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On the Emission Velocities of Photo-Electrons

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VII. *On the Emission Velocities of Photo-Electrons.*

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(*Communicated by Prof. Sir* J. J. Thomson, *O.M.*, *F.R.S.*)

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Contents.

1. *Introduction.*—Since the discovery of the photo-electric effect by Hertz, many experiments have been made on the emission of negative electricity from metallic surfaces when illuminated by light. Yet with regard to many important points the results are often indefinite and contradictory. Most theories of the photo-electric effect indicate definite relations between the velocity of emission of the electrons and (a) the nature of the metal from which they are emitted, and (b) the wave-length of the incident light. Up to the present, however, the experimental evidence as to these two relations must be regarded as quite inadequate to afford any decisive test between rival theories. This research was undertaken to obtain, among other things, quantitative evidence on these two relations.

2. *Previous Work.*—Ladenburg[*] made some valuable experiments on the velocity with which electrons are emitted from metals when illuminated by ultra-violet light. He concluded that the maximum emission velocity was inversely proportional to the wave-length. The velocity varied from metal to metal; thus, for light of wave-length λ 2010, the maximum emission velocity (measured in volts) for platinum was

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[*] Ladenburg, 'Phys. Zeits.,' VIII., p. 590, 1907.

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1·86 volts, and for zinc 1·12 volts. The source of light used by LADENBURG was a mercury arc. His metals were polished with emery and oil, and were exposed to the atmosphere for some time before the apparatus for measuring the velocity could be exhausted.

MILLIKAN and WINCHESTER* in their investigations on the photo-electric effect found enormous differences in the emission velocities from different metals. The values range from 1·34 volts for silver down to 0 volt for lead. Their apparatus was much more complicated than the type of apparatus usually used for measuring the velocities, and the interpretation of their results is correspondingly more open to doubt. As in LADENBURG'S experiments, the newly polished surfaces were unavoidably in contact with the atmosphere for some time before the apparatus was exhausted. These experiments and others show that the state of the surface is of great importance in photo-electric investigations.

Such results led to a search for methods of preparing surfaces which would show greater regularity in their photo-electric behaviour. A promising way of obtaining a clean uncontaminated surface seemed to be to sputter away the surface-layer of a metal *in vacuo*. v. BAEYER and GEHRTS† found that the emission velocities from such surfaces were much increased, and concluded that the velocities were the true velocities with which the electrons left the metal. Later experiments‡ showed that this view was incorrect, and that the electric discharge polarised the surface of the metal in such a way that the electrons were accelerated on passing through the surface film.

New surfaces of liquids can easily be prepared *in vacuo*. It seems very probable that such surfaces are (at all events initially) free from gaseous films which may retard or accelerate the electrons passing through. KLAGES§ used surfaces of mercury formed *in vacuo*, and KUNZ|| used similar surfaces of sodium-potassium alloy and of caesium. Surfaces of metals distilled *in vacuo* were used by the author,‡ and far more consistent results were obtained with them than with the surfaces treated as electrodes.

The law connecting the maximum emission velocity of the photo-electrons with the wave-length has been investigated by LADENBURG¶ for Cu, Zn and Pt, and by KUNZ** for Na-K alloy and Cs. LADENBURG concluded that the velocity of the electron was proportional to the frequency. JOFFÉ†† pointed out that the experimental results

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[*] MILLIKAN and WINCHESTER, 'Phil. Mag.,' XIV., p. 188, 1907.

[†] v. BAEYER and GEHRTS, 'Verh. d. D. Phys. Ges.,' p. 870, 1910.

[‡] HUGHES, 'Proc. Camb. Phil. Soc.,' XVI., p. 167, 1911; v. BAEYER and TOOL, 'Verh. d. D. Phys. Ges.,' p. 569, 1911.

[§] KLAGES, 'Ann. d. Phys.,' XXXI., p. 343, 1910.

[||] KUNZ, 'Phys. Rev.,' XXXIII., p. 208, 1911.

[¶] LADENBURG, *loc. cit.*

[**] KUNZ, *loc. cit.*

[††] JOFFÉ, 'Ann. d. Phys.,' XXIV., p. 939, 1907.

would satisfy equally well the law that the energy (or the square of the velocity) was proportional to the frequency. The reason for this is that Ladenburg had only a short range of wave-lengths available for producing photo-electrons. One has to decide whether the experimental results lie on a straight line or on a short piece of a parabola some distance away from its vertex. Kunz concluded that his results supported Ladenburg's law. They are, however, in good agreement with the energy law, except in the red end of the spectrum.

3. *Experiments with Surfaces Formed* in vacuo.—It was shown in an earlier experiment that the maximum emission velocities of photo-electrons from surfaces of Zn, Cd and Hg, all distilled *in vacuo*, were approximately the same. It was thought advisable to investigate the velocities of the photo-electrons from a surface of mercury prepared *in vacuo* by the method described below.

The mercury, on which the light* fell, was contained in the shallow iron dish C (fig. 1) which was 2 cm. in diameter and 1 mm. deep. (The scale of the reservoir D is ten times less than that of the rest of the apparatus.) New surfaces could be formed by opening the tap T and allowing the mercury to overflow at C. The apparatus was evacuated before this was done, and the vacuum was maintained by the liquid air method. The maximum emission velocity was measured by the minimum potential between B and C necessary to prevent electrons leaving C, and passing through the gauze to A. The brass cylinder E and B were kept at a potential of -2 volts relative to A, in order to prevent the escape of electrons from A due to reflected light. The gauze B was symmetrically situated with respect to A and C, and as a potential difference of about 2·15 volts between C and B was sufficient to stop all the electrons passing from C to B, this potential could be taken as a measure of the velocity without any correction for the "streufeld."

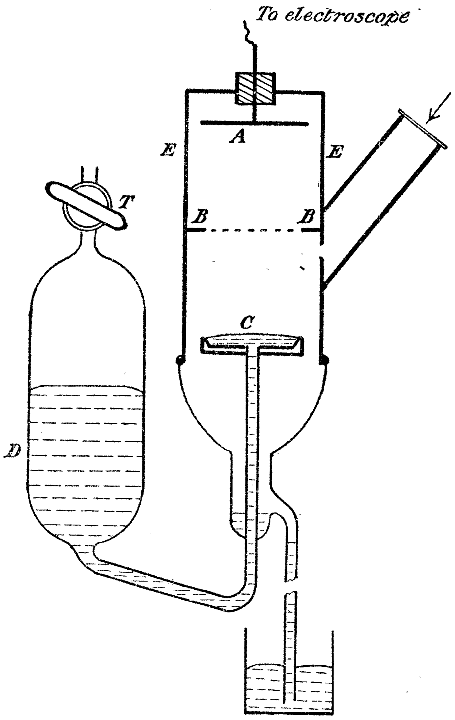

Fig. 1.

Several new surfaces were formed, and the maximum emission velocity was found to be 2·15 volts. The arrangement used by Klages was not suitable for the accurate measurement of the velocities; one can only say from his tables that the maximum emission velocity is somewhere between 2·0 and 2·6 volts. It might be urged that a surface

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* The unresolved light from the mercury arc was used in this experiment. The shortest wave-length was therefore λ 1849.

film of gas could be formed, even *in vacuo*, in a few seconds after the exposure of a new surface. To meet this objection a more drastic treatment was devised. Velocity measurements were made while the mercury was in motion. The tap T was adjusted so that the mercury overflowed at C at the rate of about 3 c.c. per second. On considering this, together with the dimensions of the dish, it is clear that no part of the surface exists for more than a small fraction of a second. Owing to the fact that the mercury in D was soon exhausted, accurate measurements could not be made. However, it can be said that the maximum emission velocity from the continuously forming mercury surface was 2·15 ± ·05 volts. This is practically the same value as that obtained for distilled Zn, Cd, and Hg. It seems extremely unlikely that any retarding film could be formed on the Hg surface in this experiment, hence it is concluded that 2·15 volts represents the actual emission velocity from Hg. The agreement with the distillation experiments supports the view that metals prepared by distillation *in vacuo* are also free from surface films.

In the course of this experiment evidence was obtained which indicates that photo-electrons are emitted nearly equally in all directions. The photo-electric current from C to A was measured in the absence of an electric field between C and B—(1) with, (2) without, a strong magnetic field along the axis of the cylinder. In the first case, when the electrons were compelled to follow the lines of magnetic force, the current was 33 times larger than when the electrons were not constrained to follow any path. The ratio of the solid angle subtended by the gauze B at the mercury surface to 2π, was about 1 to 38. This indicates that the ratio of the electrons emitted inside the cone to those emitted outside is of the order of the respective solid angles.

From the experiments described and discussed in this section, it was concluded that the most satisfactory surfaces to use in the investigation on the velocities of the photo-electrons were those prepared by distillation *in vacuo*.

4. *The Source of Light.*—The mercury arc in quartz glass was used as the source of light in this research. In the early stages of the work a very intense spark between Al terminals, produced by the primary transformer of a Tesla apparatus, was used in order to get very short wave-lengths of appreciable intensity. The results obtained with this intense spark were most irregular, frequently emission velocities as high as 10 or 12 volts were obtained. Direct experiment showed that this was not an effect due to electric waves. The spark was finally abandoned in favour of the mercury arc which gave very regular results, although the energy available in the short wave-lengths was far less.

To produce monochromatic light, a Hilger quartz spectrograph was adapted for the purpose. A sliding slit was arranged to pass over the focal plane of the camera side of the instrument. The slit having been set so as to transmit any desired wave-length, the mercury arc was placed close to it and monochromatic light emerged from the collimator. The aperture of the slit was 14 mm. by 2 mm., the collimator lens was 2 cm. in diameter, and of 20 cm. focal length. Hence the amount of light which passed through the monochromator was a very small fraction of that emitted by the lamp.

Some anomalous results in the earlier experiments led to the discovery that the monochromator did not isolate the wave-lengths perfectly. It was set so as to isolate one wave-length, and the light which emerged was analysed by means of a second quartz spectrograph. It was found that, in addition to the isolated line, all the other wave-lengths were present though much weaker. This effect leads to spurious results when working with the longer wave-lengths which are made to appear photo-electrically active when they are not. This error only becomes appreciable when using wave-lengths longer than λ 3000. Sheets of mica of different qualities were found to cut off wave-lengths shorter than λ 2967 and λ 3125, thick glass transmitted down to λ 3340, and a solution of chromium chloride absorbed all wave-lengths shorter than λ 3665. During the course of the investigation, a new wave-length λ 1849 in the mercury arc spectrum was discovered.*

5. *The Apparatus.*—The amount of energy which is transmitted by the monochromator when set to isolate any one wave-length is exceedingly small. The small photo-electric effect which would result from this feebleness in the light determined that great sensitiveness to electrical changes must be an important feature of the apparatus. Hence it is that, in the apparatus which was finally adopted, the electrical capacity is very small. The apparatus is shown approximately to scale in fig. 2.

The plate on which the light is incident is a disc, N, of nickel, 3 cm. in diameter. The disc is suspended by a thin wire from a slide, S, which runs in grooves in the tube T. The disc and wire are insulated from S by the quartz rod Q. This system can be raised or lowered by means of the winch, E, which is a glass tap with a groove cut round the barrel. S is suspended from the winch by a silk thread. The metal to be distilled is heated in a little furnace, F. This is a quartz-ignition spoon into which fits a thin quartz cup containing the metal. Between the cup and the quartz spoon there is a thin sheet of Pt or Ni, which can be heated to redness by a current. As the vacuum forms a good heat insulator, the metals can be raised to a high temperature. To get rid of occluded gases the quartz furnace containing the metal is heated for a long time in an auxiliary vacuum, until little or no gas is evolved during distillation. In this way surfaces of Ca, Bi, Sb, Zn, Cd, Se, Pb, Mg, and As were deposited on the disc, the whole process being carried out in a liquid air vacuum. When the distillation is finished the disc is raised to the position shown in the diagram.

Contact with the tilted electroscope is made by means of a spring, S′, which rests on a short cross wire behind the disc. The electroscope is placed close to the apparatus. To keep the capacity as low as possible thin connecting wires are used. The capacity of the insulated system is probably below 10 cm.

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* Hughes, 'Proc. Camb. Phil. Soc.,' XVI., p. 428, 1912.

The maximum emission velocity is given by the potential to which the disc rises when illuminated. As this frequently exceeds 2 volts there is danger of insulation leak. This is avoided by charging the case of the apparatus to a negative potential slightly less than the maximum emission velocity. The potential of N will then only rise to a fraction of a volt. Hence the ebonite insulation *e* and the sulphur insulation *f* have only to insulate for potential differences of less than ·1 volt. The quartz rod, Q, however, has to insulate the full difference of potential. Fortunately its insulating properties were found to be practically perfect. The potential to which the system rises is always measured by comparison with a potentiometer.

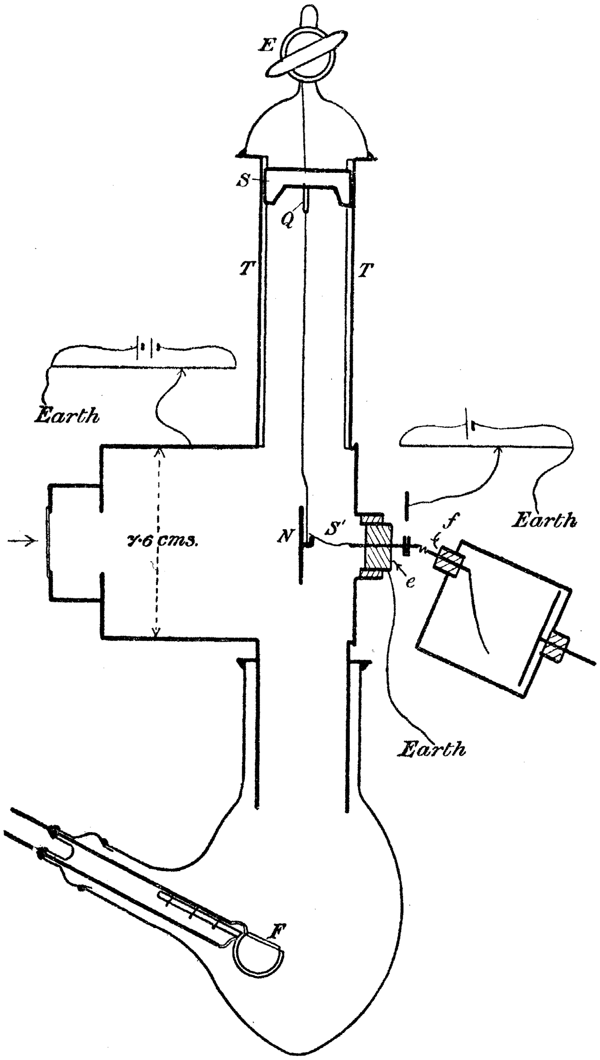

Fig. 2.

In order to produce a very good vacuum, the apparatus is always exhausted by a Toepler pump to a pressure of ·01 mm. before communication with the cooled charcoal tube is made.

6. *Velocity Distribution Curves.*—A curve giving the relation between the photo-

electric current and the potential difference between the illuminated plate and the surrounding case is called a velocity distribution curve. When the potential difference is such as to retard the electrons, then the photo-electric current is usually taken to be a measure of the number of electrons possessing velocities greater than that implied by the potential difference. Curve I., fig. 7, is a typical velocity distribution curve. Electrons whose velocities range from a maximum down to zero appear to be present, while a large number apparently require a small accelerating potential to enable them to get away from the plate. LADENBURG* and v. BAEYER† obtained curves which implied that there was a minimum velocity present as well as a maximum velocity. The majority of curves which have been published show no trace of a minimum velocity. v. BAEYER has shown that the velocity distribution curves are liable to distortion by reflection of electrons, and he says that this effect also apparently reduces the maximum emission velocities. As the accurate determination of the maximum emission velocity is of prime importance in the experiments described later, it is essential to examine very carefully all possible ways in which incorrect values may arise.

(A) *Reflection of Electrons.*—Let us assume that the illuminated plate emits electrons whose velocities range from a maximum down to zero. The distribution curve will be of the form ABC, fig. 3. If reflection of electrons by the surrounding case takes place this curve will be modified. When there is no potential difference between the plate and the case, the part bB represents the number reflected back to the plate, and hence the actual photo-electric current is Ob. A small potential accelerating the electrons from the plate is sufficient to stop all the reflected electrons, and the experimental curve AbC joins the ideal curve ABC. v. BAEYER says that the effect also reduces the maximum emission velocity as measured by the potential to which the plate rises when illuminated. It is difficult to see how this can be so, for before any electrons can be reflected to the plate a larger number must be emitted by the plate, and it should go on charging up (though more slowly) to the same potential whether reflection takes place or not.

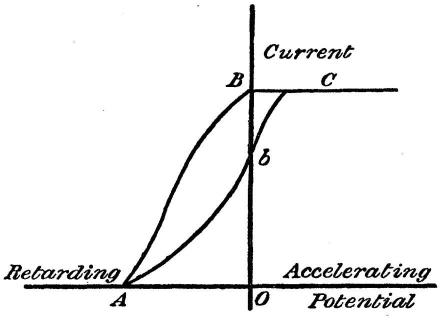

Fig. 3.

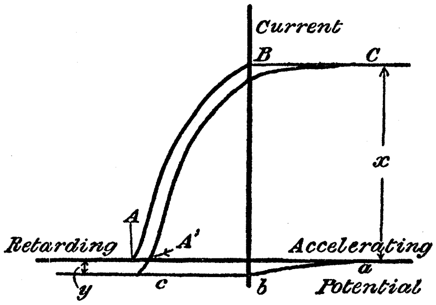

Fig. 4.

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* LADENBURG and MARKAU, 'Verh. d. D. Phys. Ges.,' IX., p. 562, 1908.

† v. BAEYER, *loc. cit.*

(B) *Reflection of Light.*—Let ABC, fig. 4, represent the velocity distribution curve from the illuminated plate. If a little light gets to the inside of the case, by reflection or otherwise, then the curve *abc* will be the velocity distribution curve for the current from the case to the plate. Experimentally the sum of these two curves is observed. A′ is the potential to which the system will charge up, and this is less than the real value A of the maximum velocity. It is clear that the difference AA′ increases as the ratio of the reflected effect y to the direct effect x increases.

(C) *Effect of an Electron approaching the Boundary Obliquely.*—Consider photo-electrons leaving the point P (fig. 5) with equal velocities and in all directions. We shall see that the velocity distribution curve is not ABC (fig. 6) but A*b*C, which implies, on the usual interpretation, that all velocities from A down to zero are present. Let V_0 be the potential required to stop the electrons travelling normally. An electron starting in the direction PN′ will describe a parabola. The potential difference, which will allow this parabola to graze the plane NN′ is $V_0 \cos^2 \theta$. If we assume that the electrons are emitted equally in all directions, then the number of electrons emitted between the cones θ and $\theta + d\theta$ is proportional to $\sin \theta$. Hence a number $n\int_0^\theta \sin \theta \, d\theta$ of electrons apparently have a velocity equal to and greater than $V_0 \cos^2 \theta$, and therefore the relation between the number possessing velocities above a certain apparent velocity and that velocity is parabolic. The experimental velocity distribution curve would be A*b*DC and not ABDC.

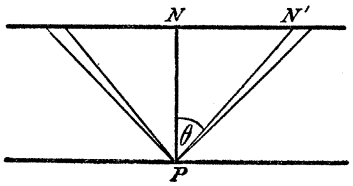

Fig. 5.

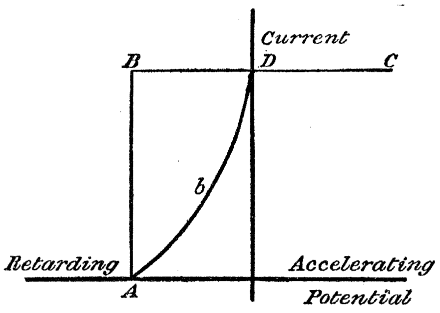

Fig. 6.

The usual experimental arrangements are not so simple as in this case, but it easily follows that whenever an electron approaches a boundary obliquely then the potential difference just necessary to stop it is less than that potential which corresponds to its actual velocity.

(D) *The Effect of Magnetic Fields.*—A weak magnetic field (such as the earth's field) is often sufficient to impose a considerable curvature on the path of a photo-electron. This would cause many electrons to approach the boundary with an increased tangential component of velocity and so give rise to the effect discussed in the last paragraph. Some of the slower electrons would never get away from the illuminated plate, for in the absence of an electric field, they would describe complete circles inside the apparatus. Thus a magnetic field would account for the part B*b*, fig. 3, which is usually attributed entirely to reflection of electrons.

From a consideration of these effects, one must conclude that the velocity distribution curves usually obtained do not give anything like the actual distribution of velocities with which the electrons emerge. Many velocity distribution curves have been given and discussed in various papers, but the complications arising from effects (C) and (D) have been completely overlooked.

Experimental.—Experiments were made to see how the velocity distribution curves could be affected by magnetic fields and the presence of gas. In particular, the corresponding effect on the maximum velocity was investigated. The apparatus used is shown in fig. 2. The disc N was covered with a layer of zinc. The unresolved light from a mercury arc was used.

In column I. the results obtained under normal conditions are given. The vacuum was obtained by the liquid air method, and the pressure was certainly below ·0005 mm. The earth's magnetic field (about ·5 gauss) was approximately parallel to the disc.

In column II. the results are given when an electromagnet was held near the apparatus. The field inside the apparatus was far from uniform, but at the centre it was about 7 gauss.

In column III. the results are given when the magnetic field was increased to 30 gauss.

The results given in column IV. were obtained with air in the apparatus at a pressure of ·03 mm.

The results given in Table I. are plotted in fig. 7.

TABLE I.

Potential.	Photo-electric current.			
	I.	II.	III.	IV.
40 volts	83		86	
30	83		85	
20	82		80	
10	82	82	72	79
4	82	80	54	71
2	82	77	38	63
1	80	72	19	52
0	35·5	22·5	3·5	18
– ·7	17·2	7·0	1·0	5
– 1·0	10·0	4·5	·5	2·5
– 1·3	5·0	2·0	0	·5
– 2·0	0	0	0	0
– 10·0	– 1·5	– 1·0	0	0
Maximum velocity . . .	1·93 volts	1·76 volts		1·86 volts

Let us consider whether reflection of electrons is adequate to explain the part AB in curve I., fig. 7. Let ω be the solid angle subtended by the disc at any part of the case in front of the disc. In the expression for the number of the electrons which get back to the disc there will be a factor $\omega/2\pi$. This is roughly ·1 for this apparatus. The other factor is less than 1, otherwise it would mean complete reflection of electrons. The ratio of AB to AO is therefore much bigger than can be accounted for by reflection of electrons. The earth's magnetic field is more likely to account for this effect. It will be noticed that the maximum velocity is apparently reduced by the magnetic field. This is due to the fact that the paths of the electrons are so curved that none of them strike the case normally. As long as a few electrons impinge on the case normally the correct maximum velocity will be given. This was shown in the following experiment. Two coils were arranged on opposite sides of the apparatus to assist or to oppose the earth's field. Light of wave-length λ 2537 caused the plate to charge up to ·70 volt. This remained the same for all magnetic fields from 0 to 2 gauss. With greater fields the maximum velocity began to diminish slightly. This shows that, for velocities of ·7 volt (and above), the effect of the earth's magnetic field (·5 gauss) can be ignored.

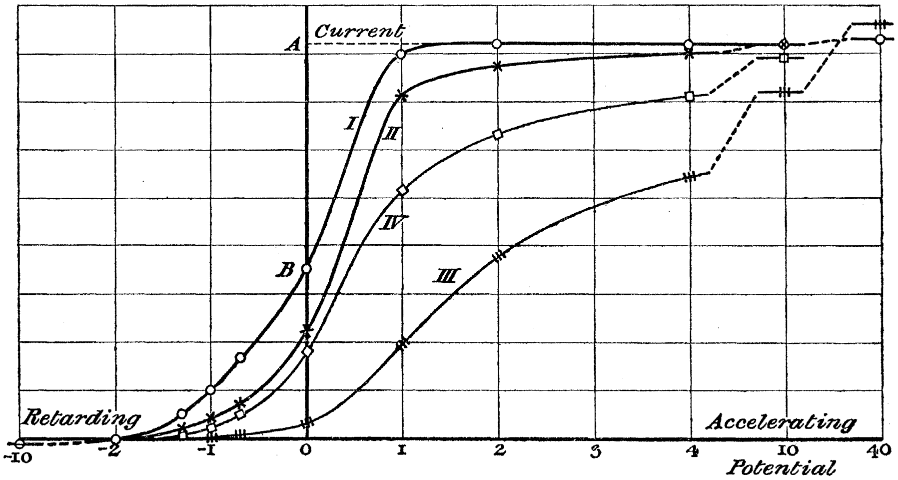

Fig. 7.

Column IV. shows that the presence of enough air to allow the majority of the electrons to collide with air molecules modifies the velocity distribution curves and reduces the maximum velocity from 1·93 volts to 1·86 volts. On opening communication with the cooled charcoal tube, the emission velocity rose to 1·93 volts in five minutes. It would take considerably longer for the pressure of the residual gas to reach its lowest value.

It therefore appears that reflection of electrons, the earth's magnetic field, and the degree of vacuum used in these experiments have no appreciable effect on the maximum emission velocities.

There remains to consider the effect due to reflected light. In column I., Table I., the ratio of the effect due to reflected light to the direct effect is 1·5 to 85. Consider what happens at the point A′ where the curve cuts the axis (fig. 4). Only the shortest wave-length has any tendency to cause the plate to charge up positively, while it receives negative electricity due to the whole range of wave-lengths reflected to the sides. When using monochromatic light the latter effect would be much less. A zinc plate charged up to 2·02 volts when illuminated by the unresolved light from the mercury arc. When the shortest wave-length λ 1849 was isolated and directed to the plate it charged up to 2·06 volts. It is evident therefore that 2·06 volts was very nearly the true velocity with which the fastest electrons were emitted.

From these considerations it seems quite justifiable to take the potential to which the disc rises as being the actual maximum velocity of emission.

7. *Experiments with Monochromatic Light.*—In the following pages experiments are described from which it is concluded that the maximum energy of emission of photo-electrons, and not the maximum velocity, is proportional to the frequency of the incident light. It seemed the best course to work not with a large number of different wave-lengths, but with three selected wave-lengths, and having fixed on these, to determine the corresponding emission velocities with the highest possible accuracy. Observations were sometimes made with other wave-lengths, but the proof rests largely on the experiments made with λ 2537, λ 2257, and λ 1849.

Nearly all the elements distilled in these experiments were pure. In most cases the distilled portion was tested chemically at the end of the experiment.

Cadmium.—The total photo-electric currents from a surface of distilled cadmium corresponding to the lines λ 2537, λ 2257, and λ 1849, were approximately proportional to 40, 20, and 1. The times taken for the disc to attain its final potential were in the inverse order. The rate at which the final potential was attained, when using λ 1849, was so slow that it always required about an hour to determine the final potential, even when the system was initially charged to a value ·1 volt below its final value. It was this excessive feebleness of the light that made the experiments difficult, even when the electrical conditions were at their best.

In Table II. the experimental results are given. The velocities, corresponding to the three wave-lengths, were determined three times each in rotation. For reasons discussed in section 4, the lines λ 2967 and λ 3340 were obtained by the transparency limits of mica and glass. In the fourth and fifth columns the theoretical values are given on the energy law and LADENBURG'S law respectively, taking the values for λ 2537 and λ 1849 as standard.

The velocity predicted by the energy law for λ 2257 is in much better agreement with the experimental value than that predicted by LADENBURG'S law. The experimental values for λ 2967 and λ 3126 are lower than the theoretical values, on account of the earth's magnetic field curling the paths of the photo-electrons so much that none of them impinge on the case normally. Though the experimental velocity for λ 3126 is given as 0 in the table, a well-marked current was obtained with an

TABLE II.—*Cadmium.*

Wave-length.	Velocities (in volts).			Mean velocities.
λ 2537	·901	·901	·890	·897
λ 2257	1·420	1·431	1·431	1·427
λ 1849	2·480	2·480	2·480	2·480

Wave-length.	Frequency, *n*.	Experimental velocities.	$V = kn - V_0$.	$\sqrt{V} = k'n - c$.
λ 1849	1623×10^{12}	2·480 volts	[2·480]	[2·480]
λ 2257	1329	1·427	1·424	1·339
λ 2537	1182	·897	[·897]	[·897]
λ 2967	1010	·148	·286	·495
λ 3126	960	0	·101	·398
λ 3340	898	No effect.	(− ·12)	·293

$V_0 = 3\cdot347$ volts; $k = 3\cdot590 \times 10^{-15}$.

accelerating potential of ·5 volt. There was no leak due to λ 3340 under the same conditions. In this region, perhaps the best test of the energy law is that there is an emission of electrons with λ 3126, but not with λ 3340, and this is exactly what theory predicts. According to LADENBURG's law, one might expect an emission of electrons down to λ 4000.

Dry oxygen at 140 mm. was admitted to the apparatus for 15 minutes. This caused a reduction (after evacuating again) in the total leak for each wave-length of about five times. The result of this was that it was impossible to measure the maximum emission velocity corresponding to λ 1849. The velocity changes are:—

λ 1849	effect too small.
λ 2257	·276 volt reduction.
λ 2537	·244 ,, ,,
λ 2967	no effect.

The results of another experiment with a fresh surface of distilled Cd are given in Table III.

As before, there is close agreement between the experimental value for λ 2257 and the value predicted on the energy law. The energy law also predicts that the effect should set in between λ 3126 and λ 3340.

The apparatus was filled with oxygen at 160 mm. for 10 minutes. A reduction in the total effect was again noticed. The velocity changes are:—

λ 1849	effect too small.
λ 2257	·213 volt reduction.
λ 2537	·244 ,, ,,
λ 2967	no effect.

TABLE III.—*Cadmium.*

Wave-length.	Velocities (in volts).			Mean velocities.
λ 2537	·869	·869	·869	·869
λ 2257	1·399	1·389	1·389	1·392
λ 1849	2·459	2·459	2·448	2·455

Wave-length.	Frequency, n.	Experimental velocities.	$V = kn - V_0$.	$\sqrt{V} = k'n - c$.
λ 1849	1623×10^{12}	2·455 volts	[2·455]	[2·455]
λ 2257	1329	1·392	1·396	1·309
λ 2537	1182	·869	[·869]	[·869]
λ 2967	1010	·159	·249	·468
λ 3126	960	·042	·070	·373
λ 3340	898	No effect.	(− ·15)	·274

$V_0 = 3{\cdot}384$ volts ; $k = 3{\cdot}597 \times 10^{-15}$.

From these two experiments with oxygen one may conclude that the effect of contact with oxygen is to move the line $V = kn - V_0$ parallel to itself, the value of V_0 being increased.

The results of a third experiment with cadmium are given in Table IV.

TABLE IV.—*Cadmium.*

Wave-length.	Velocities (in volts).				Mean velocities.
λ 2537	·716	·716	·720	·720	·718
λ 2257	1·256	1·282	1·267	1·282	1·270
λ 1849	2·380	2·395	2·385		2·387

Wave-length.	Frequency, n.	Experimental velocities.	$V = kn - V_0$.	$\sqrt{V} = k'n - c$.
λ 1849	1623×10^{12}	2·387 volts	[2·387]	[2·387]
λ 2257	1329	1·270	1·275	1·185
λ 2537	1182	·718	[·718]	[·718]
λ 2967	1010	0	·068	·334
λ 3126	960	No effect.	(− ·12)	·253

$V_0 = 3{\cdot}754$ volts ; $k = 3{\cdot}784 \times 10^{-15}$.

With a small accelerating potential there was a decided leak with λ 2967, but not with λ 3126.

From these three experiments with different surfaces of cadmium distilled *in vacuo*, it appears conclusive that the results satisfy the energy law accurately, and that LADENBURG'S law is incorrect. This conclusion is based on the results for λ 2537, λ 2257, and λ 1849. Additional support is derived from the fact that the photo-electric effect sets in at the wave-length predicted by the theory.

Zinc.—Experiments similar to those on cadmium were carried out with surfaces of distilled zinc. The energy law was found to be obeyed as accurately as in the case of cadmium. As the experimental results for zinc (and for all the metals subsequently mentioned) are very similar to those for cadmium, it is unnecessary to reproduce them here. The velocities in any experiment can be calculated from the values of k and V_0 which follow. (Each pair of values for k and V_0 represents a separate distillation and a table similar to Tables II., III., and IV.)

	k.	V_0
	$3{\cdot}70 \times 10^{-15}$	3·72 volts.
	3·82	3·79
	3·83	3·83
	3·79	3·73
Mean . . .	3·79	3·77

Magnesium.—Rather more difficulty was experienced in working with magnesium than with zinc or cadmium. Except in the experiment where $V_0 = 2{\cdot}91$ volts, the effect for λ 1849 was rather smaller than in the other experiments, and it was therefore more difficult to determine the corresponding maximum velocity. The results of the experiments are :—

	k.	V_0.
	$3{\cdot}45 \times 10^{-15}$	2·91 volts.
	3·33	3·25
Mean . . .	3·39	3·08

Bismuth.—The results for bismuth are summarised by the following values for k and V_0 :—

	k.	V_0.
	$3{\cdot}60 \times 10^{-15}$	3·49 volts.
	3·65	3·48
	3·63	3·14
Mean . . .	3·63	3·37

Antimony.—The values for k and V_0 for antimony are :—

	k.	V_0.
	$3{\cdot}72 \times 10^{-15}$	3·67 volts.
	3·66	3·54
Mean . . .	3·69	3·60

Calcium.—Owing to its high boiling point, calcium was very difficult to distil. Some trouble was experienced in getting the velocity corresponding to λ 1849. In the experiment denoted by $k = 3{\cdot}01 \times 10^{-15}$ and $V_0 = 2{\cdot}37$ volts, a slight photo-electric leak was obtained with λ 3650 which (with these constants) is just within the range of wave-lengths capable of producing a photo-electric effect on the energy law. This was the only occasion in the course of the research when λ 3650 was found to produce a photo-electric effect :—

	k.	V_0.
	$3{\cdot}30 \times 10^{-15}$	2·80 volts.
	3·01	2·37
	3·22	2·55
Mean . . .	3·17	2·57

Lead.—The experiments on lead are represented by the following values of k and V_0 :—

	k.	V_0.
	$3{\cdot}58 \times 10^{-15}$	3·51 volts.
	3·51	3·33
Mean . . .	3·55	3·42

Selenium.—All the elements that have been tested belong to groups 2, 4, and 5 of the periodic table. They are all metals, and are generally more or less electropositive in character. Selenium, which belongs to group 6, is a non-metal, and is much more electronegative. There is not very much variation in the photo-electric behaviour of the seven metals whose photo-electric behaviour has been investigated, and it is probable that one would not get much variation until one tried an element possessing widely different properties. Selenium might, therefore, be expected to show some difference in its photo-electric properties.

Not the slightest effect was obtained with λ 2537 or with λ 2257, but a well-marked effect was obtained with λ 1849. The total photo-electric effect for this wave-length appeared to be quite as big as for any of the other elements previously tested. A very thin layer of Se was distilled first, and the maximum emission velocity corresponding to λ 1849 was 1·01 volt. Then a much thicker layer was distilled, and the velocity was again 1·01 volt. The selenium was left for about fifty hours in contact with the residual gases which came out from the charcoal ($\simeq$ ·01 mm.). There was no change in the velocity. Then air at 200 mm. was admitted for 15 minutes. There was no change in the velocity even after this. It is clear that the photo-electric properties of selenium are not nearly so much affected by contact with air as those of zinc or cadmium.

As selenium would only emit electrons with λ 1849, it was not possible to find k and V_0 for selenium. If we assume selenium to have approximately the same k as Bi and Sb (which are in the next group), we find that V_0 for selenium is about 4·8 volts.

Arsenic.—Four distillations of arsenic were made. The effects of the first two were so much smaller than the effects with other metals that velocity measurements were not undertaken. Some pure arsenic from another source was obtained, but still the unusually small leak was obtained and so the effect appeared to be real. There was no photo-electric effect with λ 2537. The effect set in between λ 2386 and λ 2330. With λ 2257 the effect was far smaller than with other metals. The effect with λ 1849 was considerably smaller than with other metals, but the difference was nothing like so great as in the case of λ 2257. It was impossible to determine the emission velocities with any accuracy. One distillation gave ·44 volts for λ 2257 and 1·50 volts for λ 1849. The other distillation gave ·33 volts for λ 2257 and 1·40 volts for λ 1849. Even when the greatest precautions were taken, these values could not be determined to within ·1 volt. Hence we can only say that k lies between $3{\cdot}6 \times 10^{-15}$ and $3{\cdot}8 \times 10^{-15}$, and that V_0 is of the order 4·4–4·6 volts.

Zinc Chloride.—Zinc chloride was heated in the quartz furnace in the vacuum for some time to drive off moisture. Then the disc was lowered in order to receive a layer of the distilled salt. There was not the slightest trace of any photo-electric leak even when the unresolved light from the mercury arc fell upon the disc. An unexpected effect was then observed. Ordinary undried air was admitted to the apparatus at a pressure of 760 mm. for 15 minutes. On evacuating again, a slight photo-electric leak was obtained. Under similar conditions a zinc plate would emit a current of the order 10^5 times as great. This leak from the zinc chloride after contact with air increased by about 80 per cent. in the course of an hour. The plate charged up to about ·3 volt when the unresolved light from the mercury arc fell upon it. There was not enough effect to use the monochromator. After the exposure to air, the surface of the zinc chloride, previously quite dry, appeared slighly moist.

Quantitative experiments on the total photo-electric effect were not made, but, as far as one could judge from the rate at which the plate charged up, the effect was much the same for all metals except arsenic. The reduction in the total effect for cadmium after the admission of oxygen was certainly far greater than the differences between the effects for the metals distilled *in vacuo*.

8. *Discussion of the Results.*—(i.) It is clear from these experiments that the energy with which the fastest electrons emerge from a plate illuminated by ultra-voilet light

is proportional to the frequency of the light. The evidence is based mainly on observations made with the wave-lengths λ 2537, λ 2257, and λ 1849. The velocity V, measured in volts, is related to the frequency n by the formula $V = kn - V_0$. This implies that the emission of photo-electrons should cease below a certain definite frequency, and this was found to be the case experimentally. We may therefore consider the energy law to be established over the whole range of wave-lengths which are effective in causing the emission of photo-electrons.

(ii.) The great differences between the results of experiments on the photo-electric effect, which have been published from time to time, are no doubt very largely due to more or less tenacious gaseous films covering the surfaces. The method of distillation *in vacuo* was adopted to avoid the presence of these gaseous films, as it is impossible to get rid of them when once they are formed. If a metal distilled *in vacuo* soon became covered with a retarding film, then we should not expect the agreement which was obtained between the experiments on distilled mercury and those on the continuously forming mercury surface, where the surface is exposed to the light as soon as it is formed.

MILLIKAN* and WRIGHT† have obtained abnormally high values for the emission velocities from metals which were kept in a very good vacuum for several months. During that period the metals were frequently illuminated by intense ultra-violet light. MILLIKAN explains the results by a purification of the surfaces from gaseous films which are considered to have a marked retarding effect on the electrons. They also found that when these abnormally high values were obtained the emission velocity was a maximum (13·5 volts for Al) for the wave-length λ 2166. It is possible that, in MILLIKAN and WRIGHT'S experiments, the long-continued exposure to ultra-violet light produces a surface polarisation, for when the metal emits electrons it is acting as a cathode. There certainly seems to be more opportunity for unknown changes to take place, perhaps producing surface polarisation, than in these experiments. Here the measurements were usually complete in about four hours after the distillation had taken place.

(iii.) Do the electrons which emerge from a plate illuminated by ultra-violet light all possess the same velocity, or do their velocities range from a maximum down to zero? The latter would almost certainly be the case if the electrons suffered various amounts of scattering by the molecules in the surface before they emerged. The discussion in section 4 of this paper shows that the so-called velocity distribution curve obtained by plotting the leak against various retarding potentials is mainly a function of the obliquity with which the electrons strike the surrounding boundary. This question cannot therefore be answered from the curves given in fig. 7. In some experiments of LADENBURG, to which this consideration does not apply to the same extent, it appeared that monochromatic light produced electrons all of the same velocity.

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* MILLIKAN, 'Phys. Rev.,' XXX., p. 287, 1910.

† WRIGHT, 'Phys. Rev.,' XXXIII., p. 43, 1911.

It would follow from this, that only those electrons which do not undergo any scattering (or, more accurately, which do not suffer any reduction in velocity through scattering) can emerge. It is proposed to investigate this important point in further experiments.

(iv.) The values of k and V_0 (Table V.) for the elements investigated in this research change in the same direction, though the changes in V_0 are considerably greater than those in k. The variations in k are a little larger than the possible errors of experiment.

The photo-electric effect was one of the first phenomena to be interpreted on the quantum theory of radiation. If the energy of the photo-electron is equal to that in the quantum, hn, where h is PLANCK'S constant, then we should have

$$Ve = hn.$$

This gives a definite value for our k. The value of h/e is numerically equal to $4{\cdot}19 \times 10^{-15}$. The experimental values of k, which vary from $3{\cdot}17 \times 10^{-15}$ to $3{\cdot}79 \times 10^{-15}$, suggest, on this view, that only a fraction of the energy of the quantum is transferred to the electron. Had the experimental values for k been grouped about the theoretical value h/e, one would almost be compelled to conclude that k was a constant for all metals and equal to the quotient of these two universal constants. However, as the experimental values are well outside the theoretical value, there is no reason on the quantum theory why they should be the same for all elements, as the sharing of the energy between the electron and the parent molecule may depend on the nature of the element.

The view that the quantum is a localised vehicle for radiant energy of dimensions comparable with those of a molecule is not now accepted. The earlier view led to a very simple explanation of photo-electricity. Nevertheless, some new way of considering the phenomena in terms of the quantum theory may explain many of the results. A molecule may have to be in a condition to accumulate energy to the amount hn before it can emit an electron carrying away a definite and, for any one substance, a constant fraction of the energy away with it. In some way such as this the energy law could be accounted for.

(v.) Sir J. J. THOMSON* has given a theory of the photo-electric effect, based on resonance, which leads to the law verified in these experiments, that the energy of the photo-electron is proportional to the frequency of the light. It was shown that if an electron rotates on a certain cone at whose apex there is an electrical doublet, its energy of motion is proportional to the frequency. If light of the same period passes over the system, resonance takes place, and the electron is expelled with about the same energy as it had in its orbit.

(vi.) The experimental relation $V = kn - V_0$ suggests that the electron starts initially

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* Sir J. J. THOMSON, 'Phil. Mag.,' XX., p. 238, 1910.

with an amount of energy $e.kn$ and that $e.V_0$ represents the loss of energy by the time it has emerged from the surface. We may regard this $e.V_0$ as being made up of two parts, $V_1.e$ the loss of energy in passing out of the molecule and $V_2.e$ the loss of energy in passing through the retarding surface layer. It is very probable that V_2 is zero for surfaces prepared by distillation of metals *in vacuo*. The effect of admitting oxygen for a short time to the apparatus, when the disc was covered with a new surface of cadmium, was to increase V_2 from 0 to about ·3 volt. A previous research* showed that oxygen was effective in reducing the emission velocities from Cd and Zn and other metals while hydrogen was ineffective. This is in agreement with a view advanced by Sir OLIVER LODGE and others, that oxygen is mainly responsible for the contact potential. On this theory, however, the oxygen layer is positive with respect to the metal, while to account for the reduction in the velocity the layer should be negatively charged.

V_1e may be identified with the work required to take an electron away from a molecule. Unless the quantity kn exceeds V_1, light is incapable of producing a separation of the electron from the molecule. If the V_0 given by these experiments is equal to V_1, then the smallest frequency capable of exciting the photo-electric effect should be identical with the smallest frequency capable of producing ionisation in the vapour of the metal. An assumption is made here that ionisation in gases by light is essentially the same thing as the photo-electric effect.

An inspection of the values of V_0 in Table V. shows that the work of withdrawing an electron from a molecule is least for calcium, the most electropositive element in the table, and greatest for the more electronegative elements.

(vii.) We may apply these principles to determine the work required to ionise a molecule of oxygen. From my experiments† on the ionisation of the air by ultra-violet light, I concluded that air (or more probably the oxygen in it) is only ionised to an appreciable extent when light of wave-length shorter than about λ 1350 is absorbed in it. An examination of the results given in PALMER's paper‡ justifies this estimate. What value shall we give to k for oxygen? Fortunately the values of k do not alter much, so a mean may be taken without much error. The mean of all the k's (omitting k for the electropositive calcium) is $3{\cdot}62 \times 10^{-15}$. The mean k for Bi and Sb is $3{\cdot}66 \times 10^{-15}$, and these elements resemble oxygen somewhat more than the other elements. The value of $V_1 (= kn)$ works out to be 8·0 volts. DEMBER§ finds that the work required to ionise a molecule of air is $1{\cdot}26 \times 10^{-11}$ erg. Dividing this by $e = 4{\cdot}65 \times 10^{-10}$ we get the ionising potential to be 8·1 volts.

(viii.) When zinc is in combination with chlorine, which has a strong attraction for the electron, experiment shows that light of wave-length λ 1849 is incapable of

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* HUGHES, 'Proc. Camb. Phil. Soc.,' XVI., p. 167, 1911.

† HUGHES, 'Proc. Camb. Phil. Soc.,' XV., p. 482, 1910.

‡ PALMER, 'Phys. Rev.,' XXXII., p. 1, 1911.

§ FRANCK and HERTZ, 'Verh. d. D. Phys. Ges.,' p. 967, 1911.

producing a photo-electric effect. It was shown in a previous research* that the vapours zinc ethyl, tin tetrachloride, and carbon disulphide, could not be ionised by ultra-violet light,† although all these compounds contain elements which are photo-electric when uncombined. These results are easily interpreted on the view that the valency electron is the electron concerned in the photo-electric effect. When combination takes place the valency electron is attracted more strongly to the molecule of the compound than it was to the electropositive member when uncombined. One could get a measure of the affinities of different elements for zinc, by observing the shortest wave-length necessary to cause ionisation in various zinc compounds. The experimental difficulty is that the critical wave-lengths will usually be beyond the region that can be conveniently used in experiments.

(ix.) The inside of the apparatus surrounding the illuminated plate was covered with the same layer of soot throughout the experiments. As carbon is of marked electronegative properties it is probable that the fall of potential across the surface layer, which may be present, is not more than a fraction of a volt. To correct for this, the values of V_0 should all be altered by this small amount. This correction should be given by an experiment in which the inside of the case as well as the illuminated plate is covered with the same distilled metal.

9. *Variations in k and* V_0 *with Atomic Volume.*—POHL and PRINGSHEIM found from their investigations on the alkali metals that the photo-electric effect may be divided into two parts—the "normal" effect and the "selective" effect. In the normal effect the emission of photo-electrons is determined solely by the amount of light absorbed, and the ratio of the photo-electric current to the energy in the light increases continuously with decreasing wave-length. The emission of photo-electrons in the selective effect only occurs when a component of the electric force in the light beam is in the plane of incidence. The ratio of the photo-electric current to the energy in the incident light rises to a very well-marked maximum for a certain wave-length which varies from metal to metal. This maximum becomes less defined and moves towards the ultra-violet as the element becomes more electronegative. A selective effect has been observed for Rb, Li, Na, K and Ba, and the maxima correspond to wave-lengths within the region λ 5000 to λ 2000. The question arises as to whether the velocities of the electrons produced in the two effects are identical or not. If the two effects originated in different systems we should not expect a coincidence. Even if they are fundamentally the same, it is not self-evident that the velocity of the electrons produced near the maximum should obey the same law as the velocities at two points well away from the maximum. The selective effect is generally regarded as a resonance phenomenon, and therefore the emission velocities near the maximum of the effect might possibly possess unusually high values. No selective effect has been

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* HUGHES, 'Proc. Camb. Phil. Soc.,' XVI., p. 378, 1911.

† The shortest wave-length is given in the paper as λ 2300. It should be corrected to λ 1849, which was discovered later.

observed for the elements investigated in this research. Lindemann[*] has given a formula which connects certain constants of the elements with the maximum of the selective effect. Except in the case of Li, the agreement with experiment is fairly good. The formula is

$$\lambda_{\text{max.}} = 65{\cdot}3\,(a/n)^{1/2}$$

where a is the atomic volume and n the valency. The application of this formula to the elements used in this research is given in Table V. It is recognised that the process of extrapolation to elements of valency greater than 2, has no experimental justification.

Table V.

Element.	Atomic weight.	Atomic volume.	Valency.	$\lambda_{\text{max.}}$	k.	V_0.
Ca	40·1	25·4	2	λ 2330	$3{\cdot}17 \times 10^{-15}$	2·57 volts
Mg	24·3	14·0	2	λ 1730	3·39	3·08
Cd	112·4	13·0	2	λ 1670	3·66	3·49
Zn	65·4	9·2	2	λ 1400	3·79	3·77
Pb	207·1	18·1	4	λ 1390	3·55	3·42
Bi	208·0	21·2	5	λ 1340	3·63	3·37
Sb	120·2	18·1	5	λ 1240	3·69	3·60
As	75·0	13·1	5	λ 1060	≏3·7	≏4·5
Se	79·2	17·6	6	λ 1110		≏4·8
O_2	16·0	12·6	6	λ 940		≏8·0

The calculated value of the maximum of the selective effect in Ca is well within the range of wave-lengths used in this research, and that for Mg is not very far outside. Yet there was nothing abnormal in the emission velocities from Ca compared with those from other metals.

In looking for some connection with the selective effect, a remarkable relation between the values of k and V_0 and the atomic volume was noticed (Table V). In any set of elements of the same valency there is a regular increase in k and V_0 with decreasing atomic volume. As we pass from one valency to another, the relation is discontinuous, the discontinuity always being in the same direction. This may be expressed by saying that if each atomic volume were multiplied by a suitable fraction which becomes smaller with increasing valency, then the values of k and V_0 would change continuously with the product of the atomic volume and a factor depending upon the valency.

There is no clear connection between the changes in k and V_0 with changes in the atomic weight.

10. *Summary.*—(1) The maximum velocity of photo-electrons from the surfaces of a number of elements prepared by distillation *in vacuo* has been measured.

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[*] Lindemann, 'Verh. d. D. Phys. Ges.,' XIII., p. 482, 1911.

(2) It has been shown that the energy of the fastest electrons emitted when monochromatic light falls on the surfaces is proportional to the frequency of the light. The results are expressed in the form $V = kn - V_0$, where V is the velocity measured in volts and n the frequency. LADENBURG'S law, that the velocity is proportional to the frequency, has been shown to be incorrect.

(3) The values of k and V_0 have been found directly for the elements Ca, Mg, Cd, Zn, Pb, Sb, Bi, and As, and the values of V_0 for Se and O_2 indirectly.

(4) The values of k and V_0 for elements of the same valency change regularly with the atomic volume.

(5) The product of V_0 into e, the charge on an electron, has been identified with the work required to separate an electron from the molecule.

(6) It has been shown that the velocity distribution curves usually obtained in photo-electric experiments do not by any means represent the actual distribution of velocities of the electrons.

(7) The maximum emission velocity of photo-electrons from a continually forming mercury surface is identical with the velocity from a surface of mercury prepared by distillation.

The spectrograph used in this research was obtained by means of a Government Grant through the Royal Society.

In conclusion, I wish to express my best thanks to Prof. Sir. J. J. THOMSON for his interest and encouragement during the course of this investigation.

[*Note added July* 11, 1912.—The preceding paper will be rendered more complete by a short reference to two papers which appeared after it was written, and which bear upon some of the points discussed therein. In Table V. the maximum of the selective effect for Mg is given as λ 1730 by LINDEMANN'S formula. POHL and PRINGSHEIM ('Verh. d. D. Phys. Ges.,' p. 546, 1912) have obtained the interesting result that a freshly distilled surface of Mg does not show any selective effect, but that, in less than an hour after distillation, a well-marked selective effect appears with its maximum at λ 2500. It was mentioned in connection with Table V. of this paper that the emission velocities for Mg are quite regular, although this metal is different from the other elements (except perhaps Ca) in that it has a selective effect with its maximum within the range of wave-lengths used in this investigation. The emission velocities appear, therefore, to be unaffected by the presence of a selective effect.

From a consideration of the spectrum of the source of light used by LENARD in his recent experiments on the ionisation of air by ultra-violet light, LYMAN (' Phys. Zeits.,' XIII., p. 583, 1912) concludes that the ionisation of air by light does not take place unless the light contains wave-lengths less than about λ 1300. This confirms the experimental result which I obtained in an earlier research, and which I have used in the present paper to determine the ionising potential of oxygen.]