THE VALENCY OF PHOTO-ELECTRONS AND THE PHOTO-ELECTRIC PROPERTIES OF SOME INSULATORS.

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SYNOPSIS.

Photo-emission from insulators; the valency of photo-electrons.—Charged droplets of different insulators are suspended in the field of a parallel plate condenser by regulating the strength and direction of the electric field so that the electric force on the droplet is equal and opposite the gravitational force. Ultra-violet light of various intensities and frequencies is allowed to fall on the droplets and the photo-emission is observed. The photo-emission of several insulators is studied in this manner. By making the light intensities sufficiently low, the author finds that only one electron escapes at each emission. This is true for all insulators studied and is verified in the case of each insulator by the observation of several hundred emissions. This result is in line with similar work on ionization of gases by X-rays. γ -rays, β -particles, and α -particles by Professor Millikan and his students. By the use of different absorption screens the long wave-length limit of photo-emission from sulphur, shellac, oil and paraffine is located. These are located with greater accuracy than given by any other methods. The effect of water vapor and various surface impurities on photo-emission is discussed.

I. INTRODUCTION.

IN 1911 Millikan and Fletcher¹ furnished the first conclusive evidence ^{\cdot} that the mechanism of ionization by X-rays, gamma rays and β particles consisted in the detachment from the neutral molecule of one single elementary charge. Millikan, Gottschalk and Kelly² by using a similar method found the same to be true for ionization by α particles of several different gases and vapors. Mr. J. B. Dereux,³ at Professor Millikan's suggestion, using the same general method studied the photoemission from mercury drops. This work gave evidence which indicated that only one electron was expelled from the mercury atom in the process of photo-emission.

It would indeed be interesting if high speed particles of atomic size, high speed electrons and electromagnetic radiations of as widely differing frequencies as that of gamma rays and ultra-violet light all showed the uniform property of liberating one and only one electron from the atom in its ionization.

¹ Millikan and Fletcher, Phil. Mag. (6), 21, p. 753, 1911.

² Millikan, Gottschalk and Kelly, PHys. Rev.

⁸ J. B. Dereux, Phys. Rev., 11, p. 276, 1918.

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As mentioned above Mr. J. B. Dereux suspended single mercury drops, charged statically in the process of vaporization in the electric field of a parallel plate condenser and allowed ultra-violet light to fall directly on the drops. At the instant of a change in speed, indicating a change in the charge on the drop by its photo-emission, the light was shut off and its speed measured. It was possible to calculate from the change in speed the number of electrons liberated. The majority of the changes observed were those corresponding to emission of single electrons. Since a number of changes corresponded to emissions of more than one electron it was thought worth while to extend the investigation to other substances.

If the changes observed which correspond to emission of more than one electron were due to simultaneous emissions from different atoms on the surface, the chance of this could be decreased by using less active surfaces and decreasing the intensity of the radiation. In choosing surfaces whose emission currents would be small the insulators would naturally suggest themselves. They were selected for the further reason that this is the only method of study of photo-emission which is capable of furnishing very direct and very reliable information with regard to the photo-electric properties of insulators.

II. HISTORICAL SURVEY OF PHOTO-ELECTRIC WORK ON INSULATORS.

In the study of photo-emissions of insulators the general method of procedure has been to place a thin sheet of the insulator over the surface of one of the plates of a condenser, to apply an accelerating field, allow the radiation to fall on the surface and measure the current. In good insulators the surface charges up positively as the photo-electrons escape, until the potential gradient at the surface is sufficiently high to neutralize the accelerating potential and prevent the escape of further electrons. This gives a fatigue effect which makes consistent results difficult to obtain. Sheets of good insulators will remain for a long time in this polarized state and fresh samples of the material must be used. Using this general method Goldmann and Kalandyk1 investigated the photoelectric effect in sulphur. Photo-electric currents were obtained when a source of ultra-violet light was used and the polarization effect mentioned above was encountered and studied. They found that the photo currents completely disappeared when a plate of glass was interposed between the source and the sulphur, which would indicate the long wave limit somewhere below λ 3200. R. Reiger² investigated a number of insulating

¹ Ann. d. Phys., XXXVI., p. 589, 191**1**.

² R. Reiger, Ann. d. Physik., XVII., p. 935, 1905.

materials, and found a number including, ebonite, mica, sealing wax and glass that showed small emission currents when exposed to the light of an electric arc. W. Wilson¹ examined shellac and found no emission with ultra-violet light.

III. EXPERIMENTAL.

The apparatus as described by Millikan³ was used in the present work, with such changes as were found necessary in the problem. The apparatus consisted essentially of a parallel plate condenser with plates horizontal, the plates were 22 cm. in diameter and were separated 1.586 cm. An ebonite strip surrounded the condenser, with windows set in at proper intervals; one for the illumination of the drop, one for observation and one of quartz for admission of the ultra-violet light. Several small holes were bored in the center of the upper plate for the admission of drops and an electromagnetically controlled shutter was provided to close these holes when the drops were under observation. The condenser plates were placed in an air tight iron tank about 30 cm. in diameter and 50 cm. high. This cylinder was placed in a tank, about 50 cm. in diameter leaving a space between the walls of tank and cylinder which was filled with oil to hold the temperature constant. Tubes at the level of the condenser provided with vacuum tight, transparent windows ran from the outer tank into the inner tank at the proper places for admission of light for illuminating the drop, for observation, and for admitting the ultra-violet light. The windows in the ebonite strip were directly in front of these tubes.

The space between the condenser plates was illuminated by the light from a right-angled carbon arc. The light was focused on the drop by a cylindrical lens. A telescope having a high magnifying power was used for observing the drops. In the focal plane of the eye piece was a scale, the smallest division of which corresponded to 2 mm. Observations were made through a window 150 degrees from the one through which the light entered. A stop watch was used in timing.

The potential of the plates was furnished by 3,500 small lead cells giving a potential of about 7,000 volts. By means of a special switch the condenser could be charged, short circuited, or reversed by changing the position of a handle.

For changing the charge on the drops X-rays were used. The X-ray tube was placed just outside the apparatus near one of the windows. The source of radiation, usually a mercury vapor lamp was placed on a line of centers with the center of the condenser, and opposite a quartz window.

¹ W. Wilson, Ann. d. Physik., XXIII., p. 127, 1907.

⁸ R. A. Millikan, PHys. Rev., 32, p. 349, 1911.

SECOND SERIES. The drops of the various insulators were formed by getting the insulator in the liquid state and discharging it through an atomizer placed in the upper part of the iron cylinder and manipulated by air pressure from without. After atomizing there was always a rain of drops through the holes of the upper plate and one of proper gravity speed was selected; the shutter over the holes closed and the drop balanced by regulating its charge with X-rays. An electromagnetically controlled shutter over the quartz window was then lifted and the radiation allowed to enter until a change in speed showed an emission to have occurred, the shutter was then closed and the speed determined. From this speed and its speed under gravity the number of unit charges on the drop could be obtained and the difference between the number before and after emission gives the number of electrons emitted.

The number of charges on the droplet was determined from the relation

$$n = C\left(\mathbf{I} \pm \frac{t_1}{t_2}\right) \frac{\mathbf{I}}{V},^{\mathbf{I}}$$

where n = number of unit charges.

- C = a constant for a given drop.
- t_1 = number seconds it takes drop to traverse a certain distance d under gravity.
- t_2 = number seconds it takes drop to traverse the same distance d under the field V.

V =potential across plates.

In determining the spectral range of photo-sensitiveness of the various insulators the method followed was to balance a drop in the field and allow radiations of a certain range to fall on it and observe whether or not emissions occurred. A large number of drops were used for each range so that there was no uncertainty in any case.

IV. SULPHUR.

Drops of sulphur were obtained by heating chemically pure sulphur to a proper temperature in a specially made atomizer. The atomizer was placed in the large chamber about 20 cm. above the upper plate of the condenser and heated by a coil which kept the entire atomizer at a temperature of 150° C. At this temperature the sulphur is in the form of a pale yellow mobile liquid and atomizes quite readily. The temperature regulation had to be close in order to obtain satisfactory performance for at about 160° C., the sulphur changes to a dark viscous liquid which is too viscous to permit being atomized. The sulphur drops were always charged statically and a satisfactory drop was easily obtained.

¹ Millikan and Fletcher, Phil. Mag. (6), 21, 753, 1911.

At the beginning of the work no special precautions were taken with the gas content of the chamber; it consisted of the air of the room freed fairly well of water vapor. The sulphur drops evaporated very rapidly; in fact so fast that all calculation of the number of charges on the drop or the changes in charge were made impossible by the enormous change in the size of the drop. Table I. gives the gravity speeds, taken at 5minute intervals, of a drop held under observation for 30 minutes. The charge on the drop was varied by X-ray ionization so that as it evaporated it remained just balanced in the field. At 5-minute intervals the electric field was removed and readings were taken of its speed under gravity.

TABLE I.

Sulphur Drop No. 8. Time to pass over 50 divisions: 1. 8.2 seconds. 2. 10.4 at the end of 5 minutes. ... 3. 13.6 10 " " 4. 17.7 15 ** " 5. 28.0 30

While evaporating the drops drifted badly and were soon out of the illuminated space. It was necessary to get rid of the evaporation before observations could be made. After a number of unsuccessful attempts the trouble was eliminated by boiling sulphur in the sealed chamber until the walls were coated with flowers of sulphur, and moisture-free air then allowed to stand in the chamber for days before the observations were taken. While the drops still evaporated, the rate was slow enough so that no uncertainty was introduced into the calculations. Table II. gives data on a drop observed for one hour in the same manner as the drop in Table I.

The readings given in Table II. for each time interval are the average of a number taken at each of the intervals. I was considerably surprised to find a variation of as much as 10 per cent. in successive timings, one

 TABLE II.

 Drop No. 27.

 Time to pass over 50 divisions:

 1. 7.6 seconds.

 2. 7.6 " at end of 15 minutes.

 3. 7.4 " 30 "

 4. 7.0 " 60 "

taken immediately after the other as from experience in timing drops in another investigation I had acquired sufficient skill to check readings to .I seconds. Upon examining a number of the drops under a micro-

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scope they proved not to be perfect spheres, but spheres with minute crystal faces on the surface. The amount of this deformation varied considerably from drop to drop being apparently absent in some. This seemed to offer grounds for a satisfactory explanation of the variations, for a change in the orientation of the drop between two different excursions would change the resistance offered to its fall. In selecting drops for observation several timings of their gravity speed were taken one immediately after the other and if the variations were large the drop was discarded and another obtained.

In studying the valency of photo-electrons the following procedure was employed; after a drop with a proper gravity speed had been selected it was given a sufficient positive charge by X-ray ionization to just balance it in the field with the voltage used. The shutter covering the quartz window was opened and the radiations from a quartz mercury lamp allowed to fall on the drop until an increase in speed indicated an emission. The shutter was immediately closed and the speed determined. The shutter was again opened and the process repeated. This was continued until 4 or 5 emissions had occurred, then the drop was brought back to its initial number of charges with X-rays and the process repeated. Some of the smaller drops were started with an excess of 3 or 4 electrons and emissions allowed to occur until the drop had lost 3 or 4 electrons beyond the neutral point. This was not possible with the larger drops due to the electric force with the small number of unit charges and with voltages available being insufficient to balance the force of gravity. Some drops were kept under observation for two hours. 57 separate emissions were observed on one drop and over 500 emissions were observed under good experimental conditions and calculated.

When the observations were first begun the drops captured about as many electrons as they emitted. This was at first attributed to residual radio-activity as this same apparatus had been used by Millikan, Gottschalk and Kelly (loc. cit.) in studying ionization by α particles and had had radium open in the chamber. But on running a blank, that is observing the drop for an hour with the shutter closed, the drop was found to capture but two electrons; so it was concluded that the plates were emitting. In order to prevent this the plates were covered with lamp black, but the photo-sensitiveness was increased several hundredfold, in fact, as soon as the shutter was opened the drop would capture electrons in such rapid succession that the individual captures were indistinguishable. This emissivity was most probably due to the carbon in the lamp black as it was found that its long wave limit was $\lambda 2550$ (approx.) and this is about the limit Hughes¹ found for carbon.

Hughes, Photo-Electricity, p. 102.

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Shellac was then tried, as W. Wilson (loc. cit.) had pronounced it not photo-sensitive to the light of a quartz mercury-vapor lamp. However, it emitted electrons freely, so a thin coating of paraffine was next tried and no emission was found.

Table III. gives the results of observation on 10 droplets of sulphur.

Drop No.	No. Minutes Under Obs.	No. Emissions.	No. Singles.	No. Mult.
21	90	35	35	
22	100	40	40	
24	100	44	44	
25	120	57	56	1
26	30	12	12	
28	60	38	37	1
29	110	45	45	
30	120	40	40	
31	60	20	20	
32	100	25	25	

TABLE III.

As is shown all emissions with the exception of two were of a single electron and both of these were emissions of two electrons. As is evident from the "times under observation" the emissions were very frequent, in fact more so than the table indicates as this time includes time consumed in regulating charge on the drop, timing it and adjusting the illumination.

In order to decrease the rate of emissions a plate of fused quartz about 5 mm. thick was placed in the path of the beam. From evidence to be discussed later this plate appeared to cut off all radiation below $\lambda 2250$. This decreased the emission rate to six to eight an hour. About 200 emissions were observed at this reduced rate and 40 hours were consumed in observation. In every instance the emissions were unmistakably emissions of single electrons. Table IV. gives the data on a representative drop.

The activity of various drops differed considerably. The rate of emission from some drops was so slow that after observing them for a time to be sure they possessed activity they were discarded. This difference in activity must be attributed to surface conditions. All drops were most active initially and their activity gradually decreased with time; the rate of emission was decreased roughly one half at the end of two hours.

The surface polarization effect which was observed in sheets of sulphur was somewhat evident with the drops. If electrons were emitted until the drop became positively charged then as the positive charge increased

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 t_1 .

4.1

4.1

4.0

4.0

3.9

3.8

6.8

4.8

6.7

12.0

78.0

19.8*

20.0*

22.0

6.9

12.0

6.6

4.9

24

24

24

24

24

24

36

36

36

24

24

24

	D_{i}	rop No. 32.			
t ₂ .	K. V.	K. V. $\left(\mathbf{I} = \frac{t_1}{t_2}\right) \frac{\mathbf{I}}{KV}.$		No. Electrons Emitted.	
80.0	24	.0438	4 Pos.		
12.6	24	.0552	5	1	
7.0	24	.0660	6	1	
4.9	24	.0765	7	1	
19.5*	36	.0219	2 Pos.		
22.4	36	.0330	3	1	
7.1	36	.0436	4	1	
12.2	24	.0557	5	1	
6.8	24	.0672	6	1	
5.0	24	.0756	7.	1	
5.0	24	.0750	7 Neg.		
6.9	24	.0658	6	1	
12.8	24	.0550	5	1	
80.8	24	.0436	4	1	
19.0*	24	.0328	3	1	
21.6	36	.0326	3 Pos.		
7.0	36	.0434	4	1	
12.0	24	.0552	5	1	

.0660

.0763

.0659

.0551

.0435

.0334

.0221

.0325

.0430

.0547

.0656

.0738

6

7

5

4

3

3

4

5

6

7

6 Neg.

2 Pos.

1

1

1

1

1

1

1

1

1

1

TABLE IV.

All t_2 marked with * the drop was going downward due to the force of gravity being greater than the opposite directed force of the electric field. In these cases the minus sign is used in the formula $\left(\mathbf{I} \pm \frac{t_1}{t_2} \right)$.

by further emissions, the rate of emission was greatly decreased. A drop that had lost 25 electrons beyond its neutral value was held under observation for one hour and only three emissions observed. The excess positive charge was neutralized by X-ray ionization and the drop was found to emit at the rate that was to be expected after it had been under

observation for one hour. Data was taken on a number of drops with varying excess of positive charge hoping to find some quantitative relation of stopping potentials but the variation from drop to drop, probably due to differences in surface contamination masked any such relation, if it exists.

In order to find the long-wave limit of emission for the sulphur a Hilger quartz spectroscope was set up outside the quartz window and by means of extra quartz lenses the radiation from any desired frequency was focused at the center of the condenser in the path of the drops. No emissions were obtainable with any frequency. To test the adjustment of the light system mercury drops were suspended between the plates of the condenser and photo-emissions were obtained when the instrument was set for $\lambda 2536$. As no emission could be obtained from the mercury for the adjustments of the spectroscope at wave-lengths shorter than $\lambda 2536$ due to their low intensity, the only conclusion that could be drawn from this work was that the long-wave limit for the sulphur was some wave-length shorter than $\lambda 2536$. It was next attempted to set some closer limits for the long-wave limit by using absorption screens.

After studying a number of filters Cobalt chloride in absolute methyl alcohol was found most suitable. An absorption cell with quartz windows about 8 mm. wide was used. Solutions of Cobalt chloride in this cell, varying in strength from 2 N to .01 N were studied photographically with a quartz spectrograph and a mercury vapor lamp. The greatest precautions to prevent stray light and fogging were taken and the exposure times were made as long as fogging permitted. These photographs showed the solutions to have a narrow absorption band covering the range λ 4600 to λ 5100 and complete absorption of radiations of wave-lengths shorter than λ 2650 for the 2 N solution, and of all radiations shorter than λ 2400 for the .01 N solution. The methyl alcohol cut off all radiations of wave-length shorter than λ 2350. With the quartz mercury lamp that was used, photographing directly and using every precaution lines were obtained down to λ 2150. These photographs were repeatedly taken and the sharpness and completeness of the absorption ranges well substantiated.

No emissions from the sulphur were obtained when the radiations passed through the cell filled with any of the cobalt chloride solutions or with the methyl alcohol only. Many drops were held under observation for more than an hour each with the methyl alcohol cell before the quartz window. After a drop was secured it was exposed to the direct radiations and several emissions observed then the cell would be interposed and the emissions would immediately stop; at the end of 30 minutes the cell would be removed and emissions from the drop would begin immediately in every instance. This definitely placed the long-wave limit at some wave-length shorter than $\lambda 2350$.

An absorption screen was looked for that would transmit some frequencies to which the sulphur was photo-sensitive; some transparent commercial *fused* quartz was found which when interposed in the path of the radiation cut down the emissivity from 40 emissions to the hour to 5 an hour. These plates were about 5 mm. thick and only one was used. If a plate of crystal quartz of the same thickness was placed in the path of the radiation there was no reduction in the rate of emission. This was verified in a number of drops. On examining the transmission of this plate it was found to cut off (at least photographically) all wavelengths shorter than λ 2250.

Some time after completing this work I noticed that Hughes in his book, Photo-Electricity, had remarked that a column of water I cm. long cut off all radiations shorter than λ 2200. This was confirmed photographically and as a check on the earlier work, the emission of sulphur through this filter was examined and its rate of emission was found to be decreased in about the same ratio as with the fused quartz plate filter.

The long-wave limit of photo-sensitiveness of sulphur can be placed with a great amount of certainty between $\lambda 2400$ and $\lambda 2200$ and it is probably within the narrower limits of $\lambda 2350$ and $\lambda 2250$.

V. Shellac.

Drops of shellac were obtained by atomizing a filtered solution of shellac flakes dissolved in ethyl alcohol. The alcohol evaporates rapidly and the density of the sphere reaches a constant value in a very few minutes, as is shown by the constancy of the gravity speeds. The drops showed perfect sphericity when examined under a microscope and showed none of the variations in speed on succeeding excursions under gravity as did sulphur.

All the sulphur was washed out of the large cylinder and removed from the condenser plates. The entire interior of the iron cylinder was coated with shellac and this allowed to stand several days after which the air was pumped out of the tank several times and the air that was admitted each time was filtered and dried. A thin coating of paraffine was used on the plates as with the sulphur. The shellac drops were much more satisfactory to work with as there was no evaporation, and little, if any, fatigue effect of photo-emission.

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TABLE V.

Drop No. 49.

P.D. = 6,000 volts. Time under obs. = 90 minutes.

<i>t</i> ₁ .	<i>t</i> ₂ .	$\left(\mathbf{I} \pm \frac{t_1}{t_2}\right) \frac{\mathbf{I}}{V} \times \mathbf{IO}^3.$	No Units on Drop.	No Electrons Emitted.	Time Interval Before Emis- sion, Secs.
23.0	31.8*	.0465	1 Pos.		
	51.3*	.0920	2	1	20
	128.	.1367	3	1	90
	Inf.	.1666	4	1	10
	62.0	.2286	5	1	120
	35.6	.2745	6	1	40
	25.0	.3200	7	1	0
	18.2	.3775	8	1	80
	15.6	.4125	9	1	30
23.2	35.4	.2757	6 Neg.		
	61.0	.2296	5	1	15
	Inf.	.1666	4	1	40
	130.0*	.1370	3	1	65
	52.0*	.0926	2	1	5
	32.2*	.0466	1	1 *	10
	23.0*	.0000	0	1	12
	31.8*	.0448	1 Pos.	1	. 28
23.2	Inf.	.1666	4 Neg.		
	133.0*	.1375	3	1	68
	50.0*	.0895	2	1	70
	32.0*	.0462	1	1	10
	23.0*	.0000	0	1	-25
23.4	32.2*	.0461	1 Pos.		
	52.0*	.0916	2	1	70
	134.0*	.1375	3	1	45
	Inf.	.1666	4	1	150
	62.5	.2290	5	1	10
	35.6	.2761	6	1	35
	25.4	.3200	7	1	40
23.4	32.5*	.0466	1 Pos.		
	52.4*	.0923	2	1	140
	133.0*	.1373	3	1	30
	Inf.	.1666	4	1	25
	62.0	.2295	5	1	100
	35.4	.2766	6	1	75
	25.2	.3211	7	1	5
	18.2	.3808	8	1	2

All t_2 marked with * the drop was going downward due to the force of gravity being greater than the oppositely directed force of the electric field. In these cases the minus sign is used in the formula $\left(\mathbf{I} \pm \frac{t_1}{t_2}\right)$.

With the complete radiation from the mercury vapor lamp the photocurrent from the shellac drops was less than that obtained initially from the best sulphur drops. However there was much less variation in photo-emission from drop to drop than from the sulphur.

The time interval from the opening of the shutter until an emission had occurred was observed for about 200 emissions. This was taken when the excess positive or negative charge was never more than 5 units. The average time interval was 50 seconds, the maximum time was 4 minutes and the minimum was too small to be measured by a stop watch.

In the study of the valency of the emission data were taken on 40 drops. More than 800 emissions were observed and the number of electrons liberated at each emission determined. The same procedure was followed as in the case of the sulphur.

Table No. V. gives the data on a typical drop. The time interval given under "time of exposure" is the interval of time between the opening of the shutter and the occurrence of the emission.

Table No. VI. contains a summary of data on 10 drops.

Drop. No.	Time Under Obs.	No. Emissions.	No. Singles.	No. Mult.
17	120	47	47	0
19	80	29	29	
20	100	28	28	
21	60	23	23	
27	120	44	44	
31	120	40	40	
37	60	19	19	
38	50	17	17	
40	70	26	26	
49	90	30	30	

TABLE VI.

As seen from the table every emission observed corresponded to the liberation of a single electron, this was also true of the observations on the remaining drops. The conclusion thus seems fully warranted that the process of photo-emission liberates one and only one electron from the molecule in sulphur and shellac. This is rather interesting especially in the case of shellac in which there are complex molecules made up of a large number of atoms.

As it is generally recognized that there is an absence of free electrons in non-conductors and insulators, the actual observation and identification of electrons emitted photo-electrically from them gives added weight to the accumulating evidence that photo-electrons come from the atom structure and are not free electrons.

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The long-wave limit of the shellac was found to be quite definitely somewhat shorter than that of sulphur, although I believe not a great deal shorter. No emissions were obtained from a large number of drops when the radiations were passed through the methyl alcohol solution. A fused quartz plate was then interposed in the path of the beam and 10 drops were observed for intervals of time exceeding an hour and no emissions occurred, but immediately after the plate was removed emissions would begin quite normally. The filter of water one cm. in thickness was interposed in the path of the beam for each of the 10 drops and emission was entirely stopped, but immediately after removing the filter emission began in every case. The conclusion then seems fully warranted that the long-wave limit for shellac is shorter than $\lambda 2200$.

Allen in his book Photo-electricity, p. 83, in discussing W. Wilson's work says, "Although shellac itself is not photo-electrically active, it allows the photo-electric current to pass through it when a thin layer is laid upon a metal plate." As is evident from what has been given we found that shellac was photo-sensitive. The photo-sensitiveness of shellac in thin sheets was examined by covering the metal plates of the condenser with a thin coating. The photo-emission from the coated plates was stopped by the same filters that stopped the emission from the shellac spheres; although this was not found to be the case with the cleaned metal plates, which indicates that this emission is from the shellac and not from the plates.

VI. PARAFFINE AND OIL.

Commercial paraffine was melted and a thin coating of it placed on the condenser plates in a portion of the work with shellac and sulphur because there was no emission from it when illuminated by the mercury vapor radiation direct.

The oil used throughout the work on the evaluation of "e" by Professor Millikan was examined for its photo-emission by suspending the drops in the path of the radiation and found not to be photo-sensitive to the radiations from the mercury light direct.

As only a small piece of fluorite just large enough for a window in the ebonite strip was available, a pair of zinc electrodes were placed just inside the inner cylinder and in the narrow space between the edge of the condenser plates and the wall, directly in front of the small fluorite window. By using a tuned circuit very much energy was put into the spark. When the spark was running it caused currents of air in the cylinder which made the drops drift badly.

Great precautions were taken in sealing the condenser so that its

interior would not be affected by outer currents. By doing this, drops of either oil or paraffine could be kept under observation for more than 30 minutes while the spark was running. The drops of paraffine were obtained by melting the paraffine in the atomizer used for the sulphur. The oil drops were obtained by atomizing in the usual method.

With the radiation from the zinc spark passing through a thin fluorite window and about 12 cm. of air photo-emissions were obtained from both the oil and the paraffine drops. Several emissions were obtained from each of 20 drops of both materials and no emissions were obtained from any drops of either material when radiations from the mercury lamp fell on the drops. The conclusion that both oil and paraffine are photo-sensitive and that their long-wave limit is shorter than $\lambda 2150$ (this is the shortest wave-length photographed through the mercury lamp used) seems fully warranted.

VII. SUMMARY.

I. A method has been given for detecting very weak photo-emission currents from insulators. Photo-emission currents were observed from sulphur, shellac, oil and paraffine.

2. The long-wave limit for sulphur has been placed between λ 2400 and λ 2200.

3. The long-wave limit for shellac was found to be some wave-length shorter than λ 2200.

4. The long-wave limits for oil and paraffine were found to be below $\lambda\,2150.$

5. The photo-emission from molecules of sulphur and shellac consist in the ejection of a single electron from the molecule at each emission.

This work was suggested by Professor Millikan and carried out under his direction. I desire to express my appreciation for his interest and helpful suggestions, also to Mr. V. H. Gottschalk who was associated with me in the preliminary work.