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GENERAL CONSIDERATIONS ON THE PHOTO-ELECTRIC EFFECT

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Abstract

It is shown that the equality of the stopping potentials, which is expressed in the equation $V_{AB}=(h/\epsilon)(\nu_{oB}-\nu_{oA})$, is a consequence of the principle of detailed balancing, without any assumption about the mechanism of photo-electric emission. If the relation is not satisfied, the system cannot be in equilibrium, and there must be slow transformations taking place with evolution of energy. Differentiation of the equation above gives a hold on the numerical magnitude of the temperature coefficient of the Volta difference, and also on the magnitude of the surface heat. In potassium the latter must be much larger than the ordinary Peltier heat. In a cavity in any body the equilibrium electron density is the same whether the photo-electric or the thermionic mechanisms act separately or conjointly. This gives certain connections between the photo-electric threshold frequency and thermionic emission. It is shown that the difference between the photo-electric and the thermionic work functions must be a universal constant for all metals, as must also the difference between the specific heat of the metal and a surface charge, and the difference between the entropy of the metal and a surface charge at 0° Abs. Experiment makes it probable that these three universal constants are each zero. Applying this result to thermionic emission, it is probable that the abnormal emission from coated substances involves non-equilibrium conditions. Finally it is suggested that the considerations of this paper enable another significance to be attached to the argument of Lawrence that photoelectric and thermionic emission are identical.

As a result of a series of experiments, both by himself and by others, culminating in 1916, Millikan[1] has drawn the conclusion that the stopping potentials of all pure metals under photo-electric stimulation are the same. The meaning of this is as follows. A metal A is exposed to the action of light of frequency ν, under the stimulation of which it emits electrons toward another metal C. A difference of potential is applied between A and C by a battery of such a magnitude as just to prevent any of the electrons emitted from A from reaching C. The experimental fact now is that the potential which must be applied by the battery to accomplish this is independent of the nature of the metal A, and is the same for all metals, so long as ν and the metal C are unaltered. Assuming the Einstein photo-electric equation, Millikan showed that an equivalent way of expressing the experimental fact is contained in the relation

$$V_{AB}=(h/\epsilon)(\nu_{oB}-\nu_{oA}) \tag{I}$$

where A and B denote any two metals, V_{AB} is their Volta contact difference of potential, and ν_{oA} and ν_{oB} are the characteristic threshold frequencies of the Einstein equation.

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[1] R. A. Millikan, Phys. Rev. **7**, 18, 355 (1916).

Millikan proposed to use the relation (I) as a criterion of the "genuineness" of the contact potential difference. Two metals which satisfy the relation are said to show the "genuine" contact difference, but if they do not satisfy it, as often happens in practise, then Millikan calls the difference "spurious," and ascribes it to the action of some sort of surface layer. Millikan further drew certain conclusions about the nature of the mechanism from the relation (I).

In the report of the fourth Solvay Conference at Brussels in 1924,[2] just published, Lorentz comments on the relation of Millikan, and shows that if it can be assumed that two constants in his own analysis, which are closely connected with the coefficient in the thermionic emission equation of Richardson, are the same for all metals, then the results of Millikan follow from certain very simple assumptions about the mechanism. In the discussion, Lindemann[3] suggested, and Lorentz later gave a proof,[4] that the two constants would be expected to be the same for all pure metals, since they are intimately connected with the chemical constants of Nernst, and their equality follows from the third law of thermodynamics.

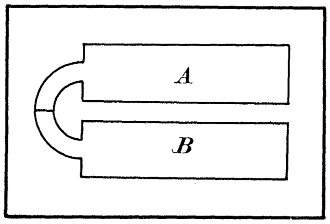

Fig. 1

More recently, Professor Hall[5] has shown that the result of Millikan can be deduced from the detailed picture of the mechanism which his theory of conduction presents.

It is the purpose of the first part of this paper to show that the equality of the stopping potentials follows from certain very general considerations, not involving any assumptions as to mechanistic details, or even the third law of thermodynamics. It follows that any consistent picture of the mechanism must give this relation, and that conversely, conclusions can not be drawn as to the correctness of a mechanism because it gives the relation.

In the deduction I shall assume the so-called principle of detailed balancing; this principle will be discussed in greater detail in a following note. The application which we shall make of it is suggested by Fig. 1. Two metals, A and B, metallically connected, confront each other in an evacuated enclosure at temperature τ. The system comes to equilibrium.

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[2] H. A. Lorentz, Conductibilité des Métaux et Problèmes Connexes. Rapport et Discussions du quatrième Conseil de Physique tenu à Bruxelles du 24 au 29 Avril 1924 sous les Auspices de l'Institut International de Physique Solvay, Gauthier–Villars, Paris, 1927, page 33.

[3] F. A. Lindemann, Fourth Solvay Report, page 64.

[4] H. A. Lorentz, Fourth Solvay Report, page 64.

[5] E. H. Hall, Proc. Nat. Acad. Sci. **11,** 111 (1925).

We assume in the first place that the photoelectric processes taking place in the system are in equilibrium for every frequency by themselves. This assumption is equivalent to one already made by Einstein.[6] The justification here is to be found in the fact that light of a definite frequency produces electrons of only a single energy. Conversely, electrons of this energy impinging on the metal give, when absorbed, light of only this frequency. Actually, of course, light of a definite frequency gradually diffuses into other frequencies, and electrons of definite energy acquire by collision other energies, but these are secondary effects, and by choosing the conditions properly, may be made to take place with arbitrary slowness. This means that a system containing light of a single frequency is in unstable equilibrium, but in equilibrium nevertheless. We now fill the cavity between A and B with light of frequency ν to such an intensity as entirely to mask the background of black radiation, and consider the equilibrium conditions for this frequency alone.

We suppose for the sake of argument that the threshold frequency ν_{oB} of B is greater than that of A, ν_{oA}, and consider equilibrium under light of the particular frequency ν_{oB}. Under this stimulation, photo-electrons are ejected from A with a definite energy, but none from B. In the space between A and B there is a retarding force due to the Volta potential difference between A and B. This Volta difference must be such that it exactly reduces to zero the velocity of the electrons emitted from A when they have completely traversed the space between A and B. For if they arrived at B with a finite velocity, charge would accumulate on B, and equilibrium would have to be maintained by the continual passage of electrons back to A through the metallic connection. If the electrons do not reach B, then by using light of slightly higher frequency, electrons may be emitted from B, which now reach A, whereas none reach B, and the return circuit must be completed from A to B through the metal. Either of these possibilities demands that equilibrium be maintained by a circulating process, which is contrary to the principle of detailed balancing.

The energy of the electrons emitted from A which can just reach B is ϵV_{AB}. But by Einstein's photoelectric equation, the energy of the electrons emitted from A under light of frequency ν_{oB} is $h(\nu_{oB}-\nu_{oA})$, which gives, on equating the two expressions,

$$V_{AB}=(h/\epsilon)(\nu_{oB}-\nu_{oA}),$$

or exactly the equation of Millikan, expressing the equality of stopping potentials.

There seems no escape from this conclusion, provided the system is truly in equilibrium. Therefore, if the relation is not satisfied, or if in other words there are "spurious" contact forces, the system cannot be in equilibrium, and there must be non-thermal energy transformations taking place not contemplated in the analysis above. It is natural to look for such in chemical

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[6] A. Einstein, Ann. d. Physik **37**, 832 (1912).

changes in the surface films; this seems consistent with the experimental evidence.

The fact that it is possible to deduce the relation (I) by a thermodynamic, non-mechanistic, method, would seem to justify us in applying the relation to other phenomena with considerably greater confidence than has been possible hitherto. We may, for example, obtain an expression for the temperature derivative by differentiating Eq. (I) with respect to the temperature, obtaining

$$\frac{dV_{AB}}{d\tau}=\frac{h}{\epsilon}\left(\frac{d\nu_{oB}}{d\tau}-\frac{d\nu_{oA}}{d\tau}\right).$$

The temperature coefficient of the Volta effect is notoriously difficult to measure, and there are no satisfactory values for it. There have, however, been a number of determinations of the effect of temperature on photoelectric emission. This effect is known to be small, in fact for common metals the statement is usually made that there is no dependence on temperature. From this we may conclude that the change with temperature of the Volta effect of common metals is certainly small. It is difficult to find in the literature data from which an estimate may be made of just how small numerically the effect probably is. It has been found by Ives[7] that the alkali metals, however, do show a pronounced temperature effect. He found that between room temperature and liquid air the work function of potassium ($=h\nu_0$) probably changes by 0.2 volts. If we assume that under ordinary temperatures the work function is of the order of 5 volts, this means a relative temperature coefficient of the Volta effect of potassium against a neutral metal of 10^{-4} per degree, or an absolute temperature coefficient of 3.3×10^{-6} Abs. C. G. S. units per degree.

This estimate of the value of $dV/d\tau$ enables us to consider again the question of the surface heat, discussed in a former paper.[8] We have the relation $\tau(dV)/(d\tau)=P'$, or

$$P_{AB}'=\tau\frac{h}{\epsilon}\left(\frac{d\nu_{oB}}{d\tau}-\frac{d\nu_{oA}}{d\tau}\right).$$

P_{AB}' here includes both the ordinary Peltier heat and the surface heats. The considerations above show that at 300°K P_{AB}' is of the order of 10^{-3} Abs. C. G. S. Now the ordinary Peltier heat between potassium and platinum is of the order of 10^{-5} Abs. C. G. S. Hence the surface heat in potassium is so much larger than the ordinary Peltier heat as to be of a different order of magnitude. In common metals the temperature variation of ν_0 is less than in potassium, and therefore the surface heat is a smaller multiple of the ordinary Peltier heat.

We can now carry our analysis of the situation further by returning to consideration of the black body state of equilibrium. For the purpose of our

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[7] H. E. Ives, Jour. Opt. Soc. Amer. and Rev. Sci. Instr. **8,** 551 (1924).

[8] P. W. Bridgman, Phys. Rev. **14,** 306 (1919).

immediate argument consider only a single body A with a cavity in it. At any definite temperature the cavity is filled with the corresponding black body radiation, and also with an electron vapor of definite density. We assume, for the present at least, that the electron vapor is produced by two different mechanisms, the photoelectric and the thermionic mechanisms. The ordinary thermodynamic argument is applicable to such a system, and in particular Clapeyron's equation, giving the change of pressure of the electron vapor with temperature, $d\tau/dp = \tau\Delta v/\eta$, is valid. As always, thermodynamics has no concern with mechanisms, and does not recognize the existence of two different methods by which the electron vapor may be produced. The η of Clapeyron's equation is the heat which must be absorbed by the system, comprising body, cavity, and vapor, to maintain it isothermal when one electron evaporates, leaving behind on the surface of the body a positive charge, and contains mingled together the contributions made by the two mechanisms. We cannot disentangle, or even give separate meaning to, the two mechanisms by experiments made under equilibrium conditions. This has an immediate application to the usual thermionic analysis. The η of our equation is exactly the η which appears in the formula for thermionic emission obtained, for example, by Richardson from a thermodynamic argument involving equilibrium conditions, and therefore contains contributions made by the photoelectric as well as by the thermionic mechanisms. The fact that so close a connection is found experimentally between this η and the heat directly measured in purely thermionic experiments under non-equilibrium conditions leads to the suspicion that the photoelectric contribution to η is not large.

To give meaning to the two mechanisms we must set up definitions obtained from experiments made under non-equilibrium conditions. We may do this in some such way as follows. Imagine a body of definite temperature in empty space, the infinitely distant boundaries of the space being at 0°K, so that the radiational field in the space is uni-directional, all the radiation traveling from the body to the confines of the space. (Of course the body strictly does not have a definite temperature under such conditions, but this state of affairs may in practice be realized very closely.) Under these conditions there is a certain emission of electrons from the body which is a definite function of its temperature, and this emission is accompanied by a certain cooling of the body, so that heat has to be continually supplied from outside to maintain it isothermal. This emission is what is usually meant by thermionic emission. Now expose this body to a beam of parallel light of definite intensity and frequency. It will be found that there is an additional emission of electrons, and this additional emission we define as the photoelectric emission for the given frequency and intensity at the given temperature. We believe that when there is such photoelectric emission the energy of the reflected beam of light is less than that of the impinging beam, or in other words that the energy of the photo-electrons is abstracted from the energy of the incident light, although I believe that this has not been tested by direct experiment. Suppose now that we have found how the photoelectric emission varies with intensity, frequency, and temperature. We recognize that any body not at 0°K contains an internal radiation field, and that therefore there is a continual liberation of photo-electrons in its interior. Some of these are absorbed before reaching the surface, but a certain number will emerge. We may subtract this number from what we above called the thermionic emission, and call the difference the "corrected" thermionic emission.

Assuming now that we can satisfactorily give meaning to the two different mechanisms, let us draw what conclusions we can about the relations between them by a thermodynamic argument. It is in the first place evident that the latent heat of evaporation η, which enters Clapeyron's equation, is the same whether the electron has been evaporated by a photoelectric or a thermionic mechanism. The reason is that the initial and the final states of the system are the same, independent of the details of the evaporation. If evaporation is by photoelectric emission, the immediate source of the energy of the electron is the radiation field, but the radiation field must absorb energy from the body to restore itself to its equilibrium intensity, so that the total heat absorbed by the system from outside to maintain itself isothermal during the evaporation process is independent of the details. Since η is the same, independent of the mechanism, the difference of the thermodynamic potentials of the solid and the vapor is also independent of the mechanism, and therefore the equilibrium conditions are also independent. This means that the same electron gas pressure is maintained at a definite temperature, whether we totally suppress one or the other of the mechanisms, or allow them to act conjointly in any ratio.

Let us now follow the consequences of assuming that the photoelectric mechanism alone functions. We return to our original system of two metals A and B in metallic connection, Fig. 1, which confront each other in temperature equilibrium. At the surfaces of A and B there are electron vapors of definite pressures depending only on the temperature and the properties of the metal. The pressure gradient in the vapor between A and B is maintained by the Volta difference of potential in a way well understood from thermionic analysis. Now here, just as above in our argument about stopping potentials, we may isolate those processes connected with any definite frequency, and apply the conditions of equilibrium to them alone. This is possible because of Einstein's photoelectric equation. Such an isolation is, however, possible under somewhat more general conditions. It is easy to see that these more general conditions demand in the first place that all the electrons which leave the surface under the stimulation of light of a definite frequency leave with a single definite energy (call this energy $E(\nu,A)$), and secondly, that the difference between the energy of electrons leaving A and B under the same frequency must just equal the work done against the Volta difference of potential when an electron moves from the surface of A to that of B. This last condition gives the equation $E(\nu,A)=E(\nu,B)+\epsilon V_{BA}$. If we give to $E(\nu,A)$ the Einstein value, we obtain at once the equation already found expressing the equality of the stopping potentials.

Apply again to this system the principle of complete equilibrium. There can be no circulation of electrons through the metal, which means that the number of electrons which approach the surface of A from the vapor must equal the number which leave A.

In order to avoid the complications arising from the fact that the electrons of a given energy may leave the surface in all directions, we simplify the problem by assuming that in the vapor the electrons move only along one or another of the three coordinate axes, one taken perpendicular, and the other two parallel to the surface. This can have no effect on the final result except to change an unimportant numerical factor.

Assume for the present that the light of frequency ν is of unit intensity, and of frequency greater than ν_{oA} and ν_{oB}. Denote by $f_A(\nu,\tau)$ the number of electrons per unit area leaving the surface of A perpendicularly in unit time under the direct stimulation of this light. This emission is accompanied by absorption of light. The radiation balance is maintained by the absorption of an equal number of electrons approaching the surface, with emission of an equal amount of radiation. If we call $\alpha_A(\nu,\tau)$ the fraction of the impinging electrons which are thus absorbed, it is evident that the number of electrons which approach the surface must be $f_A(\nu,\tau)/\alpha_A(\nu,\tau)$. Abbreviate this as $F_A(\nu,\tau)$. In the equilibrium condition, this must also equal the total number which leave the surface, including in this count the number emitted by radiation and the number reflected. Now if the frequency ν is greater than ν_{oB} as well as greater than ν_{oA}, all the electrons leaving A travel completely across the intervening space and impinge on B, and similarly all the electrons leaving B impinge on A. By a repetition of the argument above, the number of electrons leaving B is $F_B(\nu,\tau)$. Hence the condition of equilibrium, since there can be no return circulation of electrons through the metal, is:

$$F_A(\nu,\tau)=F_B(\nu,\tau).$$

In other words, $F_A(\nu,\tau)$ must be independent of the nature of the substance A when $\nu>\nu_{oA}$. F is not defined if $\nu<\nu_{oA}$. We may take as a characteristic parameter of the substance ν_{oA}. Hence $F_A(\nu,\tau)$ becomes $F(\nu,\nu_0,\tau)$, and this must be independent of ν_0 when $\nu>\nu_0$. This may be exhibited graphically, as shown in Fig. 2. At any constant temperature $F(\nu,\nu_0,\tau)$ is defined only

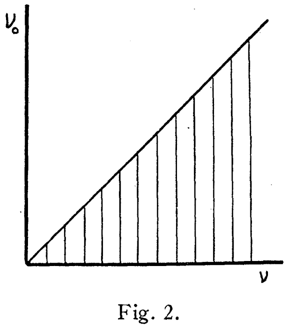

Fig. 2.

above the shaded part of the $\nu-\nu_0$ plane, and over this part of the plane the F surface is a ruled surface, with rulings parallel to the ν_0 axis.

We may now obtain another condition limiting the function F from the fact that the equilibrium electron density under photoelectric stimulation alone is equal to the equilibrium density of the ordinary thermionic analysis.

Consider the total electron vapor. If we suppose that the motion of the electrons is restricted to the three coordinate axes, and that along each axis there is Maxwell's distribution of velocities, then the number of electrons per unit volume in the velocity range dv is

$$dn_v=\frac{n}{3}\left(\frac{m}{2\pi k\tau}\right)^{1/2}e^{-mv^2/2k\tau}dv,$$

where n is the total number per unit volume, and the number striking unit surface in unit time is

$$dN_v=\frac{1}{2}v\,dn_v=\frac{n}{6}\left(\frac{m}{2\pi k\tau}\right)^{1/2}e^{-mv^2/2k\tau}v\,dv.$$

Thermionic analysis gives various possible ways of expressing n. I shall base my argument here on a form which I have developed in a recent paper,[9] namely:

$$n=\frac{(2\pi mk\tau)^{3/2}}{h^3}\exp\left[-\frac{\eta_0}{k\tau}-\frac{1}{k\tau}\int_0^\tau(C_{p\rho}-C_{pm})d\tau+\frac{1}{k}\int_0^\tau\frac{C_{p\rho}-C_{pm}}{\tau}d\tau\right].$$

Here η_0 is the latent heat of vaporization (at constant surface charge) at 0°K, and $C_{p\rho}-C_{pm}$ is the difference of specific heat between the charged and the uncharged metal. It was assumed in the deduction that the entropy of the electron vapor is given by the Sackur-Tetrode expression, and also that the difference of entropy between the surface charge and the uncharged metal vanishes at 0° K. (third law). If this last condition is not satisfied, so that the difference of entropy between metal and surface charge has a value $(S_\rho-S_m)_0$ different from zero at 0°K, then the above expression for n is to be multiplied by the constant term $\exp[(S_\rho-S_m)_o]$. In the following I shall use this more general form.

Further, we may connect the above expression for dN_v with Einstein's photoelectric equation, obtaining the relations:

$$mv^2/2=h(\nu-\nu_0),\quad v\,dv=h\,d\nu/m.$$

Now the number of electrons dN_v is also the number which are in photoelectric equilibrium under the stimulation of light of frequency ν and intensity $I(\nu)d\nu$, where $I(\nu)$ is the distribution function for black radiation of the temperature τ. Assuming that the density of the vapor in photoelectric equilibrium is proportional to the intensity of the light, we have:

$$dN_v=F(\nu,\nu_0,\tau)I(\nu)d\nu.$$

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[9] P. W. Bridgman, Phys. Rev. **27,** 173 (1926).

But

$$I(\nu)=\frac{8\pi}{c^3}\,\frac{h\nu^3}{e^{h\nu/k\tau}-1}\,.$$

Substituting the various values gives:

$$F(\nu,\nu_0,\tau)=\frac{\dfrac{n}{6}\left(\dfrac{m}{2\pi k\tau}\right)^{1/2}\dfrac{h}{m}e^{-h(\nu-\nu_0)/\kappa\tau}}{\dfrac{8\pi}{c^3}\,\dfrac{h\nu^3}{e^{h\nu/k\tau}-1}}\,.$$

The condition which we previously found was that F should be a universal function of ν and τ, independent of ν_0. Since n does not involve ν, the above expression for F can be consistent with this condition only through the condition that $ne^{\,h\nu_0/k\tau}$ must not involve ν_0. Substituting the value of n above gives

$$ne^{h\nu_0/k\tau}=\left(\frac{2\pi k\tau}{h^2}\right)^{3/2}\exp\left[(S_p-S_m)_0+\frac{h\nu_0-\eta_0}{k\tau}\right.$$
$$\left.-\frac{1}{k\tau}\int_0^\tau (C_{pp}-C_{pm})d\tau+\frac{1}{k}\int_0^\tau\frac{C_{pp}-C_{pm}}{\tau}d\tau\right],$$

which must be independent of the metal (or of ν_0). Since the coefficient on the right hand side does not involve ν_0, the condition demands that the exponent be independent of ν_0. Abbreviate $C_{pp}-C_{pm}$ by $\theta(\nu_0,\tau)$. The condition demands that

$$(S_p-S_m)_0+\frac{h\nu_0-\eta_0}{k\tau}-\frac{1}{k\tau}\int_0^\tau\theta(\nu_0,\tau)d\tau+\frac{1}{k}\int_0^\tau\frac{\theta(\nu_0,\tau)}{\tau}d\tau$$

be independent of ν_0. Differentiate this expression partially with respect to ν_0, denoting the derivative by a prime, obtaining

$$(S_p-S_m)_0'+\frac{h-\eta_0'}{k\tau}-\frac{1}{k\tau}\int_0^\tau\theta'(\nu_0,\tau)d\tau+\frac{1}{k}\int_0^\tau\frac{\theta'(\nu_0,\tau)}{\tau}d\tau=0.$$

Differentiate this expression partially with respect to τ, obtaining

$$\int_0^\tau\theta'(\nu_0,\tau)d\tau=h-\eta_0'.$$

Differentiate again by τ, obtaining

$$\theta'(\nu_0,\tau)=0.$$

Whence, $\theta(\nu_0,\tau)$ is equal to a universal function of τ, or $C_{pp}-C_{pm}$ must be independent of the metal. Putting this value back gives the condition:

$$h-\eta_0'=0,$$

or $\eta_0-h\nu_0=$ a universal constant.

Similarly $(S_p - S_m)_0 =$ a universal constant.

These three conditions give important information. The condition $\eta_0 - h\nu_0 =$ universal constant, shows that the so-called thermionic and photoelectric work functions differ for all metals by the same constant. It has often been suspected that these two work functions are the same, but only on the basis of specific pictures of the mechanism, such, for example, as assuming that both the photoelectric and the thermionic electrons have their origin in the conduction electrons in the metal, and these assumptions are questionable. The conclusion above is free from assumptions about the mechanism, and is correspondingly more satisfactory. We may further strongly suspect that the universally constant difference between η_0 and $h\nu_0$ is equal to zero, since we have no other evidence of the existence of a universal constant of these dimensions. Experimentally, if the value of the constant can be found for a single metal it is thereby found for all. Recent work by Warner[10] makes it very probable that these two functions are the same for tungsten, and therefore that the universal constant is equal to zero.

With regard to the other two conditions, I have shown in my previous paper that if the thermionic emission formula $I = A\tau^2 e^{-b_0/\tau}$ holds, where A is a universal constant $(=2\pi(k^2 m\epsilon)/h^3)$, then $C_{pp} - C_{pm}$ and $(S_p - S_m)_0$ must both vanish. But now the formula has been shown experimentally to apply with much precision to the case of tungsten, so that for this metal $C_{pp} - C_{pm}$ and $(S_p - S_m)_0$ must both be zero, and hence in general they must also equal zero.

These conclusions, reached by an examination of the photoelectric effect, have a most important bearing on the conclusions of my previous thermionic paper. Experimentally, there are many substances (in general coated, not pure, substances) for which A of the thermionic emission formula is enormously different from the universal value above. I suggested in the former paper that this might be explained by the non-vanishing of $C_{pp} - C_{pm}$ or of $(S_p - S_m)_0$. But the new argument of this paper eliminates this as a possibility. Hence we must seek in other directions for the explanation of abnormal values of A. One possibility is that the Sackur-Tetrode expression does not apply to the electron vapor under these conditions, or that the interaction between the parts of the system is so strong that the entropy of the whole is not the sum of the entropies of the parts. This does not seem a very likely explanation, particularly at low temperatures. It seems to me much more probable that an abnormal value of A indicates that the system cannot be in equilibrium, and that therefore thermodynamics cannot be applied to it, just as we saw that failure of the equality of the stopping potentials means that the system is not in equilibrium, and there are other than thermal sources of energy. Such a state of affairs does not seem intrinsically improbable in the coated metals which show the abnormal A.

The value found above for F may be analyzed into its components $f(\nu,\tau)$ and $\alpha(\nu,\tau)$ by ordinary photoelectric experiments under non-equilibrium

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[10] A. H. Warner, Proc. Nat. Acad. Sci. **13**, 56 (1927).

conditions. I shall not attempt to pursue this aspect of the subject further here.

Finally, the analysis of this paper has a bearing on a recent paper by Lawrence[11] who offers a proof that what is ordinarily called thermionic emission is entirely photoelectric in character, or that what I have called the "corrected" thermionic emission is zero. This conclusion is much at variance with conclusions reached on experimental grounds by Richardson,[12] who states that the photoelectric emission is 5000 times too small in the most favorable case to account for observed thermionic currents, and also by Ives,[13] who finds the photoelectric effect much too small. Now an examination of the details of Lawrence's argument will show that many of his steps follow equally well from the principle laid down here, namely that in equilibrium the electron vapor has the same density, whether produced by a purely photoelectric or by a thermionic mechanism. A consequence of this principle is that the electrons which enter the vapor state from the solid metal under photoelectric stimulation must have the Maxwell distribution of velocities. For in the vapor alone there is a mechanism which maintains the Maxwell distribution, as shown by ordinary kinetic theory, so that if the entering electrons did not also have this distribution, the resultant distribution would be disturbed. An argument on this basis will exactly reproduce the early equations of Lawrence's paper, including his expression $(\alpha hc^3/4\pi m^2)\ (\nu-\nu_0)/\nu^3$ for the magnitude of photoelectric emission by light of frequency ν. The only modification will be that now the constant α of this expression will not be connected in the same way with the constant A in the thermionic emission formula as in the argument of Lawrence. But Lawrence did not consider the relative *numerical* magnitudes of these constants, but contented himself with showing that certain expressions have the same algebraic form. This is evidently not sufficient. I believe that if he had gone further and considered the numerical magnitudes, he would essentially have had to reproduce the steps which led Richardson to conclude that the photoelectric effect is 5000 times too small.

THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
October 3, 1927.

Note Added on Reading Page Proof. The argument leading to the conclusions of pages 98 and 99 neglects the variation of ν_0 with temperature. This effect is so small that none of the conclusions would be essentially modified by inclusion of this term.

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[11] E. O. Lawrence, Phys. Rev. **27,** 555 (1926).

[12] O. W. Richardson, Phil. Mag. **31,** 149 (1916).

[13] H. E. Ives, Astrophys. Jour. **64,** 128 (1926).