AN EQUILIBRIUM THEORY OF ELECTRICAL CONDUCTION

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Abstract

Equilibrium electron theory of electrical conduction.—(1) *General equation.* Accepting the simple electron theory expression for specific conductivity, the concentration of free electrons is supposed to be determined by the reaction: normal atom$\leftrightarrows$positive ion $+\nu$ electrons, which is governed by the ordinary laws of chemical equilibrium, and this gives for the specific electrical resistance $\rho=C(\nu N)^{-1/(\nu+1)}\ T^a e^{b/T}$, where ν is the valence in the reaction, N the concentration of atomic nuclei, $a=(\nu+4)/2(\nu+1)$, $b=(\varphi_0-\psi_0)/(\nu+1)R$, $(\varphi_0-\psi_0)$ being the mean energy required to bring about the hypothetical reaction of 0°K. This formula shows fair quantitative agreement with experimental data for both good and poor conductors; in particular, the constant a is about 1.25 for the alkali metals and less for metals of higher valence except in the case of Fe and Ni. For the metals the requirement is that φ_0 be slightly less than ψ_0· while for poor conductors φ_0 must be considerably greater than ψ_0. (2) *Interpretation of constant b in terms of photoelectric and thermionic work functions.* φ_0 and ψ_0 are identified with the photoelectric energy function and with the corresponding thermionic function respectively. According to the theory proposed the ordinary *expression for the thermionic saturation current* becomes: $i=BT^{(4\nu+1)/2(\nu+1)}\ e^{-\omega/RT}$, where $\omega=(\varphi_0+\nu\psi_0)/(\nu+1)$ in the present notation. Therefore for metals the photoelectric φ_0 and the thermionic ω as experimentally determined should be practically identical, while for poor conductors the experimental φ_0 should considerably exceed ω. These conclusions are both in agreement with the facts. (3) *Explanation of photo-conduction.* This theory suggests that the mean value of φ_0 is diminished by absorption of radiation of the resonance frequency. For poor conductors this would bring about an increase in conductivity. While for metals at ordinary temperatures the conductivity would not be sensibly affected, at very low temperatures metals should prove photo-sensitive.

In attempting to explain the electrical conductivity of good and of poor conductors the electron theory has so far required quite different methods of treatment. In the case of poor conductors like compounds and semi-metals Koenigsberger[1] found an expression for the specific resistance, the theory of which was based upon chemical dissociation of atoms into ions and electrons, the current in general being carried by electrons. In order to obtain close agreement with experiment it was necessary to include an empirical factor of the same form as appears in the temperature variation of metallic resistance. In recent work on

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[1] Koenigsberger, Ann. der Phys. **32**, 179, (1910).

the conductivity of molybdenum sulphide,[2] a substance which may exhibit all phases between poor conduction and that of metals, the author attempted an interpretation of the behavior of this substance on the basis of Koenigsberger's theory, and found that the energy required to liberate a free electron from an interior atom on the average diminished considerably as metallic conduction was approached, an observation which led to the present paper. Probably the most successful theory to account for metallic conduction alone has been that of Bridgman,[3] in which the conductivity is given by the simple electron theory expression, with special assumptions in regard to the variation of the electronic mean free path, the concentration of free electrons being considered constant. It is the purpose of this article to show that, in an exceedingly natural and simple manner, it is possible to explain the temperature variation of electrical conductivity for both good and poor conductors on identically the same hypothesis for each. The theory proposed accepts the expression for the conductivity given by the simple electron theory, but like the theory proposed by Caswell[4] it assumes a constant or nearly constant mean free path, and explains conductivity variations by variations in the concentration of the free electrons. Like the theory of Koenigsberger it is based upon a chemical dissociation of atoms into ions and free electrons.

In the first place it is assumed that the electrons which may become free follow the ordinary laws of chemical equilibrium in their dissociation from the parent atoms. This assumes that the atmosphere of free electrons behaves like a perfect gas, i.e. that the mutual electromagnetic effects due to their charges are negligible. If we take as the simplest possible reaction $A \leftrightarrows A^{+} + \epsilon$, where A is a neutral atom, A^{+} a singly charged positive ion, and ϵ an electron, then the mass action law is $\log (C_{+} \cdot C_{\epsilon}/C) = k$ where C, C_{+} and C_{ϵ} are respectively the concentrations of atoms, ions and electrons in equilibrium. Now for this reaction, $C_{+} = C_{\epsilon} = n$, the number of free electrons per unit volume; while $C = N - n$, where N is the total number of nuclei present in unit volume whether as neutral atoms or as ions.

Hence $$\log [n^2/(N-n)] = k$$

Solving for n, $$n = \tfrac{1}{2}e^{k}(-1 \pm \sqrt{1+4Ne^{-k}})$$

Therefore, if N is large compared with e^{k};

$$n = N\tfrac{1}{2}e^{k}/2 \qquad (1)$$

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[2] Waterman, Phys. Rev. **21,** 540, 1923.

[3] Bridgman, Phys. Rev. **17,** 161, 1921; **19,** 114, 1922.

[4] Caswell, Phys. Rev. **13,** 386, 1919.

This condition appears in general to be satisfied, except for the case of good conductors when quite near absolute zero.

The equilibrium constant k is given by

$$\partial k/\partial T = q/RT^2 \tag{2}$$

where q is the average amount of energy required to bring about the reaction for a single atom.

In the case of a typical atom in its place in the solid structure, suppose the potential of the electron which may become dissociated is V_1 when held by the atom, and V_2 when free to take part in conduction. Roughly speaking then, V_1 may be the potential at the periphery of an atom, and V_2 the mean potential of the space through which the conducting electrons pass. Then $q = (V_1 - V_2)\epsilon = \phi - \psi$. Thus ϕ is the energy required to remove a bound electron completely from the substance and V_1 is this ionization potential, presumably analogous to the ionization potential of a gas but not necessarily equal to it. Ψ is the energy required to liberate a free electron from the solid and is thus identified with the energy function ϕ dealt with in the theory of thermionic emission. By analogy with the behavior of gaseous atoms it is natural to assume that ϕ of the present theory is practically independent of the temperature. On the other hand ψ is expected by thermodynamical reasoning to vary with the absolute temperature as follows:[5] $\psi = \psi_0 + (3/2)\ RT$, neglecting a relatively small term involving the specific heat of electricity.

Therefore we may write: $q = (\phi_0 - \psi_0) - (3/2)RT$. Substituting this value of q in Eq. (2), and integrating:

$$k = -(\phi_0 - \psi_0)RT - (3/2)\log T + \text{const.} \tag{3}$$

where ϕ_0 and ψ_0 are independent of the temperature and characteristic of the substance and its structure.

Eq. (1) then becomes:

$$n = A\ N^{\frac{1}{2}} T^{-\frac{3}{4}} e^{-(\phi_0 - \psi_0)2RT}$$

where n is the number of free electrons per unit volume in equilibrium. In this expression the variation of N resulting from thermal expansion is neglected, as its effect on n is comparatively small.

The specific electrical conductivity σ which, according to the simple classical theory, is $\sigma = n\epsilon^2\lambda/2\sqrt{3mRT}$,
becomes $\sigma = A'N\ T^{-5/4}\ e^{-(\phi_0 - \psi_0)/2RT}$
where $A' = A\,\epsilon^2\lambda/2\sqrt{3mR}$
or the specific resistance: $\rho = C\ N^{-\frac{1}{2}} T^{5/4}\ e^{(\phi_0 - \psi_0)/2RT}$

In case a more general simple reaction is assumed for the liberation of electrons, of the form $A \leftrightarrows A^{\nu +} + \nu\epsilon$, where ν is the valence, by similar

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[5] O. W. Richardson: "Electron Theory of Matter," p. 453.

argument (and using a similar approximation) the concentration of free electrons depends upon temperature as follows:

$$n = (\nu N)^{1/(\nu+1)}\, e^{k/(\nu+1)} = A\,(\nu N)^{1/(\nu+1)}\, T^{-3/2(\nu+1)}\, e^{-(\phi_0-\psi_0)/(\nu+1)RT} \tag{4}$$

whence $$\sigma = A'(\nu N)^{1/(\nu+1)}\, T^{-(\nu+4)/2(\nu+1)}\, e^{-(\phi_0-\psi_0)/(\nu+1)RT} \tag{5}$$

and $$\rho = C(\nu N)^{-1/(\nu+1)}\, T^{(\nu+4)/2(\nu+1)}\, e^{(\phi_0-\psi_0)/(\nu+1)RT} \tag{6}$$

where $$C = 2\sqrt{3mR}/A\,\epsilon^2\lambda$$

It is seen that the theory requires that the valence of an element should influence its conductivity. Thus for a

univalent reaction: $(\nu=1)$, $\rho \propto T^{1.25} e^{(\phi_0-\psi_0)/2RT}$;
bivalent reaction: $(\nu=2)$, $\rho \propto T^{1.00} e^{(\phi_0-\psi_0)/3RT}$;
trivalent reaction: $(\nu=3)$, $\rho \propto T^{0.875} e^{(\phi_0-\psi_0)/4RT}$;
quadrivalent reaction: $(\nu=4)$, $\rho \propto T^{0.800} e^{(\phi_0-\psi_0)/5RT}$; etc.

In any case the dependence of the specific resistance upon temperature is of the form:

$$\rho = CT^a\, e^{b/T} \tag{7}$$

where C, a and b are constants characteristic of the substance.

Now an examination of conductivity data shows that in general the temperature variation of specific resistance (at constant e.m.f. and pressure) for all solid conductors (with the possible exception of alloys) may be represented quite approximately by an expression of this type, Eq. (7).

For the best conductors, i.e. metals, a is of the order of magnitude of unity, and b/T is small at ordinary temperatures so that the exponential factor is nearly unity. At low temperatures better agreement is shown if b is negative, since the specific resistance then approaches zero exponentially as the temperature diminishes. In the theoretical expression it is seen that the exponent of T does approximate unity for all valences, while the requirement for metals that b should be small and negative may be met by assuming that ϕ_0 is slightly less than ψ_0.

For poor conductors, such as Se, B, and many compounds, the constant b is large and positive, so that the factor T^a has little effect, and the specific resistance of these solids at all available temperatures decreases exponentially with rising temperature. Thus for such conductors ϕ_0 is much greater than ψ_0.

For transitional substances such as Si, Ge, and some compounds, which show a minimum resistance, preceded by the characteristics of poor conductors and followed by metallic conduction, b, i.e. $(\phi_0-\psi_0)$, has an intermediate positive value and a is in the neighborhood of unity. As a matter of fact the theoretical expression predicts a minimum resistance at a temperature given by:

$$T = 2(\nu+1)\,(\phi_0-\psi_0)/(3\nu+4)R$$

Thus there is no minimum resistance (except at 0°K) when ϕ_0 is less than ψ_0, the case of metals. For poor conductors, where ϕ_0 is much larger than ψ_0, the temperature of minimum resistance would be impossibly high or above the melting point. Changes of structure such as polymorphic transitions involve a change in the constants of the expression and offer no difficulties.

TABLE I

Element	Valence	Obs. Exponent a' in $\rho\propto T^{a'}$	Range of Exp. Data (°C)	Constancy of a' fails
Li	I	1.30	−187 to 100	
Na	I	1.34	−200 to 93.5	below −150
K	I	1.33	−200 to 60	below −100
Rb	I	1.29	−190 to 35	
Cs	I	1.3	−187 to 27	
Ca	II	1.0	0 to 100	
Sr	II	1.0	0 to 100	
Cu	I, II	1.15	−259 to 1083	below 0
Ag	I	1.10	−259 to 960	below −150
Au	I, III	1.12	−253 to 1063	below −150
Mg	II	1.07	0 to 100	
Zn	II	1.15?	−253 to 415	below −150
Cd	II	1.02	−253 to 300	below −100
Hg	I, II	1.20	−200 to −50	below −150
Sn	II, IV	1.1	−200 to 225	below −100
Pb	II, IV	1.09	−253 to 200	below −200
Al	III	1.22	−190 to 400	
Tl	I, III	1.13	−183 to 100	below −100
Bi	II-V	0.91	−200 to 259	above 20
		mean		
Fe	II, III	1.43	−253 to 400	below −100
Ni	II, III	1.45	−180 to 100	
W	II-VI	1.24	0 to 2000	
		1.0	0 to 100	
Rh	III, IV	1.13	−186 to 100	below −80
Ir	III, IV	0.99	−180 to 100	
Pd	II, IV	0.95	−183 to 100	below 0
Pt	II, IV	0.96	−264 to 1600	below −73 above 1000

In the case of metallic conductors the extent of the quantitative agreement with experimental data is shown in the Table. The theoretical formula for this case is $\rho = CT^a e^{-b/T}$, expressing explicitly the fact that b is here negative. By plotting logarithmically the experimental values for specific resistance against absolute temperature, the slope of each curve at any point according to the theory should be: $a' = a + b'/T$, where $b' = .434\ b$, common logarithms being used. Thus the observed slope a' should exceed the theoretical exponent a by an amount

$b'T$. At ordinary temperatures or higher, b'/T is expected to be small if not negligible; consequently in this region the observed slope a' should be nearly constant and show a variation with valence from element to element similar to that of the theoretical temperature exponent a. At low temperatures on account of the additive term b'/T the observed slope a' should considerably exceed a and should increase rapidly with diminishing temperature. The approximate temperature at which the constancy of a' thus fails is given in the fifth column. The experimental data are taken from the Smithsonian Physical Tables, with the exception of the short range observations (0° to 100°C) which are Bridgman's.

For the alkali metals, for which a univalent reaction $A \leftrightarrows A^+ + \epsilon$ may with most confidence be assumed, the experimentally determined temperature variation of resistance shows striking quantitative agreement with the theory. The observed slope a' is nearly the same for all metals of this group, and exceeds the theoretical exponent a by 3 to 7 per cent, which is entirely consistent with the theory, while the customary first power of the absolute temperature is wrong by 29 to 34 per cent. Na and K show a marked departure from constancy of a' at the lowest temperatures given, which would be due to the effect of the exponential factor of the formula.

For the alkaline-earth metals Ca, Sr and Ba, the bivalent reaction alone would be expected to occur or certainly to predominate, for which a first power of the absolute temperature should be exact. The results as far as they go are in entire accord with the theory, i.e., $a = 1.00$. It is unfortunate that a greater range of temperature has not been studied and that Ba seems not to have been investigated.

A priori it appears far from certain that the reaction of an atom of a solid in liberating electrons should necessarily be governed rigidly by the valence which that atom exhibits in forming chemical compounds, except in the case of the alkali metals. Rather it seems quite likely that an atom should behave somewhat after the manner of a gaseous atom, where in general ionization may take place progressively, i.e., $A \rightarrow A^+ + \epsilon$, $A^+ \rightarrow A^{++} + \epsilon$, etc., until the possible number of free electrons is exhausted, a stage which will depend upon the highest possible valence. The ionization potentials will in general be different for each dissociation and characteristic of the atomic structure. Thus intermediate values of a will in general be expected, and especially where more than one chemical valence exists. But it seems also possible that in the solid state one or more of the outer electrons may in certain cases be strongly held in place as a bond of union between adjacent atoms and thus be prevented from becoming free. Or on the other hand the atomic structure might possibly be altered in such a direction as to facilitate the liberation of additional electrons. Thus there would appear to be two factors which may be operative in any such atomic dissociation within a solid, the atomic structure of the individual atom, and the interatomic or molecular structure.

With these considerations in mind, the agreement is seen to be good on the whole, between the experimental and the calculated data in the case of the other metals listed. It will be noted that the observed values of a' are in most cases somewhat greater than the theoretical values of a, as would be expected for the several reasons given. The valence in the conductivity reaction is distinctly different from the ordinary chemical valence for Ag, Al, W, Fe and Ni. In the case of Al and W the former valence is lower, and thus it seems that a much greater amount of energy is required to free a second electron than the first, the reason for which may lie in the nature of the interatomic structure as suggested. Ag is a surprise, with an apparent reaction which is partly bivalent. This is not so serious an exception as would be the case if one of the alkali metals showed other than a univalent reaction. Also, according to the most recent developments of the Bohr-Sommerfeld theory, the atomic structures of Cu and Ag are almost exactly similar, so that the nearly identical behavior in conductivity of these two elements, including the same type of reaction liberating electrons, would be expected. From this point of view the surprise is that Cu and Ag differ in chemical valence. Incidentally it may be mentioned that according to the Bohr-Sommerfeld theory the three valency electrons of Al are distributed with one alone in the outermost highly eccentric orbit, and two in the next orbit of smaller eccentricity. Thus there is some basis for the fact that Al appears to be univalent in its conductivity reaction. The two similar metals Fe and Ni are outstanding exceptions to the theory in its present form, and for these no explanation is offered at present, except a suggestion that these two may have a sort of molecular dissociation of the form $2A \leftrightarrows (2A)^+ + \epsilon$, for which a should be 1.50. The strongest support from experimental data comes from the case of the alkali metals, where a univalent reaction appears absolutely necessary, and where an exclusive univalent reaction is found in fair agreement.

Incidentally a characteristic of the experimental graphs in many cases was found to be a slight increase in the value of a' on approaching the melting point, which was most pronounced in the case of Bi. Pt was a notable exception where a decrease occurred.

Fig. 1 shows the graphs of specific resistance vs. absolute temperature, plotted logarithmically in the manner in which the slopes a' were obtained, for three representative metals, Na, Cu and Pt. It will be seen from the Table that Cu and Pt might be expected to give trouble, inasmuch as the constancy of the observed slope a' fails below a higher temperature than for most metals. The curves drawn represent the theoretical variation of resistance according to Eq. (7). For the Na curve the theoretical value $a=1.25$ was assumed and the agreement is excellent. For Cu and Pt no exact value of the theoretical exponent a could be predicted, so that the curves merely represent the theoretical expression with a choice of constants which approximates the observed behavior. It is observed that at the lowest temperatures for Cu and Pt a departure from agreement occurs. It is in this region however that the approximation underlying the expression (7) might be expected to break down. Better agreement here could be obtained with a more rigorous expression, as higher values of the resistance would then be obtained.

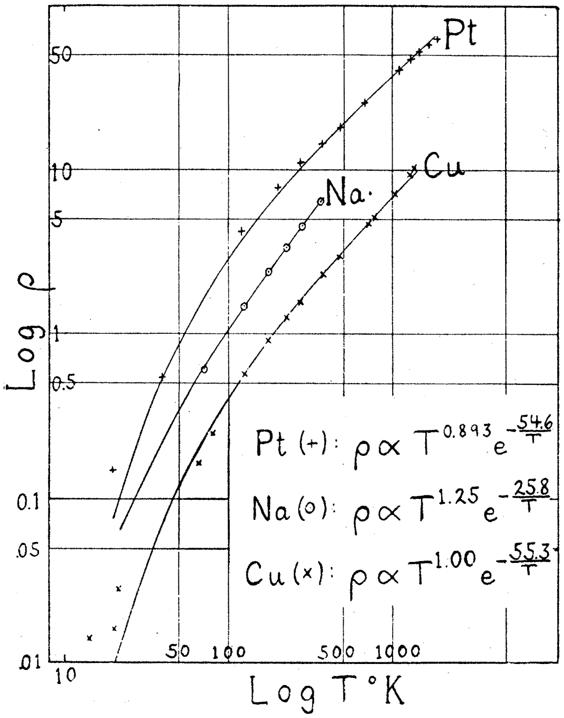

Fig. 1. Specific resistance as a function of absolute temperature.

On the basis of this theory super-conductivity might possibly be accounted for by a polymorphic transition, which as readily seen in such changes at ordinary temperatures involves a change in the difference $\phi_0 - \psi_0$.

It is hardly necessary to give data to show agreement with experiment in the case of poor conductors, as the theoretical expression here derived is of the same type as that of Koenigsberger[1] with T^a substituted for the factor $(1+\alpha t+\beta t^2)$. Taken empirically there is practically no choice between these two factors, especially when the order of accuracy of experiments with poor conductors is considered. The expression also compares favorably with Bidwell's[6] empirical formula for transitional substances. In this formula the "metallic resistance" factor is assumed to be e^{xT} instead of T^a.

It is interesting to consider the physical interpretation of the quantities ϕ_0 and ψ_0. On the basis of this theory the behavior of metals at low temperatures is explained by the hypothesis that ψ_0 is slightly greater than ϕ_0. Thus the space in which the conducting electrons travel in metals is at a higher potential than that of their normal positions when held by the atom. This may be considered to point to the conclusion that for metals the conducting electrons pass chiefly through the interiors of the atoms rather than to any extent through a real space between them, a result which is in agreement with the view of Bridgman for most metals. On the other hand in the case of poor conductors, the fact that for these substances ϕ_0 is greater than ψ_0 may indicate that the conducting electrons traverse mainly the interatomic space.

The theory derives additional confirmation in an entirely different direction. As has been stated the function ψ_0 should be identical with the theoretical thermionic function commonly denoted by ϕ_0. Suppose the function ϕ_0 of the conductivity expression to be identified with the corresponding energy function ϕ_0 in the theory of photoelectric emission. This interpretation is equivalent to assuming that thermionic emission involves directly only the free electrons while photoelectric emission affects directly only the electrons bound by the atom. Although the correctness of this view of photoelectric emission is still debated it is on general principles the most natural assumption to make, and is consistent with the fact that photoelectric emission seems to be independent of the temperature.

This interpretation makes possible a consideration of the experimental values obtained for the thermionic and the photoelectric energy functions in connection with the theoretical expression for the conductivity.

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[6] Bidwell, Phys. Rev. **29**, 447, 1922.

It is first necessary to point out that the ordinary expression for the thermionic current, namely:

$$i = B'T^2e^{-\omega/RT} \tag{8}$$

(using ω, to avoid confusion, in place of the usual notation ϕ_0) should be modified. This equation is obtained from:

$$i = BnT^2e^{-\psi_0/RT}$$

with n, the concentration of free electrons, considered constant, and thus becomes:

$$i = B''\ (\nu N)^{1/(\nu+1)}\ T^{[2-3/2(\nu+1)]}\ e^{-[\psi_0/RT+(\phi_0-\psi_0)/(\nu+1)RT]},$$

since n varies with temperature according to equation (4), or

$$i = B''\ (\nu N)^{1/(\nu+1)}\ T^{(4\nu+1)/2(\nu+1)}\ e^{-(\phi_0+\nu\psi_0)/(\nu+1)RT} \tag{9}$$

which for a univalent reaction would be: $i = B''N^{\frac{1}{2}}T^{5/4}e^{-(\phi_0+\psi_0)/2RT}$.

Thus according to the theory the experimentally determined values of the thermionic energy function ω in equation (8) are in reality values of $(\phi_0+\nu\psi_0)/(\nu+1)$ rather than ψ_0. Now in the case of metals the conductivity expression (5) indicates that ϕ_0 and ψ_0 are nearly equal, and therefore the experimental values of ϕ_0 and ω should prove also nearly equal. Although the consistency of such determinations of ϕ_0 and ω has been far from satisfactory the fact is that both appear to be closely of the same magnitude for metals. The maximum difference may even be roughly predicted from the conductivity data. Thus the probable maximum value of $(\phi_0-\psi_0)/(\nu+1)R$ in the case of any metal appears to be in the neighborhood of 100°. An approximate calculation shows this to result in a difference between ϕ_0 and ω of less than 1 per cent, the latter being greater. This is a crude maximum difference for the most favorable case; the difference would be expected to be considerably less for most metals. For example, taking the experimental value of the thermionic energy function for Na as 1.82 equivalent volts in conjunction with the value of b $(=(\phi_0-\psi_0)/2R)$ from the conductivity data (cf. Fig. 1), namely $-51.6°$, whence $\phi_0-\psi_0 = -4.5(10)^{-3}$ equivalent volts, it follows that $\phi_0 = 1.82-0.002$ equivalent volts. Therefore the difference between the photoelectric function ϕ_0 and the thermionic ω should escape experimental detection by direct methods used thus far.

It should prove extremely interesting to compute in this manner the difference between ϕ_0 and ψ_0 from the conductivity data for many elements. Unfortunately the experimental data for specific resistance over a wide range of temperature, and especially at low temperatures, are in general neither extensive nor consistent enough for this purpose. A most satisfactory beginning in such study could be obtained if data were available for all the alkali and alkaline-earth metals in solid form of highest purity, since for these metals the valence in the hypothetical conductivity reaction would be definitely known. It is important for the sake of consistency in results that the *same specimen* be observed over the entire range of temperature available, and that especial attention be paid to observations at the temperature of liquid air and below. Another and more complex method of attack would be further systematic and careful investigation of the specific resistance of poor conductors over large ranges of temperature, with especial attention to points of minimum resistance, and to polymorphic changes.

In the case of poor conductors like the oxides and sulphides the conductivity expression indicates that ϕ_0 is much larger than ψ_0. It follows that the observed values of ϕ_0 should be considerably greater than ω. This again is found to be the case for such conductors. For example Hughes[7] gives $\phi_0=5.0$ and $\omega=1.9$ equivalent volts in the case of CuO. If for the liberation of electrons within the oxide a bivalent reaction is assumed as being the predominating type and especially as approximating the reaction for metallic Cu, then since $\omega=(\phi_0+2\psi_0)/3=1.9$, $\psi_0=0.35$ equivalent volts. Hence $\phi_0-\psi_0=4.65$ and the specific resistance of CuO should be proportional to $Te^{(\phi_0-\psi_0)/3RT}$ or $Te^{18,000/T}$, which would indicate a low conductivity and a rapid exponential decrease in resistance with rise in temperature. The experimental values for ϕ_0 and ω are subject to far too much uncertainty for such numerical computation, however; indeed, if the theory is correct, more accurate comparative values of ϕ_0 and ω should be obtained by aid of the conductivity data.

The theory also affords a natural explanation of increase in conductivity under the influence of light. The explanation generally offered is that the increased conductivity is due in part at least to the presence of photoelectrons within the substance. This explanation, if correct, may be sufficient on any theory, but it encounters difficulties. In the present theory, if the analogy holds between solid and gaseous atoms, we might expect to find the ionization energy or potential of any atom affected by absorption of radiation of the resonance frequency. The effect of such absorption would be to diminish the mean value of ϕ_0, and in consequence for the case of poor conductors where $\phi_0-\psi_0$ is a large positive difference and the exponential factor most important, the conductivity should increase. This view has already been advanced by the author in explanation of the light sensitiveness of molybdenite.[2] For metals, the exponential factor being nearly negligible at ordinary

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[7] Hughes (after Millikan and Richardson), Bulletin of the National Research Council, Vol. 2, Part 2, No. 10.

temperatures, the conductivity would not be sensibly affected unless the value of ϕ_0 were greatly altered. But if this hypothesis concerning light-sensitiveness and the proposed explanation of conductivity at low temperatures are correct it follows that metals should be found light-sensitive at very low temperatures. It should be noted that this explanation of light-sensitiveness does not require an emission of photoelectrons caused *directly* by the radiation, but only that the absorption of radiation diminishes the mean amount of energy required to liberate an electron, and the equilibrium condition then necessitates an increased concentration of free electrons. This may also explain why photo-conductivity for a given substance is more readily produced than photoelectric emission from the surface.

Unless the constant of integration in Eq. (3) is evaluated by some independent method, it is impossible to compute the actual concentration, mean free path, etc. of the free electrons. With this constant at our disposal, the conductivity formula given is consistent with any values of the mean free path and concentration, as for instance Bridgman's, which do not make the concentration approach that of the atomic nuclei too closely, since when n is of the same order of magnitude as N the approximation underlying the simple conductivity formula is invalid. In regard to the variation of the mean free path λ with temperature possibly the most natural assumption is that λ varies as the mean distance between adjacent nuclei or as the inverse third power of the concentration of nuclei. As this latter concentration enters into the conductivity formula independently in the factor $(\nu N)^{1/(\nu+1)}$ it is seen that not only is the variation produced by thermal expansion quite small in either factor, but the effect on λ is always nearly offset by the direct effect on N.

It is apparent that a conductivity theory of the form here outlined possesses singular advantages in its ready application and extension to numerous allied effects. Further investigation along these lines is now in progress.

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