which was kept continually in liquid air while the apparatus was set up. At no time was there any evidence of mercury vapor in the tube *H*. For measuring the pressures the extremely sensitive ionization gauge, *G*, due to Buckley,<sup>1</sup> was used. The photo-electric tube, *H*, contained the tungsten plate,<sup>2</sup> *T*, opposite which, at a distance of about a centimeter, the tungsten filament, *F*, and, in line with both, a tube sealed with a quartz window, *W*; the last being fastened with De Khotinsky wax. The connecting tubing had a bore of about 2.5 cm. and the whole apparatus was made as compact as possible. The source of illumination was, for the most part, a spark between zinc terminals. To avoid all electromagnetic disturbances, the spark gap, together with the induction coil, storage cell and Leyden jar, were all enclosed in an iron box.<sup>3</sup> A Dolazelek electrometer served for measuring the photo-currents, a sensibility of about 300 mm. per volt being usually employed. An electric oven could be slipped over a region indicated in the figure by the dotted line.

The ionization gauge, calibrated by Buckley against both a McLeod and a Knudsen manometer, gives the pressure in millimeters of mercury according to the formula (for air),

$$p = .05 \frac{I_C}{I_A},$$

where  $I_A$  is the current, in amperes, set up by a coated filament in a field of 200 volts and  $I_C$  the resulting flow of positive ions. The former can be read on a milli-ammeter, at least for the larger values, and the latter by means of a galvanometer. In order to read the smaller currents for  $I_A$  at the higher pressures more accurately, the writer employed the following null method of measuring these small currents. Fig. 2 shows the connections. A known resistance,  $R_1$  is placed in series with the

<sup>1</sup> O. E. Buckley, Nat. Acad. Sci. Proc., 2, 683, 1916.

<sup>2</sup> This was a thorium free sample kindly furnished by Dr. Langmuir and of the same sort used by him in the determination of Richardson's "b."

<sup>3</sup> W. H. Kadesch, PHYS. REV., 3, 367, 1914.

circuit whose current it is desired to measure. Connected to one end,  $A$ , of this resistance, is a circuit containing a variable resistance,  $R_2 + R_3$

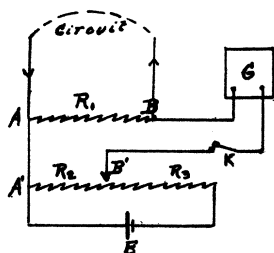


Fig. 2.

and a cell, whose E.M.F. need be known only to the degree of accuracy of the gauge itself. A Leeds and Northrup portable galvanometer was put at  $G$ . The adjustment consists simply in finding a point  $B'$  so that on closing the key,  $K$ , no deflection resulted.  $B$  and  $B'$  being then at the same potential, we have, calling the currents in  $R_1$  and  $R_2$  respectively  $C_1$  and  $C_2$ ,

$$C_1 R_1 = C_2 R_2.$$

Also

$$C_2 = \frac{E}{R_2 + R_3},$$

Therefore

$$C_1 = \frac{R_2 E}{R_1 (R_2 + R_3)}.$$

As actually used, the resistances were set in a fixed relation and the heating current of the glower of the gauge regulated for zero deflection of the galvanometer. Since  $I_A$  need not be changed very often (*i. e.*, only for a large variation in the range of pressure) a few previously calculated values of  $R_1$ ,  $R_2$  and  $R_3$  enabled one quickly to set on any desired current.

The limit of this instrument to indicate low pressures is set only by the possibility of being able to measure the current  $I_C$ . On the other hand, it was found that a maximum reading was obtained at .019 mm. This was located by plotting the values of  $I_C$  against time as the apparatus was gradually exhausted by a Gaede mercury pump.

The photo-currents measured were the saturation currents for a timed duration of the spark. The plate  $T$  (Fig. 1) was connected to one of the quadrants of the electrometer, the other being earthed. A positive potential was applied to the filament,  $F$ , the other pole being earthed, and the liberated electrons thus removed from the tube. A field of 10 to 20 volts was sufficient for saturation.

With the apparatus as first set up and no further exhaustion than simply pumping with the diffusion pump, the following readings were taken.

The photo-currents are expressed in millimeters deflection on the basis of 300 mm. per volt sensibility and 2-second illumination when the electrometer alone is used. (Sometimes an auxiliary condenser had to be connected.) These are given under  $C$  in the last column.

TABLE I.

Date.	No.	$p$ .	$C$ .	Date.	No.	$p$ .	$C$ .
May 10	1	$4.8 \times 10^{-3}$	9.6	May 13	8	$7.7 \times 10^{-3}$	9.8
11	2	"	7.2	14	9	$5.2 \times 10^{-3}$	8.7
12	3	"	7.1	"	10	$3.8 \times 10^{-4}$	7.7
"	4	"	6-6.8	"	11	$1.4 \times 10^{-4}$	8.1
"	5	"	8.2	"	12	$8.0 \times 10^{-5}$	8.9
13	6	$5.0 \times 10^{-3}$	7.9	15	13	$5.1 \times 10^{-5}$	7.8
"	7	$3.2 \times 10^{-4}$	8.7	"	14	$8.5 \times 10^{-5}$	7.3

As is to be expected from all preceding photo-electric work there is here no evidence for a relation between pressure and photo-currents. The table includes every run that was made until the apparatus was opened. On one or two occasions the writer has noticed fluctuations in excess of those here recorded, but the foregoing are representative of the sort of constancy that readings, taken days or weeks apart under apparently the same conditions, would show.

It may be mentioned, parenthetically, that readings were sometimes taken at zero fields, the filament  $F$  being earthed. Both  $T$  and  $F$  being of the same metal there should be no contact potential present. The results were very variable in this case as might be expected under the conditions. The number of electrons caught by the filament would depend on their particular distribution at any particular time, and this would be influenced by the charging of the inner surface of the glass tube. It was observed that illuminating the plate repeatedly, even when it was earthed at the time, would cut down the ensuing current greatly, doubtless because of such accumulation of charge on the walls. The effect would disappear after a short while. This phenomenon practically ceased at the saturation voltage, as it should do if the foregoing explanation is correct.

The effect upon the photo-currents,  $C$ , of denuding the tungsten plate of gases is shown in Table II. The headings have the same significance as in Table I. The denuding was done by glowing the filament while the negative potential indicated in the last column was applied to it.

So far no parts of the apparatus had been baked out or the metal parts heated, except the illuminated plate as described.<sup>1</sup>

No further readings were taken for four months. A new tungsten plate was mounted, though from the same original piece. Then the data contained in Table III. were taken.

The increase in no. 3 is not as large as was expected in view of the

<sup>1</sup> The ionization gauge and the tungsten filament in the photo-tube had been renewed since the readings in Table I. were taken.

TABLE II.

Date.	No.	$p$ .	$C$ .	Remarks.
June 9	1	$1.5 \times 10^{-3}$	1.4	Just after set up.
"	2	"	187.6	After first bombardment, for 10 minutes up to 960 volts D.C. No observable heating of the plate.
	11	$1.9 \times 10^{-3}$	133.0	No further treatment since last observation.
	12	$2.0 \times 10^{-3}$	433.0	After bombardment with 1,500 volts, about 30 minutes.
	13	$1.9 \times 10^{-3}$	449.0	No further treatment since last observation.
		(Apparatus opened.)		
July 6	6	$2.6 \times 10^{-3}$	94.0	Note decrease after exposure to the air.
"	7	$2.0 \times 10^{-3}$	1885.0	After bombarding at 1,500 volts. Not visibly heated but surface slightly altered in appearance.
"	8	$2.0 \times 10^{-5}$	1900.0	After pumping down to 1/100 value of preceding pressure. Practically no effect on the photo-current.
	7	$1.6 \times 10^{-3}$	1715.0	Day after a bombardment up to 1,400 volts, about 30 minutes. First time plate at red heat in spots.
		(Apparatus opened.)		
	18	$2.9 \times 10^{-3}$	4.0	Decrease after exposure to air.
"	11	$4.8 \times 10^{-4}$	968.0	After bombardment at 3,500 volts A.C. about 30 minutes. Plate bright red in central portion, duller at edges.

effect of other cases of bombardment. Also the spontaneous increase in no. 6 is hard to account for, unless the fact mentioned in the last column may have had some bearing on it. However in view of the results of all these observations, it appears that there is an enormous increase of photo-sensitiveness after the occluded gases are removed. No. 7 shows the final reading at the lowest pressure attained for photo-electric observations in the course of these experiments. The tube and gauge had been baked out, the metal parts all glowed (the collector plate of the gauge had shown no visible heat during the bombardment, but a subsequent bombardment that caused it to glow did not influence the pressure attained). It can then fairly represent the conditions of a pure metal in a very low pressure thoroughly out-gassed. The close agreement of the final values of  $C$  in Tables II. and III. is probably largely accidental. On account of a rearrangement of the set up, necessitated by the addition of a monochromatic illuminator, the intensity of illumination of the plate in Table III. was slightly changed.

According to Table II. the maximum photo-current occurs after only

TABLE III.

Date.	No.	<i>p.</i>	<i>C.</i>	Remarks.
Nov. 30	1	$2.2 \times 10^{-8}$	50	
Dec. 1	2	"	93	After a slight bombardment to try a new transformer.
Jan. 1	3	$6.2 \times 10^{-5}$	112	After bombarding 15 minutes at 3,500 volts A.C. Plate at red heat all over.
	2	$9.0 \times 10^{-4}$	106	No further treatment since last observation.
	3	$1.1 \times 10^{-5}$	111	After baking tube and gauge for one hour at 300° C.
	7	$1.2 \times 10^{-4}$	407	This was after the tungsten filament had been brightly glowed for one hour for a clean up experiment.
	8	$3.5 \times 10^{-6}$	964	After bombarding 15 minutes at 2,200 volts A.C. Plate at a bright orange yellow heat. Now appears for the first time a bright metallic lustre.

a moderate heating of the plate. This maximum does not appear in Table III. and is probably due to some accidental surface condition in the first case. Piersol,<sup>1</sup> however, has observed a similar phenomenon in the case of a number of other metals. When new trials along this line were undertaken some weeks later, troubles unfortunately developed with the mountings of the tungsten plate that made further tests of this kind impossible.

Pressure readings were made with this apparatus down to  $3.5 \times 10^{-7}$  mm., with the photo-tube taken off. This is below the lowest pressure which it was possible to maintain for photo-electric observations. The De Khotinsky wax, used to hold the quartz window, may account for this difference. Also, as has been mentioned above, it was impossible to bake out every part of the apparatus. An attempt to heat the parts not inclosed by the oven with a Bunsen burner, while the diffusion pump was in operation, proved a failure. With the gauge and tube in the electric oven, and the diffusion pump going, mercury vapor diffused over into the tube.

It was also found that, though taking off the liquid air caused the pressure to rise rapidly, the vacuum could be as quickly restored by replacing it, with the pump in operation. Thus in one case the pressure rose almost immediately from  $5 \times 10^{-6}$  to  $1.2 \times 10^{-2}$  mm. and returned to  $5 \times 10^{-6}$  mm. It may be remarked that the low pressures mentioned just above were read after mercury vapor had diffused through the tubing as described.

<sup>1</sup> *Loc. cit.*

## II. DIRECT OBSERVATION OF LONG WAVE-LENGTH LIMIT OF TUNGSTEN.

To determine the long wave-length limit of sensitivity of the tungsten a Hilger monochromatic illuminator was set up before the quartz window; a Heræus quartz mercury lamp being the source of light. As used with this apparatus, this lamp with direct illumination of the tungsten plate, gave a scale deflection about three times as large as that obtained previously with the zinc spark, *i. e.*, about 1,000 mm. in two seconds of illumination when no condenser was used. When the light was passed through the monochromator it was found impossible to obtain any deflection at all with any wave-length which would pass through the instrument. However some idea was gained of the limits of sensitiveness by means of two absorption media.

A solution of methyl alcohol placed in the path of the direct beam from the source<sup>1</sup> cut out the effect entirely. The first trials were made after the runs no. 2 in Table III. Other trials after no. 3 gave the same results. Finally after the last run, no. 7, a small deflection was observed. This was less than one thirteen hundredth of the deflection caused by the unfiltered light and about twice that which could still be observed with certainty. Since this sensitiveness was not attainable before the plate was thoroughly out-gassed, any conclusions as to a real change of the wave-length limit based on the absence of any observable effect under those conditions would be correspondingly doubtful.

The empty absorption cell itself, by virtue of the absorption of its fused quartz windows, cut down the deflection to only one tenth of its value, both before and after the plate was out-gassed.

Mt. M. J. Kelly, at this laboratory, found, photographically, that methyl alcohol had a sharply defined absorption region beginning with decreasing wave-length, at 2370 Å, and that the fused quartz windows had a similar absorption region beginning at 2160 Å. Now the above experiment showed that about nine tenths of the total light effect must have been due to wave-lengths shorter than 2160 Å, and all but one part in thirteen hundred to wave-lengths less than 2370 Å. The question arises whether this residual effect is due to active wave-lengths longer than 2370 Å or to a very small amount of light of shorter wave-length that was not entirely absorbed by the methyl alcohol. The latter is the more natural assumption, so that the indication of this experiment is that the long wave-length limit of tungsten is between 2100 and 2300 Å.

We can compare these results with the minimum frequency for which tungsten is light-sensitive, as calculated from Einstein's equation,

$$hv_0 = w_0$$

<sup>1</sup> The zinc spark was also used at times.



where  $w_0$  is the work done by an escaping electron against the forces which tend to retain it in the metal. If we assume that  $w_0$  has the same value as in thermionic emission, we can use its value as obtained from thermionic experiments. Lester<sup>1</sup> has made some experimental verifications of the identity of the "work function,"  $\varphi$ , of an electron escaping from a metal and "b" in Richardson's equation,

$$i = a\theta^{1/2}e^{-b/\theta}.$$

The relation is

$$\varphi e = bk,$$

where  $e$  is the charge on an electron,  $k$  the gas constant for one molecule.  $\varphi$  was calculated from experiments made on the "cooling effect." Now if we assume that  $w_0$  in Einstein's equation has the same value as in thermionic emission, using Lester's value for tungsten,  $\varphi = 4.478$  volts, we have

$$\nu_0 = \frac{\varphi e}{h} = \frac{4.478 \times 4.774 \times 10^{-10}}{300 \times 6.547 \times 10^{-27}} = 1.088 \times 10^{15},$$

or

$$\lambda_0 = 2757\text{\AA}.$$

On the assumption that the experiment with the methyl alcohol light filter does really indicate a total absence of light sensitiveness to wave-lengths longer than 2370 Å, the difference is seen to be at least 400 Å. This is much larger than the variations in either the values of  $\varphi$  as observed by Lester, or the values of  $b$  obtained by Langmuir when proper precautions were taken to have all occluded gases removed.

It may be mentioned that Lester's value of  $b$  ( $= \varphi e/k$ ) is 52,130. This agrees well with the weighted mean value,  $b = 53,130$ , which that writer has calculated from some measurements by Smith<sup>2</sup> and Langmuir.<sup>3</sup>

Lester<sup>4</sup> also found that the effect of residual gases was to increase the value of  $\varphi$ . This he tested by sealing off a tube containing a tungsten filament and allowing the glowing filament<sup>5</sup> to clean up the active gases present. Inert gases do not affect  $\varphi$ . If this fact has any direct bearing on the present experiment it would mean that the occluded gases responsible for the higher value of  $\varphi$  were such that they were not driven out by the treatment the plate received as described above.

It is, of course, not established that the work function is the same in photo-electric as in thermionic emission, or that these phenomena deal with the same type of electron. Concerning the case of platinum

<sup>1</sup> Horace Lester, *Phil. Mag.*, 31, 197, 1916.

<sup>2</sup> K. K. Smith, *Phil. Mag.*, 29, 802, 1915.

<sup>3</sup> I. Langmuir, *PHYS. REV.*, 2, 450, 1913.

<sup>4</sup> *Loc. cit.*

<sup>5</sup> *I. e.*, the same filament which was the subject of investigation.

Hughes<sup>1</sup> makes the following comparison: Richardson<sup>2</sup> gives 5.34 volts as representing the work done (per unit charge) when an electron escapes from hot platinum. But from photo-electric observations, using the most probable value of  $\lambda_0$ , viz., 2910 Å,  $V_0$  comes out 3.86 when calculated from  $V = k\nu - V_0$ . When instead of  $k$  the corresponding value from the quantum theory,  $h/e$  is used,  $V_0$  becomes equal to 4.32 volts.

The results of the present experiments indicate a value of the work function, calculated from Einstein's equation, as lying between 5.7 and 6.3 volts. The work required to remove an electron from tungsten photo-electrically thus seems to be larger than that required in the case of thermionic emission.

### III. CLEAN-UP EFFECTS.

The fact that an incandescent filament tends to improve the vacuum has been noted by many observers. It has been subjected to detailed study by Langmuir<sup>3</sup> for a number of gases.

The present attempt offers nothing new, except as it might serve to make a comparison with another sort of clean-up to be discussed later in connection with the blue haze experiments.

The mercury valve, *B* (Fig. 1), was closed and the filament glowed a little more brightly than in the ordinary Mazda lamp. The following readings were then taken.

TABLE IV.

Time (Minutes).	$\beta$ .	Absorption Cu. mm. $\times 10^6 v$ .	Per Minute.
0	$1.2 \times 10^{-4}$		
5	$6.8 \times 10^{-5}$	6.84	1.37
10	$3.5 \times 10^{-5}$	4.55	.91
20	$1.9 \times 10^{-5}$	2.20	.22
30	$1.6 \times 10^{-5}$	.40	.04
40	$1.4 \times 10^{-5}$	.26	.026
50	$1.3 \times 10^{-5}$	.13	.013
60	$1.25 \times 10^{-5}$	.07	.007

The absorbed air is given in cu. mm. at atmospheric pressure per cu. mm. of the volume,  $v$ , of the apparatus used. The last column contains the average rate per minute in the same units.

The next day but one following this run the pressure was found to have risen to  $2.8 \times 10^{-5}$  mm., when the filament was again glowed at a higher temperature, bringing the pressure down to a little below  $10^{-5}$  mm. The graph is shown in Fig. 3.

<sup>1</sup> A. L. Hughes, Photo-electricity, Cambridge University Press.

<sup>2</sup> O. W. Richardson and K. T. Compton, Phil. Mag., 24, 576, 1912.

<sup>3</sup> I. Langmuir, J. Am. Chem. Soc., 34, 1310, 1912; 35, 107, 1913; 35, 931, 1913.

Table IV. shows that the rate of clean-up, as shown in the last column, diminishes to 1/200th of its initial value while the pressure drops to 1/10th of its original amount. According to Langmuir<sup>1</sup> the rate of clean up for oxygen is proportional to the pressure. For nitrogen<sup>2</sup> it is different according to the range of pressure experimented with, but is in-

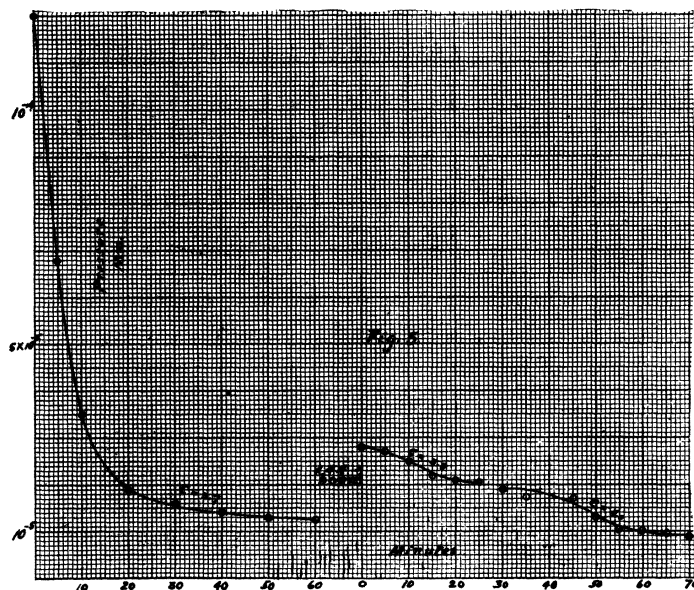


Fig. 3.

dependent of the pressure in the interval from .0065 mm. to .0001 mm. of mercury.

The present experiment indicates that the rate of clean up of air decreases at a greater rate than the pressure and that the latter reaches a fairly well defined limiting value, which is manifestly not due alone to the inert gases. Langmuir found a "fatigue effect" in the case of hydrogen, so that a continual treatment of the glowing wire in that gas brought the clean-up practically to a standstill. In view of these experiments and the fact that the rate of clean up depends on the temperature of the filament in a way widely different for the different gases, no general conclusions can be drawn from experiments on a mixture such as air.

#### IV. PHENOMENA ACCOMPANYING THE APPEARANCE OF THE "BLUE HAZE."

The bluish glow, known as the "blue haze" has often been remarked.<sup>3</sup>

<sup>1</sup> Langmuir, J. Am. Chem. Soc., 35, 107, 1913.

<sup>2</sup> *Loc. cit.*, 35, 931, 1913.

<sup>3</sup> W. R. Whitney, Proc. Am. Inst. El. Eng., 31, No. 1, 921, 1912. Saul Dushman, PHYS.

It can be seen, at a certain state of exhaustion, in the ordinary incandescent lamp. Whitney<sup>1</sup> observed that it "cleaned up" gases and was accompanied by a disintegration of the lighted filament.

The present investigation may be grouped under three heads: (A) Pressure changes and general observations; (B) Current-voltage relations; (C) Clean-up effects.

(A) *Pressure Changes and General Observations.*

To attempt to study the pressure changes preceding and accompanying the appearance of the glow, the following procedure was adopted.

The valve *B* (Fig. 1) was closed, the filament *F* glowed brightly and a positive potential applied to the plate *T*; the filament being the negative pole. The indications of the gauge were observed while the potential was gradually increased.

The first experiments were performed at a comparatively high field voltage of 900 to 2,100 volts A.C. and at pressures varying from  $6 \times 10^{-4}$  to  $5 \times 10^{-5}$  mm. of mercury. No change in the pressure was observed, even at the instant the blue haze appeared and the plate was red hot with the bombardment (showing incidentally how thoroughly the metal had been out-gassed). It was noticed that the gauge current  $I_A$  was always diminished when the field was applied to the tube *H*. But  $I_C$  was found to diminish in the same ratio, so that as far as the gauge indicated, there was no change of pressure.

In order to bring the necessary potential within lower and more accurately measurable limits, it was decided to use a pressure as high as .01 mm. A potentiometer supplied the field up to the available 220 volts, D.C.

It was then observed that the blue haze appeared very sharply, accompanied by a sudden fluctuation in the voltage downward and a break upward in the electronic current. This phenomenon has been described by Richardson and Bazzoni,<sup>2</sup> in their experiments on mercury vapor.

At the first one of such fluctuations a blue glow appears directly behind the anode; it can be made to appear and disappear within a variation of potential too small to be observed on a Weston 30-volt voltmeter, with which a change of one fifth volt could be easily detected. On increasing the field the glow spreads into the tube and, a little later, at a voltage which seemed to be constant for all pressures tried, a second "kick" occurred. Here the glow suddenly spread further into the tubing above

REV., 4, 123, 1914. A. Wehnelt and E. Liebreich, Phys. Zeit., 15, 557, 1915. O. W. Richardson and Charles B. Bazzoni, Phil. Mag., 32, 426, 1916.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

the bulb  $H$  and also increased greatly in intensity. At this point the glow was very sharply defined and a column of it could be pushed along the tubing at will by controlling the field.

The gauge showed no change in the pressure at any time, except that after some minutes it would begin to register the falling pressure due to the above-mentioned clean-up effect. The blue glow then began gradually to recede into the tube  $H$  and finally to disappear altogether. The rate of disappearance depends on the pressure of the absorbable gases present, and for the lower pressure, the rapid disappearance of the glow, once it begins to withdraw, is very striking. As shown at the end of the paper, this disappearance was accomplished at times in an interval of a second. In these experiments also, as in the first trials with A.C. fields, it was observed that the gauge current  $I_A$  was always diminished when the field was applied in the tube  $H$ . But  $I_C$  diminished in the same ratio, so that the gauge recorded no change in pressure.

(B) *Current-Voltage Relations.*

In order to maintain the pressure as nearly constant as possible during a set of observations the mercury seal  $B$  was left open. A constant P.D. of seven volts was maintained across the terminals of the filament. To the apparatus mentioned above was added a milliammeter. A typical set of readings is shown in Table V.  $V_1$  is the first "kick" voltage, when the blue color first appears behind the anode;  $C_1$  the corresponding current change. In this set the initial current was not readable on the scale used.  $V_2$  is the voltage drop at the second kick, already referred to above. The voltages are measured at the positive end of the glowing filament, the average would thus be 3.5 volts greater. Under  $C_2$  are given the current readings corresponding to the voltages,  $V_2$ .

TABLE V.

No.	$p$ .	$V_1$ .	$C_1$ .	$V_2$ .	$C_2$ .
1	.0101	18 → 14	0 → .005	26 → 22 30 → 25	.130 → .133 .135 → .140
2	.0086	22 → 16	→ .006	22 → 20	.113 → .115
3	.0068	24 → 16	→ .007	22 → 20	.118 → .122
4	.0047	33 → 18	→ .013	25 →	
5	.0023	54 → 24	→ .026		
6	.0010	92 → 44	→ .045		

Owing to the fact that even with the considerable volume in use the pressure would slowly diminish, it was usually impossible to duplicate any reading during a run. The kicks are rather hard to catch accurately

and rapid fluctuations are apt to occur at these points of instability, especially at the lower pressures. Thus in case of no. 6 the voltage and current made the jump back and forth twice, finally remaining at the "before the kick" value. This meant, of course, that the clean-up had progressed so far that the higher potential of  $V_1$  was not sufficient to start the blue glow again.

Fig. 4 is the plot from the above data. No. 1 seems to have three points of instability, though that may well be the result of the manipulation of the potentiometer. It did not occur in the other sets. The

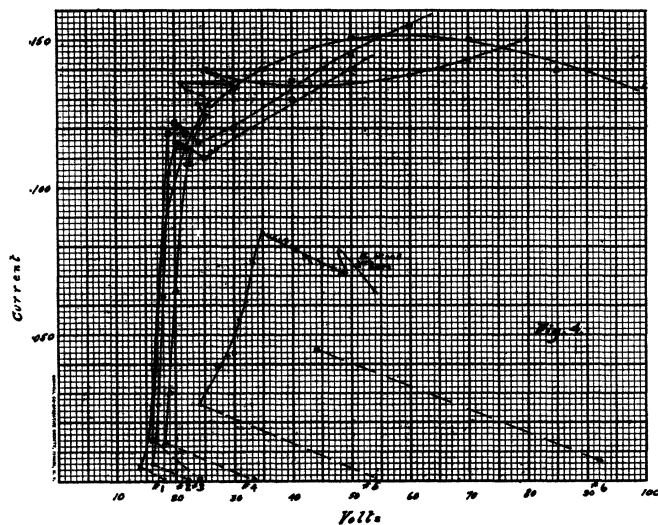


Fig. 4.

currents before the first break are not shown in the plot; they increase gradually from zero until the break. Thus the whole phenomenon resembles that described by Richardson and Bazzoni<sup>1</sup> in the case of mercury, even to the order of magnitudes involved. These observers mention also the second point of instability, but are of the opinion that it is due to the "discharge wandering in the tube" and did not regard it as of as much interest as the first. Coming as it does at approximately the same voltage for all the pressures would suggest that it is a function of the apparatus rather than of the other conditions. This would remain to be investigated.

Referring again to the curves, it seems as if in no. 5 the first break had overtaken the second, being just at that voltage; it shows also another break later. But the conditions at that stage were too variable to make

<sup>1</sup> *Loc. cit.*

any general statement. This is also evident from an inspection of the progress of the currents, after the first very rapid increase immediately after the first break. No. 6 consisted of only the first jump.

A second table is added to show the duplicability of the phenomenon. The seventh column gives the ratio of the currents, before and after the first kick. This was used by Richardson and Bazzoni as a measure of the magnitude of the kick. It shows a maximum as found by them.

TABLE VI.

No.	$p$ .	$V_1$ .	$C_1 \times 10^4$ .	$V_2$ .	$C_2$ .	Ratio of $C_1^*$ .
1	.0120	17 → 14.5	.75 → 5.9	26 → 24	.104 → .107	7.9
2	.0113	19 → 16	1.5 → 12.0	28 → 22	.136 → .148	8.0
3	.0070	26 → 16	1.8 → 40.0	22 → 21	.105 → .108	22.2
4	.0026	60 → 26	2.7 → 50.0	28 → 26		18.5
5	.0013	114 → 42	45 → 600			13.3
6	.0009	206 → 105	110 → 1270			11.5

The behavior of the voltage  $V_1$ , also, is similar to that found by those observers for mercury. Thus, an attempt to lower the voltage after the first "kick" results in a sudden drop to the initial part of the curve; *i. e.*, to a smaller current and larger voltage.

As is evident from Tables V. and VI., the minimum potential necessary to maintain the glow (which is practically the lower reading in the column under  $V_1$ ) approaches a limiting value as the pressure increases. In these experiments the minimum value for  $V_1$  was never below 14 volts, with a pressure up to .02 mm., the highest readable on the gauge. Taking account of the potential difference across the terminal of the glowing filament, the average potential would be 17.5 volts. Compared to the ionizing potential for nitrogen (using 7.7 volts), this is roughly in the same ratio as the corresponding quantities Richardson and Bazzoni found for mercury, *viz.*, 11.5 volts for the glow as compared to minimum ionizing potential of 4.9 volts. However, in the light of some recent experiments by Hebb,<sup>1</sup> who has shown that pure mercury vapor will arc at 4.9 volts, the above comparison may not have any significance. The present trials were necessarily complicated by the fact that they were made on a mixture of gases subject to a sorting-out effect due to the clean-up. A detailed study of this phase of the ionization problem on pure gases would seem to be a profitable undertaking.

The writer does not lose sight of the fact that where there is very probably a selective absorption of the gases present in air, the gauge constant would be subject to change. Nevertheless, such a variation

<sup>1</sup> T. C. Hebb, *PHYS. REV.*, 11, 170, 1918.

would not obliterate the general trend of the phenomenon in question. This also applies to the experiments on clean-up effects, which follow.

(C) *Clean-Up Effects.*

The clean-up effect of the blue haze was very marked, as was the wearing away of the lighted filament. The walls of the tube became covered with a shiny brown coating, showing interference colors. Langmuir<sup>1</sup> refers to a "clear brown" coating as being  $WN_2$ . This clean-up is characteristically different from that produced by the lighted filament without a field between the filament and a neighboring electrode. As will be shown more in detail later, the rate of clean up is quite different and increases with decreasing pressure just before the blue glow disappears. Also it operates at a considerably higher pressure than the ordinary clean-up. Thus it was always possible to evacuate with the blue haze at .02 mm. pressure, though a glowing filament, without the field, had absolutely no effect at this pressure.

In order to accelerate the progress of the phenomenon a smaller volume was used,  $B$  being closed. The first observations were taken immediately after the experiments described in part "B" above were completed; that is, after the air in the apparatus had presumably been deprived of its more easily absorbed constituents.

The filament being glowed as before and the maximum field applied (not over 220 volts) pressure readings were taken at intervals of a minute, during the first two runs. As soon as the minimum pressure was attained,  $B$  was opened a moment, thus equalizing the pressure throughout the apparatus, and  $B$  again closed for the next run.

The tube and about half of the connecting tube to the gauge was filled with intense purple glow which turned to a pure blue as the exhaustion proceeded. After a time the glow would begin to recede into the tube and, usually, disappear altogether. In the instances where a glow remained there was no difference in the pressure observed. The rapid decrease in the time required for glow to disappear as run after run was made was very striking. Table VII. gives a summary of these trials. The initial and final pressures are denoted by  $p_1$  and  $p_2$  respectively;  $t$  is the time taken for the glow to disappear, which was also the interval between the two pressure readings, as nearly as they could be taken. No great accuracy is claimed for the time in the shorter intervals, but they serve sufficiently to indicate the progress of the phenomenon. The quantities in the last two columns are the same as the corresponding ones in Table IV.

<sup>1</sup>I. Langmuir, J. Am. Chem. Soc., 35, 931, 1913.



TABLE VII.

No.	$p_1$ .	$p_2$ .	$t$ , Seconds.	Absorption Cu. mm. $\times 10^6 v$ .	Absorption Per Min.
1	.0110	.0015	360	12.5	2.10
2	.0076	.0011	240	8.55	2.14
3	.0072	.0010	30	8.16	16.3
4	.0065	.0009	20	7.37	22.1
5	.0062	.0015	4	6.2	93
6	.0058	.00061	2	6.8	205
7	.0053	.00068	1	6.0	360
8	.0049	.00099	—	5.4	—
9	.0046	.0011	—	4.6	—

Thus as the proportion of absorbable gases decreases with each run, the rate of clean-up increases. The total pressure at the beginning of the final run is only a little less than half that at the commencement of the experiment.

The matter was next tested by admitting a fresh lot of air into the apparatus. The valve *B* was left open and the entire apparatus evacuated in the above manner. Readings were taken every minute or two until a steady state was reached at a pressure of .0008 mm. at the end of 45 minutes.

The results are best represented in a graph, shown in Fig. 5. The

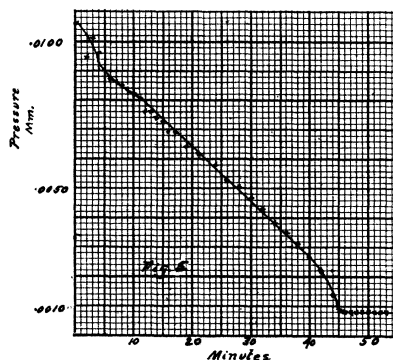


Fig. 5.

curve is practically a straight line up to a pressure of .0022 mm., when there is a rapidly increasing acceleration until the minimum pressure is attained. It is at that point the glow begins to recede and disappear.

The field and current strength were recorded. Both remained at a fairly steady state during the greater part of the time, *i. e.*, until the bend in the curve was reached, when the voltage rose and the current fell rapidly.

In the present case we are dealing with a mixture of gases, hence, since the rate of absorption increases with the diminution of the total pressure, it must vary still more rapidly with the partial pressure of the more absorbable constituents.

According to Langmuir<sup>1</sup> the oxygen atoms collide with electrons in the tungsten filament by virtue of the energy of agitation of the former, which then take on a negative charge and combine with positive tungsten atoms. A field might conceivably aid or retard this process; negative oxygen ions being repelled before chemical combination could take place; or, positive ions of the gas impelled to the negative filament.

In an investigation on the absorption of gases in vacuum tubes, Brodetsky and Hodgson<sup>2</sup> have given evidence for a mechanical theory of the phenomenon. Glass vacuum tubes were used, the current being obtained from a high potential battery. A curve for air shown by them has the general characteristics of Fig. 5.

According to their work the absorption, together with the disintegration of the cathode, is conditioned on the presence of an abnormal cathode fall: neither of the two effects appearing when the cathode fall is normal. The fact is cited (supporting the mechanical theory) that the inactive gases helium and argon are also readily absorbed. Hodgson<sup>3</sup> shows curves, similar to the above, for helium. Whatever may be the mechanism of the process, the absorption in the case of the blue haze is certainly of the same nature as the vacuum tube discharge. Just how selective it is and how it may vary with the field, which affects the ionization, remains a subject for further investigation. In all cases of absorption with the blue haze in the present experiments the minimum pressure was about 10 per cent. of the initial one. This is of course too large to be accounted for by a residue of the inert gases alone.

A number of attempts were made to obtain some information of the nature of the process by spectroscopic means.

A Schmidt and Haensch direct vision spectrometer (after Hoffmann) was employed. As has been stated above, the color of the glow changes from a sort of purple to a pure blue toward the end of the exhaustion. The spectrum of the blue haze at .01 mm. pressure showed the brighter nitrogen and oxygen lines and some of the nitrogen bands of the first and second Deslandres series as described by Kayser. No hydrogen lines were seen. After a clean-up, whenever there remained a visible glow, it was found that the nitrogen bands of the first group had disappeared and some of the second.  $H_{\alpha}$  and  $H_{\beta}$  were observed.

<sup>1</sup> I. Langmuir, *J. Am. Chem. Soc.*, 35, 107, 1913.

<sup>2</sup> S. Brodetsky and B. Hodgson, *Phil. Mag.*, 31, 478, 1916.

<sup>3</sup> B. Hodgson, *Phys. Zeit.*, 13, 595, 1912.

It was thought that the removal of a great deal of the nitrogen and oxygen might allow other lines to become more prominent, such as those of argon. In order to make possible a more careful and detailed study of the spectrum, a table was constructed showing the observed lines and the most prominent lines of the common and the noble gases in parallel columns. A number of new lines did appear that corresponded to those of argon within the limits of accuracy of the spectroscope, but they were not among the prominent ones, and could usually be duplicated by either nitrogen or oxygen, though these latter had not been seen before the clean-up. Thus it was practically impossible to draw any safe conclusions from the character of the spectrum. Also the feeble luminosity, in the bright glare of the lighted filament, made observation difficult.

In conclusion the writer wishes to take this opportunity to thank Dr. Millikan, at whose suggestion these experiments were undertaken, for his very kind assistance and numerous helpful suggestions.

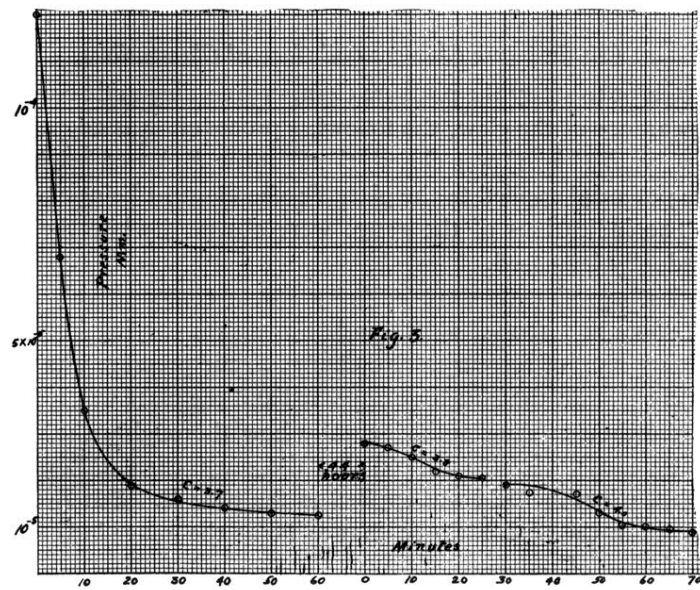


Fig. 3.