

of magnitude of the constants, yet they are seen to correspond well with the values calculated by the thermodynamic equation.

The results here presented therefore afford a striking confirmation of the general validity of the calculation of the ionization of elements from their ionization-potentials by the thermodynamic equation employed by Saha.

¹ Eggert, *Physik. Zs.*, **20**, 570, 1919.

² Saha, *Phil. Mag.*, **40**, 478, 809, 1909; **41**, 267, 1921.

³ Russell, *Astrophys. J.*, **55**, 129, 1922.

⁴ Sackur, *Ann. Physik.*, **36**, 598, 1911; **40**, 67, 1913; Tetrode, *Ibid.*, **38**, 434; **39**, 255, 1912; Stern, *Zs. Electrochem.*, **25**, 66-80, 1919; Tolman, *J. Amer. Chem. Soc.*, **42**, 1185, 1920; **43**, 1593, 1921; Lewis, *Physic Rev.*, **18**, 121, 1921.

⁵ Arrhenius, *Wied. Ann. Phys.*, **43**, 18, 1891.

⁶ H. A. Wilson, *Phil. Trans. Royal Soc.*, **A216**, 63-90, 1915.

⁷ H. A. Wilson, *Phil. Mag.*, (6) **10**, 475, 1905.

⁸ Wilson and Gold, *Phil. Mag.*, (6) **11**, 484, 1906.

AN ELECTRON THEORY OF ELECTRIC CONDUCTION IN METALS

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This is a modification and extension of the dual conception of conduction which I set forth in a paper¹ printed several years ago and to which I have referred in more recent publications. The theory in its present shape, like every other theory of metallic conduction with which I am acquainted, involves propositions that may well be questioned, but it contains certain features not present, so far as I know, in other theories, and I hope these will be found worthy of consideration, even if they are finally to be rejected.

I shall endeavor to state this theory, without extended argument, in the form of certain propositions, some of which are or involve outright assumptions. Any helpful hypothesis, not in conflict with well established facts or principles, I have considered justifiable, in view of the difficulties of the problem with which I am dealing.

Behavior of the Ions in Conduction

1. Complete metal atoms are of such hardness and symmetry that they are not subject to appreciable polarization or orientation in impressed electric fields of ordinary strength.

2. An ion is formed from an atom by loss of an electron from the outer shell and is, accordingly, unsymmetrical, essentially polarized, and therefore subject to orientation in a uniform electric field such as may be ap-

plied to a metal from without. This proposition seems to be in general accord with Langmuir's conception of atomic shells. See no. 991 in *Science Abstracts* for 1919.

3. The behavior of these ions in an electric field is somewhat like that of magnetic particles in a magnetic field, as set forth in Langevin's theory² of paramagnetism, or that of electric dipoles as described by Sir J. J. Thomson.³ But in one vital particular, indicated in the next paragraph, the formula used by Langevin and by Thomson must be modified to suit the present case.

4. When and where the equipartition law of energy holds, the Boltzmann-Maxwell distribution law can be written with the factor $e^{-V/RT}$, where V is the mean potential energy of a particle with respect to any coördinate, either of position or of direction, in the field of force, and RT is twice the mean kinetic energy of the particles with respect to any degree of freedom whatever. But when and where the equipartition law fails, we must, if we can use the Boltzmann-Maxwell formula at all, use it with regard to the particular coördinate or degree of freedom that we are dealing with. Kinetic energy along one coördinate may in this case have nothing to do with the distribution of particles along another coördinate. For example, if all the kinetic energy of air particles became rotary energy, the atmosphere would fall. So, too, if we are dealing with particles that have no rotary energy, the translatory energy of these particles will have nothing to do with their orientation in a directing field of force.

5. The atoms and the ions have a mean kinetic energy of rotation proportional to the absolute temperature but of a much smaller order of magnitude than that of the energy of translatory vibration.⁴ Accordingly we should, in the Boltzmann-Maxwell formula, use a very much smaller value than Langevin and Thomson have used in the denominator of the exponent of e , thus getting a much greater orientation, in a given field of force, than their formula would lead us to expect. This orientation will, through a great range of electric field strength, be proportional to the strength of the field and inversely proportional to the absolute temperature.

6. The time required for the orientation of an ion to reach its final value is large compared with the period of the translatory vibrations of the ion. See (21).

7. An ion has on its surface a fairly definite scar or *pit* from which an electron has been dislodged, and the ion can capture an approaching electron, thereby recovering the status of an atom, only when the electron strikes, not too violently, within this pit.

8. A free electron, approaching an ion with the kinetic energy of a gas molecule, may, though attracted toward the pit, shoot by, failing to make

connection, as a comet shoots by the sun. Accordingly, termination of the life of an ion by the taking up of a free electron may be a comparatively rare occurrence, most of the ions ending by taking up electrons directly from neighboring atoms.

9. Though the atoms have a regular arrangement in a continuous metal crystal, the individual crystals in any ordinary piece of metal are so small and so heterogeneously placed with respect to each other, that we may think of the atoms and ions as, on the whole, subject to mutual collision with any direction whatever of their line of centres. Accordingly we may think of the *pits* as *forming* anywhere on the ions, in one quarter as probably as in any other, when no impressed electric field is in operation.

10. Impressed electric fields of ordinary strength have no appreciable influence in determining or preventing the passage of an electron from an atom to a neighboring ion.⁵ Thus a potential gradient of 1 volt per centimeter, imposed from without, would be a very steep one, whereas, if the "ionizing potential" of an atom within the solid metal is of the order of 1 volt, as I believe it to be, the field of force which a neighboring ion may exert on an electron is of the order of 10^8 volts per centimeter. It is possible, however, that when extremely great current densities are used, as in attempts to pass beyond the range of Ohm's law, the impressed field may be great enough to have a perceptible effect in determining whether an electron shall stay on its present atom or pass over to an adjacent ion. Such an effect would tend to make the current increase more rapidly than the potential gradient and might do something to mask the opposite kind of change that would naturally come from the approach of the ions to a saturated state of orientation.

11. The impressed electric field does its work, under ordinary conditions, by turning the ions so that the pits upon them, wherever they at first occur, move as a positive charge would move, in the conventional direction of the field force, while the electron portion of the damaged surface shell of the ion moves as a whole in the opposite direction. Thus we have an electric *current*. The effect of the to and fro heat translations of the ion, superposed on the process of orientation, seems to be, practically, to enlarge the ion.

12. The rapidity of the process of orientation of an ion is probably controlled by various factors, one of which is, of course, the moment of inertia of the ion, but the time occupied in this process is assumed to be less than the normal life time of an ion. See (21).

Ohm's Law

13. Let the condition of the ion *i* in figure 1 represent the completed orientation due to a field the lines of which run in the direction of *F*. If the atom *a*, now in contact with *i*, loses an electron to *i*, a pit will form

on a , and the transfer will have substituted for an ion of negative potential energy an ion of equal but opposite orientation, that is, an ion of positive potential energy of orientation, and the new ion will at once begin to swing in such a way as to resume the process that had come to an end on

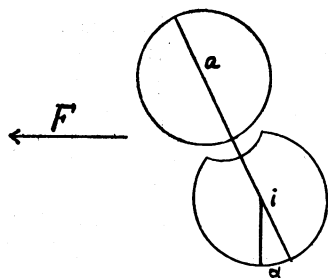


FIGURE 1

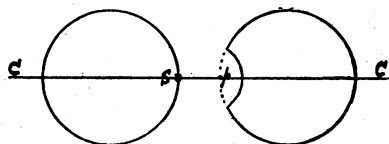


FIGURE 2

the first ion. Other things being equal, the strength of the current will be proportional to the sine of the angle of orientation, α in figure 1, which through a wide range of field strength is (see Prop. (5)) practically proportional to this strength. Thus Ohm's law is satisfied, so far as the kind of conduction now under consideration, that is, the "associated-electron conductivity," which in my previous papers I have called k_a . The "free electron conductivity," k_f , is to be considered briefly later in this paper.

The Temperature Relation

14. It is misleading to speak of the conductivity of pure metals as being proportional to the reciprocal of the absolute temperature. If this relation held, the temperature coefficient of resistance would be 0.00367 for all metals, whereas its mean value between 0°C. and 100°C. is greater than 0.00367 in most metals and is greater than 0.006 in some. Moreover, the purer the metal, the higher the value of this coefficient. Accordingly a theory of conduction that makes conductivity inversely proportional to T proves too much. It is probable that the observed rather loose relationship between conductivity and temperature is the outcome of opposing influences, the direct effect of rise of temperature being to increase resistance much more rapidly than the temperature increases, while increase in the number of ions with heating of the metal tends to reduce the resistance. This idea is elaborated in the following paragraphs.

15. The necessary relative position of an ion and an atom, with a view to the passage of an electron from the atom to the ion, is indicated by figure 2, where the circle represents an atom, the imperfect circle an ion, p the point at which an electron must lodge in order to make an atom of the

ion, cc the line of centres, and s a little three dimensional space within which the point p must be in order to capture an electron from the atom. It is to be noted that the pit in i allows the point p to pass *through* s during a very close approach of the ion and the atom.⁶

16. Let us for convenience suppose the atom to remain at rest, all the relative motion of the two particles being, for the present discussion, attributed to the ion. Ignoring any small long-period rotary oscillations the ion may have, we see that its vibrations may be resolved along three axes, one the line cc , and the other two at right angles with cc and with each other. The little vital space s , within which the point p of the ion must be in order to take up an electron from the atom, lies at the middle of the second and third of these component vibrations but nearer one end than the other of the vibration parallel to cc .

17. The probability that p will gain an electron during any single passage through s is proportional to the length of time spent in this passage. It is, then, so far as the second and third axes are concerned, inversely proportional to the product of the amplitudes of vibration parallel to these axes, each of which amplitudes is proportional to $T^{0.5}$. As to the vibrations parallel to cc , the space s lies relatively nearer the end in a short vibration than in a long one. Accordingly it may be assumed, provisionally, that, so far as motion along cc is concerned, the time spent by p in passing through s will be inversely proportional to some power of T higher than $T^{0.5}$. The result, all three component vibrations being considered, is a probability, that p will gain an electron in a single passage through s , proportional to T^{-x} , where x is some quantity a little greater than 1.5.

18. The conductivity under discussion should, other things being equal, be proportional to the amount of orientation suffered by the ions, which according to (5) varies as T^{-1} and to the frequency of transmission contacts between ions and atoms, which according to (17) varies as T^{-x} . Hence if n , the number of ions per cu. cm., remained constant, we should have this conductivity proportional to $T^{-(1+x)}$ where $(1+x)$ is somewhat greater than 2.5.

19. In the series of papers on thermo-electric action, thermal conduction, etc., which I have published in these PROCEEDINGS⁷ during the past few years, I have been led to the conclusion that the value of n can be usefully represented by the formula $n = zT^q$, where z and q are constants, the value of the latter varying in the many metals considered, from 1.2 in bismuth and in iron to 1.6 in nickel, palladium and platinum, the mean being 1.48. This general rate of increase of n with rise of temperature, taken with the propositions of (18), suggests that the conductivity k_a , now under discussion, should vary, approximately, inversely as the absolute temperature, though individual metals might depart rather widely from this relation. The relation in question is:

$$k_a \propto T^{-(1+x-q)}$$

20. Evidently it is possible, by taking for each metal an arbitrary value of x , to make the ratio of k_a at 0°C. to k_a at 100°C. agree with the observed ratio of total conductivity at 0°C. to total conductivity at 100°C. , but this would be a rather fantastic performance. Attempts to account exactly, at present, by means of the theory of conduction presented in this paper, for the details of observed fact in the relationship of conductivity to temperature would be the opposite of convincing. The value 1.6 for x serves very well for many metals.

21. I cannot in this paper reproduce the discussion by which I have sought to test the quantitative adequacy of the theory here presented. This discussion involves necessarily considerable additional conjecture and is not yet to be regarded as conclusive, but it is distinctly encouraging, provided it is allowable to use for certain factors values of an order of magnitude indicated below:

Moment of inertia of an atom, 10^{-42} gm., cm.,²

Time of orientation process, 5000 times the period of "characteristic" heat vibrations.

Life-time of an ion, at 0°C. , twice the orientation time.

n , the number of free electrons or of ions, per cu. cm., in general accord with the data given in my *Summary*,⁷ though I am now inclined to take, at 0°C. , the mean path of a "free electron" within a metal as perhaps fifty times the centre to centre distance of the atoms, instead of ten times, and so get a correspondingly smaller number for n , one of the quantities varying inversely as the other.

Under these conditions the mean kinetic energy of rotary motion of an atom (see (5)) comes out about 10^{-9} times the energy of translatory vibration.

Behavior of the Free Electrons in Conduction

22. According to the data given in any *Summary*, free-electron conductivity bears to total conductivity about the same ratio at 100°C. as at 0°C. , that is, in most metals the free-electron conductivity, k_f , is roughly inversely proportional to the absolute temperature.

23. Various writers give us the formula

$$k_f = \frac{n \lambda c e^2}{\kappa R T},$$

though they may differ in the value assigned to the constant κ . If we take as approximately true, the proposition that $k_f T$ is a constant, we have

$n\lambda c$ equally constant, and so, if we take $n\alpha T^{1.5}$ (see (19)), we have $\lambda\alpha T^{-2}$, approximately.

24. In the attempt, not hopeless, which I have been making of late to explain the various "transverse" effects in accordance with the propositions of my *Summary*, I have been led to the conclusion that the diameter of the outer electron shell of an atom may be as small as one-half the means centre to centre distance of neighboring atoms. This conception makes it comparatively easy to accept the proposition that λ may be, as already indicated in (21), fifty⁸ times as great as this centre to centre distance.

If λ really extends through many one-atom-thick layers of the metal, a slight decrease in the probability of an electron's passing through any single layer would be enough to account for the rapid decrease in λ with use of temperature, as found in (23).

¹ "A Possible Function of the Ions in the Electric Conduction of Metals," *PROC. NAT. ACAD. SCI.*, Vol. 3, March 1917.

² *Journal de Physique*, series 4, vol. 4, pp. 690-692.

³ See pp. 86-88 of his *Molecular Constitution of Matter*.

⁴ Borelius makes a like assumption regarding the kinetic energy of what he calls free electrons. See *Ann. Phys. Chem.*, vol. 57, p. 233.

⁵ In the paper referred to in footnote (1), I held quite the opposite opinion, making the effect of the field at this juncture the basis of my explanation of Ohm's law.

⁶ If this conception is sound, it would not be surprising to find very great pressure unfavorable to the state of superconductivity.

⁷ For a *Summary* see *PROC. NAT. ACAD. SCI.*, 7, No. 3, March 1921.

⁸ Bridgman has of late taken λ to be "many" times the atomic diameter.

STATIC DEFLECTION, LOGARITHMIC DECREMENT AND FIRST SEMI-PERIOD OF THE VACUUM GRAVITATION NEEDLE*

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1. *Apparatus*.—The object of the present experiments is a completion of the work of an earlier paper,¹ by carrying the exhaustion of the case as far as practicable.

In spite of the care taken to seal all parts of the extended apparatus, there remained a constant leak of .0035 mm. of mercury per hour, the seat of which I was unable to detect; but as experiments with gradually decreasing vacua were primarily contemplated, this leak was here no serious