EINSTEIN'S PHOTOELECTRIC EQUATION AND CONTACT ELECTROMOTIVE FORCE.

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§ 1. INTRODUCTORY.

EINSTEIN'S photoelectric equation for the maximum energy of emission of a negative electron under the influence of ultra-violet light, namely,

$$\tfrac{1}{2}mv^2 = Ve = h\nu - p \tag{1}$$

cannot in my judgment be looked upon at present as resting upon any sort of a satisfactory theoretical foundation. Its credentials are thus far purely empirical, but it is an equation which, if correct, is certainly destined to play a scarcely less important rôle in the future development of the relations between radiant electromagnetic energy and thermal energy than Maxwell's equations have played in the past.

I have in recent years been subjecting this equation to some searching experimental tests from a variety of viewpoints and have been led to the conclusion that, whatever its origin, it actually represents very accurately the behavior, as to both photoelectric and contact E.M.F. relations, of all the substances with which I have worked. The precision which I have been able to attain in these tests has been due to the following precautions.

1. I have made simultaneous measurements in extreme vacua of photo-currents and contact E.M.F.'s and have thus been able to eliminate the considerable influence which these latter have on photo-potentials.

2. I have worked with surfaces newly formed in extreme vacua and with very large photo-currents of saturation value of the order 20,000 scale divisions in 30 secs. so that I have thus been able to locate the intercept of the photo-current curve on the *PD* axis with much precision.

3. I have used substances which are photo-sensitive practically throughout the whole length of the visible spectrum and have thus been able to use a large range of wave-lengths all of which were above the long wave-length limit of the receiving Faraday cylinder—a matter of no little importance.

4. I have, with the aid of filters, carefully chosen for the principal lines of the mercury spectrum, eliminated from the photo-current-

potential curves corresponding to the longer wave-lengths, the effects of the scattered short wave-length light, which not infrequently falsifies entirely the shape of these curves in the neighborhood of the intercept on the potential axis.

My conclusions, however, reported briefly last year[1] and this[2] are directly at variance with results recently reported in a very notable paper by Ramsauer[3] who finds that there is no definite maximum velocity of emission of corpuscles from metals under the influence of ultra violet light. Before considering, then, any of the theoretical consequences of Einstein's equation it is necessary to first present such evidence as exists for believing that, in spite of Ramsauer's results, there is in fact a definite and accurately determinable maximum velocity of emission for each exciting wave-length.

§ 2. Proof of the Existence of a Maximum Energy of Emission of Photoelectrons and Discussion of Ramsauer's Experiments.

Ramsauer's method is notable in that he makes the first direct measurement by a magnetic deflection, of the velocity of emission of photo-corpuscles. By this method he is able to choose those corpuscles which emerge in one particular direction only, for example, the direction of the normal to the surface, and he finds that these have a certain distribution about a most frequent value. This distribution he finds the same for all wave-lengths of the incident light, for all substances, and for all angles of emission. His source, like Kadesch's, and like my own in much of my former work, is a powerful condensed spark between zinc electrodes. This source I discarded in my most recent tests on Einstein's equation because the mercury arc was found to give greater reliability in the settings and to have greater monochromatism in its lines.

The substances which Ramsauer studies are gold, brass, zinc and carbon. His range of wave-lengths, obtained with a quartz spectrometer, is quite narrow, being the same as that used by Hughes, namely, from 186 $\mu\mu$ to 256 $\mu\mu$ for gold, and 186 $\mu\mu$ to 334 $\mu\mu$ for zinc. As is well known lines of wave-length below 220 $\mu\mu$ pass with great difficulty through a quartz spectrometer. Ramsauer further works quite largely with waves which are shorter than the long wave-length limit of his receiving surface, and in fact his corrections for "falsches licht" (this term actually covers several different effects such as the emission of corpuscles from the illuminated surface itself by stray light, and the emission of corpuscles from the surrounding walls by light reflected to

[1] Phys. Rev., IV., p. 73, '14.
[2] Phys. Rev., VI., p. 55, '15.
[3] Ann. der Phys., 45, p. 1120, 1914. Also 45, p. 961.

them from the illuminated surface) are very large, amounting to as much as 1/10 of the maximum photo-currents. This seems to me to rob the lower parts of his velocity distribution curves of practically all significance. His procedure differs from mine most vitally in that while I measure very precisely, as I think, the maximum velocity of emission he measures instead the most frequent velocity of emission. This was the quantity from which Richardson and Compton[1] drew most of their conclusions and upon which they placed their chief reliance, though their method of obtaining it differed from Ramsauer's.

In his results Ramsauer agrees with Richardson and Compton in finding this most frequent velocity (expressed in energy units) a linear function of the frequency and in finding that the long wave-length limit is given by the intercept of this line on the frequency axis. Question may be raised regarding the certainty with which Richardson and Compton could determine this intercept, since its location involves the contact E.M.F. and they made no contact E.M.F. measurements in vacuo. Ramsauer eliminates contact E.M.F. entirely by surrounding the emitting surface by walls of the same metal as the emitter itself. He agrees with Richardson and Compton[1] also in finding the slopes of the volt-frequency lines differing among themselves by 20 or more per cent. and like Richardson and Compton he finds these slopes all lower than h/e by large per cents., which vary in his case, from 35 to 50 per cent. *None of these results so far are at variance either with my work or with Einstein's equation, for measurements on the most probable velocity of emission are not capable of furnishing a test of Einstein's equation.*

But Ramsauer's results are at variance with mine and with Einstein's equation in that he finds no definite maximum velocity of emission at all for when he plots energies of emission as ordinates and deflecting magnetic field strengths as abscissæ he finds these curves run off asymptotically to the axis of abscissæ. In my judgment this is because the "falsches licht" errors mask entirely the phenomenon under investigation in the region corresponding to the lower parts of his velocity distribution curves. My own experiments seem to me approximately 1,000 times better adapted to the testing of this point than are Ramsauer's, since my maximum currents are about 1,000 times larger than his, as measured in scale divisions of deflection, and if his distribution curve is the correct one, I should obtain very large currents at potentials at which, in fact, I get none at all. Thus in the case of the mercury lines 2535Å, if the potential applied to my lithium surface was .02 volt to the left of the intercept shown in Fig. 1, there was not a trace of deflection in 30 seconds.

[1] Phil. Mag., 24, p. 572, 1912.

But with lines 5461 and 4337 in the case of sodium, and line 4339 in the case of lithium, although I used a Hilgar monochromator and a narrow slit (.01 inch) I did obtain definite indications of deflections due to stray short-wave-length light, *which, however, disappeared entirely as soon as I used filters which cut out all lines of shorter wave-length than that under examination.* Fig. 1 furnishes a very good illustration of this effect. Without a filter the curves corresponding to line 4339 seemed to approach the axis asymptotically, as in Ramsauer's experiments (note the curve marked I.), but with a filter of æsculin in a glass trough which cut out entirely all lines below 4339 including the strong adjacent line 4047, the asymptotic character disappeared completely and the curve shot suddenly into the axis and gave no indications what-
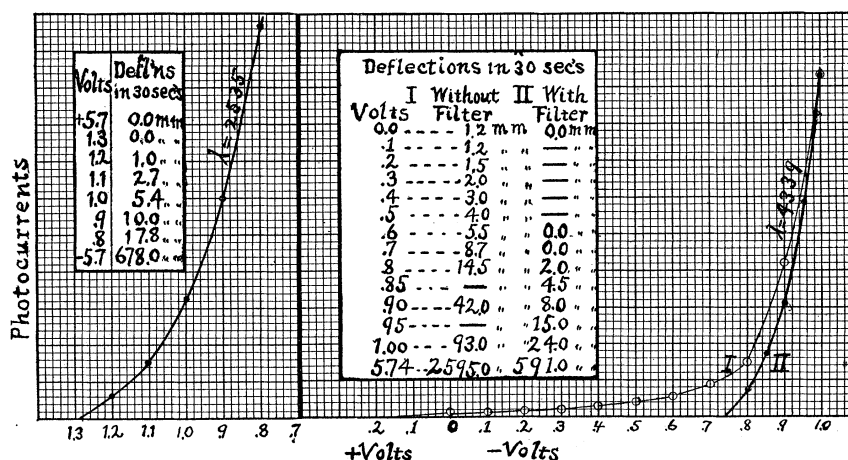

Fig. 1.

ever of deflections either at − .6 or at − .7 with volts (see Fig. 1). The curves shown in the figure and a great many other similar ones which I have taken seem to me to establish beyond question the contention that *there is a definite maximum velocity of emission of corpuscles from a metal under the influence of ultra-violet light,* or, in other words, that the curves due to a particular spectral line do plunge sharply into the potential axis and do not approach it asymptotically.

The work on the photoelectric determination of h will be reported more fully in another paper but the data furnished in Fig. 1 suffices to determine h from lithium with no little precision. Thus, since the frequencies of 2535 and 4339 are 118.2 × 10^{13} and 69.1 × 10^{13} respectively, we see from the intercepts of the figure that the slope

$$\frac{dV}{dv} = \frac{h}{e} = \frac{129 + .74}{(118.2 - 69.1) \times 10^{13}} = 4.13 \times 10^{-15} \frac{\text{Volt}}{\text{Frequency}} ; \quad (2)$$

$$\therefore h = \frac{4.13 - 10^{-15} \times 4.774 \times 10^{-10}}{300} = 6.58 \times 10^{-27} \frac{\text{Erg}}{\text{Frequency}} .$$

The error here can scarcely exceed .02 volt in 2 volts or 1 per cent.

The second conclusion of Ramsauer's which seems at variance with Einstein's equation is that each corpuscle liberated by a given wave-length does not leave the atom with a constant energy but that a given wave-length may liberate corpuscles from a given kind of atom with a large range of energies. But if the p in Einstein's equation is indeed a characteristic constant of the material as he assumed it to be, then the corpuscles are all expelled from the atom with a constant speed and any differences which may be shown by the velocities of the corpuscles which have escaped from the surface of the metal at a given angle are due to differences in the retardations which they have encountered in getting out from different depths beneath the surface. Ramsauer, however, concludes from the fact that he apparently gets the same curve of distribution of velocities for all wave-lengths and for all angles of emission that his observed external distribution of velocities is the same as the "internal distribution," that is that the corpuscles are emitted from the atoms themselves with precisely the same distribution of speeds as that which he measures outside the metal.

Now I am not at all convinced that Ramsauer's results actually do show that the distribution of velocities is the same for different wave-lengths, for the range of wave-lengths (185 $\mu\mu$ to 256 $\mu\mu$ for gold) seems to me too small and the experimental uncertainties too large to permit of such a conclusion. According to his own statement the curve corresponding to 256 $\mu\mu$, is badly falsified by stray short-wave-length light (the maximum deflections obtained with this wave-length were but 17 mm. as against the 20,000 mm. which I have used in my work with sodium). The same is true of all his curves corresponding to the longer wave-lengths. The point in question could be convincingly tested only by using widely different wave-lengths like those corresponding to the lines 2535 and 5461 as I have done in the work with sodium.

Secondly, even if the large experimental uncertainties should be reduced 10 times, and the distribution of velocities for different wave-lengths and different angles then shown to be the same, I should still consider Ramsauer's argument for the identity of the external and internal distribution of velocites to be quite unconvincing. For even though the corpuscles make perfectly elastic impact with the atoms, as Ramsauer

assumes, according to the Maxwell-Boltzmann law their energy of agitation must decrease continually with successive impacts until they are in temperature equilibrium with the atoms. In other words the corpuscles which have made many impacts before emerging in a given direction must have a smaller velocity than those which have made few. And as a matter of fact Ramsauer's observed velocity distribution curve, ignoring the asymptotic portion, is one which differs from all his suggested energy distribution curves in being too steep on the high velocity side just as would be the case if all the corpuscles had started with a common velocity and only those which came from appreciable depths beneath the surface had fallen below this velocity.

Thirdly Ramsauer in identifying the internal and external distribution of velocities appears to me to overlook the fact that the mere phenomenon of a free charge remaining on a charged conductor necessitates the existence of a surface force which prevents its escape. This is the force which Helmholtz conceived of as arising from "the specific attraction of matter for electricity." It is not a force which in any way impedes the free movement of electricity over or through the conductor, else the body would not act like a conductor, and it is with conductors alone that we are here concerned. The force considered is then one which acts on the conduction electrons, that is, on the so-called free electrons as distinguished from those which are permanent constituents of the atoms. Hence, even after an electron has escaped from the interior of an atom it cannot escape from the metal until this force is overcome. It is this force which is responsible for about 999 thousandths of the contact E.M.F. which we measure between metals. The other thousandth, measured by the Peltier effect, has a kinetic, instead of a static, origin. These relations have been the occasion of much confusion among writers on contact effects, though they have been stated with admirable clearness by Kelvin, Helmholtz and others.[1]

I am inclined to think then that neither Ramsauer's of new conclusions, (1) that there is no definite maximum energy of emission and (2) that the external and internal distribution of velocities are the same can, possibly stand. At any rate the correctness of the second has in no way been demonstrated, while the incorrectness of the first seems to me to have been established.

§ 3. The Relation of Contact E.M.F. and Einstein's Equation.

The precise tests which I have reported of Einstein's equation consist in showing (1) that there is a very exact linear relation between the

[1] A remarkably lucid presentation is found in Wüllner's Experimental Physik, Vol. III., pp. 736–755. See also Kelvin, Phil. Mag., 46, p. 82, 1898.

maximum P.D. and the frequency, (2) that the slope of this line yields very accurately Planck's *h*, and (3) that the intercept of this line on the frequency axis is the frequency at which the metal first becomes photo-sensitive.   In order to test this last point it was necessary to displace in the direction of positive potentials the observed P.D.*ν*. line by the exact amount of the measured contact E.M.F.   When this was done the observed long wave-length limit, as directly determined, agreed quite accurately with the intercept (see Fig. 2).   This means that in Einstein's
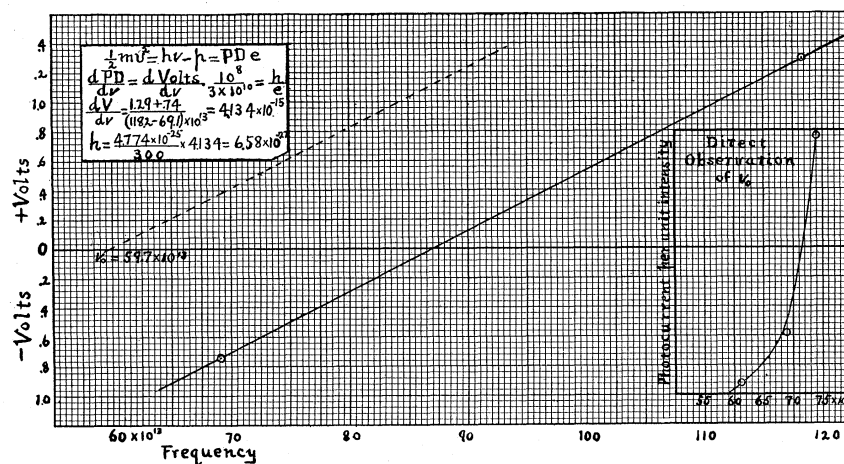

Fig. 2.

equation *p* represents not the amount of work necessary to remove the corpuscle entirely from the influence of the metal, that is, to carry it out beyond the influence of the latter's contact field, but rather the work necessary to just free it from the surface so that a relatively large accelerating field can then remove it, for it is in just this way that we actually make the test.   The quantity *p*, then, is the work necessary to just detach a corpuscle from the surface of the metal and we have, by putting in (1) *v* = 0

$$p = h v_0. \tag{3}$$

Now since both the independence of photo-emission upon temperature, and also the fact that gases show the photo-effect, indicate that the electrons which are ejected by light from metals are not the free electrons of the metal, but rather electrons which are constituents of the atoms, we would naturally consider *p* as made up of two parts, (1) the work p_1 necesary to detach the electron from its parent atom and make it a free electron of the metal, and (2) the work p_2 necessary to detach this free, or conduction, electron from the surface of the metal.

If we consider two opposed metal surfaces, for example one of pure zinc and one of pure copper separated only by the ether, and imagine that they have been put initially into the same electrical condition, so that no electrical field exists between them, then if a wire of copper be run from the copper plate to the zinc plate, we find by experiment that upon making contact an electric field is established between the plates. We say that the P.D. which now exists has arisen because of a contact E.M.F. at the junction of copper and zinc which causes an electrical flow from copper to zinc until equilibrium is set up, and we measure this contact E.M.F. by the observed P.D. which it creates, taken of course with the opposite sign. By definition then the contact E.M.F. is the amount of work which, before any electrical field exists, would be required to transfer one unit of free positive electricity from the zinc over to the copper against the superior attraction of zinc for this unit. After the contact has been made and equilibrium set up, it, of course, requires no work to carry electricity across the zinc-copper junction other than that represented by the Peltier effect, which has another cause and is of an altogether different order of magnitude. Writing then the above definition in symbols we have

$$\text{Contact E.M.F.} = \frac{p_2 - p_2'}{e}. \tag{4}$$

in which p_2 relates to the zinc and p'_2 to the copper.

If, as in the case we are considering, e is negative, then this contact E.M.F. is negative. Now if we write for each of any two opposed metals

$$h\nu_0 = p = (p_1 + p_2)$$

and

$$h\nu_0' = p' = (p_1' + p_2')$$

and subtract we obtain

$$h\nu_0 - h\nu_0' = (p_1 - p_1') + (p_2 - p_2') \tag{5}$$

which in view of (4) becomes

$$\text{Contact E.M.F.} = \frac{h\nu_0 - h\nu_0' - (p_1 - p_1')}{e}, \tag{6}$$

an expression which shows that Einstein's equation does not at all demand that the contact E.M.F., even between two pure metals, be equal to the difference between the frequencies corresponding to long wave-length limits of the two metals multiplied by h/e. If this latter relation is found by experiment to hold for any two metals it is an exceedingly interesting and important fact which, however, has no bearing on the validity or invalidity of Einstein's equation. If this equation is correct such a result would simply mean that $(p_1 - p_1') = 0$ which in

turn might mean that the energy of *escape* of the corpuscle from the atom is always equal to $h\nu$, the absorbed energy being, contrary to the physical theory which guided Einstein, greater than $h\nu$ or it might mean that, though the absorbed energy is but $h\nu$, the works necessary to detach corpuscles from the atoms of the two metals are the same, or that these works are both so small in comparison with the works necessary to detach conduction electrons from metallic surfaces that $(p_1 - p_1')$ is in any case negligible in comparison with $(p_2 - p_2')$.

Now the experimental situation is as follows: Richardson and Compton,[1] although they made their contact E.M.F. and their photoelectric measurements under different conditions, namely the former in air and the latter in vacuo, yet found that for any two metals $h/e(\nu_0 - \nu_0')$ was at least of the same order of magnitude as the contact E.M.F. between these same two metals, and last year I also found that in the case of sodium and copper oxide, while the measured contact P.D. between them was 2.51 volts, h/e times the difference in the frequencies corresponding to the long wave-length limits was 2.79 volts, a result which seemed almost near enough to be in accord with Richardson and Compton's conclusion. Furthermore if Einstein's equation is correct, this conclusion can be tested very accurately without any contact potential measurement at all by a method which has already been tried a number of times, though the results have been quite discordant, and so far as I know the relation of the result to contact E.M.F. has not been clearly pointed out. This relation appears at once as soon as we determine just what are the demands which Einstein's equation imposes on contact E.M.F.

Consider a corpuscle ejected from any conducting surface by light of frequency ν into a Faraday cylinder made for example of a metal more electronegative than the emittor. Then, if the corpuscle is to be brought to rest just as it reaches the wall of the Faraday cylinder, the energy of ejection must just equal the work done against the applied positive potential plus the contact potential and this by Einstein's equation is equal to $h\nu - p$. Thus denoting by V_0 the *observed* maximum positive potential, and by K the contact E.M.F. between the Faraday cylinder and the emittor, and remembering that $p = h\nu_0$ in which, if the emitting surface is inhomogeneous ν_0 is the long wave-length limit of the most electropositive element in the surface, that is, the element which loses negative electrons most easily, we have

$$\tfrac{1}{2}mv^2 = (V_0 + K)e = h\nu - h\nu_0.$$

Writing a similar equation for an electron ejected by light of the same

[1] Phil. Mag., 24, p. 592, 1912.

frequency from the surface of any other conducting material into the same Faraday cylinder we obtain

$$\tfrac{1}{2}mv^2 = (V_0' + K')e = h\nu - h\nu_0'.$$

By subtraction we find since the contact E.M.F. between the two metals used as emittors is $K' - K$.

$$\text{Contact E.M.F.} = \frac{h}{e}(\nu_0 - \nu_0') - (V_0 - V_0'). \tag{7}$$

If then Einstein's equation is correct this should furnish a perfectly general way of measuring contact E.M.F. between any two conducting surfaces, pure or impure, and if it can be experimentally verified, then we have one more proof of the correctness of Einstein's equation. This is the equation which I have been submitting to careful experimental test in the case of the alkali metals, and I have thus far found it in perfect agreement with experiment (see below).

If (7) may be regarded as established by the work which follows, then it will be obvious that we can test whether or not, with any particular metals,

$$\text{Contact E.M.F.} = \frac{h}{e}(\nu_0 - \nu_0') \tag{8}$$

by simply observing whether these metals, when placed before the same Faraday cylinder and stimulated by a given wave-length, show the same value of the observed maximum positive potential, *i. e.*, whether $V_0 - V_0' = 0$.

What I wish to point out then is that, though Einstein's equation does demand that certain relations exist between contact E.M.F.'s and photo-potentials, namely those stated in equation (7) it does not demand the relation (8) suggested by the experimental work of Richardson and Compton, and with about the same sort of roughness, by my results on sodium. If however (7) is a correct and perfectly general relation, as it must be if Einstein's equation is a rigorous one, then (8) can be tested for any particular substances by seeing whether, for these substances, the last term of (7) vanishes. This point was tested carefully in 1906 by Millikan and Winchester[1] who found marked differences in the V_0's for eleven different metals and whose results therefore seem to conflict with (8). It was again tested by Page in 1913[2] who found that with freshly scraped surfaces of copper, aluminum and zinc the V_0's were all alike. Kadesch[3] in 1914 measured accurately the V_0's

[1] Phil. Mag., 14, p. 201, 1907.

[2] Am. Jr. Sci., 36, p. 501, 1913.

[3] Phys. Rev., III., p. 367, May, 1914.

corresponding to freshly cut sodium and potassium in front of the same receiving chamber, and although he did not discuss the question here under consideration, a glance at his curves shows that for a given wavelength these V_0's differ by as much as .85 volt. Last winter I found that the directly measured contact E.M.F. in vacuo between lithium and copper oxide was more than a volt less than the observed value of $h/e(\nu_0 - \nu_0')$ in which ν_0 was the observed long wave-length limit of lithium freshly cut in vacuo and ν_0' the observed long wave-length limit of CuO in the same vessel. (It is to be remembered that e is here negative.) These results appear to show conclusively that (8) does not in general hold, and in a paper presented at the April meeting of the American Physical Society[1] I suggested that the failure of (8) in some cases and its apparent validity in others might be explained by the influence of surface inhomogeneities. For obviously, in measuring $(h/e)(\nu_0 - \nu_0')$ one is always making his long wave-length limit tests on the most photosensitive, $i.\ e.$, the most electropositive constituent of a given surface, while in measuring contact E.M.F.'s one is testing the *mean* effect outside the surface of all the surface constituents, so that in the case of a lithium surface which is discharging electrons into a copper oxide cylinder, if the lithium surface were a mixture of substances, some of which were much more electropositive than others, the measurement of $(h/e)(\nu_0 - \nu_0')$ would correspond, if (8) were correct for homogeneous surfaces, to a determination of the contact E.M.F. of the most electropositive element in the lithium surface. Hence the measured contact E.M.F. would be expected to fall below the value of $(h/e)(\nu_0 - \nu_0')$ as my results showed that it did.

Nevertheless this was not a necessary cause of the failure of (8), for equation (6) shows that there is no reason other than an experimental one for supposing that (8) ever holds. Accordingly, shortly after the above-mentioned meeting, I suggested to Doctors Kadesch and Hennings that they reëxamine the point tested first by Millikan and Winchester and last by Page, using as nearly as possible the latter's experimental conditions in order to find out whether the difference between the two sets of results was due to the fact that we worked in these early experiments with old surfaces while Page had tested newly scraped metals, or whether new surfaces of the ordinary metals do actually show differences in the V_0's which escaped Page's detection, as equation (6) indicates that they might well do. They found that they could use with some modification the apparatus on which Dr. Hennings had worked with contact E.M.F.'s in this laboratory some

[1] PHYS. REV., VI., p. 55, '15.

years previously. Their results are given in papers which follow and seem to support Page's conclusion for the ordinary metals when newly scraped. It is useless, however, to attempt to put any interpretation upon these results until Einstein's equation is shown to be a reliable tool with which to work, that is, until equation (7) is shown to be able to predict accurately and invariably observed contact E.M.F.'s. The following results show that in all the cases thus far examined in which (8) breaks down completely (7) nevertheless yields the most beautiful agreement.

Thus in the experiments reported in April to the Physical Society[1] the measured contact E.M.F. between lithium and copper oxide was found to be 1.52 volts. The long wave-length limit of the lithium was found to correspond accurately to $\nu_0 = 57.0 \times 10^{13}$. This was determined most reliably by displacing the P.D., ν line toward positive potentials by the amount of the measured contact E.M.F. and then taking the intercept of this line on the ν axis. Direct observation checked closely however the value thus obtained. The long wavelength limit of the receiving copper oxide cylinder was directly determined at line 2535 with an uncertainty of perhaps 50 Å. This corresponds to $\nu_0' = 118.2 \times 10^{13}$. These figures give (see equation (2))

$$\frac{h}{e}(\nu_0 - \nu_0') = 4.13 \times 10^{-15}(118.2 - 57.0) \times 10^{13} = 2.53 \text{ volts.}$$

Now line 2535 was just at the long wave-length limit of the copper oxide, so that for this line V_0' between CuO and a Faraday cylinder of CuO was zero. On the other hand, for line 2535 the V_0 between the lithium and the CuO Faraday cylinder was found to be just $+ 1.00$ volts, so that (7) becomes

$$1.52 = 2.53 - 1.00 = 1.53.$$

These measurements were made on a newly cut lithium surface. Several months later the measurements were repeated and the contact E.M.F. between the then old lithium surface and the Faraday cylinder had changed to 1.11 volts. The V_0 between the lithium and cylinder for line 2535 had changed to 1.29 volts (these are the measurements shown in Fig. 1) and the long wave-length limit ν_0 was now measured at 59.7×10^{13}. The ν_0' had not changed. These figures give

$$\frac{h}{e}(\nu_0 - \nu_0') = 4.13 \times 10^{-11}(118.2 - 59.6) \times 10^{13} = 2.42 \text{ volt}$$

and equation (7) now becomes

$$1.11 = 2.42 - 129 = 1.13.$$

[1] PHYS. REV., VI., p. 55, '15.

Although the agreements in both these cases are exceedingly close the uncertainties in the long wave-length limit of the CuO amount to possibly 50 Å. so that $\nu_0 - \nu_0'$ is uncertain by as much as 3 per cent., or possibly a trifle more.

Again, in the case of the sodium I stated above that the results of the measurements gave contact E.M.F. = 2.51 volts, while $h/e(\nu_0 - \nu_0')$ came out 2.79 volts, which looked at first like fair agreement with equation (8), but the agreement is well nigh perfect when the second term of equation (7) is taken into account, for the ν_0' for this Faraday cylinder (it was a different one from that used with the lithium) corresponded to $\lambda_0 = 2685$ Å. instead of $\lambda_0 = 2535$ Å. This gives $\nu_0' = 111.8 \times 10^{13}$. For the sodium ν_0 came out accurately 43.9×10^{13}. From the relation $(d \text{ volts})/d\nu = 4.13 \times 10^{-15}$ we can compute the maximum energy of emission V_0 of corpuscles under the influence of line 2535 from a surface for which this energy is zero at $\lambda = 2685$. It is

$$4.13 \times 10^{-15}(118.2 - 111.8) \times 10^{13} = .26 \text{ volt.}$$

This is V_0'. With line 2535 the observed V_0 for the sodium was .52 volt, so that

$$(V_0 - V_0') = .52 - .26 = .26 \text{ volt.}$$

Then equation (7) becomes

$$2.51 = 2.79 - .26 = 2.53$$

which is but one per cent. in error. All of these results then, are in perfect agreement with the demands of equation (7) although they are definitely opposed to the generality of the conclusion that contact E.M.F. $= h/e(\nu_0 - \nu_0')$, which is identical with the conclusion that the observed photo-potentials of different metals are all the same when light of a given wave-length ejects corpuscles from metals into the same Faraday cylinder. Whether the differences between the alkali metals and ordinary metals in regard to equation (8) are due to surface inhomogeneities, as I stated last April, or that it might be to intrinsic properties of the metals must be determined by further experiments. Some data has already been accumulated, but its presentation will be deferred to another occasion.

Since we are here concerned primarily with the testing of Einstein's equation, the important result already attained and so far as I am aware not hitherto shown is that Einstein's equation *appears to predict accurately and generally the relations between Contact E.M.F.'s and photo-potentials.*

§ 4. Contact E.M.F.'s and Temperature.

There are some interesting relations between Einstein's photoelectric equation and the effect of temperature on contact E.M.F.'s which, so far as I am aware, have not hitherto been pointed out.   In 1906 Millikan and Winchester[1] and Lienhop[2] independently established the lack of dependence upon temperature of the v of equation (1).   Since v is not dependent on temperature it follows from (1) that $p(= hv_0)$ also is not a function of temperature.   It follows then from equation (7), since all the terms on the right were definitely shown in Millikan and Winchester's experiments to be independent of temperature, that contact E.M.F. must also be independent of temperature.

Now W. Schottky[3] has recently made measurements on contact E.M.F.'s at incandescent temperatures and obtained results which are the same, within the rather wide limits of uncertainty, as those commonly obtained at ordinary temperatures, that they are the same as at ordinary temperatures, so that, so far as experiment has now gone, Einstein's photoelectric equation, whatever may be said of its origin, seems to stand up accurately under all of the tests to which it has been subjected.

§ 5. Summary.

The tests of Einstein's photoelectric equation which I have considered and, save in the case of the last, subjected to accurate experimental verification are:

1. The existence of a definite and exactly determinable maximum energy of emission of corpuscles under the influence of a given wavelength.
2. The existence of a linear relationship between photo-potentials and the frequency of the incident light.   (This has not been shown in the present paper.)
3. The exact appearance of Planck's h in the slope of the potential-frequency line.   The photoelectric method is one of the most accurate available methods for fixing this constant.
4. The agreement of the long wave-length limit with the intercept of the P.D., v line, when the latter has been displaced by the amount of the contact E.M.F.
5. Contact E.M.F.'s are accurately given by

$$\frac{h}{e}(v_0 - v_0') - (V_0 - V_0').$$

[1] Phys. Rev., 24, p. 16, and Phil. Mag. (6), 14, 188.

[2] Ann. d. Phys. (4), 21, 284.

[3] Ann. d. Phys., 44, p. 1011, 1914.   Phys. Zeit., 15, p. 624, June 15, 1914.

6. Contact E.M.F.'s are independent of temperature. This last result follows from Einstein's equation taken in conjunction with the experimentally well established fact of the independence of photo-potentials on temperature. If the surface changes in the heating so as to change the photoelectric currents, the contact E.M.F. should change also, otherwise not.

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