Some Contemporary Advances in Physics—V

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ELECTRICITY IN SOLIDS

IN considering such topics as the flow of electricity through solids and the outflow of electricity across their boundaries, we have to forego the assistance of the great system of laws, models, and word-pictures which constitutes the contemporary theory of the structure of the atom. This imposing and truly powerful theory, which nowadays seems to bulk larger than all of the rest of physics, is after all limited to certain restricted fields; it deals successfully with particular properties of isolated atoms, and also with certain qualities of atoms which seem to be localized in their inner regions; but it avails little or nothing in the study of the behavior of liquids and solids. Much of the present-day theory of electrical conduction in solids is based only on the very simplest assumptions as to the nature of the atoms of which they are built, some would even remain valid under the old-fashioned ideas of continuous electrical fluids; and profoundly as we may believe that solids are built of atoms resembling Bohr's famous model, it is highly doubtful whether that model has ever helped to interpret a single one of the phenomena of conduction or done more than to provide a new language for old ideas.

We have first to make the distinction between the substances in which atoms migrate along the path of the flowing current and apparently carry the moving charge, and the substances in which the atoms stand still while the current flows past them. It is universally conceded that elements, and likewise the alloys of metals and a number of solid compounds, belong to the latter class; whatever it is that carries the current flows through and past the substance, leaving it at the end as it was at the beginning. Weber said in 1858, "In the metals there are electrically-charged particles as well as atoms; some of the former are freely mobile and others vibrate about the atoms; they are the cause of the conduction of electricity and of heat, and of magnetic phenomena as well." Considering that in Weber's day electricity had never been observed apart from ponderable matter and electrons were unknown, this is entitled to rank as a daring anticipation.

Next we have to distinguish between conduction by metals and conduction by non-metallic elements. Strictly we should begin by defining a "metal"; but this task had better be left to the chemists, as being really their affair; and they have found it no easy affair to

PERIODIC CLASSIFICATION OF THE ELEMENTS[1]

	I	II	III	IV	V	VI	VII	VIII	O
1	1 H								2 He
2	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F		10 Ne
3	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl		18 A
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe 27 Co 28 Ni	
	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br		36 Kr
5	37 Rb	38 Sr	39 Yt	40 Zr	41 Nb	42 Mo	43—	44 Ru 45 Rh 46 Pd	
	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I		54 Xe
6	55 Cs	56 Ba	Rare Earths	72 Hf	73 Ta	74 W	75—	76 Os 77 Ir 78 Pt	
	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85—		86 Nt
7	87—	88 Ra	89 Ac	90 Th	91 Pa	92 U			

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[1] The atomic numbers are given in front of the abbreviations of the elements.

set up a definition by which every element can be confidently assigned to one class or to the other. In fact there is a tendency to begin by defining metallic conduction, and then define metals as the elements which display it! The difficulty, as usual, is to make the definition sharp enough to decide a few intermediate or transitional cases. Anyone even slightly acquainted with chemistry or physics would instantly recognize as metals the elements in the first column of the Periodic Table, and those at the bottom of the table in all the columns; and as non-metals, with the same ease, the elements in the topmost row of the table and down the right-hand side. The first element of every column after the first two is non-metallic, and the non-metallic character advances farther and farther down the columns as one proceeds across the Table from left to right. One might say that the elements which are not metals occupy the northeast sector of the Table, and the debatable ones cross in a diagonal band from northwest to southeast. The elements which are gases under the usual circumstances of temperature and pressure are extreme instances of non-metals; but some of the definitely non-metallic elements, and all of the debatable ones, are solid or liquid under the usual conditions.

Very little could be said about the elements which under ordinary conditions are gases, for very little is known about the manner in which they conduct electricity when liquefied or frozen. Probably the reason is that the experimental conditions would be unusually difficult, and the substances probably very bad conductors; it is not easy to imagine solid hydrogen moulded into a cylinder, drawn into a wire, clamped or sealed between electrodes, or filled into a sheath less conductive than the hydrogen itself. The difficulties may not be insuperable; but they have not been generally overcome.

As for the solid elements which are definitely not metals, or which belong to the debatable group, there is an abundance of data in print, and yet not nearly so much as we need. In general their resistances are tremendously greater than the resistances of metals; "tremendously" for once is not an extravagant word, for the conductivities of the elements are spread over a sweeping range of orders of magnitude which few if any other qualities of theirs can rival. The mass of the heaviest known atom differs from the mass of the lightest only by a factor of 240; the densities of the solidified elements, their compressibilities, their other mechanical and thermal properties range over not more than one or two, at the most three orders of magnitude; even the energy required to extract the innermost electron of an atom rises by a factor of only 10^5 in passing from the first to the last element of the series; but the conductivity of silver stands to the conductivity of sulphur in the ratio 10^{21}. The distance from the sun to the nearest star is some 10^{18} cm.; we see that a sheet of sulphur a thousandth of an inch thick would offer more of an obstacle to the passage of electricity than a cable of silver of the same diameter, extending from the earth to Alpha Centauri. The variations of conducting-power from element to element are thus as fantastically great as the variations in scale from the world of common life to the world of interstellar spaces. The conductivities of the metals, however, are confined within a narrow fraction of this range; it is between the metals and the non-metals, and between one non-metallic element and another, that the leaps are surprisingly great.

In general, too, the resistance of a non-metallic element decreases as its temperature is raised; the curve of resistance versus temperature (I shall often call it *characteristic*, henceforward) slants downward, the derivative and the temperature-coefficient of resistance are negative. Near room-temperature this is the usual behavior, but not always over the entire accessible range; of some elements it is observed that the resistance declines less rapidly as the temperature is raised, the curve is concave upward; eventually the decline ceases, the resistance passes through a minimum value at a certain characteristic temperature, and thereafter increases with the temperature as the resistances of metals do. At least one element of the debatable class (germanium) exhibits a characteristic curve that slants upward instead of downward at room-temperatures; but when the curve is followed towards lower temperatures, it too is found to be concave upward with a minimum of resistance below $-100°$ C. This suggests that for all of the non-metals the resistance-temperature curve may be a loop bulging downward, with a minimum at a certain temperature that varies from element to element; on this generalization one of the contemporary theories is founded.

These rules can be illustrated by mentioning briefly the behavior of the non-metallic elements one by one. Beginning at the foot of the procession of elements, we pass over hydrogen (no data), lithium and beryllium (metals), and commence with boron. *Boron* has a very high resistance at room temperature, which drops a hundredfold when it is heated to 180° C. and ten-million-fold when it is raised to a red heat. On *carbon* a tremendous amount of work has been done, which unfortunately largely goes to show that the word "carbon" usually signifies a framework of carbon atoms packed with occluded gases, organic compounds, and impurities of divers kinds, which no known mode of treatment avails to expel entirely, although almost anything which is done to the substance alters its constitution enough to affect its resistance. (We shall later see that the situation with many of the metals is almost as bad.) Most of the experiments reveal a steady decline of resistance as the temperature is raised, whether the sample used be amorphous or crystalline (graphitic) and whatever its history; but Noyes recently traced several very concordant curves for several samples of graphite (all however of the same provenience) showing a minimum of resistance near 800° C. Diamonds have exceedingly high resistances, which fall when they are heated.

Passing over four gases and three metals, we come next to *silicon*; the curve traced by Koenigsberger shows the resistance descending as the temperature is increased, until at a certain critical temperature it leaps sharply upward; from the new high value it descends again as the silicon is further warmed, only to make a second upward jump; from this second maximum it drops steadily away, at least as far as the highest temperature attained in the experiment. This illustrates another perplexing property of some elements; they have several distinct "allotropic" forms, each of them more or less stable over a distinct range of temperature which may or may not overlap with the ranges of the others; each must be regarded, so far as its conducting-power is concerned, as a distinct element. In some instances the several forms of an element are vividly contrasted in appearance and in general behavior; such is the case with *phosphorus*, all of the forms of which have high resistances, but little is known about their trends with temperature. In other cases the anomalous changes of temperature with resistance are not accompanied by other striking changes; and there is a tendency to explain any deviation from an expected trend—such as, for example, a maximum in a resistance-temperature curve—by saying that the substance is gradually changing from one form into another.

Sulphur is the extreme case of high resistance. I know of no data for *scandium*, which is to be regretted, as there is some reason from general atomic theory for supposing that this element stands at a turning-point of the Periodic Table. *Titanium*, like silicon, has several modifications, in some of which the characteristic rises while in others it descends. *Germanium* has been studied lately by Bidwell; it is the element mentioned above which displays a minimum of resistance at −116° C. *Arsenic* resembles the metals. *Selenium* in the dark has an extremely high resistance; its character when illuminated is too much of a subject to be discussed in this place. *Zirconium* was found, at least by one observer, to display a minimum of resistance at 70° C., though in conductivity it compares favorably with the accepted metals. *Antimony*, although ranked among the metals, is usually to be found among the exceptions to any rules laid down for them; the same can be said of *bismuth*. *Tellurium* is an outstanding instance of an element with two modifications, and a sample taken at random is likely to be a mixture of them in unpredictable proportions, which change when it is heated; the characteristics are correspondingly crooked, and rarely agree. *Iodine* has a very high resistance.

Comparing the metals as a group with the non-metals, the first striking rule is that their conductivities are much higher and rather close together; from silver (the most conductive of all substances at room-temperature), to bismuth, the most resistant of the elements commonly accepted as metals, the conducting-power descends in the relatively small ratio of 75 to 1. The next and familiar rule is, that increasing temperature and increasing resistance always go together; the characteristic always slants upward to the right, the derivative and the temperature-coefficient of resistance are positive. It is customary to say that the resistance is always approximately proportional to the temperature, and that the temperature-coefficient of resistance always has approximately the one universal value, which is the value of the temperature-coefficient of volume of an ideal gas at constant pressure (or its temperature-coefficient of pressure at constant volume). That is to say, when the temperature of a piece of metal is increased by a given amount, its resistance increases approximately in the same proportion as would the pressure of a fixed quantity of an ideal gas, enclosed in a non-expanding container and raised from the same initial to the same final temperature as the metal. Were these statements literally true, all the resistance-temperature curves for metals would be straight lines intersecting the axis of temperatures at absolute zero. But the second statement cannot even be considered a good approximation, unless one is willing to confer the title "good approximation" on a numerical value .00365 which is expected to agree with a set of observed values which ranges upwards to .0058 (potassium) and .0063 (iron). (I refrain from giving a lower limit for the range, for a reason which will presently be made clear.) Also the characteristic curves are not rigorously straight lines, although it is not unreasonable to call some of them *approximately* straight, when one considers how wide is the interval of temperature over which some of them have been traced. In some cases a quadratic term added to the linear expression, resulting in a formula $R=R_o+at+bt,^2$ is sufficient to express the data. Usually, but not always, the extra coefficient b is positive; the characteristic is concave upward. "Usually but not always" is a phrase much in demand when one is laying down rules for conducting bodies. In this case metals of the platinum triad furnish the exceptions. In other instances cubic terms must be added to the formulæ, and in still others even these are inadequate. One of the longest characteristics ever traced, the one determined by Worthing and Forsythe for tungsten from 1400° to 3250° C., conforms to the equation $R = const.\ T^{1.2}$.

All these details about values of resistances and shapes of resistance-temperature curves are sedate and commonplace enough; but there is one quite extraordinary phenomenon in this field, one of the strange discontinuities which appear here and there in the theatre of nature and contribute more of dramatic interest to the spectacle than any amount of smooth correlations between continuous variables. Extensions of the characteristics downwards toward the absolute zero have to follow upon improvements in the art of producing and maintaining very low temperatures; and for the last twenty years the advances in this art have been made in the Cryogenic Laboratory of the University of Leyden, and there the curves have been extended downwards step by step as additional ranges of cold were made accessible. The temperatures down to 14° K. attained with liquefied hydrogen did not affect the resistances of metals in any very startling way, although the characteristics are generally more sharply curved there than at ordinary temperatures; but when with the aid of liquefied helium Kamerlingh Onnes penetrated to within five degrees of the absolute zero, something astonishing took place.

Kamerlingh Onnes had been experimenting with platinum wire, and he had found that over the interval of temperatures newly made available, the interval from 4.3° to 1.5° K. (a small range when measured in degrees, but a great one when considered in terms of the distance between its lower limit and the absolute zero) the resistance of the wire did not change. This he thought might mean that the proper resistance of the metal had become exceedingly small, leaving as the chief component of the observed resistance a term unaffected by temperature and due possibly to some such thing as discontinuities in the wire, for example between the platinum and bits of impurities mixed into it. To have a purer metal he replaced the platinum by repeatedly-distilled mercury. It was contained in a slender glass capillary tube, forming so fine a filament that the resistance at room-temperature was rather considerable; in one specified instance, 173 ohms. When he lowered this filament of mercury to the temperature of frozen helium, at a certain point the resistance suddenly vanished. Literally it vanished; the word is justified, for the value to which it had dropped was, if not truly zero, at all events not so much as one five-billionth of its value at room-temperature, and not so much as one ten-millionth of its value just before, at about 4.1° K., it suddenly disappeared. The mercury had altogether lost what had always seemed to be as inseparable a quality of matter as its inertia or its weight.

A few other elements were later found to share this property; tin, of which the resistance vanishes at 3.78°; lead, having its threshold-temperature at 7.2°; thallium, at 2.3°. Three of these four are consecutive in the procession of elements. Other elements were definitely found not to become "supra-conductive" within the accessible range: gold, cadmium, platinum, copper and iron. In the vicinity of the absolute zero each of these metals has a constant resistance independent of temperature. This as I mentioned was interpreted to mean that these metals, or at least these samples, behaved thus because they were impure—that impurities prevented the vanishing of resistance—but since mercury contaminated intentionally with gold or with cadmium was found to become supraconductive, and tin amalgam likewise, it has become necessary to save this interpretation, if at all, by assuming that in the five specified metals the impurities coalesce with the metal in some particular way. It is interesting to note that the threshold-temperature of tin amalgam lies above that of either of its components—at 4.29° K., to be compared with the 4.1° of mercury and the 3.78° of tin. These thresholds are not entirely independent of circumstances; they diminish when a large current-density is used, and also when a magnetic field is applied, possibly from the same reason in both cases.

A number of fantastic things could happen in a world from which electrical resistance had vanished, and one of them was actually realized by Kamerlingh Onnes within the compass of his helium-cooled chamber, when a current of three hundred and twenty amperes flowed for half-an-hour around and around a leaden ring with no applied E.M.F. whatever to maintain it, and did not lose as much as one one-hundredth of its initial strength. In another experiment a current of forty-nine amperes flowed for an hour around a coil of lead wire of a thousand turns, wound upon a brass tube, and did not lose quite one per cent. of the intensity with which it had been started by removing a magnet of which the field had interlaced the coil. At this rate it would have taken over four days for the current to drop to the $1/e$th part of its initial value, if the coil could have been kept cold so long. This corresponds to a resistance lower than 3.10^{-7} ohms; the resistance of the coil at room-temperature was 734 ohms. Few discoveries in physics can have been so exciting as this one, and further news from Leyden is awaited with keen anticipation. Until the present liquefied helium has been made nowhere else, but from now on the process will be carried on at Toronto also.

Pressure affects the resistance of a metal much less than temperature; that is to say, doubling the hydrostatic pressure upon a metal makes no perceptible difference with its resistance if the initial pressure is one atmosphere or less, and usually alters it only by a few per cent. if the intial pressure amounts to thousands of atmosphere. The art of applying enormous pressures under controllable conditions has been developed furthest by Bridgman in the Physical Laboratory of Harvard University, which through his work holds the same unique rank in high-pressure investigations as Kamerlingh Onnes' laboratory at Leyden in low-temperature research. The highest pressure which Bridgman has applied to metals during resistance-measurements exceeds 12,000 kg/cm^2, which amounts practically to twelve thousand atmospheres. No one has ever applied temperatures twelve thousand times as great as room-temperature, nor even four thousand times as great as the lowest accessible temperature; but when the pressure is altered in this enormous ratio the resistance changes only by a few per cent. The volume likewise changes by only a small fraction, which rather suggests that it is the change in closeness of packing of atoms rather than the creation of intense internal stresses which is responsible for the change in conductivity; however, there is no close correlation between relative change in volume and relative change in resistance; sometimes the two are of opposite signs. Usually, but not always, the conductivity increases with the pressure; as if squeezing the atoms together facilitated the flow of electricity across the metal. The rule applies to thirty-five elements, distributed as follows in the Periodic Table: in the first column, 11 Na, 19 K, 29 Cu, 47 Ag, 79 Au; second column, 12 Mg, 30 Zn, 48 Cd, 80 Hg; third, 13Al, 31 Ga, 49 In, 81 T1; fourth, 6C, 22 Ti, 40 Zr, 50 Sn, 82 Pb; fifth, 15 P, 33 As, 73 Ta; sixth, 42 Mo, 52 Te, 74 W, 92 U; seventh, 53 I; eighth, 26 Fe, 27 Co, 28 Ni, 45 Rh, 46 Pd, 77 Ir, 78 Pt; rare earths, 57 La, 60 Nd. Several of the non-metallic elements are found in the list. The exceptions are the five curiously assorted metals 3 lithium, 20 calcium, 38 strontium, 51 antimony, 83 bismuth—five elements distributed over three columns of the Periodic Table, each of which contains several other elements which conform to the rule. One modification of 55 caesium belongs under the rule, another among the exceptions. This illustrates how the behavior of metals in conducting electricity is liable to cut across the classification of the Periodic System, which controls nearly all of the properties of elements except those that vary uniformly from one element to the next all along the series.

As for the magnitude of the effect, the resistances of most metals are decreased through less than 10% by applying a pressure of ten thousand atmospheres, some only through one or two per cent.; but the decrease is 40% for sodium, 70% for potassium, 70% also for the "debatable" element tellurium, and 97% for black phosphorus; bismuth gains about 25% in resistance and antimony about 10%. The curves representing resistance as function of pressure are somewhat curved, but not greatly so; however the curvature frequently varies along the curve to such an extent that a two-constant formula is not sufficient to express the data. It is an interesting fact that the percentage by which a given pressure changes the resistance of a metal is approximately independent of its temperature, and consequently the percentage by which a given rise in temperature changes the resistance is approximately independent of the pressure; so that the combined effects of a pressure-change Δp and a temperature-change ΔT on a metal change its resistance from R_o to $R_o\ (1+a\Delta p)(1+b\Delta T)$.

Tension, which is equivalent to negative pressure acting along a particular direction (there is no way of applying a negative hydrostatic pressure) results in lengthening the metal along one direction, shortening it along all directions perpendicular to that one, and dilating it as a whole. Most of the information about what it does to electrical resistance is owed to Bridgman. Usually, but not always, tension increases the resistance to current-flow along the direction of the stress. The exceptions are bismuth and strontium. Comparing the data about the effects of pressure and of tension, we see that Bi and Sr are exceptions to the common rules for both, while Li, Ca and Sb are exceptions to the usual rule for pressure but not to the usual rule for tension. This helps to show why it is so difficult to set up a thoroughly satisfactory theory of conduction in metals.

By melting a substance its density can be altered without altering either its temperature or its pressure; of course, the balance of interatomic forces is also altered in some mysterious but very potent way. Melting a solid usually brings about a decrease in density; the solid sinks in the liquid; but there are exceptions (bismuth, antimony, gallium). The conductivity always changes in the same sense as the density; hence for most metals the solid is more conductive than the liquid, but bismuth, antimony, and gallium have greater resistances frozen than molten. This is one of the few rules in this field to which no exceptions have yet been discovered. The observed values of the ratio (resistance of liquid)/(resistance of solid), when tabulated and examined, show a tendency to cluster about values which are ratios of simple integers, such as 2:1, 1:3, 1:4. It would probably require a careful and expert analysis to show whether this tendency is more pronounced than a quite random distribution might reasonably be expected to display. Mercury has the highest ratio of all, 4:1.

Other agencies which are harder to measure or control may have distressingly great effects on the conductivity of a metal. The various metallurgical processes, annealing, cold-working and the rest, affect the resistance; sometimes the sign of the change can be explained by saying that the process has caused the many small crystals forming the metal to fuse into a few large ones, diminishing the resistance offered by the intercrystalline partitions; sometimes this explanation fails to work. Impurities may have a serious effect; for example Bridgman remarks of bismuth that "a fraction of a per cent. of lead or tin may change the temperature-coefficient from positive to negative and increase the specific resistance severalfold." Often impurities betray themselves by an abnormally low temperature-coefficient of the metal; this means that the absolute rate of increase is unusually small compared to the value of the resistance itself. This is so generally the case that a value of temperature-coefficient which (at 0° C.) is much below, say, .004 is usually taken to mean that the sample of metal under investigation is impure; and the "standard" values for individual metals set down in tables have often taken sudden jumps upward, when better-purified samples became available for measurements. For this reason I laid more stress, in a preceding paragraph, on the values which far exceed .00365 rather than the values which fall far below it. A metal contaminated by a small admixture of another metal may be regarded as the limiting case of an alloy. There is an enormous literature of the electrical behaviour of alloys, and some of the results can be extended to this limiting case. It is found, for example, that if two metals A and B form mixed crystals with one another, an alloy formed by mixing a small percentage or a fraction of one per cent of A into B, has a surprisingly greater resistance than B; and vice versa. The temperature-coefficient of the alloy is on the other hand much smaller than that of the metal, and may even be negative. Thus, although an alloy of this type may seem to be as thoroughgoing a metal as either of the pure elements of which it is made, it has a thoroughly anomalous electrical behaviour; and the alloys as a whole, instead of assisting us to understand conduction in metals, contribute generously to the already abundant supply of difficulties. It remains to be seen whether the measurements upon single crystals of metals, which are being published at a steadily-increasing rate, are going to clarify the situation or increase the perplexity.

While I have left unmentioned a large number of the phenomena which a theory of conduction must be required to explain, the few which I have described will give quite an adequate basis for beginning a discussion of some of the extant theories. It must be conceded at once that the situation is bad. Perhaps there is some set of assumptions or of postulates by which the whole chaotic crowd of phenomena can be unified into a harmonious system; but if so, no one has yet formulated it. The theories, such as they are, may be divided into two groups: theories in which the electrons are supposed to move freely within the atoms and be stopped when they reach an interspace, and theories in which the electrons are assumed to move freely within the interspaces and be stopped when they collide with atoms. Those of the first kind start out with the advantage of being better adapted to the usual effect of pressure on resistance; most metals become more conductive when compressed, as if conduction were assisted by squeezing the atoms closer together. Still the oldest, the best-known, and the most highly elaborated of all the theories belongs to the second kind. This is the one formally known as the electron theory of metallic conduction, or more briefly as the electron theory of metals, and quite commonly as the "classical" theory of conduction (it does not take an idea so long to become "classical" in physics as it does in the arts). Founded by Riecke and by Drude in the closing years of the last century, it was developed by Lorentz and has since been worked over by Planck, Wien, Bohr, and other savants of the first eminence. Its popularity is largely due, I suspect, to the fact that it can be formulated with great if specious exactness: that is to say, as soon as a few definite assumptions are made (such as the simple, if unplausible, assumptions that the atoms are big elastic spheres and the electrons little ones), numercial consequences can be calculated with any degree of precision. In this respect most of the competing theories are sadly defective. Two or three of the numerical deductions made from simple auxiliary assumptions have agreed rather well with experimental data; and they have contributed to the feeling that there must be some kernel of truth in the mathematics, even if not in the physics of the thing, although it breaks down in so many other comparisons with experiment.

Fundamentally the theory is very simple, and has not been helped to any great extent by the more sophisticated mathematics which its emendators have introduced into it. What is observed in electrical conduction is this: when a potential-difference is established across a piece of metal, the electrons do not fall freely clear across it and emerge at the positive end with all the kinetic energy which the P.D. should have communicated to them; they ooze gradually through the metal, heating it as they go along and emerging with no unusual amount of energy, as if they had rubbed along through the metal like heavy particles dropping at constant speed through a gas. "Rubbing along" being a concept foreign to the atomic scale, we have to interpret that each electron falls freely through a small distance, collides with something to which it gives up the energy acquired from the field during its fall, falls again across another short distance, gives up its new quota in another collision, and so forth from side to side of the metal. Furthermore the energy which it gives up at each stoppage must find its way directly or indirectly into the heat of the metal, i.e., into thermal agitation of its atoms. Representing by T the time-interval between two consecutive collisions, by E the fieldstrength in the metal, by e and m the charge and mass of the electron, by U the average kinetic energy acquired by the electron from the field in its free fall between two collisions, we have

$$U=\tfrac{1}{2}(eET/m)^2m. \tag{1}$$

If there are n electrons in unit cube of the metal, and each is stopped $1/T$ times in unit time, the rate at which heat appears in the unit cube is nU/T; but this rate is by definition the product of the conductivity σ by the square of the fieldstrength E, hence

$$\sigma=\tfrac{1}{2}\, ne^2T/m \tag{2}$$

The same equation (2) can be reached, if one prefers to think of conductivity as the ratio of current-density to fieldstrength, by considering that during each free fall, the field augments the speed of each electron in the direction of the field-vector by the amount eET/m, which on the average is lost at the collision terminating the fall; so that the result is as if the field imprinted a constant drift-speed equal to $\frac{1}{2}eE/m$ upon all the electrons. Multiplying by ne to get the current-density and dividing by E to get the conductivity, we arrive again at (2).

Equation (2) is the fundamental equation of the electron theory of conduction, and indeed of most of the other theories. Let us begin by trying the supposition that the electrons are at rest until the field is applied, and are brought to a full stop at each collision. Represent by l the average distance traversed between collisions. The proposed assumption leads to $T=\sqrt{2ml/eE}$. The conductivity therefore would depend on the fieldstrength, which would violate Ohm's law. Ohm's law being rigorously valid except under extreme conditions (Bridgman found the first slight deviations from it, in gold and silver, at current-densities of the order of 10^6 *amps/cm*^{2}) we have to discard the idea. The lesson is, that the electrons must be supposed to be normally in motion at speeds enormously greater than the speed imparted by the field during a free fall. Let u stand for the natural average speed of the electrons; we have $T=l/u$, and

$$\sigma=\tfrac{1}{2}ne^2l/mu, \tag{3}$$

provided always that $u \gg eET/m$.

This condition is abundantly fulfilled if we make the obvious and appealing assumption that the electrons are moving with the same average kinetic energy as atoms of a gas at the same temperature; in fact, if the free path l is no longer than the average distance between atom-centres, the deviations from Ohm's law should not appear even under such extreme circumstances as those of Bridgman's experiments. Making therefore this assumption, which in symbols is $\tfrac{1}{2}mu^2=\dfrac{3}{2}kT$, we find

$$\sigma=\tfrac{1}{2}\frac{e^2}{\sqrt{3km}}\;\frac{nl}{\sqrt{T}}. \tag{4}$$

Not much attention should be paid to the numerical factor, which would be slightly different if we should assume Maxwell's law of distribution for the velocities of the electrons; the essential factor is the last one, $nl/\sqrt{T}$. Examining (4) in the light of the fact that the conductivity of most metals decreases distinctly more rapidly than $1/\sqrt{T}$=in fact, as rapidly as $1/T$ or still more so—as the temperature increases, we see that the product nl will have to be supposed to vary with temperature. It seems natural to suppose that l depends altogether on the distance between adjacent atoms, which varies comparatively little with temperature, and anyway varies in the wrong direction for the purpose of the theory; so that the burden of accounting for the proportionality of σ to the first or a higher power of $1/T$ must be laid upon n.

Now it has occurred to a number of people that the free electrons are dissociated from the atoms, and the number of free electrons is given by the degree of dissociation, which in turn should vary with the temperature in a manner prescribed altogether by the amount of work necessary to remove an electron from an atom into the (presumed) interspace where it plays about freely. But we should certainly expect that this work would be positive, as it is for the extraction of electrons from free atoms; in which case the degree of dissociation and the number of free electrons should increase with temperature. The theory is therefore adapted to explain a resistance which decreases steadily with increasing temperature, as do the resistances of some non-metallic elements; it is adapted to explain a resistance which at first diminishes and then, as the temperature increases further, goes through a minimum and rises, for the decrease in the factor $l/\sqrt{T}$ finally predominates over the increase in the factor n; it is not adapted to explain a resistance increasing with temperature over the whole range, as do those of the metals. One might assume that the work of extracting an electron from an atom inside the metal is negative. This is essentially the alternative embraced by Waterman, who postulates that the work in question is a function of temperature, of the form $W=W_o-cT$, $c>0$. For metals W_o is to be chosen negative or zero, so that W shall be negative throughout; for non-metallic elements W_o is to be given some positive value, so that W shall change in sign at some point in the temperature-range. This unusual theory must be judged by its effectiveness; that it should reduce conduction in all elements, metallic and non-metallic alike, to a phenomenon of a single type is a feature appealing strongly in its favor; but Noyes' curves of resistance versus temperature for graphite did not agree with its demands in a satisfactory manner.

The assumption underlying (4) has however involved us in a collateral difficulty. If we believe that the n free electrons per cc. of the metal have an average energy $\frac{3}{2}kT$ and a total kinetic energy $\frac{3}{2}nkT$, we are certainly forced to admit that when the unit cube of metal is heated through 1° the electrons must take their share $\frac{3}{2}nk$ of the heat imparted to it; but the specific heat of most metals is such that it seems that the atoms must take it all and leave none over for the electrons. If we evade this difficulty by assuming n to be quite small compared with the number of atoms per cc., a few per cent. of it or less, we lose certain numerical agreements which will be mentioned later, and we have also to make l quite large, amounting to several times the distance between adjacent atoms;

yet all the tendency of modern atomic theory is to make it seem likely that the atoms fill almost the whole space within the metal.

Another way to avoid the difficulty with the specific heats consists in assuming that the high natural speed with which the electrons fly about is altogether independent of temperature; the burden of making σ as expressed in (3) vary in the proper manner with temperature is then laid upon l, which, Wien suggested, should be supposed to vary inversely as the amplitude of vibration of the atoms—that is, a free electron collides with an atom only if and when it is in vibration, and the chance of a collision increases with the amplitude of the vibration. The variation of resistance with pressure may then be explained, so far as the usual sign goes, by saying that when an ordinary metal is compressed the amplitude of oscillation of its atoms diminishes, though the temperature remain the same; the frequency of oscillation must then vary inversely as the amplitude, to keep the average energy of oscillation constant; there is some reason for expecting this to happen. Bridgman's theory somewhat resembles this one, except that the electrons are supposed to glide through the atoms and collide with the gaps; gaps between atoms are comparatively unusual, and occur chiefly when two atoms are vibrating with great amplitudes in opposite senses, so that the variation of conductivity with pressure again has the proper sign. But to explain the behavior of the three metals of which the resistance increases with pressure and with tension, Bridgman went back to the idea that in these the electrons glide through the interspaces.

As I have given only the phenomena of conduction which the electron-theory explains with difficulty, I must in justice mention the ones on which its reputation chiefly depends. In the first place it is a theory of thermal conduction as well as electrical conduction; the electrons in the hotter part of a metal maintained at an uneven temperature are assumed to have a greater average energy than the electrons in the cooler part, so that they diffuse down the temperature-gradient and realize a convection-current of heat. The theory leads to as definite a numerical value of the one conductivity as of the other, and the ratio of electrical to thermal conductivity is predicted as

$$\frac{\lambda}{\sigma}=2\left(\frac{k}{e}\right)^2.T, \tag{5}$$

a universal constant for all metals, multiplied into the absolute temperature, and devoid of the quantities n and l which have caused us so much trouble. This is one of the predictions which is nearly enough true to be impressive; the ratio $\lambda/\sigma T$ does indeed vary surprisingly little over a wide range of metals at room-temperature and over a fairly wide range of temperatures for each of many metals. It is usually somewhat larger than the predicted value (5); but this can be conveniently explained by saying that there must be an additional mechanism for transmitting heat, something in the nature of the elasticity of the substance, which superposes its conducting-power upon the conducting-power of the electrons, and so inflates the numerator of the ratio in (5). The reason for supposing such an extra mechanism is primarily that there must be some such mechanism to perform the thermal conduction in substances which are electrical insulators. No element conducts heat as badly as sulphur and boron conduct electricity; and if we imagine a special elastic mechanism for conducting heat in boron and sulphur, we can hardly deny it to copper and silver. Bridgman found that for six metals out of eleven tested, the thermal conductivity decreased when high pressure was applied, although the electrical conductivity increased. We must hope to find an explanation for this anomaly in the behaviour of the elastic mechanism; likewise an explanation for the deviations from (5) which occur at high and at low temperatures. In theories such as the one mentioned over Wien's name in the last paragraph, in which the average *vis viva* of the electrons is supposed not to vary from a hotter place in a metal to a cooler place, we have to lay the entire burden of thermal conduction upon the elastic mechanism. This makes it difficult to explain the universal relation (5).

Another striking feature of the theory is that Lorentz succeeded in deducing the Rayleigh-Jeans radiation-law from it. He obtained from it an expression for E, the radiant emissivity of a thin stratum of metal, as a function of temperature T of the metal and wavelength λ of the radiation; another for A, the absorbing-power of the metal, likewise a function of T and λ; divided the first by the second, and obtained a definite quotient. By Kirchhoff's thermodynamic laws, E/A is equal to E_o, the radiant emissivity of a perfectly black body. The expression deduced by Rayleigh and by Jeans for E_o and the expression deduced by Lorentz for E/A are identical. Lorentz assumed that the collisions of the electrons with the atoms (or whatever it is they collide with) are very short in duration compared with the intervals of free unaccelerated flight from one collision to the next, and that the speeds of the electrons are distributed according to Maxwell's law about the mean value corresponding to the mean energy $3kT/2$. He also made certain assumptions which restrict the validity of his expression for E/A to radiations of great wavelength; the Rayleigh-Jeans expression for E_o is restricted in exactly the same way. At least as much, it seems, should be demanded from any theory of conduction offered in competition with the "classical" one.

The conception of free electrons in metals also gives a beautiful qualitative explanation of the thermoelectric effects, although unfortunately it does not do very well as a quantitative theory. If in two metals at a certain temperature the densities of free electrons are different—n_1 free electrons per cc. in one and n_2 in the other—and these two metals are brought into contact with one another, electrons will flow from the one where the density is greater into the one where it is less; and this flow will continue until arrested by a counter-electromotive-force V, of which the equilibrium-value can be shown, in any one of a variety of ways, to be

$$V=\frac{kT}{e}ln(n_1/n_2)$$

Such an electromotive force would account for the Peltier effect; and conversely, if the theory were correct, measurements of the Peltier effect between two metals at a given temperature and pressure would give the ratio between the densities of free electrons in the two metals under the specified conditions. Such data, combined with data on conductivity interpreted by such an equation as (4), should give information about the free paths l_1 and l_2 in the metals. The Thomson effect is more difficult to deal with, as thermal equilibrium does not prevail; however it can be seen that there will be a counter E.M.F. in an unevenly-heated metal. Measurements on the Peltier and Thomson coefficients for many metals, over wide ranges of temperature and pressure, would be very valuable; but they are so extremely hard to make even under the best of conditions, that the outlook for obtaining a really extensive set is unpromising. Possibly there is a better chance with the indirect method (determining the first and second derivatives of the curve of thermal electromotive force versus temperature). Such data of the Thomson effect as exist are not helpful to the simple theory.

Another phenomenon which lends itself very readily to explanation by the theory, and so contributes a certain amount of support to it, is the thermionic effect—the spontaneous outflow of electrons through the surfaces of hot metals. (But carbon likewise exhibits it very efficiently, and we must beware of formulating any theory of it which reposes on specific properties of metals not shared by carbon!) To interpret the thermionic effect only one new feature need be added to the theory, and this a feature which in fact was all the time latent in it—the idea that there is a certain fixed potential-difference between the interior of a metal and the region outside of it, resulting in a potential-drop localized in a thin stratum at the surface, which an electron within the metal must surmount in order to escape from the metal into a contiguous vacuum. Such a potential-drop would for instance result from a "double layer" along the surface of the metal, a sheet of positive charges within and a sheet of negative charges opposite, parallel, and close to the positive sheet on the outside. It has been pointed out that, since probably half of the orbital electrons belonging to the atoms at the frontier of a metal lie outside the plane containing the nuclei of these atoms, they with the nuclei constitute a sort of double-layer; it has also been suggested that after a certain number of electrons issue from the metal, they are held as an electron-atmosphere above it by the forces due to the distribution of residual positive charge within the metal (Kelvin's electrical-image conception), and the electron-atmosphere with the positive surface-charge together form a double-layer. However we may conceive this double-layer, it is obvious that if we postulate free electrons within the metal, we must also postulate a barrier in the shape of an opposing potential-drop between the metal and the exterior world to keep the electrons from wandering away.

Designate this potential-drop by b, so that eb is the energy which an electron must give up in traversing it from inside to outside. Assume further (disregarding the old specific-heat difficulty) that the velocities of the electrons inside the metal are distributed isotropically in direction, and according to Maxwell's distribution-law in speed, with the mean kinetic energy $\frac{3}{2}kT$ appropriate to the temperature T of the metal. Imagine the metal surface to occupy the plane $x=0$, metal to the left and vacuum to the right. Consider the electrons which come from within the metal and strike unit area of the boundary in unit time; those of them which have velocities of which the x-component lies between u and $u+du$ are in number equal to

$$dI=\frac{nu}{\sqrt{2\pi kT/m}}e^{-\frac{mu^2}{2kT}}du, \tag{6}$$

n meaning as heretofore the number of electrons per unit volume of metal. The total number which strike unit area of the boundary from within is equal to the integral of this expression from $u=0$ to $u=\infty$, which is

$$I_o=n\sqrt{kT/2\pi m}. \tag{7}$$

Those which escape are those for which $\frac{1}{2}mu^2$ exceeds eb; we obtain the number of them by integrating (6) from $u=\sqrt{2eb/m}$ to $u=\infty$, and find

$$I_e = n\sqrt{kT/2\pi m}\, e^{-eb/kT}. \tag{8}$$

This, supposing n and b to be independent of temperature, is Richardson's well-known formula for the saturation-current from a hot body as function of temperature. All of the multitudinous observations agree with it; but this does not mean so much as might be thought, for the experts inform us that all the data, no matter how accurately taken, would agree quite as well with a formula in which T, or T^2, or even T^0, stood in the place of the factor $T^{1/2}$ by which the exponential is multiplied. Incidentally this would permit us to make n vary as some small power of temperature, such as the inverse square root, if we chose to make the resistance-temperature relation in (4) agree with experiment at such a price. Or if we assume n independent of temperature, we can calculate it from measurements on thermionic saturation-currents. The measurements usually give for n values of the order of magnitude of the number of atoms per unit volume.

What is more definitely significant is, that the velocities of the emerging electrons are actually distributed in a manner compatible with the assumptions made. Let us enquire how many of the electrons issuing from unit area of the metal have velocities of which the x-component lies between u and $u+du$. These are the very same electrons which struck the surface from within, having velocities of which the x-component lay between u' and $u'+du'$; u' and du' being related to u and $u+du$ by the equations:

$$\tfrac{1}{2}mu^2 + eb = \tfrac{1}{2}m(u')^2, \quad u'du' = udu. \tag{9}$$

The number of these electrons is by (6)

$$dI' = \frac{nu'}{\sqrt{2\pi kT/m}}\, e^{-\frac{(mu')^2}{2kT}}\, du', \tag{10}$$

which by virtue of the relations (9) reduces to

$$e^{-\frac{eb}{kT}} \cdot \frac{nu}{\sqrt{2\pi kT/m}}\, e^{-\frac{mu^2}{2kT}}\, du, \tag{11}$$

which is identical with (6) except for a constant factor; which means in turn that the distribution-function of the emerging electrons is identical with the distribution-function of the internal electrons, being in fact the Maxwell distribution-function with the same mean kinetic energy $\frac{3}{2}kT$. The argument as given proves the point only for the distribution in the velocity-component u; but the distribution-functions in v and w, the velocity-components parallel to the boundary of the metal, are unaffected by the double-layer, since v and w for any particular electron are unaffected by the passage through it; and since it is the essential feature of the Maxwell distribution-law that the distributions in v and w are identical for each and every value of u, the conclusion follows as stated. Nevertheless it does sound paradoxical.

This conclusion has been verified repeatedly by experiment. Richardson began by simulating the simple mathematical conditions of infinite plane electrodes as closely as practicable; he inserted a small flat incandescent surface in an aperture in the middle of a large flat cold plate, charged the two to the same potential, and placed opposite and parallel to them a large flat collecting-electrode. Charging this latter to various potentials V inferior to the potential of the emitting surface, he plotted the electron-current which it received as function of V; this is the distribution-function of the speed u of equation (6) and the following equations translated into terms of the corresponding kinetic energy $\frac{1}{2}mu^2$ as independent variable. To ascertain the distribution-functions in v and w he isolated a small area of the collecing-electrode, moved it to and fro in a plane parallel to the plane of the emitting surface, and measured the current into it in its various positions. Many measurements have since been made upon the currents into cylindrical collectors from hot wires stretched along the axes of the cylinders; it is somewhat more difficult to write out the formula for the expected relation between current and retarding-potential, but the experimental conditions are much more under the experimenter's control. All these investigations have confirmed the theorem, except a single discordant one which was later explained away; the strongest verification is furnished by the experiments of Germer, whose precautions of preparation and accuracy of measurements far surpassed everything that had gone before.

The evidence thus is quite favorable to the idea of an electron-gas within the metal with its electrons moving with velocities as prescribed by Maxwell's distribution-law, and kept from diffusing away by a double-layer covering the surface. Other evidence for the existence of a double-layer is furnished by the photoelectric effect and by the existence of contact-potential-differences. When light of frequency ν falls upon a metal, electrons emerge from it with velocities which are distributed in a manner quite distinct from Maxwell's distribution and have nothing to do with the temperature of the metal. The kinetic energies of some of the electrons attain a certain upper limit W_m, but none surpasses it; W_m is a linear function of ν given by the equation

$$W_m = h\nu - P, \tag{12}$$

h being Planck's constant, P a positive constant characteristic of the metal. This is an exceedingly strong intimation that each of the emerging electrons, while still inside the metal, suddenly absorbed a quantum of energy $h\nu$ from the light and departed with it, giving up a fixed quantity P in passing through the surface. (Those which issue with energies clearly less than W_m can be supposed to have started distinctly beneath the surface and to have lost additional energy in struggling through the metal to it). Translating P into potential-drop, we see that it represents the potential-difference or the "strength" of the surface double layer. It may be determined by measuring W_m for light of various frequencies, plotting it against frequency, and extrapolating the resulting straight line to its intersection with the axis of frequencies. Or it may, in principle, be determined by plotting the photoelectric current as a function of frequency, and extrapolating the curve to its intersection with the axis of frequencies, where no electrons escape and the photosensitiveness ceases; but curves are not so easy to extrapolate as straight lines, and there are some anomalous results which are still unexplained.

It would seem an easy matter to measure the strength of the double-layer by both photoelectric and thermionic methods upon a single substance. But it is rather difficult; for one reason, the substances for which the photoelectric currents are easy to produce and measure are precisely the metals upon which good thermionic measurements are next to impossible, and vice versa. The best photoelectric measurements have been made upon the alkali metals, which are very sensitive to visible light; but they cannot be formed into wires, and volatilize furiously when heated enough to produce an important thermionic effect, filling the evacuated tube with dense vapors which ruin the accuracy of the measurements. The best thermionic measurements have been made upon platinum and tungsten, which are not sensitive at all to visible light, and begin to be sensitive far out in the ultraviolet where experiments with radiation are difficult. Furthermore there is the capital difficulty that the photoelectric measurements must be confined to temperatures where the thermionic current is imperceptible; if one were to irradiate an incandescent tungsten filament the extra current of photoelectrons would be too small to notice. If we assume outright that P does not vary greatly from room-temperature up to the temperatures of incandescence, and therefore compare photoelectric data upon cool metals with thermionic data upon the same metals when hot, we find that there is a fairly good agreement. Values of the thermionic constant b between 4 and 5 volts correspond to photoelectric sensitiveness commencing between 3,100 and 2,500 Angstrom units, and this correctly describes the behavior of several of the heavy high-melting-point metals; photoelectric sensitiveness extending well up into the visible spectrum, such as the alkali metals display, corresponds to values of P/e of the order of 2 volts and lower, and such values are indicated by the thermionic experiments made upon sodium and potassium by Richardson under the inevitably bad conditions.

Contact-potential-difference, one of the longest known of all electrical phenomena—Volta discovered it—agrees admirably with this interpretation of the photoelectric constant P. Imagine that we have pieces of two metals, potassium and silver for example, which are drawn out and welded together at one end, and at their other ends are spread out into plates and face one another across a vacuous space. We know that the opposing faces behave as if they were at essentially different potentials, the potential-difference V between them being characteristic of the two metals and independent of the size or separation of the opposing faces. Yet this potential-difference V is not equal to, is indeed usually much greater than the potential-difference between the interiors of the metal across the welded joint, which is deduced from the Peltier effect. The only way to resolve the contradiction is to assume that it is the region just outside the potassium which differs by V from the region just outside the silver; the metals themselves are at nearly the same potential, but there is a double-layer at the surface of each which establishes a fixed potential-drop between it and the vacuum. Representing by P_1/e and by P_2/e the voltage-drops at these two double-layers, by M the potential-difference between the interiors of the metals as inferred from the Peltier effect, by V the potential-difference between the regions just outside the metals which we identify with the contact potential difference, we find

$$P_2/e - P_1/e = V + M \tag{13}$$

in which M is so small compared with the other terms that henceforth we will leave it out.

Now imagine that light of a high frequency ν_o falls upon the potassium; it elicits electrons of which the maximum energy at emergence is $h\nu_o - P_1$; these highest-speed electrons arrive at the silver plate with energy $(h\nu_o - P_1/e - V)$, having had to overcome the additional potential-drop V in passing from the region just outside the potassium to the region just outside the silver. (The reader can make the changes in language required if V happens to be of the sign corresponding to a potential-rise). From (13) we see that this energy of arrival is equal to $(h\nu_o$—$P_2/e)$—an expression from which P_1, the only quantity characterizing the irradiated metal, has fallen out! Therefore the electrons arrive at the silver plate with the same maximum speed, whether the irradiated metal be potassium, sodium, silver, or any other metal! (unless we hit upon a metal for which $h\nu_o < P_1/e$, in which case we shall never get any at all).

This experiment is usually performed by putting a battery between the silver and the irradiated metal, and adjusting its E.M.F. until the fastest electrons are just turned back before reaching the silver; this is known as "determining the stopping potential." If our interpretation of contact-potential-difference is correct, the stopping-potential must be independent of the irradiated metal, and depend only on the material of which the collecting-electrode is made; further, the difference between the stopping-potentials observed with two different metals as collecting-electrodes should be equal to their contact potential difference. These predictions have been verified in several sets of experiments, notably by Richardson and Compton. Millikan developed the interesting theoretical consequences which they suggest. There should be similar relations involving thermionic currents; observations confirming them have been made, but not so extensively published; they are more difficult to make with accuracy because the thermionic electrons have no definite recognizable maximum velocity.

We seem to have marshalled a formidable amount of evidence in favor of the electron-theory of conduction with the associated idea of the surface double-layer. Yet it would be misleading not to point out that an equation quite as satisfactory as (8) in representing the thermionic current as function of temperature can be deduced by reasoning in an entirely different fashion from entirely different postulates. This, the thermodynamical method of speculating about the thermionic effect, was originated by H. A. Wilson; it consists essentially in assuming a thoroughgoing analogy between the outflow of electrons from a hot metal and the evaporation of molecules from a solid or a liquid. We know that if an evacuated chamber is partly filled with liquid water or solid $CaCO_3$, the remaining space inside the chamber is quickly pervaded with H_2O or CO_2 molecules composing a gas, its pressure and density being determined absolutely by the temperature T. We infer that if an evacuated chamber, with its walls made of some insulating substance, contains a piece of metal and is heated to a high temperature, the whole evacuated space will be pervaded with electrons composing a gas, its pressure p and density n being determined absolutely by the temperature of the system, T. We must assume that the electron-gas outside the metal conforms to the ideal-gas law

$$p = nkT \tag{14}$$

and we shall also presently assume that its specific heats have the values characteristic of monatomic ideal gases,

$$C_v = \frac{3}{2}Nk, \qquad C_p = \frac{5}{2}Nk. \tag{15}$$

I use n to represent the number of electrons per unit volume of the gas, as the number within the metal no longer enters in any way into the reasoning; N to represent the number in a gramme-molecule (Avogadro's constant). These are the only assumptions which involve a kinetic theory in any way.

Imagine now a wire of which one end projects into an evacuated chamber of the sort described, maintained at T, and the other into another such chamber maintained at $T+dT$. We consider a process which consists of increasing the volume of the first chamber by just enough to require N additional electrons to come out of the wire to fill the additional space, and simultaneously decreasing the volume of the second chamber by just enough to crowd N electrons into the wire; so that in effect N electrons are transferred from the one chamber to the other through a wire of which the two ends are at temperatures $T+dT$ and T. This process will be carried on reversibly. Designate by L the heat which must be imparted to the metal at T, to remove one electron from it under the circumstances of the experiment; by sdT the heat which is absorbed when one electron is transferred through the metal from a point where the temperature is T to a point where the temperature is $T+dT$. s is the coefficient of the Thomson effect, referred to a single electron instead of a coulomb. L contains a term kT, which corresponds to the mechanical work done in forcing back the walls of the chamber to make place for the evaporated electron-gas. Subtracting it we obtain $(L-kT)$, to be called $e\phi$, as the actual energy expended in putting the electron across the boundary of the metal.[*]

In the process which I have just described, the *input of heat* consists of the following terms: NL which goes to extract the N electrons from the metal in the first chamber, $-N\left(L+\frac{dL}{dT}dT\right)$ which is liberated when N electrons condense into the metal in the second chamber, and $-NsdT$ which is absorbed by the electrons in travelling through the wire. The *output of work* is NkT during the expansion of the first chamber, $-NkT-NkdT$ during the contraction of the second chamber. The *input of entropy* is NL/T during the evaporation in the first chamber, $-N\left(L/T+\frac{d(L/T)}{dT}\right)dT$ during the condensation in the second chamber, and $(-Ns/T)dT$ during the flow of electrons through the wire.

We now complete the cycle by changing the pressure and temperature of the gramme-molecule of electron-gas in the first chamber from p, T to $p+dp$, $T+dT$, after which it becomes equivalent with the gramme-molecule in the second chamber at the beginning of the process. Calculated in the usual way—isothermal contraction at T from p to $p+dp$, isobaric expansion at $p+dp$ from T to $T+dT$—we find: *input of heat*, $\frac{5}{2}NkdT-NkT[d(ln\ p)/dT]dT$; *output of work*, $NkdT-NkT[d(ln\ p)/dT]dT$; *input of entropy*, $\frac{5}{2}(Nk/T)dT-Nk[d(ln\ p)/dT]dT$.

The two processes together constitute a complete reversible cycle. We therefore equate the sum of the inputs of entropy to zero, and obtain:

$$\frac{e\phi}{T}-e\frac{d\phi}{dT}-s+\frac{5}{2}k-kT\frac{d(ln\ p)}{dT}=0. \tag{16}$$

and equate the difference of the inputs of heat and the outputs of work to zero, which gives:

$$-e\frac{d\phi}{dT}-s+\frac{3}{2}k=0 \tag{17}$$

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[*] This definition suggests a thermal method of measuring L, which has several times been put into practice. The experiments are difficult and the data must be corrected for many influences, but the best results indicate that $(L-kT)$ is approximately equal to eb of (8). The data of Darisson and Germer indicate a slight difference, which may be an important test of suggested theories of conduction.

and combine the equations into

$$\frac{e\phi}{T}+k=kT\frac{d(ln p)}{dT} \tag{18}$$

which integrated, yields

$$p=ATe^{\int\frac{e\phi}{kT^2}dT}. \tag{19}$$

We still have to make the bridge between this formula, which relates to the pressure of the electron-gas in equilibrium with the metal, and the quantity actually observed, which is the saturation-current out of the metal surface in an accelerating field. In the equilibrium-state, the number of electrons which issue from the metal is equal to the number which, coming from the external electron-gas, strike its boundary and do not rebound. This is indisputable; to make it useful we have to make two new assumptions: one, that the number of electrons which issue from the metal is the same in an accelerating field as in the equilibrium-state; the other, that no electrons rebound from the surface. The first assumption had to be made in the preceding deduction—that is, we had to assume tacitly that the uncompensated outflow of electrons through the surface of the metal did not appreciably distort the Maxwell distribution within; the second is a drawback peculiar to the thermodynamic method. Accepting these two assumptions along with all their predecessors, we finally reach the expression for the number of electrons emitted per unit area per unit time from the surface of the hot metal:

$$I=CT^{\frac{1}{2}}e^{\int\frac{e\phi}{kT^2}dT}. \tag{20}$$

This is the equation for the thermionic saturation-current attained by the thermodynamical reasoning.

Let us finally try some hypotheses about the variation of ϕ with temperature: for a first one, the hypothesis ϕ=constant. The general equation becomes

$$I=CT^{\frac{1}{2}}e^{-\frac{e\phi_o}{kT}}, \tag{21}$$

which is perfectly identical with (8) which was deduced from the electron-theory with the additional assumption of a double-layer independent of temperature. We cannot however freely make an assumption like this, for our equation (17) shows that an assumption about $d\phi/dT$ implies, and conversely is implied by, an assumption about the value of the Thomson coefficient s. In making ϕ independent of temperature we in effect assumed that the Thomson coefficient has the value $s=\frac{3}{2}k$ (per electron), which happens to be precisely the value demanded (and vainly demanded) by the electron-theory of conduction. If on the other hand we choose to accept from the experiments the fact that s is extremely small compared to $\frac{3}{2}k$, the equation (16) compels us to set

$$\phi=\frac{3}{2}kT/e+\phi_o. \tag{22}$$

Inserting this into (19) we obtain

$$I=CT^2e^{-\frac{e\phi_o}{kT}}, \tag{23}$$

which is commonly known as the T^2-law, and is at the moment the favorite way of expressing the variation of thermionic current with temperature. As I said earlier, experiment is thus far powerless to distinguish between (8), (20) and (22).

This brief and superficial sketch of the thermodynamic argument is meant partly to familiarize the reader with the T^2 formula, and partly to show that the observations upon the dependence of thermionic current on temperature do not necessarily sustain the particular type of theory which has figured most in these pages, as against its rivals actual or conceivable. Of course it would be unjustifiable to say that any argument of the thermodynamical type is *ipso facto* stronger than any argument based on a physical model. It may be true that the laws of thermodynamics are valid everywhere without exception; but it is certainly true that in any particular case it is extremely difficult to feel sure just how they should be applied to arrive at absolutely binding conclusions. In this case, for instance, we have assumed as both possible and reversible a process which no one has ever carried through, and no one, in all likelihood, ever will; and in the course of analyzing the transfers of energy between the system and the external world in this imagined process, we have classified some as transfers of heat and some as transfers of mechanical work, and possibly ignored yet others, so that the analysis requires careful thought and has in fact been made in different ways by different authorities. There is for example the problem of the allowance to be made for work done in transferring the electrons from place to place against electromotive forces, which might or might not be *nil* when summed around the complete cycle; H. A.

Wilson has recently made a specific assumption regarding these. For still further subtleties Bridgman's theoretical articles may be consulted. I must however add that an extension of the thermodynamical argument, with the assistance of Nernst's "third law of thermodynamics," leads to the conclusion that the constant C of equation (23) should have for all elements, if not indeed for all substances, the same universal value, calculable in terms of certain universal constants. There is some evidence that this may be true for emission from pure elements. Were it so, the result would be of fundamental importance; but another article almost as long as this one would be required to explain it properly.

The general tone and character of this article will probably leave the final impression that the electrical behaviour of solids is an utterly confused and chaotic department of physics, a hopeless entanglement of incongruous rules diversified by numberless exceptions. I fear that this impression—except perhaps for the hopelessness of the situation—is substantially the correct one. In fact this presentation has put the state of affairs in rather too favorable a light, for I have passed over a number of the perplexities. I have scarcely mentioned the thermoelectric effects, or spoken of the complexities of the photoelectric effect, or of the emission of electrons from metals which are bombarded by other electrons or by ionized atoms; and I have not mentioned at all the galvanomagnetic and thermomagnetic effects, the most baffling and bewildering of all. In fact it seems only too probable that if one should succeed in erecting a theory by which all the phenomena I have described could be brought into one coherent system, some galvanomagnetic effect would be lying in wait for it to bring it to the dust. Clairaut is said to have been saddened by feeling that Newton had discovered all the laws of celestial mechanics, leaving nothing for men born after him to do except to improve the methods of calculation. Ambitious students of physics who, through too exclusive a study of the radiations from atoms, may have come to feel in the same way about Bohr, should find consolation in contemplating the present status of the Theory of Conduction in Solids.

LITERATURE

The chief recent compilation of data upon conduction in solids is Koenigsberger's article in Graetz' *Handbuch der Elektrizitat.* K. Baedeker wrote an excellent short account of the data and the theories, entitled *Die elektrischen Erscheinungen in metallischen Leitern*, which although published in 1911 is not yet superseded. Bidwell's paper on germanium is in Phys. Rev. (2) *19*, pp. 447–455 (1922); Noyes' article on carbon in Phys. Rev. (2) *24*, pp. 190–199 (1924). The investigations on supraconductivity are reported chiefly in the *Leyden Communications*; Crommelin

has given a comprehensive account of them in Phys. ZS. *21* (1920), with a bibliography of all of the work; two or three subsequent communications are reviewed in Science Abstracts. Bridgman's work on the effect of pressure and of tension on the electrical and thermal conductivities of the elements is printed chiefly in the *Proceedings of the American Academy of Arts and Sciences* from 1917 onward, with occasional announcements in the Physical Review, where also his theoretical papers are published (Phys. Rev. *14*, pp. 306–347 (1919); *17*, pp. 161–195 (1921) and *19*, pp. 114–134 (1922). For the effect of melting, consult Bridgman's papers, and one by von Hauer, in Ann. d. Phys. *51*, pp. 189–219 (1916).

The "classical" theory of conduction is presented in Lorentz' book *The Theory of Electrons*, which bears his signature as of 1915. Bohr wrote a dissertation upon it which is highly praised by those who have succeeded in reading it in the Danish. Wien's and Planck's modifications of it are published in the *Sitzungsberichte* of the Berlin Academy for 1912 and 1913. In the Philosophical Magazine of 1915 there are a number of articles on the theory by G. H. Livens, like Baedeker a victim of the war. The conception of quantity of free electrons determined by dissociation of atoms is presented by Koenigsberger in Ann. d. Phys. *32*, pp. 170–230 (1910) and Waterman's extension of it is in Phys. Rev. *22*, pp. 259–270 (1923). Some chapters in J. J. Thomson's *Corpuscular Theory of Matter* deal with the theories; in an article in Phil. Mag. *29* (1915) he offers a theory involving an attempt on supra-conductivity, which the others do not touch.

The field of thermionics is thoroughly covered in Richardson's *Emission of Electricity from Hot Bodies* (2d edition, 1921). Subsequent theoretical papers by Richardson are in Proc. Roy. Soc. *A105*, pp. 387–405 (1924) and Proc. Phys. Soc., London, *36*, pp. 383–399 (1924), and one by H. A. Wilson on what I have called the "thermodynamical argument" in Phys. Rev. (2) *24*, pp. 38–48 (1924). For various interpretations of the surface double-layers see Debye, Ann. d. Phys. *33*, pp. 440–489 (1910); Schottky, ZS. f. Phys. *14*, pp. 63–106 (1923); and Frenkel, Phil. Mag. 33, pp.297–322 (1917). Germer's investigation of the distribution-in-energy of thermionic electrons is briefly reported in Science, *42*, 392 (1923), and a fuller account is to be published; Davisson and Germer's determination of L in Phys. Rev. *20*, pp. 300–330 (1922). For the photoelectric measurements establishing equation (12), consult Millikan, Phys. Rev. *7*, pp. 355–388 (1916); for the relation between values of P and contact-potential-difference consult Page, Am. Journ. Sci. *36*, pp. 501–508 (1913) and Millikan, Phys. Rev. *7*, pp. 18–32 (1916). Values of the thermionic constant b are tabulated in Richardson's book and in Dushman's article, Phys. Rev. (2) *21*, pp. 623–636 (1923). Values of the photoelectric constant P are tabulated by Kirchner, Phys. ZS. *25*, pp. 303–306 (1924) and by Hamer (Journ. Opt. Soc. *9*, pp. 251–257 (1924). For the arguments that the constant C of equation (23) is a universal constant, consult the references given by Dushman (*l. c. supra*) and Richardson, Phys. Rev. (2) *23*, pp. 153–155 (1924); for the data, Dushman in Phys. Rev. (2) *23*, p. 156 (1924).