

## A DIRECT PHOTOELECTRIC DETERMINATION OF PLANCK'S "h."<sup>1</sup>

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### I. INTRODUCTORY.

QUANTUM theory was not originally developed for the sake of interpreting photoelectric phenomena. It was solely a theory as to the mechanism of absorption and emission of electromagnetic waves by resonators of atomic or subatomic dimensions. It had nothing whatever to say about the energy of an escaping electron or about the conditions under which such an electron could make its escape, and up to this day the form of the theory developed by its author has not been able to account satisfactorily for the photoelectric facts presented herewith. We are confronted, however, by the astonishing situation that these facts were correctly and exactly predicted nine years ago by a form of quantum theory which has now been pretty generally abandoned.

It was in 1905 that Einstein<sup>2</sup> made the first coupling of photo effects and with any form of quantum theory by bringing forward the bold, not to say the reckless, hypothesis of an electro-magnetic light corpuscle of energy  $h\nu$ , which energy was transferred upon absorption to an electron. This hypothesis may well be called reckless first because an electromagnetic disturbance which remains localized in space seems a violation of the very conception of an electromagnetic disturbance, and second because it flies in the face of the thoroughly established facts of interference. The hypothesis was apparently made solely because it furnished a ready explanation of one of the most remarkable facts brought to light by recent investigations, viz., that the energy with which an electron is thrown out of a metal by ultra-violet light or X-rays is independent of the intensity of the light while it depends on its frequency. This fact alone seems to demand some modification of classical theory or, at any rate, it has not yet been interpreted satisfactorily in terms of classical theory.

While this was the main if not the only basis of Einstein's assumption, this assumption enabled him at once to predict that the maximum energy

<sup>1</sup> An abstract of this paper was presented before the Am. Phys. Soc. in April, 1914. (PHYS. REV., IV., 73, '14.) The data on lithium were however first reported at the meeting of the Am. Phys. Soc. in April, 1915. (PHYS. REV., VI., 55, '15.)

<sup>2</sup> Ann. d. Phys. (4), 17, 132, 1905, and (4), 20, 199, 1906.

of emission of corpuscles under the influence of light would be governed by the equation

$$\frac{1}{2}mv^2 = V \cdot e = h\nu - p, \quad (1)$$

in which  $h\nu$  is the energy absorbed by the electron from the light wave, which according to Planck contained just the energy  $h\nu$ ,  $p$  is the work necessary to get the electron out of the metal and  $\frac{1}{2}mv^2$  is the energy with which it leaves the surface, an energy evidently measured by the product of its charge  $e$  by the P.D. against which it is just able to drive itself before being brought to rest.

At the time at which it was made this prediction was as bold as the hypothesis which suggested it, for at that time there were available no experiments whatever for determining anything about how P.D. varies with  $\nu$ , or whether the hypothetical  $h$  of equation (1) was anything more than a number of the same general magnitude as Planck's  $h$ . Nevertheless, the following results seem to show that at least five of the experimentally verifiable relationships which are actually contained in equation (1) are rigorously correct. These relationships are embodied in the following assertions:

1. *That there exists for each exciting frequency  $\nu$ , above a certain critical value, a definitely determinable maximum velocity of emission of corpuscles.*
2. *That there is a linear relation between  $V$  and  $\nu$ .*
3. *That  $\frac{dV}{d\nu}$  or the slope of the  $V \nu$  line is numerically equal to  $h/e$ .*
4. *That at the critical frequency  $\nu_0$  at which  $v = 0$ ,  $p = h\nu_0$ , i. e., that the intercept of the  $V \nu$  line on the  $\nu$  axis is the lowest frequency at which the metal in question can be photoelectrically active.*
5. *That the contact E.M.F. between any two conductors is given by the equation*

$$\text{Contact E.M.F.} = h/e(\nu_0 - \nu'_0) - (V_0 - V'_0).$$

No one of these points except the first<sup>1</sup> had been tested even roughly when Einstein made his prediction and the correctness of this one has recently been vigorously denied by Ramsauer.<sup>2</sup> As regards the fourth Elster and Geitel<sup>3</sup> had indeed concluded as early as 1891, from a study of the alkali metals, that the more electro-positive the metal the smaller is the value of  $\nu$  at which it becomes photo-sensitive, a conclusion however which later researches on the non-alkaline metals seemed for years to contradict.

<sup>1</sup> Lenard (Ann. d. Phys. (4), 8, 149, 1902) discovered a maximum velocity though he did not find the effect of frequency upon it.

<sup>2</sup> Ann. d. Phys., 45, 1120, 1914 and 45, p. 961.

<sup>3</sup> Wied. Ann., 43, 225, 1891.

During the ten years which have elapsed since Einstein set up his equation the fifth of the above assertions has never been tested at all, while the third and fourth have never been subjected to careful experimental test under conditions which were even claimed to permit of an exact and definite answer, nor indeed can they be so subjected without simultaneous measurements *in vacuo* of both contact potentials and photo-potentials *in the case of metals which are sensitive throughout a long range of observable frequencies*. In making this statement I am not under-rating at all the exceptionally fine work of Richardson and Compton,<sup>1</sup> who in common with most other observers interpreted their results in terms of Einstein's equation, but who saw the significance of that equation much more clearly than most of their predecessors had done. I am merely calling attention to the fact that the slope mentioned in (3) and the intercept mentioned in (4) cannot possibly be determined with any approach to certainty unless the region of wave-lengths open to study is larger than it is in the case of any save the alkali metals, and also, in the case of (4) unless simultaneous measurements are made in vacuo upon photo-potentials and contact E.M.F.'s. The fact that Richardson and Compton's slopes vary by more than 60 per cent. is sufficient evidence of the correctness of this statement. Also on the one alkali metal, sodium, on which they made measurements, they made no attempt at contact E.M.F. determinations.<sup>2</sup> Furthermore, since their work appeared two or three theories have been developed to explain their observed departures from the relationships predicted by Einstein's equation<sup>3</sup>—departures which the work at the Ryerson Laboratory appears to prove to be altogether non-existent. In a recent review Pohl and Pringsheim<sup>4</sup> whose own large experience with photoelectric work possibly predisposes them to see the difficulties even too clearly, go so far as to assert not only that any conclusions regarding the validity of (3) and (4) are premature and quite unsupported by any experiments with light waves, but that (2) also, to the testing of which practically all of the work on the energies of photo-emission has thus far been directed, is not deducible from existing data. Furthermore Sir J. J. Thomson<sup>5</sup> writing in December, 1914, says: "the experimental results hitherto obtained seem on the whole to confirm

<sup>1</sup> Phil. Mag. (6), 24, p. 575, 1912.

<sup>2</sup> Professor Richardson in his note in the PHYS. REV., IV., p. 523, 1914, rightly states that they developed a "novel" method of estimating contact E.M.F.'s *in vacuo*, and for this they deserve much credit. But they could not use this method in the case of sodium, for they definitely state that on account of fatigue effects, they were unable to obtain any complete photo current-potential curve for sodium. Further my own work shows that this novel method is not *always* a valid one for determining contact E.M.F.'s.

<sup>3</sup> See Hughes, Phil. Mag. (6), 25, 683, '14 and Sutton, Phil. Mag., 29, 734, '15.

<sup>4</sup> Phil. Mag., 26, 1017, 1913.

<sup>5</sup> Proc. Phys. Soc., London, XXVII., 105, December 15, 1914.

this result [that stated in (2)] though it must I think be confessed that the direct experimental evidence in favor of the strict proportionality is too meagre to enable us to maintain that it is a direct result of experiment."

The difficulties which have stood in the way of reaching a reliable conclusion even as to (2) will be seen from the following review. The first measurements on the relation between the frequency and the maximum energy of emission (which has always been measured by the retarding P.D. necessary to just stop the discharge of electrons under the influence of ultra-violet light) were made in 1907 by E. Ladenburg<sup>1</sup> who concluded that  $\sqrt{V}$  was proportional to  $\nu$ , *i. e.*, that the maximum *velocity* rather than the maximum *energy* of emission was proportional to frequency. Joffe<sup>2</sup> worked over Ladenburg's experimental data and showed that it fitted just as well the Einstein relation  $V \propto \nu$ . The reason for this wide uncertainty lay simply in the fact that the range within which the relation between  $V$  and  $\nu$  could be followed in Ladenburg's experiments was between 2,000 and 2,600 Ångstroms, and with so small a strip of wave-length to investigate, and relatively large experimental errors in making the settings, practically any kind of a theoretical curve might be fitted by the experimental data.

Unquestionably the most reliable work in this field is that done by Richardson and Compton<sup>3</sup> and by Hughes.<sup>4</sup> But Hughes like Ladenburg made his observations at but three frequencies, viz., those corresponding to  $\lambda = 1,849$ ,  $\lambda = 2,257$ , and  $\lambda = 2,537$  and the first of these he finds very hard to get on account of the extreme feebleness of the light. He uses the observations at two of these points, viz., 1,849 and 2,537 to fix his line, and then finds that the third point is slightly closer to this line when  $\nu$  is assumed proportional to  $V$  than when it is assumed proportional to  $\sqrt{V}$ . This is evidence favorable to the first law as opposed to the second, but it obviously does not show a linear relation between  $V$  and  $\nu$  as opposed to a relation of the type  $V \propto \nu^{\frac{3}{2}}$  as implied by Lindemann's theory,<sup>5</sup> or as opposed to any one of several other relations which might be suggested. Hughes indeed adds to his case the argument that his straight line cuts the  $\nu$  axis at about the frequency at which the metal is found to first become photo-sensitive, but since he fails to take any account of the contact E.M.F.'s between his opposing plates these crossing points should be incorrect as Pohl and Pringsheim have pointed out. According to these latter authors, barring the very uncertain points at  $\lambda = 1,800$  and  $\lambda = 2,000$  Å., even a  $V \propto \nu^2$  relationship is

<sup>1</sup> Verh. d. D. Phys. Ges., 9, 504, 1907.

<sup>2</sup> Ann. d. Phys. (4), 24, 939, 1907.

<sup>3</sup> L. c.

<sup>4</sup> Phil. Trans. Roy. Soc. London, A, CCXII., 205, 1912.

<sup>5</sup> Verh. d. D. Phys. Ges., 15, 637, 1913.

just as well fitted by both the Richardson and Compton and the Hughes work as a  $V \propto \nu$  relationship. The whole argument, according to these critics, rests, in Richardson and Compton's case, on the value of the potential at  $\lambda = 2,000$  which is so far in the ultra-violet as to yield a  $V$  which they think unreliable and which in fact fits neither curve well, while in Hughes's case the argument rests on the value of the potential at  $\lambda = 1,894$  which they think even more unreliable.

The work at the Ryerson Laboratory on energies of emission began in 1905. How the present investigation has grown out of it will be clear from the following brief summary of its progress and its chief results.

1. It was found first that these energies are independent of temperature,<sup>1</sup> a result unexpected at the time but simultaneously discovered by Lienhop<sup>2</sup> and thoroughly confirmed by others later. This result showed that *photoelectrons do not share in the energies of thermal agitation as they had commonly been supposed to do*, and this result still stands.

2. The apparent energies of emission, that is, the volts which had to be applied to just stop the emission were determined for eleven different metals and found to differ among themselves by more than one volt.<sup>1</sup> This point has recently been tested again by Richardson and Compton<sup>3</sup> and by Page,<sup>4</sup> both of whom find *no* differences. The present work shows that differences do in general exist though possibly not under the conditions used by the other experimenters.

3. The energy of emission was found to vary considerably with time and illumination, a result which I interpreted as due to the disturbing influence of a surface film which exerted under different conditions different retarding influences on the escape of electrons.<sup>5</sup>

4. The results in 3 revealed the necessity of questioning the validity of all results on photopotentials unless the effects of surface films were eliminated either by removal of the films or by simultaneous measurement in vacuo of photopotentials and contact E.M.F.'s, or by both procedures at once. Accordingly I initiated in 1910 on a somewhat elaborate scale simultaneous measurements on photoeffects and contact E.M.F.'s in vacuo on film free surfaces. Some of the results of these measurements on the common metals have been recently reported by Mr. Hennings.<sup>6</sup> Others are contained in this paper, and still others will be reported in a later paper.

<sup>1</sup> Phil. Mag. (6), 14, 188, 1907.

<sup>2</sup> Ann. d. Phys. (4), 21, 284.

<sup>3</sup> Phil. Mag. (6), 24, 582, 1912.

<sup>4</sup> Am. Jr. Sci., 36, 501, 1913.

<sup>5</sup> PHYS. REV., 30, 287, 1910, and 34, 68, 1912.

<sup>6</sup> PHYS. REV., 4, 228, 1914.

5. The marked difference between the apparent effects on the energy of emission of different types of sources such as the spark and the arc, even when the same wave-length was employed, were traced to the extreme difficulty of eliminating disturbances when spark sources are employed—a difficulty of course appreciated from the first, but thought to have been disposed of because screening of the direct light from the arc removed the differences.<sup>1</sup> After these disturbing influences were eliminated powerful spark sources of given wave-length were found to produce exactly the same energies of emission as arc sources of the same wave-length and of about the same mean intensity, but of only one thousandth the instantaneous intensity.<sup>2</sup> *This furnished very exact proof of the independence first discovered by Lenard of the energy of emission upon intensity, even when the intensity of illumination in one wave-length, viz.,*

$$\lambda = 3650, \text{ was as high as } 10000 \frac{\text{erg}}{\text{cm}^2 \text{ sec}}.$$

6. The relation between  $V$  and  $\nu$  was tested with spark sources without bringing to light at first anything approaching a linear relationship. These results were reported by Dr. Wright.<sup>3</sup> A question as to their validity was, however, raised by my subsequent proof of the insufficiency of such screening devices as had been used in the case of spark sources. Accordingly Dr. Kadesch took up again the relation between  $V$  and  $\nu$  with powerful spark sources, using film-free sodium and potassium surfaces, and obtained results which spoke definitely and strongly in favor of a linear relation between the maximum P.D. and  $\nu$ . The range of wave lengths studied was from 3,900 Å. to 2,200 Å. These results have been published<sup>4</sup> since Pohl and Pringsheim wrote their critique, else I think they would not have felt that the common assumption since 1905 of a linear relation between  $V$  and  $\nu$  rested upon so insecure an experimental basis.

7. At the same time I undertook to investigate with as much exactness as possible, using as a source the monochromatic radiations of the quartz-mercury arc, the third, fourth and fifth of the above assertions of Einstein's equation, and in the vice-presidential address before the American Association for the Advancement of Science in December, 1912, expressed the hope that we should soon be able to assert whether or not Planck's  $h$  actually appeared in photoelectric phenomena as it has been usually assumed for ten years to do.<sup>5</sup> At that time the papers of Hughes and of

<sup>1</sup> Verh. d. D. Phys. Ges., XIV., 720, 1912.

<sup>2</sup> PHYS. REV. (2), I, 73, 1913.

<sup>3</sup> PHYS. REV., 33, 41, 1911.

<sup>4</sup> PHYS. REV., 3, 63, May, 1914.

<sup>5</sup> Science, 37, 119, 1913. The following is the quotation from that address: "But not only

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PLATE I.  
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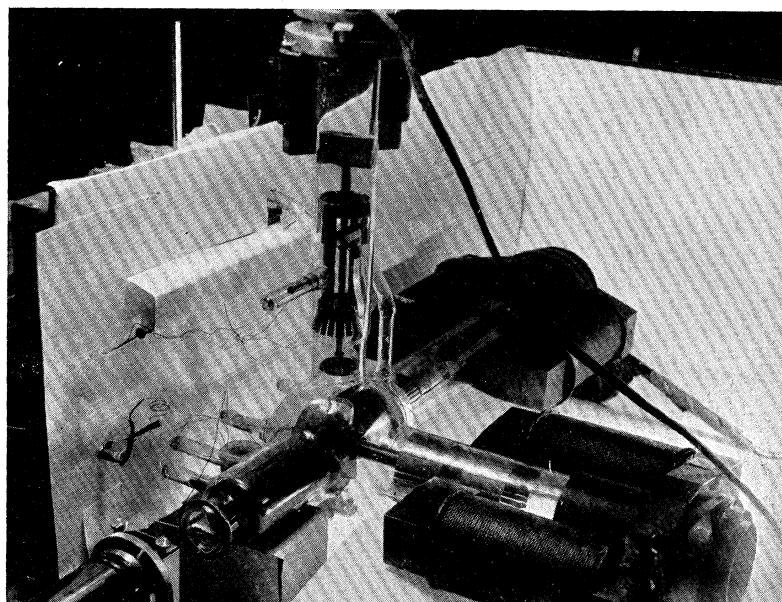


Fig. 1.

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Richardson and Compton had just appeared, though the latter paper I had unfortunately not seen at the time of writing and hence made no reference to it. These authors found the value of  $h$  in the Einstein photoelectric equation varying in the eight metals studied from  $3.55 \times 10^{-27}$  to  $5.85 \times 10^{-27}$ . Planck's  $h$  was  $6.55 \times 10^{-27}$ , a difference which Hughes tried to explain by assuming either that only a fraction of the energy  $h\nu$  was absorbed or that the energy of emission against the direction of the incident light was less than that in the direction of the incident light.

## 2. EXPERIMENTAL ARRANGEMENTS.

In all of this photoelectric work at the Ryerson Laboratory the same general method has been employed, namely, the substances to be studied or manipulated have been placed in the best obtainable vacuum on an electromagnetically controlled wheel and all the needed operations have been performed by movable electromagnets placed outside. As new operations have been called for the tubes have by degrees become more and more complicated until it has become not inappropriate to describe the present experimental arrangement as a machine shop in vacuo. The operations which are now needed in all the tubes which are being used are

1. The removal in vacuo of all surface films from all surfaces.
2. The measurement of the photocurrents and photopotentials due to these film-free surfaces.
3. The simultaneous measurement of the contact E.M.F.'s of the surfaces.

To construct tubes in which these operations can all be performed in rapid succession, particularly when the substances to be studied are, as in this case, the inflammable alkali metals, sodium, potassium and lithium, is not at all easy, and such success as is being obtained in these experiments is due in no small degree to the skill and experience of the mechanician, Mr. Julius Pearson, who has from the start made all the tubes and contributed not a little toward their design. Dr. A. E. Hennings and Dr. W. H. Kadisch, whose papers have already been referred to, have also assisted materially in the evolution of these tubes. That shown in Fig. 1 is the ninth tube of this general plan which has been constructed. Since the detail in the photograph is not very clear it will be explained in connection with the diagram shown in Fig. 2. This diagram, however, relates to a tube used before that shown in the photograph and one in which the motions of the plate  $S$  in the measurement of the contact is the absorption of energy by an electron from a light wave proportional to  $\nu$ ; its numerical magnitude is approximated at least by multiplying the frequency of the light by Planck's,  $h$ . It is true there is here no accurate agreement as yet for part of the energy absorbed by the electron is lost in getting out of the metal and the exact amount of this loss has not been measured with as much accuracy as we hope soon to be able to obtain," etc.

E.M.F.'s were made mechanically instead of electromagnetically, otherwise the tubes are identical.

The three metals on the periphery of the wheel  $w$  (Fig. 2) are cast cylinders of sodium, potassium and lithium. The measurements, here-with reported relate only to the sodium and the lithium, an accident having prevented the inclusion of data on potassium at the present time. The wheel  $w$  is rotated by the electromagnet (not shown in Fig. 2) which is nearest the observer in Fig. 1, until it is opposite the rotary knife  $K$ . The electromagnet  $F$  (Fig. 2) is then energized and slipped slightly for-

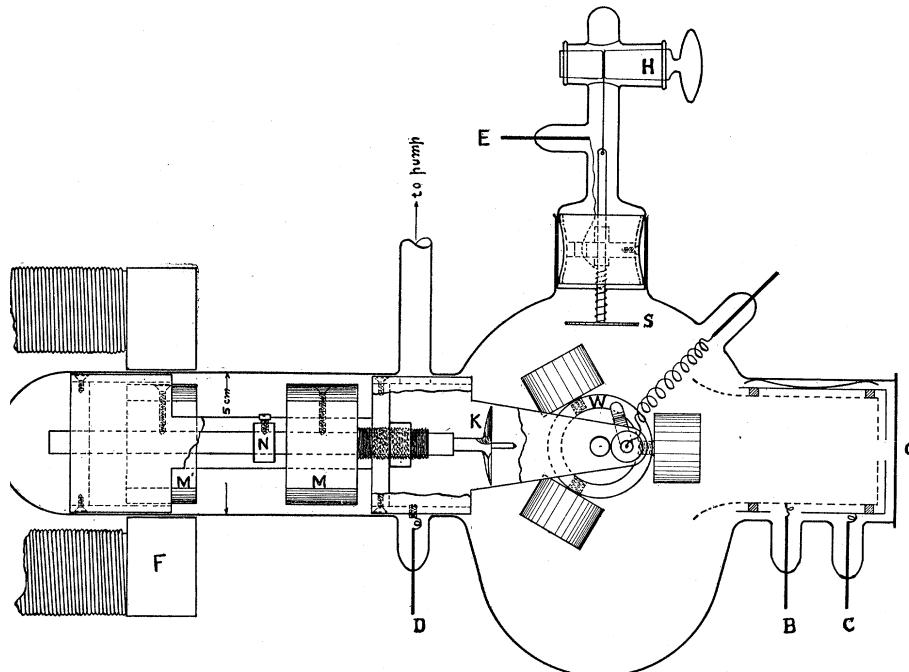


Fig. 2.

ward. It thus advances the armature  $M'$  which is rigidly attached to the knife  $K$  by a rod which slips freely through the second armature  $M$  until the stop  $N$  strikes against  $M$ . In this motion the small centering rod which projects in front of the knife  $K$  enters a small cylindrical hole in the middle of the sodium cylinder. The magnet  $F$  is then demagnetized and slipped still farther forward until it is opposite the armature,  $M$ , re-energized and rotated on an axis coinciding with the axis of the tube. This motion advances the knife  $K$ , which is rigidly attached to  $M$ , by pushing the screw between  $K$  and  $M$  forward in the brass nut carried by a frame which is rigidly attached to the walls of the tube (Fig. 2).

*K* is thus advanced far enough so that upon rotation it will cut a thin shaving from the face of the sodium cylinder. *F* is then demagnetized, slipped back to its position opposite *M'*, energized and rotated and the shaving cut off. It will be clear that by suitably setting *M* the thickness of the shaving can be regulated at will. The shaving falls down into the enlargement on the bulb beneath the wheel where it is of use in freeing the tube from residual oxygen. The knife *K* is next withdrawn from the sodium by slipping back the electromagnet *F*. The wheel *W* is then rotated until the freshly cut sodium surface is normal to the beam of monochromatic light entering at *O*, and a number of photocurrents (see below) are taken corresponding to various P.D.'s applied between the sodium and the Faraday cylinder into which it projects. This Faraday cylinder consists of an inner cylinder of copper gauze and an outer one of solid copper. The gauze cylinder, of mesh 1/20 cm., is strongly oxidized by dipping it into a solution of copper nitrate and then holding it in a bunsen flame. The inner gauze cylinder and the outer solid one are insulated from each other by ebonite rings 3 mm. thick, though in this experiment they were always at the same potential because of the joining of the electrodes *B* and *C*. This type of Faraday cylinder, originally designed by Ladenburg and Markow, was here used for the sake of giving the corpuscles which have just enough energy to reach the gauze a chance to go through the mesh and be caught between the gauze and cylinder, the idea being that the photocurrent-potential curve would plunge into the potential axis more suddenly and thus locate the maximum positive potential more accurately than if a single cylinder were used. Furthermore, the gauze projected out beyond the sodium so as to catch all electrons which left the latter (see Figs. 1 and 2).

At any desired time the freshly cut sodium or lithium surface was rotated until it was opposite the test plate *S*, which was of copper treated as to oxidizing, washing, drying, etc., exactly as was the copper cylinder, so that the contact E.M.F. between the sodium and *S* should be the same as that between the sodium and the gauze cylinder. This contact E.M.F. was measured by the Kelvin method, *i. e.*, by applying, with a potentiometer system, just such a P.D. between the sodium and the plate *S* that lifting *S* from a position say two tenths millimeter above the face of the sodium caused no motion in an electrometer needle connected to *W*. The accuracy of this determination was better than  $\frac{1}{2}$  per cent. All potentials measured in this work were in terms of the indications of a Weston Standard Laboratory voltmeter certified correct to 0.1 per cent. by the Bureau of Standards at Washington.

Since the aim was to test with the utmost possible accuracy the slope

of the line connecting frequency with the maximum P.D. it was necessary first to know  $\nu$  with great precision and second to see that no trace of light of frequency greater than that plotted got through the slit of the spectroscope. To this end a Heracut 200 volt quartz-mercury lamp was used as a source, the lines of a powerful spark source such as that used by Kadesch and also by Lenard and Ramsauer having been found much too impure for the purpose in hand. A grating photograph of the spectrum of the mercury lamp was taken and only such lines were chosen for use as had no companions anywhere on the short wave-length side. This photograph is shown in Fig. 3. The central lines belong to the iron comparison spectrum, the mercury lines being above and below it. The lines chosen for use were  $\lambda = 5,461$  (not shown in the photograph)  $\lambda = 4339.4$ ,  $\lambda = 4046.8$ ,  $\lambda = 3650.2$ ,  $\lambda = 3125.5$ ,  $\lambda = 2534.7$  and  $\lambda = 2399$ . The wave-lengths were kindly determined by Mr. Walter T. Whitney. A glance at the photograph will show how well adapted these lines are for use as accurately determined monochromatic sources so far at least as the short wave-length side is concerned. Light filters to cut out stray short wave-length light were also used as described below. Since the measurement was to be made on the maximum P.D. and since this increases with decreasing wave-length it was not of great importance that the source be of great purity on the long wave-length side. The spectroscope used was a Hilgar monochromator, the end of which is shown in Fig. 1. The slit width was uniformly .01 inch save in the case of lines 2,535 and 2,650 with which slit-widths as large as .04 inch were sometimes used.

The pressure in the apparatus, which was exhausted by a Gaede molecular pump, assisted by the chemical action of the sodium shavings, was carried down to a ten-millionth of a millimeter or less as measured by a McLeod gauge sensitive enough to permit estimates as low as the value mentioned. Such a gauge gives, of course, no indication as to the amount of mercury vapor present, but there appears to be no reason for thinking that this is not carried out by the molecular pump (which ran continuously throughout the observations unless otherwise stated) nearly as completely as are other gases. I have, however, made no tests upon this point and hence can make no positive assertions.

### 3. SOURCES OF ERROR AND THEIR ELIMINATION.

(a) *Magnitude of Photocurrents.*—Since photopotentials are independent of light intensity, it is evident that the accuracy with which the point of intersection of the photocurrent-potential curve with the potential axis can be determined is directly proportional to the magnitude of the

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PLATE II.  
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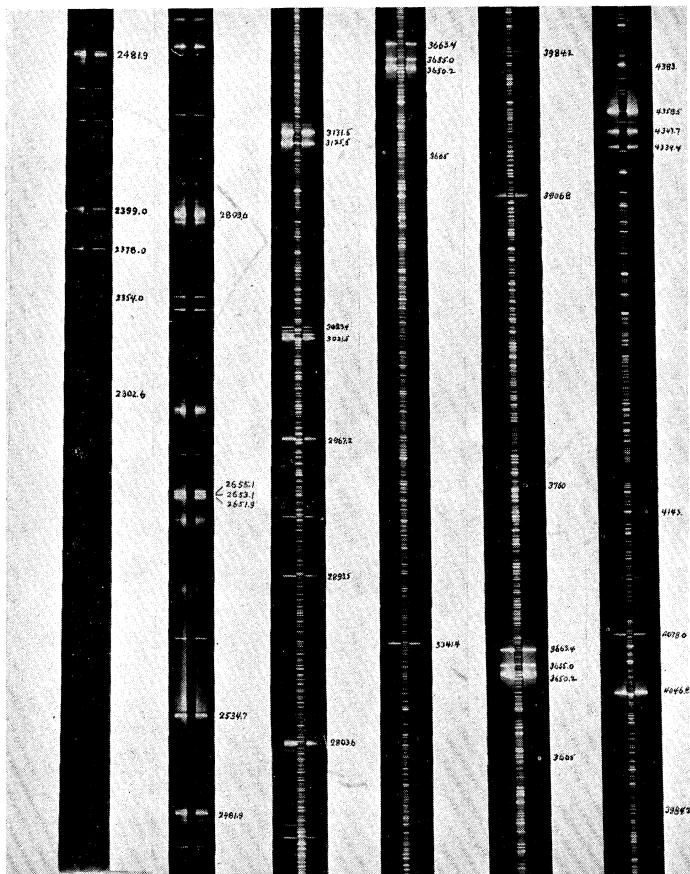


Fig. 3.

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photocurrents at any particular potential, for example at saturation. The photocurrents from a freshly shaved sodium surface are, in the best attainable vacuum, hundred of times larger than those from surfaces a few hours old. Results of especial interest in this connection will be found in a following paper.

The method employed for obtaining the maximum energy of emission in volts was not to attempt to locate experimentally just that retarding potential which would prevent the escape of electrons from the sodium or lithium to the gauze—a very uncertain procedure at best—but rather to plot the photocurrent-potential curve in the neighborhood of the balance point and then to locate this point graphically. These currents were measured with a Dolezalek electrometer connected to the joined electrodes *B* and *C* (Fig. 2). This electrometer had a sensibility of 2,500 mm. per volt, and the scale could be read to 0.2 mm.

The currents were measured by the deflections obtained in an illumination of 30 seconds, and the deflections used in the location of the balance potentials in the case of the sodium ranged from 3 mm. to 80 mm. *But with all the lines studied the saturation currents were from 75 to 500 times these maximum currents used in locating the balance points.* Thus the saturation current for line 5,461 was 3,000 mm., that for line 4,339 was 6,000 mm., that for line 4,047 was 6,000 mm., that for line 3,650 was 31,000 mm., that for line 3,125 was 17,000 mm., that for line 2,652 was 3,000 mm. and that for line 2,535 was 7,800 mm. This means that the complete curves the beginnings of which are shown in Fig. 5 would be from three to twenty meters high. These enormous currents, when measured in scale divisions, make the location of the intercepts on the potential axis a matter of much precision. Smaller currents were used in part of the measurements to be reported both because light filters were introduced (see below) and because a considerable portion of the energy passing through the slit was absorbed in a thermopile introduced for the sake of making simultaneous photoelectric and energy measurements.

(b) *Electrons Liberated by Reflected Light.*—In general the balance potential does not correspond at all to the potential necessary to stop the electrons having the highest energy of emission, but rather to the potential at which the stream of electrons escaping from the illuminated surface is equal to the stream liberated from the walls opposite that surface by light reflected to these walls. With small photocurrents the difference between the two potentials may be very large. Of course, the attempt is usually made to measure and allow for this reverse electronic current by applying a large positive potential to the illuminated

electrode and noting the apparent positive leak, but a correction made in this way is very uncertain. It was because of this error that Richardson and Compton placed less reliance on their determination of maximum energy of emission than on that of mean energy. But the validity of Einstein's equation can only be tested by accurate determinations of the maximum energy. This "back leakage" was here eliminated completely by using only *light for which the illuminated electrode was photoelectrically sensitive, but for which the surrounding walls were not photo-sensitive.* In the following experiments with sodium the long wave-length limit of the oxidized copper walls was  $\lambda = 2688 \text{ \AA}^1$ , but the sodium was sensitive up to  $\lambda = 6800 \text{ \AA}$ . *For any intermediate wave-lengths, though the saturation currents were measured by a deflection of from 3 to 31 meters, there was not a quarter of a mm. of deflection in 30 seconds when the sodium was given a positive potential of 6 volts.* Hence the balance potentials corresponding to the lines from 3,125 to 5,461, inclusive, were obtained with very great precision, so far as this effect alone was concerned. Line 2,535 was below the long wave-length limit of the walls of the Faraday cylinder which was used in the measurements on sodium, so that a positive potential of 6 volts applied to the sodium produced a back leak of 20 mm. in 30 seconds, because of electrons liberated by the reflected light. This was corrected for in plotting line 2,535, but I consider the balance potential for this line as less reliable than those for the other lines. When it is remembered that most photopotential-frequency curves have been obtained from observations on lines between 2,500 and 1,800 where this positive leak is always very large it is not to be wondered at that most erratic and uncertain results have been obtained.

(c) *Contact Electromotive Forces.*—The measurement of the contact E.M.F. between the alkali metals and the test plate showed that it varied from 0.4 volt up to 3.0 volts—depending upon the condition as to age, absorbed gas, etc., of the surfaces tested. This shows the futility of attempting to obtain accurate information about photopotential-frequency relations in the case of the alkali metals without simultaneous measurement in vacuo of photopotentials and contact E.M.F.'s. Furthermore, these changes in contact E.M.F. were found to take place quite rapidly immediately after a fresh surface had been formed by shaving. These results will be more fully reported in a following paper. For the purpose of this study it was more convenient and more accurate to find conditions under which the contact E.M.F. would remain constant over a

<sup>1</sup> In the experiments with lithium the receiving cylinder has been changed and its long wave-length limit was distinctly and definitely lower, namely  $\lambda = 2535 \text{ \AA}^o$ .

time sufficiently long to make possible a full series of photopotential-frequency measurements, than to correct each photopotential measurement by a simultaneous contact E.M.F. determination. Such conditions were found after considerable experimenting and oddly enough they were obtained not in the best obtainable vaccum, but with a pressure of as much as .01 mm. of gas in the bulb. Under such conditions there was obtained the very desirable combination of a constant contact E.M.F. and very large and fairly constant photocurrents so that the most reliable photopotential frequency curve yet taken on sodium (that shown in Figs. 5 and 7) was taken at a pressure as high as .01 mm. of mercury. These results were in perfect agreement, however, so far as concerns "h," with others obtained in the best obtainable vaccum by another method (see below).

(d) *The Length of the Photopotential-Frequency Curve.*—The smallness of the range of frequencies throughout which reliable photopotentials can be measured has already been mentioned as the gravest source of uncertainty in attempting to test any one of assertions 2, 3, 4 or 5 of page 356. Ladenburg's whole wave-length range, viz., from  $260 \mu\mu$  to  $201 \mu\mu$  gave him a curve of length but  $59 \mu\mu$  and that in a region in which, in view of the sensitiveness to the reflected light of all substances of which the collecting Faraday cylinder can be made, accurate measurements of photopotentials cannot be obtained. Hughes's range of  $69 \mu\mu$  was in a less favorable region  $185 \mu\mu$  to  $253 \mu\mu$  even than Ladenburg's. All of Richardson and Compton's published photocurrent-potential curves save those on Al and Na correspond to wave-lengths between  $\lambda = 210 \mu\mu$  and  $\lambda = 275 \mu\mu$ , *i. e.*, the range is  $65 \mu\mu$  or about the same as in Ladenburg's experiments, and the spectral region is the same. With aluminum the range was from  $200 \mu\mu$  to  $310 \mu\mu$ , or a total of  $110 \mu\mu$ , and it was against the validity of the conclusions from the work on Al that Pohl and Pringsheim critique was chiefly directed. On sodium, Richardson and Compton obtained no complete photocurrent-potential curve, but made measurements on maximum positive potentials with wave-lengths  $436$ ,  $366$ ,  $313$ ,  $254$ , and  $210 \mu\mu$ . The settings on  $254$  and  $210$  are subject to the same difficulty due to reflected light as are my own readings on these lines, so that although they made no measurements of contact E.M.F.'s of sodium in vacuo, their range of wave-lengths at which reliable settings on maximum energy of emission might have been made if the contact E.M.F.'s had been known was from  $430 \mu\mu$  to  $313 \mu\mu$  or  $117 \mu\mu$ .

Kadesch's observations on sodium and potassium covered the range of  $390 \mu\mu$  to  $220 \mu\mu$  or  $170 \mu\mu$ .

The present observations on sodium cover the range from  $680 \mu\mu$ , to  $240 \mu\mu$ , or a total of  $440 \mu\mu$  and the potentials determined with a very high precision (about .01 volt) cover the range 577.0 to 265.0 or  $312 \mu\mu$ , *i. e.*, the range is four times that of Ladenburg and Hughes and the region in which thoroughly trustworthy settings can be made is nearly three times that of Richardson and Compton or of Kadesch.

(e) *Scattered Short Wave-Length Light.*—With the very large sensibility of from 2,000 to 31,000 mm. of deflection for saturation currents, settings on the potential necessary to entirely stop a negative discharge would be incorrect if there were the slightest trace of scattered light of wave-length considerably shorter than that of the line being studied. There were in these experiments slight indications of such traces of short wave-length light, deflections of several millimeters in 30 seconds persisting in some cases considerably beyond the potential at which the photocurrent-potential curve was approaching the potential axis. In other words with increasing positive potential this curve would fall very rapidly toward the potential axis until it almost touched it and then shoot out nearly horizontally and approach it asymptotically. That these flat "feet" to the photocurrent-potential curves were due to stray short wave-length light diffusely reflected from the prism faces, lenses, or the plane reflector of the Hilgar monochromator was rendered probable by the fact that they were more pronounced with the longer wave-lengths than with the shorter, and also by the fact that they changed in amount when the plane reflector furnished with the instrument was replaced by one of speculum metal made in the laboratory. It was conclusively proved when it was found that the interposition of filters which absorbed all wave-lengths shorter than the one under investigation caused these "feet" to disappear entirely. Figure 4 shows a rather extreme case of the falsification of the true photocurrent-potential curve by such stray short-wave-length light. The metal studied was here lithium. The slit width was .02 inch and a considerable portion of the light which came through it was intercepted by a thermopile so that the saturation currents were smaller than those mentioned above, as the data on the figure shows. It will be seen from this data that line 2,535, which is the last strong line at the short-wave-length end of the mercury arc spectrum, did not show any trace of this stray light effect, for at +1.3 volts, only .01 volt beyond the intercept there was not a trace of a deflection although .2 mm. could have been easily detected. It will be seen too that at +5.7 volts there was also no trace of a deflection, thus showing that in this case line 2,535 was above the long-wave-length limit of the receiving Faraday cylinder. These readings together with the shape of the curve

constitute the best of evidence that neither stray short-wave-length light nor reverse electronic currents (Richardson and Compton's "back leakage") vitiate in any way this curve corresponding to line 2,535. But the curve corresponding to line 4,339 has a very pronounced "foot" (see Curve I.) which however disappeared completely upon interposing a filter of aesculin in a glass trough—a combination which was found to cut out entirely all lines below 4,339 including the strong adjacent

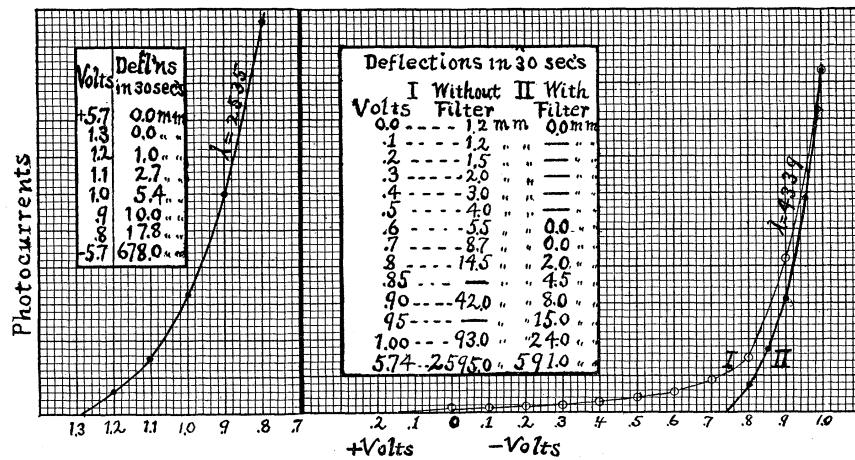


Fig. 4.

line 4,047. Note that there was now no trace of a deflection either at  $-0.6$  or at  $-0.7$  volt (see Curve II.). *These curves and a great many similar ones which I have taken seem to me to establish beyond question the contention that there is a definite, exactly determinable maximum velocity of emission of corpuscles from a metal under the influence of light of a given frequency.* Ramsauer's<sup>1</sup> recent conclusion to the contrary is due, I think, to the fact that the errors caused by stray short-wave-length light (*falsches licht*) were so large as to falsify entirely the lower parts of his velocity distribution curves. His correction for "*falsches licht*" actually amounted to as much as 10 per cent. of his saturation currents.<sup>2</sup> It will be seen that the effect of this stray short-wave-length light is to push the maximum potentials corresponding to the longer wave-lengths too far in the direction of positive potentials, while the effect of reverse electronic currents is to push the intercepts corresponding to the shorter wave-lengths, which alone they influence, in the opposite direction. These two errors are probably chiefly responsible for the fact that the slope  $h/e$  has heretofore come out so erratically and so low.

<sup>1</sup> Ann. der Phys., 45, p. 1120, 1914.<sup>2</sup> For more complete discussion of Ramsauer's experiments see R. A. Millikan, PHYS. REV., January, 1916.

In the present work there were selected, for each line studied, filters which absorbed all, or nearly all, of the energy of wave-length shorter than that of the line under investigation. Since, however, these filters diminish largely the total saturation currents their use tends to diminish the accuracy of locating the intercepts. Hence after it has been established that the flat "feet" of the curves are due to stray light, it is perhaps just as well to reduce these feet as much as possible, without the use of filters, that is, by having all transmitting and reflecting surfaces as clean and as perfect as possible and all absorbing surfaces as black as possible, and then simply to cut the feet off. Thus even in the extreme case shown in Fig. 4, Curve I., very little error in the intercept would have been made by drawing the curve altogether without reference to the last eight small readings. In the work on the sodium, after a study of all the lines had been made with filters and the stray light effects reduced to the order of a millimeter in 30 seconds, the filters were dispensed with entirely and curves plotted corresponding to observed deflections between 3 mm. and 80 mm. The result is shown in Fig. 5.

(f) *Maximum Energy of Emission vs. Most Frequent Energy.*—Richardson and Compton place least reliance upon their determinations of maximum energies of emission and draw most of their conclusions from a consideration of the *most frequent* energy of emission, making the assumption that with all wave-lengths the ratio between the most frequent energy and the maximum energy is a constant. In the present experiments with sodium this was not found to be the case, and in general it seems probable that the assumption cannot be strictly true. For even if the surface of the sodium were a perfectly homogeneous substance (evidence against this view will be brought forward in a second paper), the differences in the penetrating power of light of different wave-lengths into the sodium, as well as the differences in the absorptions of electrons of different speeds in the layers of sodium through which they emerge, would seem to require differences in the velocity distribution curves obtained with different spectral lines. Hence, there would seem to be no warrant for expecting to obtain a reliable test of any of the assertions of Einstein's equation by comparing the most frequent velocities of emission produced by different lines. *If Planck's "h" is actually involved in photoelectric phenomena its presence can be expected to be brought to light only by accurate measurements on the maximum energies of emission under the influence of lights of different frequencies.* Attention was, therefore, here directed entirely to this end.

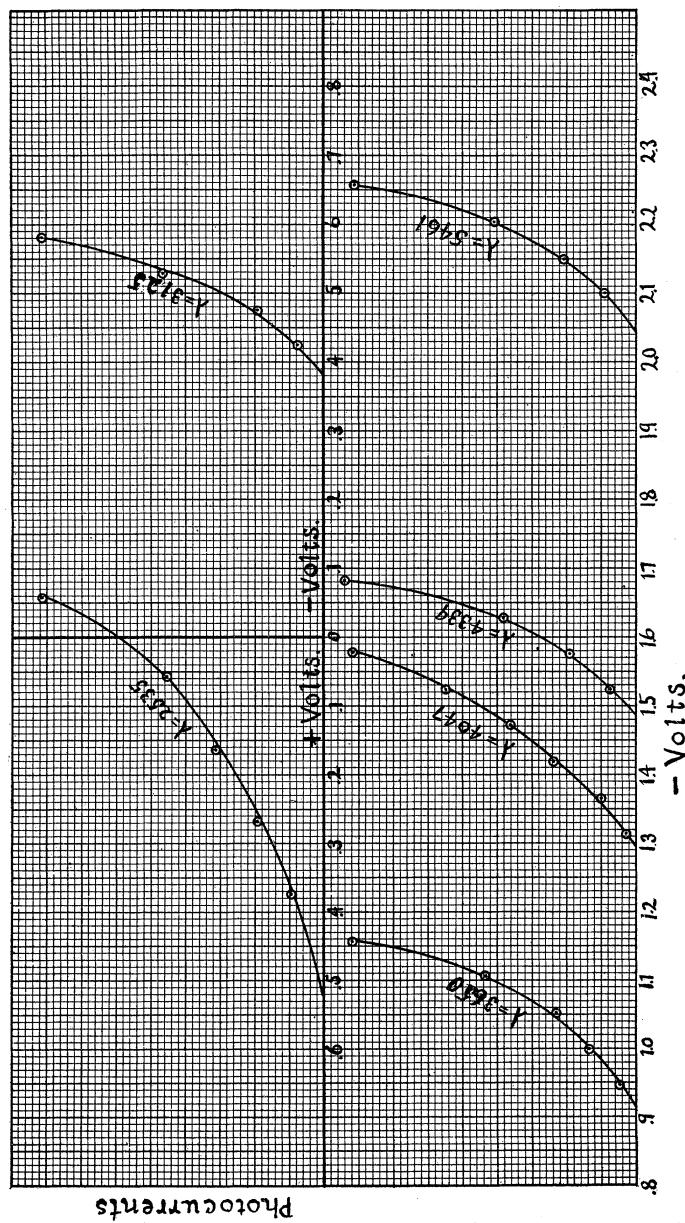


Fig. 5.

4. THE DETERMINATION OF  $h$ .

Fig. 5 shows the most reliable single set of photocurrent potential curves yet taken for the different lines. For compactness the whole right half of the figure, namely the half containing lines 3,650 to 5,461, is placed below the half containing lines 2,535 and 3,125. It will be seen that all the curves, save that corresponding to  $\lambda = 2,535$ , strike the potential axis on the side of negative volts. This means simply that  $e$  times the contact P.D., which, since sodium is positive with respect to copper, acts as a retarding potential, exceeds the energy of emission save in the case of line 2,535. It will be seen also that the maximum possible error in locating any of the intercepts is say two hundredths of a volt and that the total range of volts covered by the intercepts is more than 2.5. Each point, therefore, of a potential-frequency curve should be located with not more than a per cent. of uncertainty. The frequencies are, of course, known with great precision. In the case of a group of lines such as that about 3,650 or 4,339 (see Fig. 3) the shortest wave-length of the group is taken since it alone determines the position of the intercept. The actual potentiometer readings and the corresponding deflections in mm. for all these lines are given in Table I. In the plotting the deflections

TABLE I.

5,461.		4,339.		4,047.		3,650.		3,126.		2,535.	
Volts.	Def'n., mm.	Volts	Def'n., mm.								
2.257	28	1.581	44	1.576	82	1.157	67½	.5812	52	-.0576	68
2.205	14	1.629	20	1.524	55	1.105	36	.5288	29	+.0576	38
2.152	7	1.576	10	1.471	36	1.0525	19	.4765	12	+.1620	26
2.100	3	1.524	4	1.419	24	1.0002	11	.4242	5	+.2670	16½
				1.367	3	.9478	4	.3718	2½	+.3720	8

in mm. were multiplied by such factors as were necessary to give all the curves practically the same maximum ordinate. No corrections of any kind were applied to the readings save in the case of line 2,535 (see section 3, b above).

The result of plotting the intercepts on the potential axis against the frequencies is given in Fig. 6. It will be seen that the first result is to strikingly confirm the conclusion reached successively by Joffé, Hull, Kunz, Hughes, Richardson and Compton and Kadesch as to the correctness of the predicted linear relationship between maximum P.D. and  $v$ , no point missing the line by more than about a hundredth of a volt.

The slope of this line was fixed primarily by a consideration of the five

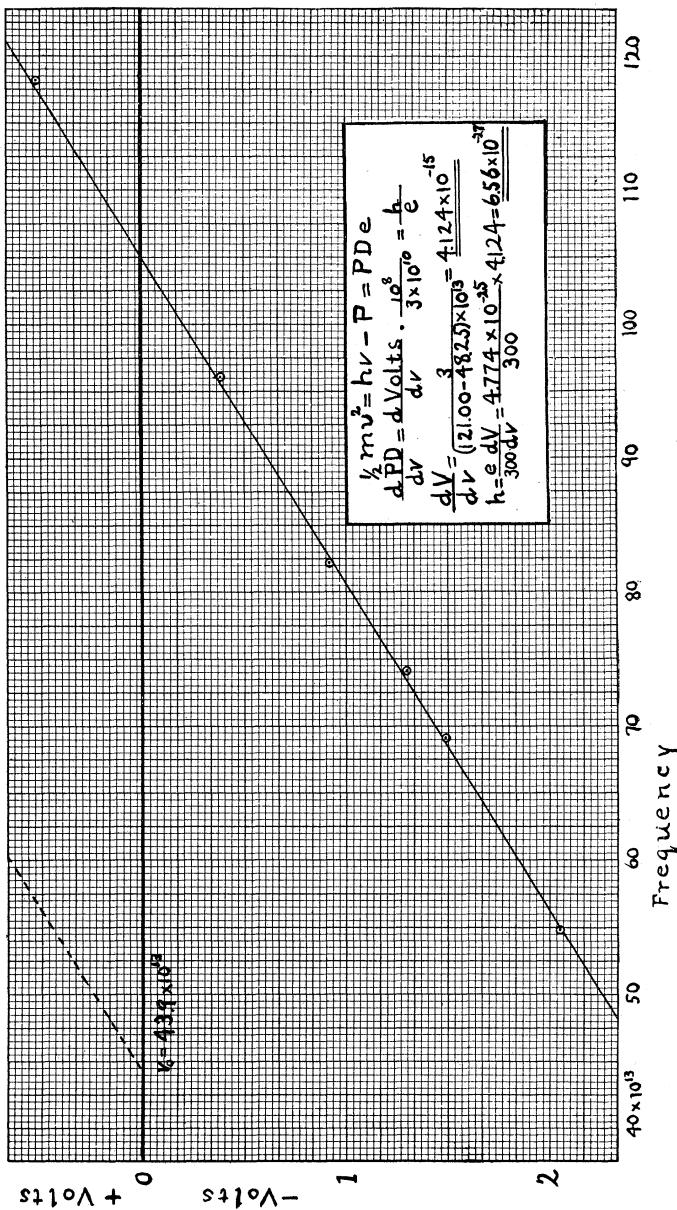


Fig. 6.

points corresponding to lines 5,461, 4,339, 4,047, 3,651 and 3,125, of which the first, the fourth and the fifth are particularly reliable.

Since no potential departs from the line by more than .01 volt and since the range of volts is about 2, it is a conservative estimate to place the maximum uncertainty in the slope at about 1 in 200 or 0.5 per cent. The value of this slope in volt-frequencies is  $4.124 \times 10^{-15}$ . Setting this, when reduced to absolute units, equal to  $h/e$  and inserting my value of  $e$ , namely  $4.774 \times 10^{-10}$ , there results  $h = 6.56 \times 10^{-27}$ .

The measurements thus far reported were all made upon a particular surface several hours after it had been cut, the conditions being exactly the same with all the lines, the only change made throughout the whole series of observations consisting in shifting the incident light from one wave-length to another by the adjustments provided on the Hilger monochromator. Such a shift required but a couple of minutes at the most. The gas pressure within the bulb amounted to as much as a hundredth of a millimeter, for the reason that after considerable experimenting it was found that under these conditions, though the contact E.M.F. varied rapidly and largely immediately after shaving, in an hour or so it reached a constancy which it maintained for several hours. Furthermore, this constant contact E.M.F. was accompanied by very large and fairly constant photocurrents—a condition very essential to accuracy in the determination of photo-potentials. In a high vacuum, though the contact E.M.F. does not change rapidly after shaving, the photocurrents often decay to a third or a fourth of the initial value in half an hour, so that it is impossible to get a complete set of curves like the above.

Having placed beyond a doubt, however, the fact of the linear relation between  $V$  and  $\nu$ , it was possible to determine the slope of the line in the highest attainable vacuum by locating two distant points on it in rapid succession. Wave-length 5,461 was always chosen for one of these points because its great intensity and large wave-length *i. e.*, steep slope, adapt it admirably to an accurate determination of the intercept on the potential axis. This intercept was determined a few minutes after shaving, while the molecular pump was kept running and the McLeod gauge showed a pressure of perhaps a ten millionth of a millimeter, then the intercept of the other chosen line was found as quickly as possible by the method used above, after which the intercept of 5,461 was again taken. If the contact E.M.F. was changing uniformly this change should be eliminated by taking the mean intercept of line 5,461. The results of nine different determinations of slope made in this way on different days and with different wave-lengths to compare with 5,461 are given in Table II.

TABLE II.

Wave-Length Compared with 5,461.	Slope in Volt-Frequencies.
3,126	$4.11 \times 10^{-15}$
3,650	4.14 "
3,126	4.10 "
3,650	4.12 "
3,126	4.24 "
4,047	3.98 "
2,535	4.04 "
3,126	4.24 "
4,047	4.21 "

Mean . . . . .  $4.131 \times 10^{-15}$ 

The estimated uncertainties in these slopes, as set down at the time of taking, range from 1 per cent. to 4 per cent., those corresponding to lines 3,650 and 3,120 being most reliable. I have not, however, attempted to weight the individual observations in taking the mean. This is seen, however, to be in very close agreement with the value found from Fig. 5. We may conclude then that the slope of the volt-frequency line for sodium is the mean of 4.124 and 4.131, namely  $4.128 \times 10^{-15}$  which, with my value of  $e$ , yields

$$h = 6.569 \times 10^{-27} \text{ erg. sec.}$$

The measurements on lithium were made in a new tube and the new receiving Faraday cylinder was found to have a long wave-length limit 150 Å. lower than its predecessor so that the maximum positive potential due to line 2,535 could now be determined with precision. Lithium was found to differ from sodium in that the surface formed by shaving in vacuo remained strongly photo-sensitive for an indefinite period. It was studied without shaving through a period of six months during which time it showed no marked decay. The set of observations in Table III was taken a few days after shaving without filters but with

TABLE III.

4339.		4047.		3650.		3125.		2535.	
Volts.	Def'n., mm.								
-6.00	1,300.0	-6.000	1,950.0	-6.000	6,000.0	-6.000	6,000.0	-6.000	3,500.0
-1.200	10.0	-1.087	21.5	-0.680	19.0	-.077	16.0	+0.736	18.0
-1.153	5.7	-1.027	10.5	-0.628	9.5	.000	6.3	+0.777	10.5
-1.103	2.7	-0.984	6.7	-0.575	5.0	+.058	2.3	+0.814	6.7
-1.058	1.7	-0.941	3.5	-0.539	2.7	+.100	1.1	+0.873	4.0
-1.000	1.1	-0.900	2.5	0.495	1.5	+.151	.5	+3.928	2.0
-.950	0.6	-0.845	1.0	0.437	.6	+.200	.2	+0.969	1.0
-.870	0.5	-0.793	0.5	0.390	.2			+1.019	0.5
		-0.737	0.25					+1.069	0.0
								+6.000	0.0

all the precautions for avoiding stray short-wave-length light which had been used with the sodium. Line 5,461 was entirely above the long-wave-length limit of the lithium, but the other lines gave readings as follows:

It will be seen that the observations were purposely extended down to very minute deflections where the effects of stray short-wave-length light

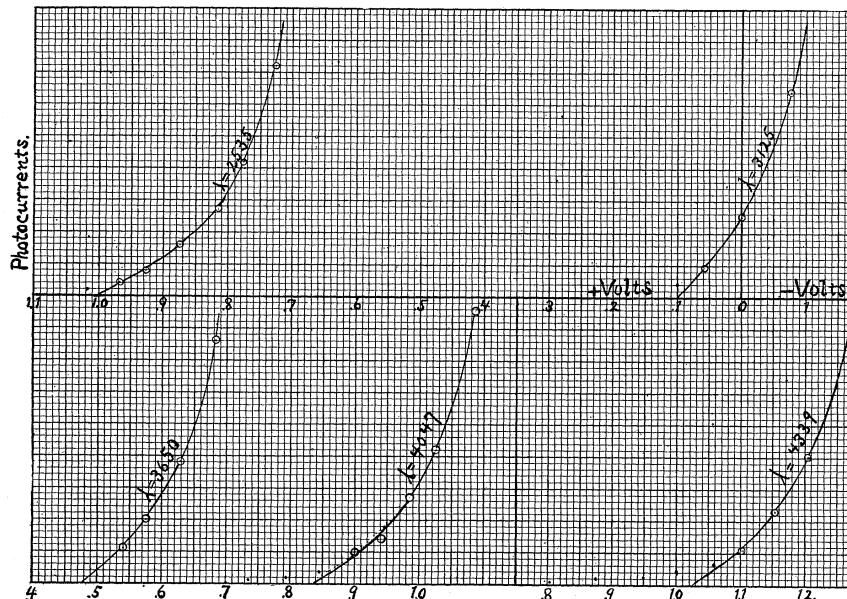


Fig. 7.

are observable, but in drawing the curves it was planned beforehand to ignore all deflections under 3 mm., so as to have the results comparable in every way with those on sodium. In this way the intercepts in Fig. 7 were all determined precisely as they now stand before plotting as in Fig. 8 was tried at all. It will be seen from Fig. 8 that the points so found are in perfect alignment, and that the slope of the line is extraordinarily close to that found with sodium. Several months later, on the then old lithium surface, another set of observations was taken using a new spectrometer. The observations are those shown in Fig. 4. Fig. 9 shows the same observations graphed so as to determine  $h$ . This quantity is seen to come out exceedingly close to the value found several months earlier on the new surface. From the two determinations on lithium we obtain the mean

$$h = 6.584^{-27} \text{ erg. sec.}$$

the uncertainty here being perhaps as much as 1 per cent. In the matter of precision I place the greater reliance on the value  $6.57^{-27}$  obtained from

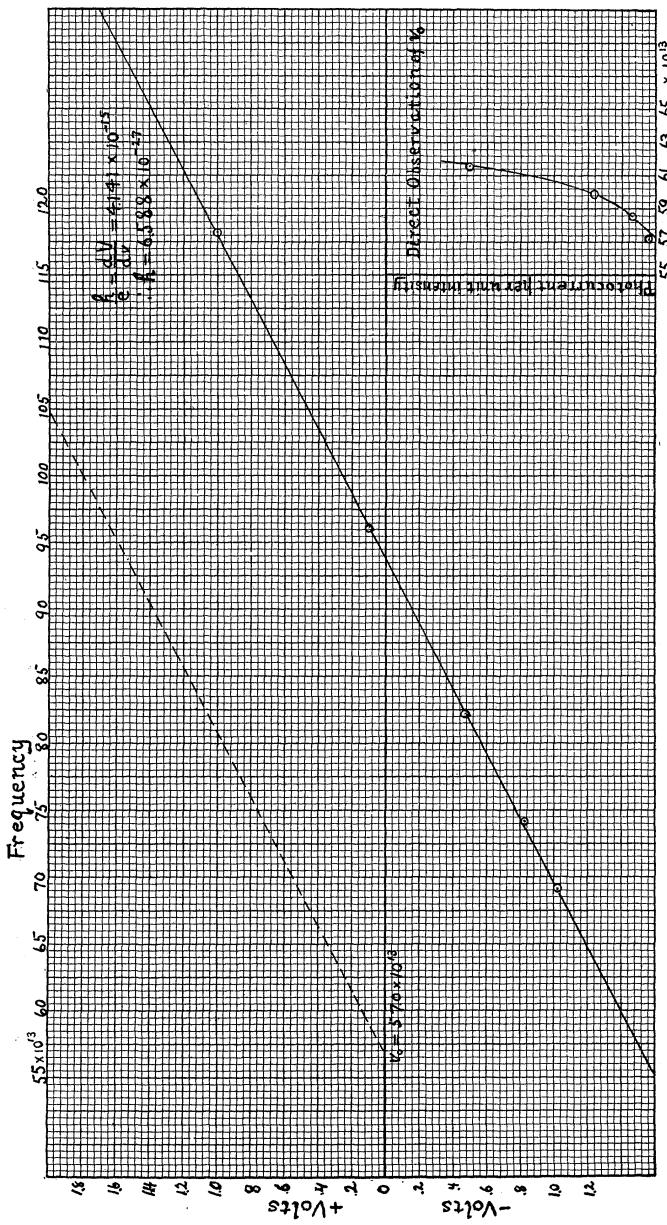


Fig. 8.

the experiments on sodium. If, as estimated above, this is in error by no more than .5 per cent. it is by far the most reliable value of  $h$  which is thus far available. Planck's original value was very close to this, namely  $6.55 \times 10^{-27}$ , but it was obtained from a product  $ab^4$  in which Planck used  $a = 7.061 \times 10^{-15}$  (erg./cm.<sup>3</sup> degree<sup>4</sup>) and  $b = .294$  cm. degrees. In the latest edition of the "Wärmestrahlung," published in 1913, the value taken for  $a$  is  $7.39 \times 10^{-15}$ , while that for  $b$  is 0.289. The

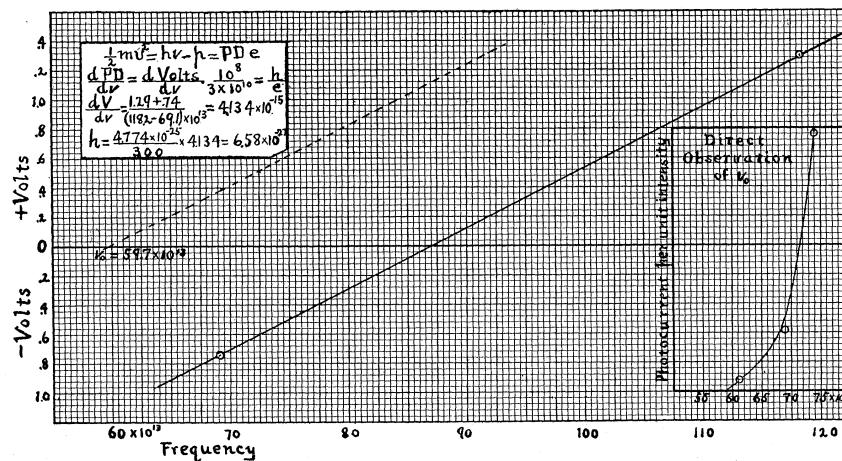


Fig. 9.

original value of  $h$  was obtained, then, from the product of two factors, the first of which Planck has since changed by 4.7 per cent. (the actual uncertainty in it was twice this amount), the second by 1.7 per cent.  $\times 4 = 6.8$  per cent. so that the original value of  $h$  contained at the lowest possible estimate, an uncertainty of  $\sqrt{(4.7)^2 + (6.8)^2} = 8$  per cent. The value of  $h$  at which Planck arrives in the last edition of the Wärmestrahlung is  $6.415 \times 10^{-27}$ , but Westphal whose value of  $a$  Planck used, has now raised his value by 2.35 per cent. while the uncertainty in  $b$  (*i. e.*, in  $c_2$ ) is still at least 0.6 per cent., since this is the difference between the Reichsanstalt value  $c_2 = 1.436$  and Coblenz's value  $c_2 = 1.4456$ . There is still, then, in each of the factors  $ab^4$  an uncertainty of at least 2.5 per cent. and hence an uncertainty in  $h$  of  $\sqrt{(2.5)^2 + (2.5)^2} = 3.5$  per cent.

Planck's equations combined with radiation data are not then as yet able to yield a value of  $h$  which is comparable in accuracy with that obtained from these photoelectric measurements.

If, however, Planck's equation is correct we can determine  $h$  with much precision from my value of  $e$  and recent data on the total radiation constant which is related to the  $a$  of Planck's equation through  $a = 4\sigma/c$ ,  $c$  denoting the velocity of light.

Thus Planck's equation is

$$h = \frac{k^{\frac{1}{3}}}{c} \left( \frac{48\pi\alpha}{a} \right)^{\frac{1}{3}}$$

and if we insert my value of  $k$ ,<sup>1</sup> which has the same precision as  $e$  and the value of  $a$  corresponding to Westphal's latest conclusions as to the value of  $\sigma$ , namely  $5.67 \times 10^{-5}$ , we obtain

$$h = \frac{(1.372 \times 10^{-16})^{\frac{1}{3}}}{2.999 \times 10^{10}} \left( \frac{48 \times 1.0823}{7.56 \times 10^{-15}} \right)^{\frac{1}{3}} = 6.57 \times 10^{-27}$$

The above value of  $\sigma$  Westphal has kindly sent me by letter as the result of new work at the Physical Institute in Berlin. It agrees exactly with Shakespear's value,<sup>2</sup> and Coblenz's recent work on  $\sigma$  seems to indicate that it is not likely to be in error by more than a per cent. If its error is no greater than this, then the above value of  $h$ , which involves  $a^{\frac{1}{3}}$  should be in error by no more than  $\frac{1}{3}$  per cent. This value will be seen to be in exact agreement with the present photoelectric determination which I have estimated as involving an uncertainty of  $\frac{1}{2}$  per cent.

We are now in position to compute with the aid of Planck's equation both of the constants  $\sigma$  and  $c_2$  of black body radiation from my direct measurements on  $e$  and  $h$ .  $\sigma$  is of course seen from the preceding calculation to come out  $5.67 \times 10^{-5}$ , while the value of  $c_2$  is found to be  $1.436$  cm. degrees.<sup>3</sup> This is exactly the Reichsanstalt value found in 1913.<sup>4</sup>

*Planck's "h" appears then to stand out in connection with photo-electric measurements more sharply, more exactly and more certainly than in connection with any other type of measurements thus far made.* The reason it has not appeared with greater certainty before despite the fact that the experiments of Ladenburg, Kunz, Hull, Hughes, Richardson and Compton and Kadesch have all been interpreted in terms of Einstein's theory is found, I think, chiefly in the uncertainty in determining volt-frequency relations when special precautions are not taken to avoid stray short-wave-length light, and when the wave-lengths used are below the long-wave-length limit of the receiving surface, i. e., below about  $\lambda = 2,700$ . Richardson and Compton's work was all done below this limit save in the case of sodium and aluminum and although the values of  $h$  obtained with these substances should have been the most reliable, the sodium gave  $h = 5.2$  or 20 per cent. too low, while the Al gave  $h = 4.3$ , or 35 per cent. low.

<sup>1</sup> PHYS. REV., Vol. II., p. 143, 1913.

<sup>2</sup> Proc. Roy. Soc., 86, 180, 1911.

<sup>3</sup> See PHYS. REV., II., 142, 1913.

<sup>4</sup> Ann. der Phys., 40, 609, 1913.

## 5. THE LONG-WAVE-LENGTH LIMIT OF PHOTOSENSITIVENESS.

The observations corresponding to Figs. 5 and 6 were all taken between one and seven hours after shaving when the gas pressure within the bulb amounted to one or two hundredths of a millimeter. A contact E.M.F.-time curve was then taken under identical conditions, and with the following results. The contact E.M.F. before shaving was 2.819 volts, it fell upon shaving to 2.30 volts. Then rose at a fairly uniform rate for half an hour to 2.520 volts, where it remained so nearly constant for nine hours that an observation made 6 hours after shaving gave a value 2.495 volts, while one made nine hours after shaving gave 2.493 volts. After nine hours the molecular pump was started and the gas all pumped out, whereupon the contact E.M.F. rose at once to 2.820 volts, its initial value. The contact E.M.F., then, during the period of taking the photopotential curve remained constant at a value which was within a hundredth of a volt of 2.51 volts. Accordingly, in order to find the value of the frequency at which, if there were no contact field, the light could just cause an electron to escape from the metal, *i. e.*, in order to find the frequency which causes an electron to leave the surface of the metal with zero velocity it is only necessary to push up the volt frequency line of Fig. 6 by the amount of the contact E.M.F., viz., 2.51 volts, and then to find its intercept on the frequency axis. The dotted line of Fig. 6 shows this line thus displaced. The intercept is seen to be at  $\nu_0 = 43.9 \times 10^{13}$  which corresponds to  $\lambda_0 = 6,800 \text{ \AA}$ . This is far above the long-wave-length limit of sodium as computed by Richardson and Compton who published the two estimates 5,770 and 5,830. Yet it was found by direct measurement that the long-wave-length limit of this sodium was at least in the neighborhood of 6,800. For the yellow lines 5,790 and 5,770 produced together a saturation current which was  $\frac{5}{11}$  of that produced by line 5,461. Indeed the balance potential for these lines was determined and found to lie on the straight line of Fig. 6 within the limits of error of its determination, but the point corresponding to 5,461 was so near to it and could be determined with so much greater accuracy, that no attempt to use the former point in the determination of  $h$  was made and it was not placed on the diagram of Fig. 6. Also the red line 6,235 produced a marked saturation current of value  $\frac{1}{20}$  of that of the yellow group. With the aid of Mr. Wilmer Souder who is making in this laboratory photoelectric-efficiency measurements on these same surfaces, the energies in the lines 5,461, 5,780 and 6,235 were found with a thermopile to be in the ratios 71, 100, 10, respectively. From these data the saturation photocurrents per unit intensity for these three lines are found to have the ratios 140, 50, 25. Plotting these numbers against wave-lengths and

drawing a smooth curve, we can locate the intercept on the wave-length axis that is, the long-wave-length limit, within perhaps 100 Å. The result is shown in Fig. 10. This procedure is probably the simplest way of avoiding the disturbing effects of stray short-wave-length light in determining directly the long-wave-length limit. Evidence will be presented in a later paper to show that this limit is by no means a constant—a fact also emphasized by Pohl and Pringsheim,<sup>1</sup> but the two sorts of measurements upon it herewith reported are made at practically the same time so that their agreement is a real test of the validity of Einstein's equation.

Lithium is better suited to this sort of a test than is sodium for the reason that its long-wave-length limit falls in the middle of the visible spectrum where all the elements necessary to the comparison are most easily and reliably observable. Both Fig. 8 and Fig. 9 show such comparisons, the first on a new lithium surface, and the second on the same surface several months later. It is to be particularly noted that while the measured contact E.M.F. between the lithium and the oxidized copper plate was 1.51 volts in the observations shown in Fig. 8, it was only 1.11 volts at the time the observations shown in Fig. 9 were taken, yet the displacing of the  $V\nu$  line by the amount of this measured contact E.M.F. yields in each case excellent agreement between the  $\nu_0$  determined from the intercept on the  $\nu$  axis and that determined by direct observation (see lower right hand corners of Figs. 8 and 9). I should be unwilling to claim that the direct observations fix the long-wave-length limit with a precision greater than 100 Å. Nevertheless these observations seem to leave no room whatever for doubt that the agreement demanded by Einstein's equation between the two methods of determining  $\nu_0$  actually exists.

#### 6. CONTACT E.M.F. AND LONG-WAVE-LENGTH LIMITS.

I have shown elsewhere<sup>2</sup> that Einstein's equation demands that the contact E.M.F. between any two conductors be given in terms of photoelectrically measured quantities thus

$$\text{Contact E.M.F.} = \frac{h}{e} (\nu_0 - \nu_0') - (V_0 - V_0^1), \quad (2)$$

in which  $\nu_0$  and  $\nu_0'$  are the long-wave-length limits of the two conductors and  $V_0$  and  $V_0^1$  are the maximum potentials which must be externally

<sup>1</sup> Phil. Mag., 26, 1917, 1913.

<sup>2</sup> Phys. Rev., January, 1916.

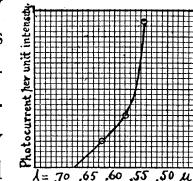


Fig. 10.

applied to just prevent corpuscular discharge by light of any particular wave-length from these two conductors to any third conductor. If the long-wave-length limit of the copper oxide receiving cylinder can be determined this equation can be quite accurately tested by means of the experiments recorded above. The desired measurement on the Faraday cylinder was made with no little precision by utilizing the observation mentioned in section 3b that when the sodium for example was charged to a positive potential of say 6 volts, if the wave-length used was longer than the long-wave-length limit of the cylinder, there was no trace of an apparent positive leak to the cylinder upon illuminating the sodium, but as soon as, with decreasing wave-length, the long-wave-length limit of the cylinder is reached, such a leak will appear because of the liberation of electrons from the walls of the cylinder by the light reflected to them. I have already mentioned that with line 3,125 although it produced with -6 volts on the sodium a current of 17,000 mm. in 30 seconds, when the sodium was given a potential of +6 volts and illuminated there was not a quarter of a millimeter of deflection. Since the greater part of the light incident on the sodium is reflected back to the Faraday cylinder, this shows that line 3,125 is completely and definitely above the long-wave-length limit of the copper oxide. Lines 3,022 and 2,967 and 2,804 are weaker and their indications are accordingly less definite, but no positive leak was obtained with them. But with wave-length 2,652, which with -6 volts give a deflection of 5,300 mm., +6 volts produced a deflection in 30 seconds of 3 mm. and with  $\lambda = 2,535$ , which with -6 volts gave 7,800 mm., +6 volts produced a deflection of 20 mm. The energies of the two lines were found in the ratio 5.3 to 9.1. Plotting then deflections per unit intensity, viz.,  $20/9.1 = 2.2$  and  $3/5.3 = 5.66$  against the corresponding wave-lengths and extending the straight-line connecting these two points to the wave-length axis we find the intercept at  $\lambda = 2,688 \text{ \AA}$ . which may be taken as the long-wave-length the limit of the copper oxide, and in view of the steepness of the curve it is not likely that this point is in error by more than say 30  $\text{\AA}$ . The corresponding  $\nu_0'$  is  $111.6 \times 10^{13}$ . From the relation  $d \text{ volts}/d\nu = 4.128 \times 10^{-15}$  we can compute the maximum energy of emission in volts of corpuscles under the influence of line 2,535 (which corresponds to  $\nu = 118.2 \times 10^{13}$ ) from a surface for which this energy is zero at  $\lambda = 2,688 \text{ \AA}$ . It is

$$4.128 \times 10^{-15}(118.2 - 111.6) \times 10^{13} = .27 \text{ volt.}$$

This is  $V_0^1$ . With line 2,535 Fig. 5 shows that the observed  $V_0$  for sodium was .52 volt, so that  $V_0 - V_0^1 = .52 - .27 = .25$  volt. But  $h/e(\nu_0 - \nu_0') = 4.128 \times 10^{-15}(118.2 - 43.9) \times 10^{13} = 2.79$  volts. The

measured contact E.M.F. at this time was 2.51 volts (see p. 382 and Fig. 6). Hence equation 2 becomes

$$2.51 = 2.79 - .25 = 2.54,$$

which is but about 1 per cent. in error.

Similar computations made with lithium showed equally good agreement. As stated above the Faraday cylinder used with the lithium was a new one and with line 2,535, +6 volts on the lithium failed to reveal any trace of a reverse electronic current. But with line 2,400 Å this reverse current was distinctly and definitely present, although line 2,400 is weak in energy compared with 2,535. Line 2,535 was then in this case very close to the long-wave-length limit. Considering the limit at this line we have  $V_0' = 0$ . But Fig. 8 shows that at that time the contact E.M.F. was 1.52 volts, while  $V_0$  for line 2535 was 1.00 volt and  $\nu_0 = 57 \times 10^{13}$ . Hence  $h/e(\nu_0 - \nu_0') = 4.128 \times 10^{-15} (118.2 - 57.0) \times 10^{13} = 2.526$  volts, and equation (2) becomes

$$1.52 = 2.526 - 1.00 = 1.526.$$

In the measurements taken six months later, although the contact E.M.F. had dropped to 1.11 volts, equation 2 still predicts the observed value. For now (see Fig. 9)  $h/e(\nu_0 - \nu_0') = 4.128 \times 10^{-15} (118.2 - 59.7) \times 10^{13} = 2.415$  volts and  $V_0 = 1.29$  volts, so that equation 2 becomes

$$1.11 = 2.415 - 1.29 = 1.125.$$

Einstein's equation appears then to stand up accurately to all of the five quantitative tests demanded of it on page 356.

#### 9. THEORIES OF PHOTO EMISSION.

Perhaps it is still too early to assert with absolute confidence the general and exact validity of the Einstein equation. Nevertheless, it must be admitted that the present experiments constitute very much better justification for such an assertion than has heretofore been found, and if that equation be of general validity, then it must certainly be regarded as one of the most fundamental and far reaching of the equations of physics; for it must govern the transformation of all short-wave-length electromagnetic energy into heat energy. Yet the semi-corpuscular theory by which Einstein arrived at his equation seems at present to be wholly untenable. I have pointed out elsewhere<sup>1</sup> that this theory was but a very particular form of the ether-string theory advanced by J. J. Thomson<sup>2</sup> two years earlier, for it simply superposed upon that theory the additional hypotheses (1) that the bunches of energy which are as-

<sup>1</sup> Science, Vol. XXXVII., p. 130, 1913.

<sup>2</sup> Electricity and Matter, pp. 62-70.

sumed to travel along the ether strings are proportional to the impressed frequency and (2) that they are transferred upon absorption as wholes to an electron. This being the case, the objections to an ether-string theory, that is, to any theory in which the energy remains localized in space instead of spreading over the entire wave-front, must hold for the Einstein theory. Lorenz<sup>1</sup> and Planck<sup>2</sup> have pointed out some of these. Despite these objections, however, Sir J. J. Thomson<sup>3</sup> and Norman Campbell<sup>4</sup> still adhere to it. I wish to call attention to one more difficulty which in itself seems to me to be very serious.

If a static electrical field has a fibrous structure, as postulated by any form of ether-string theory "each unit of positive electricity being the origin and each unit of negative electricity the termination of a Faraday tube,"<sup>5</sup> then the force acting on one single electron between the plates of an air condenser cannot possibly vary *continuously* with the potential difference between the plates. Now in the oil-drop experiments<sup>6</sup> we actually study the behavior in such an electric field of one single, isolated electron and we find, over the widest limits, exact proportionality between the field strength and the force acting on the electron as measured by the velocity with which the oil drop to which it is attached is dragged through the air.

When we maintain the field constant and vary the charge on the drop, the granular structure of electricity is proved by the discontinuous changes in the velocity, but when we maintain the charge constant and vary the field the lack of discontinuous change in the velocity disproves the contention of a fibrous structure in the field unless the assumption be made that there are an enormous number of ether strings ending in one electron. Such an assumption takes all the virtue out of an ether string theory.

Despite then the apparently complete success of the Einstein equation, the physical theory of which it was designed to be the symbolic expression is found so untenable that Einstein himself, I believe, no longer holds to it. But how else can the equation be obtained?

Before attempting to answer this question, let us consider the energy relations which it imposes. It requires the absorption at some time or other by the escaping electron of at least the energy  $h\nu$  from incident waves of frequency  $\nu$ . The total luminous energy falling per second from

<sup>1</sup> Phys. Zeit., 11349, 1910.

<sup>2</sup> Ann. der. Phys., 39, 1912. Berliner Ber., 723, 1911.

<sup>3</sup> Proc. Phys. Soc. London, XXVII., 105, December 15, 1914.

<sup>4</sup> Modern Electrical Theory, Cambridge Press, 1913, p. 248.

<sup>5</sup> J. J. Thomson's Electricity and Matter, p. 9.

<sup>6</sup> PHYS. REV., 2, 109, 1913.

a standard candle on a square centimeter at a distance of three meters is one erg.<sup>1</sup> Hence the amount falling per second on a body of the size of an atom, *i. e.*, of cross section  $10^{-15}$  cm. is  $10^{-15}$  ergs. But the energy  $h\nu$  for light of wave-length equal to 5,000 Å is  $4 \times 10^{-12}$  ergs or 4,000 times as much. Since not a third of this energy is in wave-lengths shorter than 5,000 Å, a photoelectric cell which is sensitive up to 5,000 Å should require at least 12,000 seconds or 4 hours of illumination by a standard candle 3 meters away before any of its atoms could absorb enough energy to discharge a corpuscle, yet the corpuscle is observed to shoot out the instant the light is turned on. If then we must abandon the Thomson-Einstein hypothesis of localized energy, which is, of course, competent to satisfy these energy relations, *there is no alternative but to assume that the corpuscles which are ejected are already possessed of an energy almost equal to  $h\nu$ .* Since this energy must have come from the incident frequency, for otherwise it could not be proportional to this frequency, it is necessary to assume, if the absorption is due to resonance (and we know of no other way in which to conceive it after eliminating as above the possibility that a single ether pulse drives out a free electron) that there are oscillators of all frequencies within the absorbing body and that these oscillators are at all times in all stages of energy loading up to the value  $h\nu$ . But this is impossible if the oscillators, when not exposed to radiation, emit any energy at all; for if they did so, they would in time lose all their store and we should be able, by keeping bodies in the dark, to put them into a condition in which they should show no photoelectric effect until after at least 4 hours of illumination with a standard candle. Since this is contrary to experiment, we are forced, even when we discard Einstein's theory of localized energy and discontinuous absorption, to postulate electronic absorbers which do not radiate at all while they are absorbing until the absorbed energy has reached a certain critical value when explosive emission occurs. The photoelectric effect then, however it is interpreted, if only it is correctly described by Einstein's equation, furnishes a proof which is quite independent of the facts of black-body radiation of the correctness of the fundamental assumption of the quantum theory, namely, the assumption of a discontinuous or explosive emission of the energy absorbed by the electronic constituents of atoms from ether waves. It materializes, so to speak, the quantity "h" discovered by Planck through the study of black body radiation and gives us a confidence inspired by no other type of phenomenon that the primary physical conception underlying Planck's work corresponds to reality.

But to return to a substitute for Einstein's theory. Planck<sup>2</sup> and Som-

<sup>1</sup> Drude, Lehrbuch der Optik, 1906, p. 472.

<sup>2</sup> Ann. d. Phys., 37, 644, 1912.

merfeld<sup>1</sup> have both made alternative suggestions, neither of which, however, seems competent, in general, to furnish a physical basis for the Einstein equation. Indeed Sommerfeld and Debye<sup>2</sup> definitely admit the inadequacy of their theory to account for the normal photoelectric effect, which is precisely the effect herewith investigated, while Planck's theory as thus far formulated does not yield the Einstein equation at all. Originally it had nothing whatever to say about the escape of corpuscles from atoms under the influence of ether waves, and even in the 1912 formulation<sup>3</sup> the energy of an oscillator was assumed to be given up only in the form of electromagnetic waves, but in 1913<sup>4</sup> the theory was extended so as to permit part of the energy to be emitted in the form of an ejected corpuscle. The oscillator of frequency  $\nu$  was assumed to absorb energy continuously without radiating any of it until its energy content became  $n_1 h\nu$ , in which  $n_1$  is an integer, the value of which on the average depends on the intensity of the incident waves. This energy was then assumed to shoot out explosively, the amount  $\sigma h\nu$ ,  $\sigma$  being a fraction less than one, going off in the form of an ether wave, and the amount  $(n - \sigma)h\nu$  appearing in the form of the kinetic energy of the escaping corpuscle. This energy  $(n - \sigma)h\nu$  was then assumed to be transformed entirely into electromagnetic waves of frequency  $\nu_2$ , when the corpuscle fell into a new oscillator of natural frequency  $\nu_2$ .

Now when we compare this theory with the above experimental results we observe that there is not the slightest indication in the latter that the energy absorbed by an escaping corpuscle from an incident light wave of frequency  $\nu$  is ever more than  $h\nu$ , or that  $\sigma$  has any value at all and yet the setting of  $n_1 = 1$  and  $\sigma = 0$  in the above expression of Planck is not consistent with his way of deducing his black body radiation law.<sup>5</sup>

Further the assumption that all bodies which show the normal photoelectric effect, and there is some evidence that even gases when stimulated by waves of frequency  $\nu$  shoot off corpuscles with energy  $h\nu$ , contain

<sup>1</sup> Phys. Zeit., 12, 1057, 1911, Solvay Congress, 1911.

<sup>2</sup> Ann. d. Phys., 41, 873, 1913.

<sup>3</sup> Sitz. Ber. d. k. Preuss. Akad., 18, 350, 1913.

<sup>4</sup> Ann. d. Phys., 37, 644, 1912.

<sup>5</sup> My experimental results might perhaps be reconciled with Planck's theory if, under the conditions under which I work, his expression  $\frac{1-\eta}{\eta} = \phi I$  (Wärmestrahlung, p. 159) were a quantity very much smaller than unity. As a matter of fact, however, the intensity of illumination  $K$  which I used in these experiments was measured and found, with line 5461, to be about  $10 \frac{\text{erg}}{\text{cm}^2 \text{sec}}$ . Since  $K = I \frac{32\pi^2}{3c}$  (see "Wärmestrahlung," p. 162) and  $\phi = \frac{3c^3}{32\pi^2 h\nu^3}$  we see that  $\phi I = \frac{c^2 K}{h\nu^3}$ . Inserting  $c = 3 \times 10^{10}$ ,  $h = 6 \times 10^{-27}$ ,  $\nu = 6 \times 10^{14}$  we find  $\phi I = 7000$ —a very large quantity instead of a very small one. This seems to make my results irreconcilable with Planck's theory.

sharply tuned oscillators possessing every conceivable natural frequency is a somewhat troublesome one. Certainly both the phenomena of absorption and of emission show that in most substances the great bulk of the oscillators possess natural frequencies of one or two particular values and the characteristic waves which they emit are of these frequencies, the condition for such emission being in general merely that the stimulating frequency be greater than the characteristic frequency.

In spite of these difficulties, however, a modification of Planck's formulation seems to me able to account for all the relations thus far known between corpuscular and ethereal radiations. Most of the oscillators of a given substance may be assumed to have a particular frequency or frequencies characteristic of the substance, but, just as the line spectrum of a gas is always superposed upon a faint continuous spectrum, so a few oscillators of every conceivable frequency may with no little plausibility be assumed to be mixed with the enormously larger number of oscillators which have a frequency or frequencies characteristic of the given substance. This is only making for all substances precisely the assumption which Planck makes with such conspicuous success for black substances. In other words it is assuming that all substances are to a certain degree black. If any particular frequency is incident upon such a substance the oscillators in it which are in tune with the impressed waves may be assumed to absorb the incident waves until the energy content has reached a critical value when an explosion occurs and a corpuscle is shot out with an energy  $h\nu$ . This free corpuscle may then be assumed to fritter away some, and in many cases all, of its energy by impacts with atoms, but if it strikes an oscillator of any frequency  $\nu_2$  while its energy exceeds  $h\nu_2$ , it either stimulates directly new ether waves of frequency  $\nu_2$ , or else it modifies the condition of the atom in such a way that in a subsequent readjustment it emits waves of this frequency. If the substance possesses these particular oscillators  $\nu_2$  in great abundance then these emitted waves are its characteristic X-rays. Whether they are stimulated by the return of a displaced corpuscle or by the act of displacement by a corpuscle of energy greater than  $h\nu_2$  may be left unsettled, though the former view is at present the more attractive.

In the photoelectric effect we study not the stimulation of these characteristic ether waves but the antecedent emission of corpuscles from the atom, this emission appears to take place to some extent at all frequencies of the incident light, though the emitted corpuscle never leaves the metal unless its energy of emission from the atom is greater than  $h\nu_0$ , but it takes place especially copiously when the impressed frequency coincides with a "natural frequency." According to this point of view the selective

photoelectric is simply the normal effect taking place in the neighborhood of an absorption band where oscillators of one particular frequency predominate. This is little more than Planck's theory with the possibility of a corpuscle being emitted from an atom with an energy greater than  $h\nu$  eliminated for the sake of reconciling it with the experimental facts above presented. It is to be hoped that such a theory will soon be shown to be also reconcilable with the facts of black body radiation.

I have to thank Mr. Wilmer H. Souder for able assistance during the latter portion of this investigation.

#### 10. SUMMARY.

1. Einstein's photoelectric equation has been subjected to very searching tests and it appears in every case to predict exactly the observed results.
2. Planck's  $h$  has been photoelectrically determined with a precision of about .5 per cent. and is found to have the value

$$h = 6.57 \times 10^{-27}.$$

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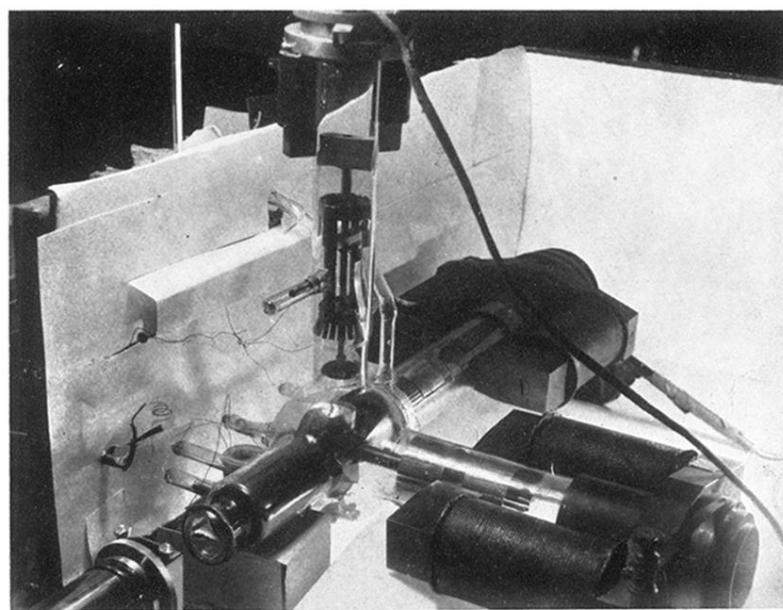


Fig. 1.

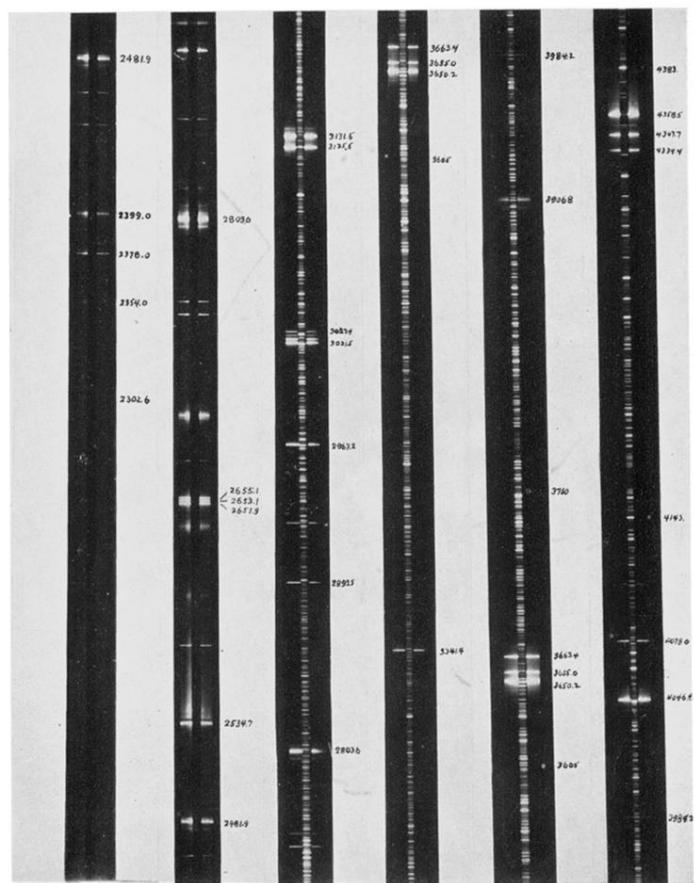


Fig. 3.