THERMIONIC EMISSION

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BY

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PREFACE.

If one compares the present state of our knowledge of thermionic phenomena with that of ten to fifteen years ago, one cannot fail to be impressed by the progress that has been achieved in the intervening period. On the experimental side, thanks mainly to the employment of modern high-vacuum technique, there has been a considerable increase in the quantity and accuracy of the data available. On the theoretical side there have been developments of a quite fundamental nature. The most important of these have been due, on the one hand, to the replacement of the classical by the quantum statistics in the theory of electrons in metals and in a vacuum, and on the other, to the application to the thermionic problem of the wave-mechanical theory of the transmission of electrons through potential barriers. Modern thermionic theory has been found to be in very satisfactory agreement with the great bulk of acceptable experimental data.

Not only specialists in the field of thermionics, but also to some extent students of physics generally, have now for some time felt the need for a comprehensive work on the subject which gives an account, from the modern viewpoint, both of the older and of the more recent developments. The present book is an attempt to supply this need.

Apart from a brief introduction, the book is divided into six chapters. A general survey of the whole field is given in Chapter I. Chapters II, III and IV deal with electron emission from clean metals, contaminated metals and oxide cathodes respectively. In Chapter V an account is given of the modern theory of electron emission. Finally, Chapter VI deals with the emission of ions, (1) from electrolytes, and (2) from metals. Lists of references to the original literature are appended at the ends of the chapters.

In accounts of experimental work, I have, wherever possible, given some sort of indication of the probable accuracy and reliability of the results obtained, or else given sufficient information to enable the reader to judge for himself. I hope that the general enhancement of the value of the data derived from their critical presentation may be deemed to outweigh any errors of judgement I may have committed, and that the latter may therefore be excused. Incidentally, I hope that the discussion of experimental details may in certain cases be of use in drawing the attention of those who are planning researches of their own to some of the pitfalls to be avoided.

The theory has everywhere been presented in as simple a form as could be contrived, and should be fairly easily readable by anyone who has attained a degree standard in physics and mathematics. Naturally it has not been possible to discuss in any detail such branches of physics as quantum statistics and the modern electron theory of metals, some of whose results are of fundamental importance in the theory of thermionic emission. I have, however, given qualitative accounts of these theories, and have tried to show by what processes of reasoning the results used in thermionic theory have been arrived at. These results are then stated, without, in general, being actually derived. For their mathematical derivations the reader must be referred to books dealing specifically with the branches of physics in question, or to the original literature.

My best thanks are due to my colleagues of the Research Laboratories of the General Electric Company, Mr. J. W. Ryde and Mr. N. L. Harris, for placing at my disposal the results of their unpublished work on the emission of electrons from thin films of barium and oxygen adsorbed on tungsten. I also wish to express my thanks to the Director, Mr. C. C. Paterson, for his leave to write about this and certain other items of hitherto unpublished work carried out in the

G.E.C. Laboratories on behalf of the Marconi-Osram Valve Company.

I am greatly indebted to Professor R. H. Fowler for the advantage of many discussions I have had with him on various points which have arisen during the preparation of the manuscript. Finally, I wish to thank my colleagues, Dr. N. R. Campbell, Mr. B. S. Gossling and Mr. J. T. Randall, for reading parts of the manuscript and offering helpful criticisms.

A. L. REIMANN.

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MEANINGS OF MOST IMPORTANT SYMBOLS USED.

T = Absolute temperature.
R = Gas constant.
k = Boltzmann's constant.
ϵ = Base of Napierian logarithms.
e = Electronic charge.
m = Electronic mass.
i = Electron emission.
i_p = Positive-ion emission.
i_a = Rate of evaporation of neutral atoms.
χ = Electron work function.
χ_p = Positive-ion work function.
χ_a = Atom work function.
U_i = Work of ionization.
l_0 = Molecular latent heat of evaporation of electrons at absolute zero.
λ_0 = Photoelectric threshold wave-length.
C = Product of inner potential of a metal and electronic charge.
μ = Zero-temperature critical energy of Fermi distribution.
h = Planck's quantum of action.
$\bar{r}$ = Mean reflexion coefficient.
$\bar{D}$ = Mean transmission coefficient.
A = Emission constant.
$A_0 = A/(1 - \bar{r}) = A/\bar{D}$.
θ = Fraction of maximum number of foreign atoms that can be adsorbed in a single layer on an emitting surface.

INTRODUCTION.

WHEN a conducting body is heated to a sufficiently high temperature, electrically charged particles are emitted from it and may be drawn off by a suitable electric field. The emission of these particles ("thermions") is now generally known as "thermionic emission." The particles may be either electrons or ions, according to the nature of the emitter and the prevailing conditions. The more important case, both on account of its theoretical interest and because of its practical applications, is that in which they are electrons. It is therefore mainly with thermal *electron* emission that we shall deal in the following pages.

The principal thermal electron emitters are the metals and certain other electronic conductors, and thus it has generally been assumed that the electrons available for emission are the same as those available for conduction. According to both the classical and the modern theory of metals, these, the so-called "free electrons," move about within the conductor, having a distribution of velocities which depends upon the temperature. The higher the temperature, the more does the distribution spread towards high velocities. That electrons are not ordinarily emitted in appreciable quantities by cold conductors can only be due to their being turned back whenever they come into the region of the surface by repulsive forces which they encounter there. As the temperature is raised, however, an increasing proportion of electrons must approach the surface with sufficient velocities to enable them to pass right through it, in spite of the repulsive forces, and so to escape. We thus have a very simple picture of the mechanism of the emission.

The success of any quantitative emission theory based on this picture must naturally depend on what assumption is made regarding the velocity distribution of the internal electrons available for emission. In the classical theory of metals this distribution was supposed to be Maxwellian, and in 1901 O. W. Richardson derived a corresponding emission formula which could be made to fit experimental data very well when its constants were given suitable values. But the classical theory subsequently became involved in such hopeless difficulties that it finally had to be abandoned, and with it the emission formula that depended on it. Happily, however, we now have a new and successful theory of electrons in metals, due in its original, incomplete form to Pauli and Sommerfeld, and since modified and extended by Bloch and others. In this the existence of effectively free electrons is assumed whose velocity distribution, instead of being Maxwellian, is governed by the new quantum statistical principles of Fermi and Dirac. And it has been shown by Nordheim and Sommerfeld that the substitution in Richardson's derivation of his original formula of the Fermi-Dirac distribution for the Maxwellian leads to an emission formula concerning whose essential validity there can be no reasonable doubt.

Fortunately, the derivation of an acceptable thermionic emission formula did not have to await the discovery of the true velocity distribution of the internal electrons. Shortly after the publication of Richardson's pioneer work, H. A. Wilson showed that an emission formula might be obtained by a thermodynamical reasoning, without its being necessary to make any assumption regarding the actual mechanism of the emission. The thermodynamical theory was subsequently further developed in a series of papers by Wilson and Richardson. The emission formula was derived by finding the condition of equilibrium at any temperature between the emitting body and a supposed external electron gas, and assuming that the electrons leaving the hot body in such equilibrium are emitted from it and would be emitted at the same rate into a vacuum. The latter assumption seems plausible enough, but the former is probably too crude, as it takes no account of reflexion of electrons at the emitting surface. It is, however, a simple matter to allow for reflexion by an extra factor in the emission formula. This was done in the later versions of the theory. Another quantity about which some assumption has to be made in deriving the formula is the specific heat of the internal electrons. On taking account of the smallness of this quantity as found experimentally, one obtains a formula which disagrees with Richardson's original formula, but which is capable of representing experimental data equally well. Later developments of the thermodynamical theory are due to M. v. Laue, W. Schottky and S. Dushman. In its final form, the formula derived thermodynamically agrees perfectly with that obtained more recently by Nordheim and Sommerfeld by the quantum-statistical method. It must be regarded as cause for considerable satisfaction that the same formula should have been arrived at by two such different methods.

The place of our subject in the scheme of physics will be apparent from the foregoing. It is directly concerned with the electrical constitution of conductors and with field conditions at their surfaces. Also thermal emission of electrons is related to other electron emission phenomena, such as those in which the surface of a conductor is exposed to electromagnetic radiation of sufficient frequency (photoelectric effect), to the action of incident electrons, positive ions or metastable molecules of sufficient energy, or to an intense electron-accelerating field.

It is found that traces of contamination at the surface of a conductor profoundly affect its thermionic properties, and, in view of the fundamental part electric forces in this critical region play in determining the emission, this is hardly to be wondered at. The importance of having clean surface conditions in experimental work has not always been so fully appreciated as it is now, neither have the means for their realization been so fully available. In consequence, many of the earlier results—indeed most of those obtained prior to about 1914 —have little or no quantitative value. It is only in more recent years that advances in vacuum and other experimental technique have made it possible to obtain in certain cases surfaces which are either almost entirely clean or have well-defined and controllable contaminations and which give, therefore, consistent and repeatable thermionic emissions.

The practical applications of thermionic phenomena are numerous and varied. In the laboratory, not only do thermionic emitters serve as a most convenient source of electrons (and occasionally of ions) in various physical researches, but in addition, the thermionic valve in its several forms has proved itself an invaluable piece of apparatus as an oscillator, amplifier and rectifier. The technical and engineering applications of the thermionic valve are no less important, e.g. in radio transmission and reception, in long distance line telephony and in alternating current rectification. Thermionic emission also plays an essential part in the operation of vacuum X-ray tubes, carbon arcs and hot-cathode gas-discharge tubes. Whilst it is not intended to deal with any of these applications in the present volume, their existence goes to show that the phenomena we are about to study are no less important from a utilitarian than from a strictly scientific point of view.

CHAPTER I.

GENERAL SURVEY.

Early History.—About two hundred years ago it became known that air, when exposed to the surface of a hot solid, loses its insulating properties. During the nineteenth century much work was devoted to the study of this phenomenon by Becquerel,[4] Blondlot,[6] Guthrie,[32] Elster and Geitel,[20] and Branly,[7] as a result of which the effect was shown to be due to the emission from the hot surface of electric charges. It was further established that whilst at relatively low temperatures and high gas pressures a conductor loses a positive charge more readily than a negative, at higher temperatures and lower pressures the reverse is the case.

In 1883 Edison [19] observed a transport of electricity across a relatively good vacuum within the bulb of a carbon-filament electric lamp. He found that if an independent electrode, mounted within the bulb, was connected through a galvanometer to the positive terminal of the incandescent filament, the galvanometer registered a current, but that no current could be observed when the connexion was made to the negative terminal. Some years later, Preece [63] and Fleming [25] showed this effect to be due to a loss of negative electricity by the negative end of the filament and its collection, after traversing the intervening space, by the auxiliary electrode at the relatively positive potential. Shortly afterwards Fleming, modifying geometrically Edison's experimental lamp, constructed a practical thermionic rectifier or "valve." This consisted of a filament which could be heated to incandescence by a current, mounted close to a metal plate within an evacuated bulb. With the filament hot, the valve behaved as a conductor or as an insulator according as the potential of the plate was made positive or negative with respect to the filament.

The precise nature of the carriers of the negative charge emitted by an incandescent conductor in a vacuum was revealed in 1899 by J. J. Thomson,[90] who found their ratio of charge to mass to agree within the limits of experimental uncertainty with that of electrons.

Fundamental Thermionic Phenomena.—The thermionic current flowing in a valve such as that of Fleming is a function both of the filament temperature and of the difference of potential between the filament and plate. Strictly speaking, there is, of course, no single filament temperature, for the ends are not as hot as the centre, being cooled by conduction to the supports. Neither is there a single potential difference between the filament and plate, owing to the potential drop along the filament. It is, however, a simple matter to confine one's observations to the current from only a very short, central portion of the filament, and so effectively to avoid both complications. To do this, it is best to have a straight filament stretched along the axis of a cylindrical anode which is divided into three sections only just separated from one another, a short central one opposite that part of the filament whose thermionic current one wishes to observe, and two end sections (" guard rings ") which are kept at the same potential as the central one but are not included in the current-measuring circuit. Finally, there is a possible complication of a different nature which early workers in the thermionic field used to find very troublesome, and that is the ionization of residual gases, which may cause the observed space current to be greatly increased. With modern vacuum technique, however, this may easily be avoided.

With a constant filament temperature, the variation of the thermionic current with the anode potential (relative to the filament) may be represented by a curve like one of those in Fig. 1. When the anode is negative to the filament, practically no space current flows. Then, as the anode is made increasingly positive, the space current grows, first at an increasingly, then at a decreasingly rapid rate, and finally it " saturates," a further increase in anode potential producing practically no corresponding increase in current.

Actually, the saturation is never perfect. An increase in anode potential always produces *some* increase in space current. This effect varies somewhat with the class of emitter, clean metals, for example, giving better saturation than emitters with composite surfaces. Thus the curves marked I, II and III in Fig. 1 were obtained with geometrically identical systems in which the cathodes were of clean tungsten, tungsten covered with a monatomic layer of adsorbed thorium, and an "activated" alkaline earth oxide respectively, the temperatures having been so adjusted that each of the three cathodes would give about the same "saturated" current. The failure of the current to saturate completely is, however, only a second-order effect, and we shall do well, for the present, to ignore both this and certain other second-order effects, confining our attention to the main phenomena.

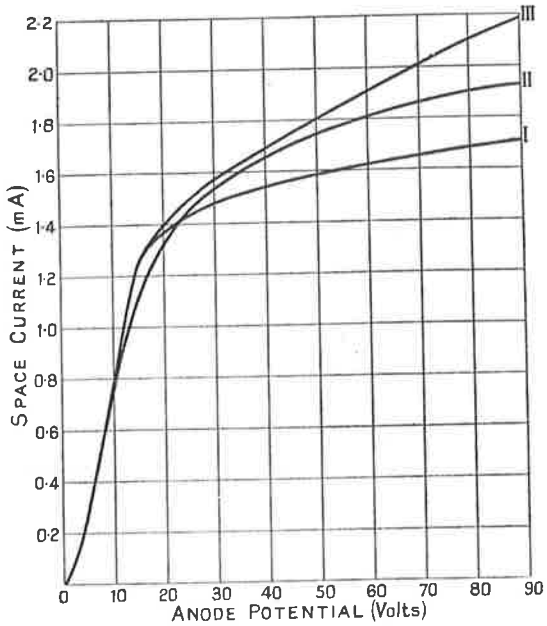

Fig. 1.—Relationship between thermionic current and potential of anode with respect to the filament in three typical cases.

Curves similar to those of Fig. 1 are obtained at all cathode temperatures, but the higher the temperature, the higher the value at which the space current saturates. This is shown in Fig. 2, where a number of curves obtained with a tungsten cathode at a series of different temperatures are reproduced.

One of the most striking things about these curves is that the lower part of each, from the origin nearly as far as the point of inflexion, coincides with a part of the *same* curve C. Here the space current is limited only by the potential of the anode. On the other hand, the saturated space currents are limited only by the temperature of the cathode. It would appear then, that the saturated currents are the fundamentally really important quantities, while the infra-saturation currents, determined as they are by field conditions, are of merely incidental interest. We shall see later that the saturated current represents all the electrons emitted by the cathode, while in the infra-saturation condition some of the emitted electrons return to the cathode. The reason why they return is that there is an electron-retarding field in the region of the cathode due to the " space charge " of the electrons present at any instant in the inter-electrode space. Only when the anode potential is sufficiently high are the electrons drawn away so

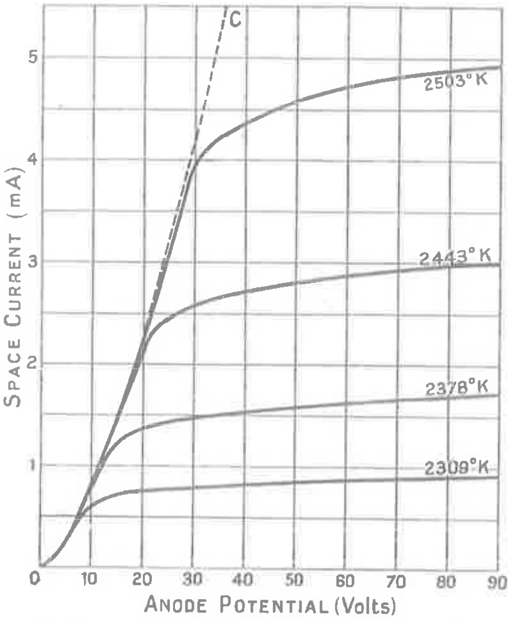

FIG. 2.—Illustrating the dependence of the thermionic current-voltage characteristic on the temperature of the emitter.

rapidly that the field is electron-accelerating in the whole inter-electrode space, in spite of the presence of the space charge. The saturated space current is called the " emission " from the cathode.

The variation with temperature (T) of the emission (i) from a tungsten filament is shown in Table I. These data were obtained by Dushman, Rowe, Ewald and Kidner[18] with a filament 0·010 cm. in diameter and 15 cm. in length, the emitting area thus being 0·474 cm.^{2}. With a filament of this length the effect of the cold ends could not have been very important. The anode was kept at 100 volts positive to the filament throughout. It will be seen at once that the growth of emission with temperature is very rapid indeed. It increases roughly by a factor of 10 for every 8 per cent. increase in the absolute temperature.

TABLE I.

VARIATION WITH TEMPERATURE OF EMISSION FROM CLEAN TUNGSTEN.

T (deg. K.).	i (amps.).	T (deg. K.).	i (amps.).
1470	$1{\cdot}61 \times 10^{-8}$	1897	$0{\cdot}910 \times 10^{-4}$
1543	$1{\cdot}020 \times 10^{-7}$	2065	$0{\cdot}996 \times 10^{-3}$
1640	$0{\cdot}905 \times 10^{-6}$	2239	$0{\cdot}984 \times 10^{-2}$
1761	$0{\cdot}975 \times 10^{-5}$	—	—

Similar data for a much lower temperature emitter, an activated lime-coated cathode, are given in Table II. These were

TABLE II.

VARIATION WITH TEMPERATURE OF EMISSION FROM LIME-COATED PLATINUM-IRIDIUM.

Temp. Rising.		Temp. Falling.		Temp. Rising.	
T (deg. K.).	i (mA.).	T (deg. K.).	i (mA.).	T (deg. K).	i (mA.).
1091	0·3	↑ 1085	0·28	—	—
1173	1·28	1173	1·25	1173	1·3
1240	3·72	1253	3·9	1240	3·8
1314	10·1	1327	11·2	1309	10·2
↓ 1389	29·5	—	—	↓ 1383	29·5

obtained by Espe[22] with a platinum-iridium ribbon 5 cm. × 0·025 cm. × 0·005 cm., whose hot, central portion (length 3 cm., area 0·18 cm.^{2}) was coated with calcium oxide. There was no appreciable emission from the uncoated ends. It will be seen that the emission per cm.^{2} from this cathode is greater at 1100°K. than that from tungsten at 2000°K. It increases roughly tenfold for every 17 per cent. increase in temperature.

If a certain proportionate increase in the temperature of a given emitter produced exactly the same proportionate increase in emission at all temperatures, then log i would be a linear function of log T. Actually it is found that the relationship between these two quantities is not quite linear. A straight line always *is* obtained, however, when log i is plotted against 1/T. In Fig. 3, for example, the data of Tables I and II are plotted in this way. And since the slopes of these plots are always negative, the temperature dependence of the emission may be expressed by the empirical formula

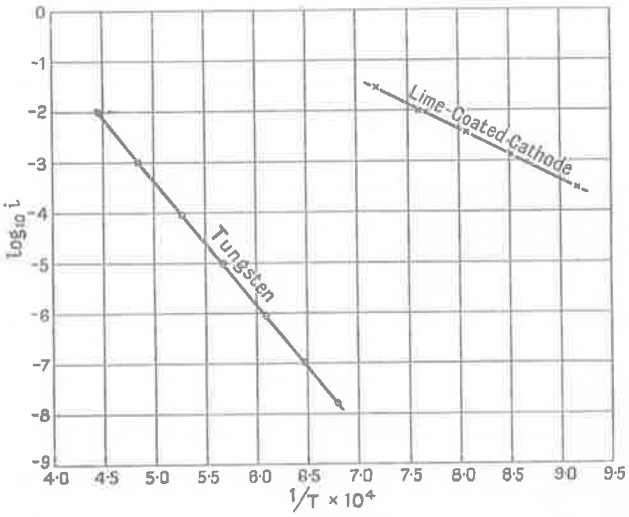

FIG. 3.—Showing the linear relationship between log i and 1/T in two cases.

$$i = f \,.\, \epsilon^{-\omega/kT}, \quad . \quad . \quad . \quad . \quad (1)$$

in which k is Boltzmann's constant and f and ω are constants characteristic of the emitter. The constant ω has the dimensions of work, and since k is the gas constant for one molecule, we should hardly be surprised to find that ω represents the work required to extract one electron from the emitter. Actually, as we shall see, although this work is not exactly ω, it is something very near it.

The thermal emission of electrons, like that of neutral molecules, gives rise to a definite loss of heat from the emitter. In certain cases the effect is very striking and is obvious to the unaided eye. Thus a well-activated alkaline earth oxide coated cathode at a red heat or a tungsten filament at about 3000°K. may be seen to become quite appreciably cooler when electrons are suddenly drawn from it. Careful measurements of the heat effect accompanying thermionic emission have established the fact that the mechanical equivalent of the heat lost per emitted electron is equal to the quantity ω in the empirical emission formula (1). However, just as, in the evaporation of neutral molecules, the actual work of separation of a molecule from the condensed phase is something less than the latent heat per molecule, so the work of extraction of an electron from a thermionic emitter is something less than ω. The actual work of extraction is the quantity χ in the formula

$$i = AT^2\epsilon^{-\chi/kT} \quad . \quad . \quad . \quad . \quad (2)$$

which fits the emission data, A being a constant. The constant χ is called the "work function" and is less than ω by $2kT_m$, where T_m is the mean temperature of the range over which the emissions have been measured.

Perhaps it will be objected that it is impossible for the formulæ (1) and (2) both to represent the same set of emission data, and strictly speaking that is, of course, quite true. Actually it is only *within the limits of experimental uncertainty* that they can both do so. The value of ω/k is generally of the order of a few tens of thousands of degrees, and thus the variation of $\epsilon^{-\omega/kT}$ with T is exceedingly rapid. The accuracy with which temperatures and emissions are measurable is not great enough to establish anything beyond the fact that the temperature variation of emission is dominated by a factor of the type $\epsilon^{-\omega/kT}$, and thus it may be represented by any formula like (1) in which f, instead of being a constant, is a moderately varying function of T, such as the product of a constant and a low power of T.

Different Kinds of Thermal Electron Emitter.—The electron emitters which we shall study in this book may be divided into three groups. These are (1) clean metals, (2) metals whose surfaces have some well-defined contamination of only a monomolecular order of thickness, and (3) electron emitting non-metals.

The number of clean metals for which really reliable thermionic data are available is rather limited. This is due in large part to the fact that in the case of all but the most refractory metals it is extremely difficult to free the emitting surface of contaminations, such as a film of oxide or of an adsorbed gas. A further difficulty with many of the less refractory metals (e.g. copper, nickel, etc.) is that even when their surfaces have, by some means, been freed of contaminations, their emissions up to temperatures near their melting-points are so excessively small that it is by no means easy to measure them accurately. Such work functions (χ in formula (2)) of clean metals as are known range from 1·8 electron-volts in the case of cæsium, the most electropositive metal of all, to 6·3 e.v.* in the case of platinum. In general, the work function increases from bottom to top and from left to right of the periodic table, that is to say, with decreasing electropositiveness.

Of the innumerable cases of metals having molecular surface contaminations, only a few are sufficiently well defined and experimentally reproducible for their quantitative study to have been possible. In these, the contamination generally forms a layer only a single atom in thickness. Such are, for example, thorium, cæsium, barium, or oxygen, adsorbed on the surface of tungsten. Certain cases of multiple layers have also been studied, in which, however, generally no two adjacent layers are of the same kind. Examples of these are cæsium on oxygen on tungsten, barium on oxygen on tungsten, etc. If the adsorbed layer—or, in the case of multiple layers, the outermost layer—consists of atoms which are electropositive to those of the metal on which they are adsorbed, the work function of the emitter is depressed by the contamination even below the value characteristic of the adsorbed substance in bulk. For example, the work function of tungsten

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* The abbreviation "e.v." will, henceforward, generally be used for "electron-volts."

is 4·54 e.v. and that of thorium in bulk 3·38 e.v., but that of a single complete atomic layer of thorium on tungsten is only 2·63 e.v. On the other hand, if the adsorbed kind of atom is more electronegative than that on which it is adsorbed, the work function is thereby increased.

The most important non-metallic emitters are the so-called "oxide cathodes" or "Wehnelt cathodes," which consist of a metal carrier or "core," coated with an alkaline-earth oxide, which has been subjected to a suitable activation treatment. These cathodes are in wide use commercially, and the most efficient of them give an emission of the order of 1 amp./cm.^{2} or even more at quite a dull red. Their action is much more complex than is that of clean or contaminated metals and is only now beginning to be understood. Although they are called "oxide cathodes," it is now known that their high thermionic activity is due not to the oxide *per se*, but to the presence of free alkaline earth metal both on the surface and in a state of solution in the oxide. Their work functions are somewhat variable, but are generally found to be of the order of 1 or 2 electron-volts. Other things being equal, cathodes whose coatings are of calcium, strontium and barium oxides have work functions decreasing in the order named.

Free Electrons in Metals.—Since emitted electrons must be derived either directly or indirectly from the interior of the emitting body, it is necessary to know something about the condition of the internal electrons if we wish to arrive at a quantitative theory of the process of emission.

In the classical theory of electrons in metals, due to Thomson, Riecke and Drude, it was assumed that every metal contains a number of "free" electrons, whose velocities are distributed in the same way as those of the molecules of an ordinary gas, and whose collisions with the atoms of the metal are comparable in their effects with the collisions of ordinary gas molecules with the walls of the containing vessel. With these assumptions it was at first found possible to account fairly satisfactorily for certain of the observed properties of metals, but the success of the theory was short-lived. As its consequences were worked out and compared with experimental data the position of the theory appeared more and more hopeless, until finally it was felt to be quite untenable. No values assumed for the orders of magnitude of the concentration and free paths of internal electrons having a Maxwellian velocity distribution could be reconciled with all the observed electrical, thermal and optical properties of metals. And in particular it was found impossible to account for the observed smallness of the molecular heat of the internal electrons compared with $\frac{3}{2}$R, the theoretical value for any Maxwellian gas at constant volume. The logical inference was that if an internal free-electron " gas " exists at all, its velocity distribution certainly cannot be Maxwellian.

In statistical theories of the velocity distribution of the molecules of a gas, it is found convenient to represent the instantaneous position and momentum of each molecule by the components of a " representative point " in an imaginary six-dimensional " phase space," three components defining the position and the other three the momentum. The phase space is divided into a large number of equal " phase cells," and the various possible distributions of the representative points among these cells consistent with any given energy and volume of the gas as a whole are considered. Any such distribution of the representative points is called a " complexion " and must on no account be confused with a velocity distribution of the molecules, each of which in general embraces many complexions. The most probable, or normal velocity distribution of the molecules is then taken to be that which is given by the largest number of complexions. In different statistical theories, different assumptions are made as to what complexions are possible and distinguishable from one another and also concerning the " sizes " of the phase cells. And different sets of assumptions naturally lead to different expressions for the normal distribution of velocities.

The statistical theory whose assumptions are of the least restrictive character is the classical. No particular value is assigned to the sizes of the cells, neither is any limit imposed on the number of representative points any given cell may contain. A further assumption of the classical statistics is that it is possible, in complexion counting, to assign an individuality to each molecule, so that an interchange between two representative points in different phase cells leads to a new complexion. The normal distribution obtained on the basis of these assumptions is the Maxwellian. The energy of a

Maxwellian gas is proportional to the absolute temperature and thus vanishes at absolute zero.

The classical assumptions are not reconcilable, however, with certain well-established principles of modern quantum physics. Accordingly they have been replaced by new assumptions which seem to be logical extensions of these principles to the realm of statistics. The new assumptions are (1) that to each phase cell must be assigned a " volume " in phase space of exactly h^3, where h is Planck's quantum of action, (2) that it is impossible for two or more representative points simultaneously to occupy the same phase cell, and (3) that no individuality can be assigned to the molecules in complexion counting. The distribution formula based on these assumptions has been worked out independently by Fermi [24] and by Dirac.[16]

Although the formulæ for the Maxwellian and the Fermi distributions look quite different, it may be shown that for sufficiently low concentrations and high temperatures the two distributions are indistinguishable from one another. The reason for this is not difficult to see. If the amounts of phase space occupied by the representative points in the various complexions consistent with the total energy and volume of the gas are of a higher order than h^3 times the number of molecules, then the chance that any given phase cell of magnitude h^3 is occupied even by a single representative point must be small, and so the question of how many representative points may simultaneously occupy one cell hardly arises—at least it is of no quantitative importance in complexion counting. And if there are on either set of assumptions as many occupied cells as there are molecules, then to each Fermi complexion there must correspond a certain constant number of classical complexions in which the same cells are occupied, this number being N !, where N is the total number of molecules. Hence the same molecular velocity distribution is given by the largest number of complexions in both cases.

If, however, the molecules are so crowded together that with an assumed Maxwellian distribution there would be, on the average, several representative points in each phase cell of magnitude h^3, then obviously the Fermi distribution must be very different from the Maxwellian. For one thing the total energy of a Fermi gas must be much greater than that of a

Maxwellian gas at the same temperature, for only so can the Fermi condition that there must be at least as many phase cells as there are molecules be satisfied. Even at the absolute zero of temperature, a Fermi gas must have finite energy, and the more condensed the gas the greater must the energy be. With a high degree of crowding the energy is never much greater, however, than is necessary for all the representative points to be accommodated, and at 0°K. it is no greater at all. At this temperature there is only one possible complexion, and the molecules are, so to speak, " frozen " into their lowest possible energy states, so that there is an abrupt " cut-off " in the distribution beyond the highest energy represented. In Fig. 4 is shown the dependence on the energy ε of the so-called " energy distribution function " $F(\varepsilon)$, which gives the number $F(\varepsilon)d\varepsilon$ of molecules of a Fermi gas having energies between ε and $\varepsilon + d\varepsilon$. The full and dashed curves represent the distributions at 0°K. and at a higher temperature respectively. The value of the energy μ at which the abrupt cut-off of the zero-temperature distribution occurs depends on the degree of crowding of the molecules and on the molecular mass.

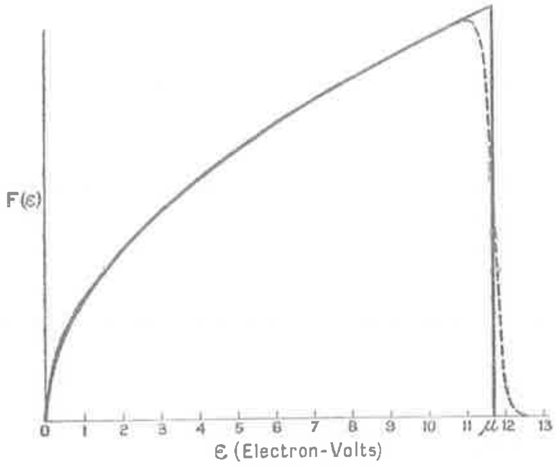

FIG. 4.—Energy distribution of free electrons in nickel at 0°K. and at 1500°K.

Except for the case of helium at the lowest temperatures and highest pressures, the crowding of the molecules in ordinary gases is not sufficient for the Maxwellian and Fermi distributions to be appreciably different from one another. In the case of an electron gas whose concentration is anything like that of the atoms in metals, however, the two distributions must be profoundly different. Let us consider, for example, the valency electrons in nickel. There are two of these per atom, and if they constitute a Fermi gas, the μ of this gas must, as we shall see in Chapter V, be 11·7 electron-volts. If the μ of Fig. 4 represents this value, then the dashed curve represents the Fermi distribution at 1500°K.

In 1927 Pauli,[58] assuming the valency electrons of the alkali metals to have a Fermi distribution, was able, for the first time, to give a satisfactory theoretical account of the temperature-independent paramagnetism of these metals. Shortly afterwards, Sommerfeld [88] showed that, by substituting the Fermi distribution for the Maxwellian in Drude's theory of metals, formulæ could be derived for a number of the properties of metals not dependent on the free paths of the electrons which were in much better agreement with experimental data than were the corresponding classical formulæ. In particular it was shown that the energy of a Fermi free-electron gas would change very much less rapidly with the temperature than would that of a Maxwellian gas, and so the specific-heat difficulty was overcome.

Those properties which depend on the free paths could not be so satisfactorily accounted for, however. This was not because there was anything wrong with the assumption of a Fermi distribution, but because nothing was really known about the free paths. Sommerfeld assumed these to be terminated by collisions between the electrons and the ions of the lattice, as in the classical theory, and thus to depend on the number of ions per unit volume and the effective combined radius of an ion and an electron. On this assumption he obtained an expression for the electrical conductivity involving the number of free electrons per unit volume, the mean free path and certain constants, but not the temperature. Now in the case of pure metals the conductivity actually has quite an important negative temperature-coefficient. Sommerfeld's theory could account for this only by assuming that an increase in the temperature brings about a diminution either in the number of free electrons (degree of ionization) or in the mean free path. The former alternative may be dismissed at once as altogether improbable. And although it does not seem unreasonable to suppose that the free path may vary with the velocity of an electron, the velocities of the electrons of a concentrated Fermi gas are affected so little by the temperature that it would be difficult to account for a temperature variation of the mean free path of the order required.

This difficulty has since been overcome by a theory due to Bloch.[5] According to the wave-mechanical theory advanced in 1924 by L. de Broglie, there is associated with every particle of mass m moving with a velocity v a wave-train, whose wave-length λ is given by the formula

$$\lambda = \frac{h}{mv}. \qquad . \quad . \quad . \quad . \quad (3)$$

This theory, as applied to moving electrons, has since been beautifully verified experimentally by the observations of Davisson and Germer, G. P. Thomson and others, on the diffraction of "electron-waves" by crystal lattices, and there can now be as little doubt of its truth as of that of the wave theory of X-rays. Bloch has considered the interaction between the de Broglie waves of a Fermi free-electron gas and the field of force associated with the lattice. At the absolute zero of temperature the lattice field is strictly periodic, the period being that of the lattice, and, as Bloch has shown, electron waves travelling through it can suffer no dispersion, so that the free paths are infinite. At higher temperatures, however, the elastic vibrations of the lattice give rise to a finite dispersion, whose importance increases as the temperature rises. The theory of Bloch correctly accounts for the order of the conductivities of the pure metals and for their normal temperature-variation, as well as for several other properties. While the theory fails to give a detailed quantitative account of all the observed properties of metals, there can be little doubt but that this is due merely to the crudeness of certain assumptions that have had to be made in order to simplify the mathematical treatment.

Bloch's result that electrons can move unhindered through a periodic field of force applies not only to the valency electrons but to those of the inner atomic "shells" as well. Thus in a sense *all* the electrons in a metal are "free," not merely one or two per atom, as was assumed by Sommerfeld. We shall find it convenient, however, to use the term "free electrons" in a somewhat restricted sense, applying it only to those electrons which, in addition to being able to move about in the metal, are also available for conduction and emission. These are by no means all the electrons in the lattice, for if they were there would be no such bodies as crystalline insulators.

We shall perhaps understand the case of metals most easily if we consider that of insulators first. The field of a crystal lattice is periodic in three dimensions. Now it has been shown that in a *one*-dimensional periodic field not all electron energy levels are possible. The effect of the field is to break up the energy levels into a number of bands of allowed energies separated by bands of forbidden energies. (We may think of this as analogous to the existence of allowed and forbidden electron orbits about atomic nuclei.) The same thing is true, as A. H. Wilson [98] has shown, in a three-dimensional periodic field, only now it is possible for some of the allowed bands to overlap. The less the electrons are attracted to the atomic nuclei, the more likely it is that the bands occupied by them will overlap with others. Actually such overlapping never occurs with any but the bands that may be occupied by the valency electrons. The bands of lower energies, corresponding to the inner electron shells of the atoms, are always separated by considerable gaps. And, as Wilson has shown, these bands are always completely "filled up" with electrons—that is to say, there are no more phase cells available whose energies are within the limits of one of these bands than are necessary to accommodate the representative points of all the electrons in the corresponding shell. Thus there is only one possible complexion of the representative points, and since any acceleration of the electrons as a whole would necessarily result in the appearance of a new complexion, such acceleration is impossible. The electrons of the inner shells take no part in conduction.

If the valency electrons also completely fill up an allowed band and this does not overlap with any other unoccupied allowed band, then even these cannot be accelerated by an applied field and the body must be an insulator. Wilson has shown that the first condition is fulfilled when the number of valency electrons is even, and the second when the " binding " (in the classical sense) of the valency electrons is sufficiently tight. If either of these conditions is not fulfilled, however, then there will be unoccupied allowed levels immediately above the critical energy of the Fermi distribution and so the electrons whose energies are near the critical value can be accelerated by the applied field. Only these are properly called " conduction electrons." According to this theory the alkali elements, which are monovalent, are of necessity metals, whether their valency electrons are " tightly bound " or not. Wilson has shown that the valency electrons of the alkali metals just half fill their allowed band. On the other hand, the alkaline-earth elements, whose atoms have two valency electrons, are metals only by virtue of the looseness of their binding.

The valency electrons, being those of highest energy, are also the only ones of whose emission there is any question.

One should be careful not to confuse the number of valency electrons per atom in a metal with the number of the column of the periodic table in which the metal appears. By the valency electrons is meant simply those in the outermost electron-shell of the atom. Actually the number of these *is* equal to the number of the column of the periodic table for all the elements of the *first two columns*, but beyond the second column the rule no longer applies. Thus nickel, which is in the eighth column, has only two valency electrons per atom. It must also be remembered that the number of valency electrons in a solid metal is not necessarily the same as that in the isolated atoms. For example, an isolated atom of palladium has no valency electrons at all, but there is reason to believe that in solid palladium there are two valency electrons per atom.

The Nature of the Surface Forces.—We have seen that the free electrons of metals have, on account of their high concentration, very considerable energies. Even at 0°K. the maximum energy μ of the Fermi distribution is, in the case of most metals, of the order of 10 electron-volts. That in spite of this energy the electrons do not ordinarily escape can obviously only be due to the existence of a potential difference between the inside and outside of the metal greater than μ/e, where

e is the electronic charge, the metal being positive to free space. This potential difference is generally known as the "inner potential" of the metal.

Now let us consider what can be the nature of the surface forces to which the existence of an inner potential is due. In the first place, each atom in the region of the surface must, by reason of the absence of similar atoms beyond, be acted upon by a system of unbalanced forces due to its neighbours. These forces must give rise to a polarization of the surface atoms. Idealized, the surface polarization may be thought of as an electric double layer, which, as is well known, is equivalent to a potential discontinuity. In reality, of course, there will be no actual discontinuity, but only a rather steep potential gradient at the surface, the steepness depending on the strength and thickness of the polarized layer. As to the *sign* of the potential gradient, these general considerations do not, of course, yield any information.

The polarization of the surface atoms is not the only thing that gives rise to a surface force, however, for even after emergence an electron is still attracted to the conductor by its own electrostatic image in the surface. Exactly where we should regard the image attraction as beginning it is impossible to say. We can hardly speak of an electric image in the ordinary sense until the electron has travelled at least an atomic diameter or two from the surface. On the other hand, as we shall see later, beyond about 10^{-6}–10^{-5} cm. from the surface the contribution of the image attraction to the work of exit becomes negligibly small. It is convenient to think of the image force as if it were derived from an image field,* and then to visualize the polarization and image fields as contributing to a single potential barrier or "hill" at the surface.

The work of extraction must be the same for all electrons having a given internal energy, irrespective of the particular paths they take between or through the surface atoms in their exit. This follows at once from the fact that at a sufficient distance from the surface (actually beyond an atomic diameter or two)

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* Clearly, no such field actually exists apart from the presence of the electron. It is interesting to note that with a reversal in the sign of the charge of the escaping particle the direction of the "field" also reverses, for a positive ion would still be *attracted* to the surface.

continuous equipotential surfaces exist which nowhere pass between atoms or charges belonging to atoms. Thus, *for the purposes of mathematical treatment* we are encouraged to idealize the problem of the escape of an electron to one in a single dimension, and to think of the charges of the polarized atoms at and near the surface as " smeared out " into uniform sheets of charge lying in planes parallel to the surface. Further considerations which would appear to justify our ignoring the atomic structure of a conductor will be discussed in Chapter V.

The picture of a potential hill at the surface of a conductor is a very convenient one in thermionic theory. Thus it has been made use of in a gravitational analogue of an emitting body by W. Schottky.[77] This consists of a flat-bottomed bowl with sloping sides. The bottom of the bowl corresponds to the interior of the metal and its sides to the potential hill in the region near the surface. Corresponding to the electrons are a number of perfectly elastic spheres rolling about within the bowl. These have a two-dimensional velocity distribution on the bottom of the bowl corresponding to the three-dimensional velocity distribution of the electrons within the metal. In most cases a sphere, on coming to the side of the bowl, will roll up it a certain distance, until it has lost all its vertical velocity, when it will fall back again. If, however, a sphere approaches the side with sufficient velocity, it will be able to roll up all the way, drop over the edge, and so escape.

On the classical view, the electrons are all at the bottom of the hill at 0°K., and in order that they may escape, energy must be imparted to them, either by heating the conductor or otherwise, so that they may " climb " to the top. The modern picture differs from the classical in that, even at absolute zero, a considerable proportion of the internal electrons are regarded as having sufficient kinetic energy to enable them to climb up an important part of the hill. In order to make them escape it is then merely necessary to impart to them sufficient energy for the remainder of the climb.

Richardson's " $T^{\frac{1}{2}}$ " Emission Formula.—A theoretical formula connecting the thermal electron emission of a conductor with the potential step at the surface and the temperature was first obtained by Richardson[65] in 1901. Richardson based his derivation on the classical electron theory of metals, and he calculated the emission on the assumption that all those electrons escape whose normal velocity component is sufficient to enable them to climb the surface potential hill. The effects of collisions between the electrons and atoms—or rather ions—was ignored on account of their statistical mutual compensation.

We now know that the classical theory of metals is certainly not true, and that therefore the emission formula based on it must be inaccurate. This formula is, nevertheless, sufficiently good, empirically, for it to have served, for two decades, not only as an inspiration for countless experimental researches in the field of thermionics, but also as a most useful tool in the interpretation of the results obtained. If only for this reason, therefore, it will be worth while to reproduce its derivation here.

Let C be the product of the inner potential of the emitter and the electronic charge, and let N be the number of free internal electrons per unit volume. Then in order for an electron, of mass m, to escape, its velocity component u, normal to the surface, must exceed u_0, where

$$\tfrac{1}{2}mu_0^2 = \mathrm{C}. \qquad (4)$$

With a Maxwellian velocity distribution, the number $d\mathrm{N}$ of electrons per unit volume having normal velocity components between u and $u + du$ is given by

$$d\mathrm{N} = \mathrm{N}\sqrt{\frac{m}{2\pi k\mathrm{T}}}\,\epsilon^{-\frac{mu^2}{2k\mathrm{T}}}, \qquad (5)$$

where T is the temperature of the emitting body and k is Boltzmann's constant. Thus the number of electrons that escape from unit area of surface in unit time is

$$\begin{aligned} n = \int_{u=u_0}^{u=\infty} u\,d\mathrm{N} &= \mathrm{N}\sqrt{\frac{m}{2\pi k\mathrm{T}}}\int_{u_0}^{\infty} u\epsilon^{-\frac{mu^2}{2k\mathrm{T}}}\,du \\ &= \mathrm{N}\sqrt{\frac{k\mathrm{T}}{2\pi m}}\,\epsilon^{-\frac{mu_0^2}{2k\mathrm{T}}}. \qquad (6) \end{aligned}$$

The emission current i per unit area is of course equal to ne, and thus, on account of (4), we have

$$i = \mathrm{N}e\sqrt{\frac{k\mathrm{T}}{2\pi m}}\,\epsilon^{-\mathrm{C}/k\mathrm{T}}. \qquad (7)$$

If we assume N not to vary with temperature, we may put

$$\mathrm{N}e\sqrt{\frac{k}{2\pi m}} = a, \qquad (8)$$

where a is a constant characteristic of the emitting body, and so write Richardson's formula

$$i = a\mathrm{T}^{\frac{1}{2}}\epsilon^{-\mathrm{C}/k\mathrm{T}}. \qquad (9)$$

Now an *empirical* formula of this type, viz.

$$i = a'\mathrm{T}^{\frac{1}{2}}\epsilon^{-\phi/k\mathrm{T}}, \qquad (10)$$

is capable of representing actual emission data perfectly well when the constants a' and ϕ are given suitable values. To find these, all that is necessary is to plot $\log i - \frac{1}{2}\log \mathrm{T}$ against $\frac{1}{\mathrm{T}}$, when a straight line will be obtained whose slope is $-\frac{\phi}{k}\log \epsilon$ and whose intercept on the $\log i - \frac{1}{2}\log \mathrm{T}$ axis is $\log a'$. We now know, however, that the a' and ϕ obtained in this way from the emission data do not correspond at all to the quantities a and C as defined above.

The "T^2" Emission Formula.—Shortly after Richardson had, by the above reasoning, derived the theoretical formula (9), H. A. Wilson [99] showed that an emission formula could also be obtained by a thermodynamical method, involving the use of Clapeyron's equation, and this method was subsequently further developed by both Wilson [100] and Richardson.[66]

Let us suppose we have an external electron gas in equilibrium with the hot conductor. Since the "molecules" of this gas exert repulsive forces on one another, due to their electric charges, it might be wondered whether an electron gas obeys the same laws as a gas whose molecules are uncharged. As will be shown later, however, in practically all cases actually arising in nature the effects of the mutual repulsions between the electrons may be neglected and the electron gas may be regarded as to all intents and purposes perfect. Let us assume this result for the time being. Then if we know the pressure of the gas, we know also how many electrons impinge on unit area of the hot conductor per second. Of these, a certain fraction will be absorbed and the remainder reflected. Since the number of electrons that impinge on the surface of the conductor must be equal to the number that leave it, those that are absorbed must be compensated for by electrons that are emitted. Thus the emitted electrons are $1 - \bar{r}$ of those incident on the surface, where $\bar{r}$ is the mean reflexion coefficient. It is assumed that the rate at which electrons are emitted into the external electron gas is the same as the rate at which they would be emitted at the same temperature into a vacuum.

Let us now inquire into the condition of equilibrium between the hot conductor and the external electron gas.

A consequence of the second law of thermodynamics is that the most general condition of equilibrium in terms of a reversible virtual change in which the work done on the system is $-p\delta V$ is

$$\delta S - \frac{\delta U + p\delta V}{T} = 0,^* \quad . \quad . \quad . \quad (11)$$

where S, U, p, V and T denote the entropy, internal energy, pressure, volume and absolute temperature, respectively, of the system. If the virtual change occurs at constant temperature and pressure, the equilibrium condition reduces to

$$\delta\Phi = 0, \quad . \quad . \quad . \quad . \quad (12)$$

where

$$\Phi = S - \frac{U + pV}{T}. \quad . \quad . \quad . \quad (13)$$

Now we are particularly interested in the dependence of the pressure of the external electron gas on the temperature when the distribution of the electrons between the two phases remains unchanged. If this condition is imposed, each change dT in the temperature of the system determines uniquely the change dp in the pressure which must accompany it. Let us compare with the equilibrium of the system at the temperature T and pressure p that at the temperature $T + dT$ and pressure $p + dp$, no electrons being transferred from one phase to the other in the transition. Since both conditions are of equilibrium, in neither is a virtual transference of electrons at

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[*] See, for example, M. Planck, "Treatise on Thermodynamics," Longmans, Green & Co.

constant temperature and pressure accompanied by an increase in the function Φ; that is, we have both

$$\delta\Phi = 0$$

and
$$\delta(\Phi + d\Phi) = 0, \qquad (14)$$

and hence
$$\delta d\Phi = 0. \qquad (15)$$

Now $d\Phi$ is given by

$$d\Phi = dS - \frac{dU + pdV + Vdp}{T} + \frac{U + pV}{T^2}dT, \qquad (16)$$

which, on account of the definition of entropy, viz.

$$dS = \frac{dU + pdV}{T}, \qquad (17)$$

reduces to
$$d\Phi = \frac{U + pV}{T^2}dT - \frac{V}{T}dp. \qquad (18)$$

Remembering that virtual transferences of electrons are supposed to be carried out at constant temperature and pressure, we thus see that our condition (15) becomes

$$\frac{\delta U + p\delta V}{T^2}dT - \frac{\delta V}{T}dp = 0. \qquad (19)$$

Since the numerator of the first term represents the virtual heat supplied to the system, this leads at once to Clapeyron's equation, viz.

$$l = vT\frac{dp}{dT}, \qquad (20)$$

where l is the latent heat of evaporation of one gram-molecule of electrons and v is the increase in volume of the system accompanying the evaporation of this quantity of electrons.

It will, on a moment's consideration, be evident that v is, practically, simply the molecular volume of the external electron gas, and since this is assumed to be a perfect gas we may write

$$v = \frac{RT}{p}, \qquad (21)$$

where R is the gas constant, and hence

$$\frac{dp}{p} = \frac{l}{RT^2}dT. \qquad (22)$$

In order to integrate this equation it is necessary to know what function l is of T. It is a well-known consequence of the first law of thermodynamics that

$$\frac{dl}{dT} = c_p - c_p', \quad . \quad . \quad . \quad (23)$$

where c_p and c_p' are the molecular heat capacities at constant pressure of the material transferred (electrons in the present case) in the gaseous and condensed phases respectively. Integrating eqn. (23), we have

$$l = l_0 + \int_0^T (c_p - c_p')dT, \quad . \quad . \quad . \quad (24)$$

where l_0, the constant of integration, is obviously equal to the molecular latent heat at absolute zero. According to the classical electron theory of metals used by Richardson in the derivation of his original emission formula, c_p' would be practically $\frac{3}{2}R$.* For a monatomic gas, c_p is of course equal to $\frac{5}{2}R$, so that (24) would reduce to

$$l = l_0 + RT, \quad . \quad . \quad . \quad (25)$$

which, substituted in (22), would give us

$$\frac{dp}{p} = \frac{l_0}{RT^2}dT + \frac{dT}{T}. \quad . \quad . \quad . \quad (26)$$

On integrating this equation we should obtain

$$\log_\epsilon p = -\frac{l_0}{RT} + \log_\epsilon T + c,$$

where c is a constant of integration, or

$$p = \epsilon^c T \epsilon^{-l_0/RT}. \quad . \quad . \quad . \quad (27)$$

From the kinetic theory of gases we know that the rate at which electrons impinge on and therefore also leave a given area of the emitting body is proportional to $p/\sqrt{T}$. The thermionic emission would therefore be given by

$$i = (1 - \bar{r})a_0 T^{1/2} \epsilon^{-l_0/RT}, \quad . \quad . \quad . \quad (28)$$

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* c_v', the molecular heat at constant volume, would be *exactly* $\frac{3}{2}R$, and on account of the smallness of the coefficient of thermal expansion of solids, we may take $c_p' \doteqdot c_v'$.

which, if we may take $\bar{r}$ to be practically independent of the temperature, is a formula of the same type as (9).

We now know, however, that c_p' is nothing like as great as $\frac{3}{2}$R. The molecular heat of the internal electrons deduced from measurements of the Thomson effect is, in the case of almost all metals, negligibly small in comparison with R. As a good approximation to the truth, then, we may neglect c_p'. The definite integral in (24) then becomes $\frac{5}{2}$R, and in place of (26) we have

$$\frac{dp}{p} = \frac{l_0}{\mathrm{RT}^2}d\mathrm{T} + \frac{5}{2}\frac{d\mathrm{T}}{\mathrm{T}}, \qquad . \quad . \quad . \quad (29)$$

which on being integrated gives us

$$\log_\epsilon p = -\frac{l_0}{\mathrm{RT}} + \frac{5}{2}\log_\epsilon \mathrm{T} + c,$$

or

$$p = \epsilon^c \mathrm{T}^{5/2}\epsilon^{-l_0/\mathrm{RT}}, \qquad . \quad . \quad . \quad (30)$$

and our emission formula becomes

$$i = (1 - \bar{r})\mathrm{A}_0\mathrm{T}^2\epsilon^{-l_0/\mathrm{RT}}, \qquad . \quad . \quad . \quad (31)$$

where A_0 is a constant, or, if we may assume that $\bar{r}$ is constant with temperature,

$$i = \mathrm{AT}^2\epsilon^{-l_0/\mathrm{RT}}, \qquad . \quad . \quad . \quad (32)$$

where A is a new constant, usually known as the "emission constant."

The formula (32) is similar to that by means of which, on page 11, we defined the work function. The definition there given was not intended to be more than a rough, provisional one, however, and it is now time to replace it by a more rigorous definition. By the work function, χ, is meant that part of the latent heat of evaporation per electron which is not concerned with the supply of kinetic energy to the electrons in the vapour phase or with the work of expansion. Thus, since c_p' is very small in comparison with R, we may write, with negligible error,

$$\frac{\chi}{k} = \frac{l_0}{\mathrm{R}}, \qquad . \quad . \quad . \quad . \quad (33)$$

and so our emission formula (31) becomes

$$i = \mathrm{A}_0(1 - \bar{r})\mathrm{T}^2\epsilon^{-\chi/k\mathrm{T}}, \qquad . \quad . \quad . \quad (34)$$

or, if $\bar{r}$ is assumed to be a constant,

$$i = AT^2\epsilon^{-\chi/kT}. \quad . \quad . \quad . \quad . \quad (2)$$

The emission formula may also be written in the form

$$i = AT^2\epsilon^{-T_\chi/T}, \quad . \quad . \quad . \quad (35)$$

where the relationship between T_χ (the so-called "work function expressed in degrees") and χ is

$$T_\chi = \chi/k. \quad . \quad . \quad . \quad . \quad (36)$$

Now k is $1{\cdot}371 \times 10^{-16}$ erg per degree, or $8{\cdot}62 \times 10^{-5}$ electron-volt per degree. Thus if, as is usual, χ is expressed in electron volts, we have the numerical relationship

$$T_\chi = 11{,}600\chi. \quad . \quad . \quad . \quad . \quad (37)$$

A few years ago, it was shown by Fowler,[26] Nordheim [54] and Sommerfeld [88] that a derivation of a formula like (34) could also be based directly on the assumption of a Fermi distribution of the internal electrons. Actually the formula so obtained, although equivalent to (34), looks a little different. It is

$$i = \bar{D}A_0T^2\epsilon^{-\frac{C-\mu}{kT}}, \quad . \quad . \quad . \quad (38)$$

where $\bar{D}$ is the so-called "mean transmission coefficient" characteristic of the emitting surface, C is the product of the inner potential of the emitter and the electronic charge, and μ is the zero-temperature critical energy of the Fermi distribution. This formula will be derived in Chapter V, where it will be shown that $\bar{D}$ is the same as $1 - \bar{r}$ and $C - \mu$ the same as χ.

In order to find the values of A and χ from any given set of emission data, all that is necessary is to plot $\log (i/T^2)$ against $1/T$, when a straight line will be obtained whose slope is $- T_\chi \log \epsilon$ (from which χ may be obtained by means of (37)), and whose intercept on the $\log (i/T^2)$ axis is log A.

Relationships between the Constants in Different Emission Formulæ.—The results of most of the earlier thermionic measurements were given in terms of the constants a' and ϕ of the older emission formula

$$i = a'T^{\frac{1}{2}}\epsilon^{-\phi/kT}. \quad . \quad . \quad . \quad . \quad (10)$$

It is easy to transform these results into terms of the more accurate formula

$$i = \mathrm{A}\mathrm{T}^2\epsilon^{-\chi/k\mathrm{T}} \quad . \quad . \quad . \quad . \quad (2)$$

if the mean temperature T_m of the range in which the emissions were measured is known.

In order to make the discussion more general, let us suppose that the two alternative formulæ by which a given set of data may be represented are

$$i = \alpha_1\mathrm{T}^{\gamma_1}\epsilon^{-\omega_1/k\mathrm{T}} \quad . \quad . \quad . \quad . \quad (39)$$

and

$$i = \alpha_2\mathrm{T}^{\gamma_2}\epsilon^{-\omega_2/k\mathrm{T}}. \quad . \quad . \quad . \quad . \quad (40)$$

Then by equating the expressions for $\frac{d \log i}{d\mathrm{T}}$ found from the two formulæ we obtain

$$\omega_2 = \omega_1 + (\gamma_1 - \gamma_2)k\mathrm{T}_m. \quad . \quad . \quad . \quad (41)$$

Substituting this value of ω_2 in (40) and equating the right-hand sides of (39) and (40) we then obtain for α_2 the value

$$\alpha_2 = \alpha_1\mathrm{T}_m{}^{\gamma_1-\gamma_2}\,\epsilon^{\gamma_1-\gamma_2}. \quad . \quad . \quad . \quad (42)$$

Thus, in particular, if $\gamma_1 = \frac{1}{2}$ and $\gamma_2 = 2$, we have

$$\chi = \phi - \tfrac{3}{2}k\mathrm{T}_m, \quad . \quad . \quad . \quad (43)$$

and

$$\mathrm{A} = a'\mathrm{T}_m{}^{-3/2}\epsilon^{-3/2}. \quad . \quad . \quad . \quad (44)$$

If ϕ and χ are expressed in electron-volts, we have, from (43), the numerical relationship between the two :

$$\chi = \phi - \frac{3}{2}\,\frac{1}{11600}\mathrm{T}_m = \phi - \frac{\mathrm{T}_m}{7740}. \quad . \quad . \quad (45)$$

It is generally found that χ is something like 5 per cent. less than ϕ.

The Reflexion Coefficient.—The mean reflexion coefficient entering into the formula (31) is that of electrons of very low velocity, for the mean kinetic energy corresponding to the normal velocity component of the molecules of a Maxwellian gas (and the external electron gas *is* Maxwellian) is only about 0·03 electron-volt per 1000° of the temperature.

Experiments with such slow electrons are very difficult to perform, and the results are subject to rather uncertain corrections, so that it is not surprising that the experimental data at present available are somewhat conflicting. Early experiments by Richardson,* Gehrts [30] and v. Baeyer [1] indicate that a very considerable proportion of very slowly moving electrons may be reflected. Thus Richardson has estimated the reflexion from a brass surface to be about 30 per cent. On the other hand, extrapolations from the results of more recent work generally indicate an almost negligibly small reflexion of slow electrons from gas-free metal surfaces. For example, Hull [34] has found that the reflexion of electrons from copper decreases from 40 per cent. at 50 e.v. to only 10 per cent. at 0·4 e.v. According to Farnsworth,[23] electron reflexion from gas-free nickel diminishes rapidly with falling primary energy down to 0·2 e.v., where he could only just detect it. Petry [60] has given curves of electron reflexion from tungsten, copper and gold as a function of primary energy, all of which have a steep positive slope in the region of 1 e.v., and if extrapolated backwards would give negligibly small or zero reflexion at a small fraction of an e.v. Such extrapolation is, however, a rather unsatisfactory procedure, particularly in view of the irregularities exhibited by some of the reflexion-voltage curves.

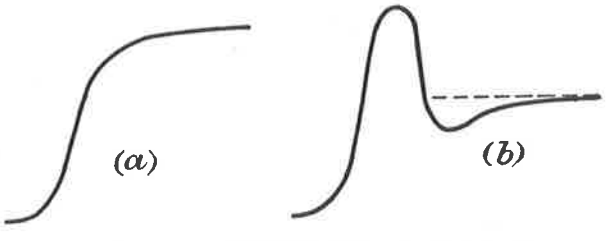

FIG. 5.—Two types of surface potential barrier.

Classical theoretical reasoning does not lead to the expectation of any appreciable reflexion at low incident velocities, not only because it is difficult to imagine any mechanism that would account for it, but also for more positive reasons. Let us first consider the negative side of the question. A surface potential hill of the shape of Fig. 5*a* could only accelerate electrons into the metal; it could not reflect them back. The only kind of hill that would, classically, account for a reflexion is

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* O. W. Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co., 2nd edition (1921), p. 170.

one with a hump, such as that of Fig. 5*b*. As we shall see later, there is reason to believe that such humps actually exist in the case of metals having an adsorbed electropositive layer of foreign atoms (or ions) on the surface. But with a potential hill of this shape we are involved in another difficulty. Classically, electrons could not escape without climbing over the top of the hump, and those having sufficient energies to do this would all have to fall down the slope of the hump on the other side and would thus all leave the metal with energies at least as great as that corresponding to the height of the hump above the final image level. The velocity distribution of the emitted electrons, therefore, instead of spreading from zero upwards, would only begin at some finite value. Yet no evidence of such a velocity distribution has been found experimentally.

Two positive objections to any assumption of an appreciable reflexion of slow electrons have been advanced by Compton and Langmuir.[10] In 1916 Langmuir,[42] employing classical particle dynamics, calculated from the measured heat conductivity in several metals the time of relaxation of electrons in them, i.e. the time it takes for an electron having unusually high energy to dissipate all but $\frac{1}{\epsilon}$th of its energy. From the order of the times found, Compton and Langmuir estimate that by the time an electron accelerated into a metal from an external electron gas has passed but a few per cent. of an atomic diameter beyond the surface layer of atoms it can no longer have sufficient energy to escape from the metal. Classically, perhaps the only conceivable mechanism of reflexion would be the attraction of an incident electron by the nucleus of a surface ion close to which it passes, in consequence of which the electron would have its direction of motion practically reversed, just as the sun reverses the direction of motion of a comet. According to the reasoning of Compton and Langmuir, in order to be reflected before it has lost too much of its energy an electron would have to pass very close indeed to the nucleus of a lattice ion, and presumably no important fraction of the incident electrons would do this. Their other objection is that neighbouring electrons (of the metal) would be repelled by the incident electron, that they would redistribute themselves very rapidly, and that the local positive space charge thus created would strongly damp out the motion of the incident electron.

These arguments do not now appear so cogent, however, as they did a few years ago. For not only is it true, in general, that the classical particle-mechanics as applied to electrons in metals has failed in several important respects, but in particular the modern electron theory of metals which replaces it, and about whose essential correctness there can no longer be any serious doubt, requires that the internal electrons shall have enormous free paths, equal to hundreds of atomic diameters. This requirement does not appear reconcilable with the conclusion of Compton and Langmuir that an appreciable part of the energy of an electron is dissipated before it has moved as much as the distance of a single atomic diameter.

The de Broglie wave-lengths of the electrons in which we are interested are, in general, great compared with the interatomic distances in the lattice. This leads one to hope that it may be possible at least to arrive at a first approximation to the truth by ignoring the atomic structure of the metal and confining one's attention simply to the action of the surface potential hill on the electron waves. This has been done by Nordheim,[54, 55] who has in this way developed a theory of electron reflexion at metal surfaces which appears to be at least qualitatively successful.

While reserving the fuller discussion of Nordheim's theory to Chapter V, we shall do well to take note of one or two of its results now. In the first place, it appears that potential hills of the type depicted in Fig. 5*a*, having no hump, cannot reflect electrons incident on them to any appreciable extent. When there is a hump, however, as in Fig. 5*b*, an important reflexion of electrons always occurs, except for such electrons as have sufficient energy to go right over the top of the hump. It may be thought that this is almost self-evident, indeed that electrons which cannot go over the hump must *all* be reflected. That is not so, however. According to the wave-mechanics, there is a finite probability that an electron incident on the hump will go right through it, even when its energy is less than that corresponding to the top of the hump, provided only that the hump is not too thick. As R. H.

Fowler[27] has pointed out, this is analogous to a well-known phenomenon in optics. When a beam of light, travelling in an optically "dense" medium, is incident on the boundary between this and a lighter medium at an angle of incidence greater than the critical angle, it is totally internally reflected and there is no beam in the second medium. There is, however, an electromagnetic disturbance in the second medium which dies away exponentially with the distance and which does not convey energy. In consequence, if the second medium is only a few wave-lengths thick and beyond it is the first medium again, a beam of light will re-form in this and travel in the forward direction, although with much diminished amplitude. Similarly, if our potential hump is not too high, and only a few Ångströms thick, the electron wave-train may re-form on the other side, also, of course, with diminished amplitude, so that a fraction of the incident electrons is transmitted through the hump. For example, with a potential hump 1 volt in height and 3 Ångströms thick—dimensions of the order we should expect to occur in nature—the calculated transmission, $1 - \bar{r}$, of slow electrons is of the order of 0·05. The theoretical transmission actually increases (as it should do) with the mean energy of the incident electrons, i.e. with the temperature, so that, strictly speaking, $1 - \bar{r}$ is not a constant. Its temperature variation is never (or hardly ever) sufficiently important, however, for it to have any effect on the measured value of χ.

The Constant A_0.—It may be shown that the constant A_0 of the emission formula (34) for metals must approach to universal constancy. This was first done by O. W. Richardson,* although the actual value of the constant was not found until some years later. Richardson's reasoning was substantially as follows:

Let the emission formulæ for two different metals be

$$i_1 = (1 - \bar{r}_1)A_{01}T^2\epsilon^{-\chi_1/kT} \quad . \quad . \quad . \quad (46)$$

and

$$i_2 = (1 - \bar{r}_2)A_{02}T^2\epsilon^{-\chi_2/kT}. \quad . \quad . \quad (47)$$

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* See O. W. Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co., 1st edition (1916), pp. 39-42; 2nd edition (1921), pp. 41-44.

Let the temperature T of both metals be the same. Then taking logarithms of the two formulæ and subtracting, we obtain

$$\log_\epsilon \frac{A_{01}}{A_{02}} = \log_\epsilon \frac{i_1(1-\bar{r}_2)}{i_2(1-\bar{r}_1)} + \frac{\chi_1-\chi_2}{kT}. \quad . \quad . \quad (48)$$

We may learn something concerning the right-hand side of this equation by considering the state of affairs that must exist when the two metals are in contact both with one another and with a common vacuum containing electrons (Fig. 6), after the system has settled down to a condition of equilibrium. Let us suppose that $i_1/(1-\bar{r}_1)$ is greater than $i_2/(1-\bar{r}_2)$, so that the electron concentration in the neighbourhood of the first metal is greater than that in the neighbourhood of the second. These two electron concentrations can only be in equilibrium with one another if there is a force tending to drive electrons from the region of the metal 2 to the region of 1, i.e. if the potential V_1 near 1 is greater than the potential V_2 near 2. The potential difference $V_1 - V_2$ is the contact difference of potential between the two metals.

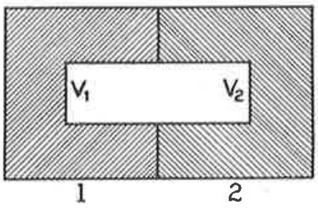

FIG. 6.

Now there is a definite relationship between the difference of potential between two regions in an electron gas at uniform temperature and the corresponding numbers of molecules per unit volume. As will now be shown, if n_1 and n_2 are these numbers where the potentials are V_1 and V_2 respectively, then

$$\log_\epsilon \frac{n_1}{n_2} = \frac{e}{kT}(V_1 - V_2).$$

Let us for simplicity consider a one-dimensional potential variation and let us suppose that there are n electrons per unit volume and that the pressure is p and the potential V at the point x. Then the condition that there shall be no resultant force acting on the electron gas at this point is

$$ne\frac{dV}{dx} = \frac{dp}{dx}. \quad . \quad . \quad . \quad . \quad (49)$$

But $p = nk\mathrm{T}$, and T is constant. Hence

$$ned\mathrm{V} = k\mathrm{T}dn,$$

or

$$\frac{dn}{n} = \frac{e}{k\mathrm{T}}d\mathrm{V}. \quad . \quad . \quad . \quad . \quad (50)$$

On integrating this, we have at once

$$\log_\epsilon \frac{n_1}{n_2} = \frac{e}{k\mathrm{T}}(\mathrm{V}_1 - \mathrm{V}_2). \quad . \quad . \quad . \quad (51)$$

Since the thermionic currents are proportional to $(1 - \bar{r})$ times the electron concentrations, we may write in place of this last equation

$$\log_\epsilon \frac{i_1(1 - \bar{r}_2)}{i_2(1 - \bar{r}_1)} = \frac{e}{k\mathrm{T}}(\mathrm{V}_1 - \mathrm{V}_2), \quad . \quad . \quad (52)$$

and this, substituted in (48), gives us

$$\log_\epsilon \frac{\mathrm{A}_{01}}{\mathrm{A}_{02}} = \frac{e(\mathrm{V}_1 - \mathrm{V}_2) + (\chi_1 - \chi_2)}{k\mathrm{T}}. \quad . \quad . \quad (53)$$

Now the work that must be done on an electron to take it from the region 1 to the region 2 in the electron gas, thence into the metal 2, through the inter-metallic boundary 2/1, and finally back into the region 1 of the electron gas is necessarily zero. The condition for this is that

$$e(\mathrm{V}_1 - \mathrm{V}_2) + (\chi_1 - \chi_2) + e\mathrm{P}_{12} = 0, \quad . \quad (54)$$

where P_{12} represents the Peltier effect at the junction between the two metals in volts. In consequence of this (53) becomes

$$\log_\epsilon \frac{\mathrm{A}_{01}}{\mathrm{A}_{02}} = -\frac{e\mathrm{P}_{12}}{k\mathrm{T}},$$

or

$$\frac{\mathrm{A}_{02}}{\mathrm{A}_{01}} = \epsilon^{\frac{e\mathrm{P}_{12}}{k\mathrm{T}}} = \epsilon^{\frac{1\cdot16 \times 10^4 \mathrm{P}_{12}}{\mathrm{T}}} \quad . \quad . \quad . \quad (55)$$

P_{12} is not generally of a greater order than about $10^{-4}\mathrm{T}$. Thus $\epsilon^{\frac{1\cdot16 \times 10^4\mathrm{P}_{12}}{\mathrm{T}}}$ will usually not exceed about ϵ, and so we shall not expect the values of A_0 for different metals to differ by factors of more than a few units.

In the case of emitters which have a negligibly small mean reflexion coefficient $\bar{r}$, the so-called "emission constant" A, defined by (2), must be equal to A_0. If there are any such, they are most probably the pure, uncontaminated metals. On the other hand, metals on whose surfaces are adsorbed monomolecular films of an electropositive contamination may have potential humps which give rise to an appreciable reflexion. We should therefore expect the emission constants of such contaminated metals to be, if anything, smaller than those of clean metals.

In Table III are given the measured values of A and χ for a number of emitters. Where a simple chemical symbol is given, it is to be understood that the emitter is the corresponding uncontaminated pure metal. Where two or more symbols are connected by hyphens, the first stands for the bulk metal and the remaining one(s) for the contaminating layer(s) of atomic thickness. Where one atomic layer is of oxygen it is to be understood that its concentration is the maximum possible. The surface concentration of a metallic contamination, on the other hand, is such that it makes the emission at any given temperature a maximum. This concentration is not necessarily the greatest possible for a single layer. Thus W-Th stands for tungsten having an optimum single layer of thorium atoms on its surface, and W-O-Ba stands for tungsten on whose surface is adsorbed a full monatomic layer of oxygen and on top of this an optimum monatomic layer of barium.

TABLE III.

EMISSION CONSTANTS AND WORK FUNCTIONS OF VARIOUS EMITTERS.

Emitter.	A. (amp./cm.^{2} deg.^{2}).	χ (electron-volts).	Emitter.	A (amp./cm.^{2}deg.^{2}).	χ (electron-volts).
Cs	162	1·81	W-Cs	3·2	1·36
Ba	60	2·11	W-Ba	1·5	1·56
Zr	330	4·12	W-O-Ba	0·18	1·34
Hf	14·5	3·53	Mo-Th	1·5	2·59
Th	70	3·38	W-La	8·0	2·71
Ta	60	4·1	W-Ce	8·0	2·71
Mo	55	4·15	W-Yt	7·0	2·70
W	60-100	4·54	W-Zr	5·0	3·14
Re	200	5·1	W-Th	3·0	2·63
Pd	60	4·99	W-U	3·2	2·84
Pt	17000	6·27			

It will be observed that of the eleven clean metals whose thermionic data are given, nine have emission constants not differing by a factor of more than about 3 from 100 amp./cm.^{2} deg.^{2}. It is possibly significant that the remaining two, viz. hafnium and platinum, are among those which it is most difficult to free from surface contaminations.

From the experimental evidence it is to be concluded either that A_0 is of the order of 20,000 amp./cm.^{2} deg.^{2} or more and that for all the emitters other than platinum $1 - \bar{r}$ is not of a higher order than 10^{-2}–10^{-5}, or else that for some reason the experimental results for platinum are not to be taken at their face value and that A_0 is probably something like 100 amp./cm.^{2} deg.^{2}. We shall see in Chapter V that, according to a quantum-statistical theory of emission in which the effect of the specific heat of the electrons in the condensed phase is ignored, the value of A_0 should be given by

$$A_0 = \frac{4\pi mek^2}{h^3} = 120 \text{ amp./cm.}^2 \text{ deg.}^2 . \qquad (56)$$

The Condition of the External Electron Gas.—We have now to consider the question of whether or not the effects of the mutual repulsions between the external electrons are small enough to be neglected, as we have assumed them to be in the derivation of the T^2 emission formula. This question was first seriously raised by M. v. Laue [49] in 1918, and in a subsequent discussion between v. Laue [50] and W. Schottky [78] it was shown that under conditions actually realized in practice the effects of the repulsions are, in fact, almost always negligibly small and that it is consequently permissible to regard the external electrons as constituting a practically perfect gas. The argument upon which this conclusion depends has been presented by Schottky and Rothe * substantially as follows :

It is obvious that the more the electrons are crowded together at any given temperature, the greater will be the proportion of the electron paths in which their motion is appreciably affected by the repulsive forces due to other electrons, and the greater, therefore, must be the departure from the ideal

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* W. Schottky and H. Rothe, "Physik der Glühelektroden," Wien-Harms' Handbuch der Experimentalphysik XIII (2), Akadem. Verlagsgesellschaft m.b.H., Leipzig (1928), pp. 35-37.

gas state. We wish to find at what concentrations the intermolecular forces may no longer be neglected and to compare these concentrations with those actually arising in practice.

Let us consider the region where, in the thermodynamical discussion, there is assumed to be equilibrium between the external electron gas and the metal, viz. that just beyond the range of the image force. Let there be n electrons per c.c. in this region, the corresponding mean distance of separation being therefore $(1/n)^{1/3}$ cm. In order that the effects of the mutual repulsions shall be negligible, in the sense we require, over all but a very small fraction of the electron paths, it is necessary that the mutual potential energy of two electrons at a distance $(1/n)^{1/3}$ cm. apart shall be a negligible fraction of the mean kinetic energy, i.e.

$$\frac{e^2}{(1/n)^{1/3}} \ll \frac{3}{2} k\mathrm{T}. \quad . \quad . \quad . \quad . \quad (57)$$

Now it will be more convenient to have our condition in terms of the thermionic current density i than of n, since the former is directly measurable. The concentration-number n may be expressed in terms of i and the mean reflexion coefficient $\bar{r}$ by means of the relation

$$n = \frac{i}{1-\bar{r}} \cdot \frac{1}{e}\sqrt{\frac{2\pi m}{k\mathrm{T}}}, \quad . \quad . \quad . \quad (58)$$

and so, combining this with (57), we have for the condition to be fulfilled

$$\frac{2}{3}\left(\frac{i}{1-\bar{r}}\right)^{1/3} \frac{e^{5/3}(2\pi m)^{1/6}}{(k\mathrm{T})^{7/6}} \ll 1, \quad . \quad . \quad . \quad (59)$$

or, writing for the constants their known values, viz. $k = 1{\cdot}37 \times 10^{-16}$ erg/deg., $e = 4{\cdot}77 \times 10^{-10}$ e.s.u., $m = 9{\cdot}0 \times 10^{-28}$ gm., and remembering that 1 ampere is equal to 3×10^9 e.s.u.,

$$\frac{38\left(\frac{i}{1-\bar{r}}\right)^{1/3}}{\mathrm{T}^{7/6}} \ll 1, \quad . \quad . \quad . \quad (60)$$

where i is expressed in amperes per cm.^{2}

In order to see whether this condition is fulfilled, let us examine two extreme cases, viz., that of a monatomic layer of cæsium on tungsten and that of clean tungsten, whose emissions have been observed at very low and at very high temperatures respectively.

Langmuir and Kingdon [48] have found the emission from an optimum monatomic layer of cæsium on tungsten to vary from about $2{\cdot}5 \times 10^{-6}$ amp./cm.^{2} at 590°K. to about $2{\cdot}5 \times 10^{-3}$ amp./cm.^{2} at 780°K. We shall see in Chapter III that for this emitter the measured value of A is 3·2 amp./cm.^{2} deg.^{2} and that this is probably not in error by more than a factor of 3. Thus, since A_0 is 120 amp./cm.^{2} deg.^{2}, $1 - \bar{r}$ is probably not less than about 1/100. Assuming this unfavourable value, then, we find the variation of the left-hand side of (60) to be from $1{\cdot}4 \times 10^{-3}$ at 590°K. to $1{\cdot}0 \times 10^{-2}$ at 780°K. Both these quantities are sufficiently small for our electron gas to be regarded as very nearly perfect.

Now let us consider the case of tungsten at the extremely high temperature of 3000°K., where the emission density is 14 amp./cm.^{2} It is possible that for this metal $1 - \bar{r}$ is about $\frac{1}{2}$, but it is certainly not much less than this. Assuming this value, we find that the left-hand side of (60) becomes $1{\cdot}0 \times 10^{-2}$. And since i changes with T much more rapidly than as $T^{7/2}$, our condition must be even better fulfilled at lower temperatures.

If we examined other cases in the same way, we should find that the condition (60) is almost always sufficiently well fulfilled for the assumption of a perfect external electron gas to be justified.

Even in certain cases where the left-hand side of (60) is not negligibly small, the conclusions based on the assumption of a perfect external electron gas may still hold good. For when electrons are being drawn from the emitter by an accelerating field, their actual concentration in the region just beyond the range of the image force must always be less than that in an external electron gas *in equilibrium* with the emitter, and in certain cases it will be very much less. The absence of returning electrons halves the concentration even when there is no reflexion, but where there is reflexion the concentration will be diminished by the additional factor of $1 - \bar{r}$. If the concentration of the electrons under emission-current-measuring conditions is substituted in (60) for that in a supposed external electron gas in equilibrium with the emitter, the less exacting condition

$$\frac{30i^{1/3}}{T^{7/6}} \ll 1 \quad . \quad . \quad . \quad . \quad (61)$$

is obtained. If this condition is fulfilled, it is difficult to see why we should not argue *as if* the effects of mutual repulsions in an electron gas in equilibrium with the emitter were also negligible and still draw valid conclusions.

That is the " microscopic " side of the question. But there is also a " macroscopic " side. If the volume of the external gas is sufficiently great, the field due to the space charge will appreciably affect the equilibrium conditions at the surface of the emitter. It is to be understood, then, that the volume of the gaseous phase considered in the thermodynamical discussions is always to be taken so small that the disturbing effect of the space charge is negligible.

Finally, it is convenient to imagine the " cylinder and piston " containing walls of the electron gas to be of the same emitting material and to have the same temperature as that whose thermionic properties are under consideration.

The Velocity Distribution of Thermally Emitted Electrons.—If we have an external electron gas in equilibrium with an emitting body, not only must the same *total* number of electrons leave the surface of the emitter in a given time as reach it from outside, but the numbers *belonging to any particular velocity group* leaving and arriving at the surface must also be equal, for otherwise there could be no true equilibrium. We shall see in Chapter V that for degrees of crowding such as occur in external electron gases at realizable temperatures the Fermi distribution is indistinguishable from the Maxwellian. Thus we shall expect the velocities of the electrons leaving the surface under the supposed equilibrium conditions to be distributed according to the Maxwellian law.

Of course not all of these electrons are necessarily emitted. Some of them may be merely reflected. Therefore, unless the reflexion coefficient is negligibly small, or else is the same for all incident velocities, we shall not expect to find the emitted electrons alone to have a Maxwellian distribution. Now there is, according to Nordheim's theory, one case in which the reflexion should not be important for electrons of any incident velocity, viz. that of a potential hill at the surface of the emitting body which has no hump projecting above the final image level, such as has been depicted, for example, in Fig. 5*a*. The electrons emitted from such a body should therefore have a Maxwellian velocity distribution. On the other hand, if there is a projecting hump, as in the hill of Fig. 5*b*, the reflexion will be negligible only for those electrons whose normal velocity components are large enough for them to go *over the top* of the hump. For those, however, whose velocities normal to the surface are so small that they would have to go *through* the hump, the reflexion coefficient will no longer be negligible, and must increase as the normal velocity diminishes. Thus in this case, while the velocity distribution of emission should still be Maxwellian corresponding to the temperature of the emitter for electrons emitted with normal velocities great enough for them to go over the top of the hump, it should not be for those that have to go through the hump.

It may, perhaps, be objected that we know from experiment that electrons which approach the surface with quite high velocities may be appreciably reflected and that Nordheim's theory therefore cannot be correct. There is reason to believe, however, that the reflexion of fast electrons is an effect depending on the atomic lattice structure, which Nordheim's theory ignores, and which is much more important for electrons whose velocities are high and whose wave-lengths are, therefore, short, than for relatively slow electrons, whose wave-lengths are large compared with inter-atomic distances. For the latter, we may probably take Nordheim's theory as a sufficiently good guide.

The method that has been most commonly employed experimentally in order to determine the velocity distribution of the emitted electrons has been to apply various negative potentials to the anode and to measure the electron currents that flow against the corresponding retarding fields. It is essential that the anode should be made sufficiently negative with respect to the cathode, for otherwise there will be a potential minimum between the two electrodes, due to the space charge, and it will be this, not directly the potential of the anode, which will determine the extra potential hill the emitted electrons have to climb. Thus, unfortunately, the method does not lend itself to the determination of the velocity distribution of the slowest electrons. In Fig. 7 is shown qualitatively the way in which the potential distribution between the two electrodes depends on the potential applied to the anode. The higher the temperature of the cathode, and the greater, therefore, its emission, the more negative must the anode be made in order that there shall be no space-charge potential minimum.

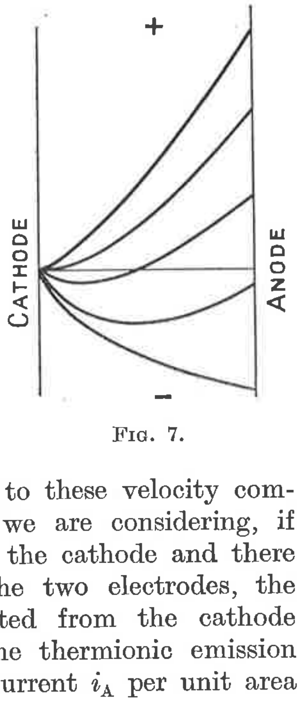

FIG. 7.

The relationship between the retarding potential and the current of electrons emitted with a Maxwellian velocity distribution which will flow against it is simplest in the case where the electrodes are infinite parallel planes. Let us examine this case first. We saw on page 23 that of a number of electrons whose velocity components in a certain direction are distributed according to the Maxwellian law, a fraction $\epsilon^{-C/kT}$ have greater kinetic energies corresponding to these velocity components than C. Thus in the case we are considering, if the anode is at a potential V below the cathode and there is no potential minimum between the two electrodes, the fraction $\epsilon^{-eV/kT}$ of the electrons emitted from the cathode will reach the anode. Or, if i is the thermionic emission per unit area from the cathode, the current i_A per unit area collected by the anode will be given by

$$i_A = i\epsilon^{-eV/kT}. \quad . \quad . \quad . \quad . \quad (62)$$

Thus, if $\log_{10} i_A$ is plotted against V, a straight line should be obtained whose slope is $-\frac{e}{kT}\log_{10}\epsilon$, and if V is in volts this is $-\frac{5040}{T}$.

The case of infinite concentric cylinders, the inner one being the cathode and the outer the anode, has been investigated mathematically by W. Schottky.[79] This case is not quite so simple as that of infinite parallel planes, since not only the radial but also the tangential components of the velocities of ejection are of importance in determining the anode current. The reason for this is, of course, that the latter as well as the former are directed toward the anode. Schottky has shown that if the radius of the inner cylinder (the cathode) is less than $\frac{1}{30}$ that of the outer and the anode is made sufficiently negative to the cathode, the dependence of i_A upon V corresponding to a Maxwellian distribution of emission is given within $\frac{1}{2}$ per cent. by the formula

$$i_A = i\frac{2}{\sqrt{\pi}}\left[\sqrt{\frac{Ve}{kT}}\,\epsilon^{-\frac{Ve}{kT}} + \int_{\sqrt{\frac{Ve}{kT}}}^{\infty}\epsilon^{-x^2}dx\right] . \qquad . \quad (63)$$

Except for very small values of V, the second term on the right-hand side is small compared with the first and the relationship between log i_A and V is approximately linear.

One would, perhaps, naturally expect this formula to be valid for all values of the anode potential which are negative to the cathode by more than V_0, where V_0 is the value for which there is just no potential minimum between the electrodes. Schottky has worked out formulæ by means of which the value of V_0 may be estimated, and he has found that with the usual order of electrode dimensions V_0 grows from $\frac{1}{10}$ volt or less to something like 1 volt as the emission, i, increases from 10^{-9}–10^{-8} amp./cm.^{2} to 10^{-5} amp./cm.^{2}. It has more recently been shown by Davisson,[13] however, that the non-existence of a potential minimum in the inter-electrode space is not a sufficient condition for the validity of (63), but that this formula must fail for $V = V_0$ and also for a certain range of values of V greater than V_0.

For really reliable and accurate determinations of the velocity distribution by the retarding field method it is, of course, necessary to avoid having either a potential drop along the cathode or a magnetic field surrounding it. Thus, if the cathode is in the form of a wire or a ribbon, heated by a current, it is usual to make the current intermittent, with a high make-and-break frequency, and to so arrange the circuit that thermionic currents are measured only during the "off" periods.

The first experimental test of the distribution of the normal velocity components of emitted electrons was made by Richardson and Brown,[69] in 1908, for the case of parallel plane electrodes, the cathode being a platinum ribbon let into a slit in a plane sheet of metal. They obtained linear plots of log i_A against V and found the mean of eight determinations of the slopes of these plots to agree within less than 1 per cent. with that required by Maxwell's law for an electron gas at the temperature of the emitter. Individual slopes differed from the theoretical by nearly 20 per cent., however.

Shortly afterwards, Richardson [67] also tested the distribution of the components of velocity parallel to the emitting surface, again with platinum, in the form of a ribbon nearly filling up a slit in a metal plate, as the cathode. Opposite the cathode and at a short distance from it was placed a plate containing a slit parallel to the ribbon. This plate was moveable in its own plane, in a direction perpendicular to the slit. Behind the slit was placed a Faraday collecting cylinder, and the current collected by it measured as a function of the position of the slit either when the movable plate and cylinder were at the same potential as the fixed plate and platinum ribbon, or when they were at some positive potential to the latter and electrons thus accelerated to them. Corresponding to different positions of the slit and collector, electrons emitted with different sideways velocities were collected. In this way the velocity components parallel to the surface were found also to have a Maxwellian distribution corresponding to the temperature of the emitter.

In 1914 Schottky [79] made use of the coaxial cylinder arrangement in order to determine the velocity distributions of the electrons emitted from filaments of carbon and tungsten at various temperatures. In each case he found the current-voltage relationship to be expressible by a formula like (63), in which, however, T was not the measured temperature of the emitting filament, but some higher temperature, which we may call the "distribution temperature." The distribution temperature generally exceeded the measured filament temperature by a few hundred degrees. The filament temperatures were calculated from the emissions, using thermionic data for carbon and tungsten found by other observers. In view, however, of the important effects surface contaminations are known to have on thermionic emissions, this method of temperature measurement cannot, perhaps, be regarded as entirely satisfactory.

Later experiments on platinum and tungsten by Sih Ling Ting,[85] using both the parallel plate and the coaxial cylinder methods, seemed to indicate a distribution of the Maxwellian type with the distribution temperature about double that of the emitter. However, this result was subsequently attributed by Jones,[38] who continued the work begun by Sih Ling Ting, to a faulty circuit arrangement, and when this was corrected the distribution temperature obtained agreed in every case very closely with that of the emitting filament.

Potter,[62] using the coaxial cylinder arrangement, confirmed Jones' result for platinum wires heated in a good vacuum, but found that when the wires were exposed to hydrogen at a pressure above about $\frac{1}{20}$ mm. the distribution temperatures were much greater than the filament temperatures. It would be difficult, however, to attribute this to the effects of surface contaminations, since Potter was unable to detect any change in the emissions due to the gas. Similar results were obtained by Congdon [11] for wires of tungsten in a vacuum and in hydrogen. Neither Potter nor Congdon found the distribution temperatures at any given filament temperature to be determined uniquely by the pressure of hydrogen, so it does not appear that the observed discrepancies between the distribution and filament temperatures can have been due merely to collisions between electrons and gas molecules. Indeed, Congdon found that while the distribution temperature was increased quite considerably by hydrogen, even when the pressure was less than $\frac{1}{10}$ mm., argon had no effect on it up to a pressure of as much as 3 cm.

The experiments of Potter and Congdon were repeated a few years later by del Rosario,[72] who failed, however, to confirm their results. He was unable to detect any effect on the velocity distribution of the electrons emitted from platinum or tungsten filaments due to exposure to hydrogen of pressures up to $\frac{1}{4}$ mm. In all cases, irrespective of the presence or absence of hydrogen, the observed distribution agreed within 2 or 3 per cent. with the Maxwellian corresponding to the temperature of the emitter.

Perhaps one of the most painstaking and accurate experimental determinations of the velocity distribution of electrons thermally emitted in a good vacuum that has yet been made is one that was carried out by Germer [31] in 1925, using a tungsten filament. A very considerable range of temperatures (1440°–2475°K.) and of retarding potentials was covered, and the distribution was at all temperatures found to be Maxwellian and the distribution temperature to agree with the actual temperature of the filament within 5 per cent. or less.

Several determinations have also been made of the velocity distribution of the electrons emitted from oxide cathodes. One of the earliest of these was made by Rössiger [73] with a cathode coated with a mixture of BaO, SrO and CaO, employing a method of magnetic analysis of the electron velocities due to Hull,[35] instead of the usual retarding field method. Within the limits of experimental uncertainty, which were rather wide, the distribution found by Rössiger agreed with the Maxwellian corresponding to the temperature of the cathode.

Later determinations made by the retarding field method by Koller [40] and Rothe [74] did not confirm this result. Both found distributions of the Maxwellian type, but corresponding to a much higher temperature than that of the emitter. It is possible, however, that this was due, at least in large part, to the unsuitability of the electrode geometry. Koller used a coated *ribbon*, instead of a round wire, stretched along the axis of a cylindrical anode. The lengths of ribbon and anode were not stated. Rothe carried out his experiments on commercial oxide-coated-filament valves, the grid and anode connected together serving as collector. In general, however, commercial valves are by no means ideal for this kind of experiment. Quite apart from the question of shape (in section) of the electrodes, they are usually so short that the field cannot be regarded as effectively two-dimensional. In addition to this, a serious error must be introduced if the temperature of the filament is calculated, as it was by Rothe, from its resistance, and the filament is so short that the resistance of the relatively cool ends is an important part of the whole. As Demski [15] has pointed out, the electrons collected by the anode must, in such a case, come mainly from the hot central portion of the filament, whose temperature is, of course, higher than that calculated from the resistance. Yet another possible source of error is, according to Demski, patchiness of the emitting surface. Such patchiness is often difficult to avoid in the case of oxide cathodes, and if it occurs the local fields associated with it will cause the measured values of the distribution temperature to be too high. After eliminating this and other sources of error, Demski has found distribution temperatures in close agreement with the corresponding temperatures of the oxide cathodes. Maxwellian distributions of the electrons emitted from oxide cathodes corresponding to the cathode temperatures have also been observed by Davisson (reported by Germer [31]) and by Möller and Detels.[53]

Two experimental determinations of the velocity distribution of the electrons emitted from fully activated thoriated tungsten have recently been made, one by Reynolds,[64] the other by Nottingham,[56] both employing the coaxial cylinder arrangement. Reynolds found the distribution to be Maxwellian, corresponding to the temperature of the emitting filament, at least for the electrons emitted with high velocities. Nottingham obtained the same result for electrons emitted with velocities of more than about 1·5 equivalent volts, but for those emitted with lower velocities he found a distribution which, while still Maxwellian, corresponded to a temperature some hundreds of degrees higher than that of the filament. By keeping the filament temperature low and thus minimizing the disturbing effect of space charge, he was able to observe the distribution down to as low a retarding potential as about 0·3 volt.

A series of observations made by Nottingham for a filament temperature of 1160°K. is plotted in Fig. 8. The nearly horizontal part of the curve corresponds to the saturation current. To the left of this the anode potentials are electron-retarding. (That they are nevertheless marked positive in Nottingham's figure is presumably due merely to his not having taken account of contact potentials and perhaps also certain circuit voltages.) The dashed curve corresponds to Schottky's formula (63) for a temperature of 1600°K. This, it will be noted, goes through the observed points for retarding potentials between about 0·3 and 1·5 volts. For retarding voltages appreciably above 1·5 the observed points lie on a somewhat steeper line whose slope corresponds to the temperature of the filament, viz. 1160°K.

Now a (log i_A)-V curve having a rather sharp change in slope at a certain point such as we have in Fig. 8 is precisely what must, according to the wave-mechanical theory, be expected in the case of an emitter at whose surface there is a potential hump. The retarding voltage at which the sharp change in slope occurs corresponds to the effective height of the potential hump, i.e. the height above the final image level. Thus, according to Nottingham's data, the effective height of the hump in the case of W-Th is something like 1·5 volts.* This is rather less than corresponds to the difference between the work functions of clean tungsten and W-Th, viz., 1·9 e.v.

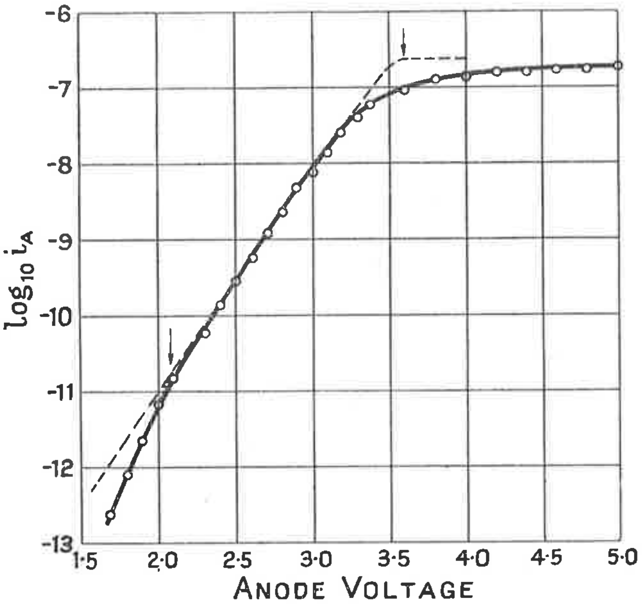

FIG. 8.—Variation with anode voltage of the electron current from a W-Th filament flowing against an electron-retarding field.

Theoretically, we should expect the effective height of the

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* Nottingham's own interpretation of his results differs slightly from that given here and leads to a value of 1·3 volts for the effective height of the hump.

hump to correspond to less than the depression of the work function due to the adsorbed film. This will at once be evident on reference to Fig. 9. In this we may suppose the continuously rising curve to represent the upper part of the potential hill at the surface of a clean metal, say tungsten. The last part of it is due to the image field and is asymptotic to a line marked W. Let us suppose the curve with a hump is the corresponding part of the potential hill for the same metal on whose surface there is an adsorbed electropositive film, say of thorium atoms. The last part of this must also be due to the image field and must therefore also rise. This will be asymptotic to some line W-Th. Obviously only the part (shaded) of the hump above the line W-Th can be effective in producing electron reflexions and the height of this part must necessarily correspond to less than the depression of the work function, $\chi_W - \chi_{W-Th}$.

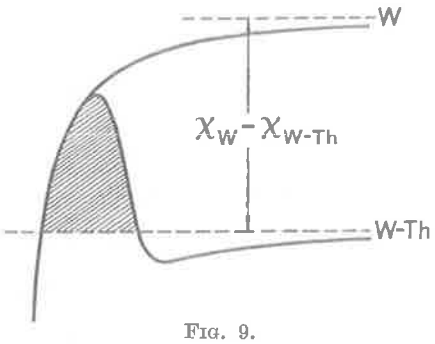

Fig. 9.

The Calorimetric Measurement of the Work Function.—We had on page 27 the equation

$$l = l_0 + \int_0^T (c_p - c_p')dT, \quad . \quad . \quad . \quad (24)$$

which, on substituting $\frac{5}{2}$R for c_p becomes

$$l = l_0 + \frac{5}{2}\,RT - \int_0^T c_p'\,dT. \quad . \quad . \quad (64)$$

The quantity l is the heat per gram-molecule of electrons lost by the conductor when a small quantity of electrons is virtually transferred at constant temperature and pressure from it to the gaseous phase. It is important to remember that the system is supposed to be completely isolated from its surroundings, so that no fresh electrons are supplied to the conductor to compensate for those lost.

The heat loss, λ per gram-molecule of electrons, suffered by an emitting cathode in consequence of saturated space current being drawn from it is, for three separate reasons, not quite the same as l. In the first place the kinetic energy per gram-molecule of a *current* with a given (say Maxwellian) velocity distribution is different from the energy per gram-molecule of a *gas* with the same kind of velocity distribution, for the faster molecules make a relatively greater contribution to the current than they do to the mass of the gas. Secondly, when saturated thermionic current is drawn there is no mutual interchange of energy between the two phases ; the condensed phase " knows nothing," so to speak, of what happens to the evaporating particles after they have left it, and therefore no work-of-expansion term enters into λ. And finally, the heat loss of which λ is a measure is not necessarily entirely uncompensated, for the electrons fed into the conductor to take the place of those lost by emission have whatever energy may correspond to the temperature of the point at which the conductor receives them.

In the expression (64) for l, the term $\frac{5}{2}$RT represents the sum of the kinetic energy ($\frac{3}{2}$RT) and the work of expansion (RT) of one gram-molecule of the external electron gas. It is clear that in the corresponding expression for λ, $\frac{5}{2}$RT should be replaced by the average kinetic energy of ejection per gram-molecule of *current* drawn minus some quantity $F(T_0)$, where T_0 is the temperature of the point at which the electron current flows back into the emitting cathode.

In order to determine the former of these quantities it is necessary to know the law of distribution of velocities of the emitted electrons. This, as we have seen, is frequently Maxwellian, although apparently it is not always so. Let us, however, here confine our attention to the cases where it *is* Maxwellian, with a distribution temperature equal to the temperature of the emitter.

Let us imagine a unit cube constructed within a Maxwellian electron gas at a temperature T. Then the mean kinetic energy of the current constituted by the electrons passing in one direction through one face of such a cube must also be the mean kinetic energy of the thermionic current due to electrons emitted with a Maxwellian distribution from the cathode at this temperature. If N represents the total number of electrons within the cube at any instant, then the number whose velocity components normal to the cube-face chosen lie between u and $u + du$ is $d\mathrm{N}$, where

$$d\mathrm{N} = \mathrm{N}\sqrt{\frac{m}{2\pi k\mathrm{T}}}\epsilon^{-\frac{mu^2}{2k\mathrm{T}}}du. \quad . \quad . \quad . \quad (5)$$

The number of electrons belonging to this velocity group which pass through the face of the cube in unit time is obviously $ud\mathrm{N}$, and that part of their kinetic energy which corresponds to the normal velocity component is $\frac{1}{2}mu^3d\mathrm{N}$. Hence the mean kinetic energy per electron of the current corresponding to the normal velocity component is

$$\frac{\int_{u=0}^{u=\infty}\frac{1}{2}mu^3d\mathrm{N}}{\int_{u=0}^{u=\infty}ud\mathrm{N}},$$

or, by (5),

$$\frac{m}{2}\frac{\int_0^\infty u^3\epsilon^{-\frac{mu^2}{2k\mathrm{T}}}du}{\int_0^\infty u\epsilon^{-\frac{mu^2}{2k\mathrm{T}}}du},$$

which is equal to $k\mathrm{T}$.* The contributions to the kinetic energy corresponding to the velocity components in the two directions parallel to the face of the cube are of course each $\frac{1}{2}k\mathrm{T}$, so that, finally, the total mean kinetic energy is $2k\mathrm{T}$ per electron or $2\mathrm{RT}$ per gram-molecule of the current. The expression for λ which is the counterpart of eqn. (64) must therefore be

$$\begin{aligned}\lambda &= l_0 + 2\mathrm{RT} - \mathrm{F}(\mathrm{T}_0) - \int_0^{\mathrm{T}} c_p{}'d\mathrm{T} \\ &= l - \tfrac{1}{2}\mathrm{RT} - \mathrm{F}(\mathrm{T}_0). \quad . \quad . \quad . \quad . \quad (65)\end{aligned}$$

Now we had on pages 28 and 29,

$$\frac{l_0}{\mathrm{R}} = \frac{\chi}{k} = \mathrm{T}_\chi.$$

Thus the work function expressed in degrees is given by

$$\mathrm{T}_\chi = \frac{\lambda}{\mathrm{R}} - 2\mathrm{T} + \frac{1}{\mathrm{R}}\Big[\int_0^{\mathrm{T}} c_p{}'\,d\mathrm{T} + \mathrm{F}(\mathrm{T}_0)\Big]. \quad . \quad (66)$$

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* For the solutions of these integrals see, for example, Appendix A to J. H. Jeans' "Dynamical Theory of Gases," Cambridge University Press.

If c_p' were equal to $\frac{3}{2}$R, as it would be if Richardson's original picture of a Maxwellian internal electron gas were true, we should have in place of (2) or (35) the emission formula (9) in which C/k would be given by

$$\frac{C}{k} = \frac{\lambda}{R} - \frac{T}{2} + \frac{F(T_0)}{R}, \quad . \quad . \quad . \quad (67)$$

and $F(T_0)$ the energy per gram-molecule of electrons of the current fed into the emitting body, would be $2RT_0$, so that finally, we should obtain for C/k the expression

$$\frac{C}{k} = \frac{\lambda}{R} - \frac{T}{2} + 2T_0. \quad . \quad . \quad . \quad (68)$$

If, on the other hand, we take $c_p' = 0$, then $F(T_0) = 0$, and we have

$$\frac{\chi}{k} = T_\chi = \frac{\lambda}{R} - 2T. \quad . \quad . \quad . \quad (69)$$

Thus, taking account of the relation (41), we see that we could replace (68) and (69) by

$$\frac{\omega}{k} = \frac{\lambda}{R} + 2T_0 \quad . \quad . \quad . \quad (70)$$

and

$$\frac{\omega}{k} = \frac{\lambda}{R} \quad . \quad . \quad . \quad . \quad (71)$$

respectively, where ω is the quantity appearing in the *empirical* emission formula

$$i = f \, . \, \epsilon^{-\omega/kT}, \quad . \quad . \quad . \quad . \quad (1)$$

f being a constant.

In practice, $2T_0$ is generally of the order of 2 per cent. of ω/k. With present-day experimental technique it is generally not possible to be certain of the accuracy of a determination of ω to within less than about 1 per cent., and, if anything, the accuracy with which λ can be measured is rather less. Thus an *experimental* test as to whether the term $2T_0$ should or should not appear seems to be only just on the borderline of possibility. There is, however, no longer the need for such a test that there was formerly. We now know enough about the metallic state to enable us to say without hesitation that the term $2T_0$ should *not* appear, and that the true work function, χ, is given by the formula (69).

Now let us consider the case where the distribution of velocity of the emitted electrons is not Maxwellian corresponding to the temperature of the emitter. In such a case the distribution may not even be strictly of the Maxwellian type, but it will probably not be possible to detect any departure from this type experimentally. Let us suppose that the distribution of the *normal* velocity components for the slower electrons corresponds to a distribution temperature T_d. We have seen that the effect of a potential hump must be to make T_d different from T, the temperature of the emitter, and a moment's reflexion will show that T_d must be greater than T. Of course for the electrons ejected with sufficient normal velocities to go over the top of the hump, T_d must be equal to T, but these electrons will in general form such a small proportion of the whole that they may be neglected. As for the tangential velocities, there does not seem any reason why these should be affected by the hump in any way. Thus for an emitter at whose surface there is a potential hump we should expect to have to replace (69) by

$$\frac{\chi}{k} = T_\chi = \frac{\lambda}{R} - T - T_d. \qquad (72)$$

Judging by the case of thoriated tungsten, we should expect $T_d - T$, the difference between the right-hand sides of (69) and (72), to be only of the order of T/2, or something like 2 or 3 per cent. of T_χ. It is rather doubtful if the limitations of present-day technique would permit of such a small difference being established experimentally.

Attention was first drawn to the possibility of determining work functions calorimetrically by O. W. Richardson [68] in 1903. Five years later Wehnelt and Jentzsch [96] attempted to measure the work function of a lime-coated platinum filament by this method. The filament formed one arm of a Wheatstone bridge. After the bridge had been balanced with the filament at a certain temperature and with no thermionic current flowing, saturated space current was drawn and the heating energy supplied to the filament increased until the bridge again balanced. The amount of this increase was taken to be equal to the heat lost by the filament on account of the evaporation of the electrons, and the work function calculated on this basis. It was found, however, that the value so obtained differed widely from that deduced from the temperature variation of the emission of the same filament. The failure to obtain concordant results by the two methods is now known to have been due to (1) proper allowance not having been made for the disturbing effect of the thermionic current on the balance of the bridge and on the temperature distribution along the filament, and (2) the rather unfortunate choice of cathode, from which (see Chapter IV), with the very imperfect vacua realizable at that time, it was impossible to obtain consistent thermionic behaviour. The experiments were repeated by Schneider [76] in 1912, who, however, had no better success. In the following year, Cooke and Richardson,[12] by a modification of the experimental method employed by their predecessors, succeeded in eliminating the worst of the electrical and thermal secondary effects produced by the thermionic current and obtained very tolerable agreement between the work function determined calorimetrically and that deduced from the slope of the Richardson line in the case of osmium and tungsten, but still failed to do so in the case of lime-coated platinum, as did also Wehnelt and Liebreich [97] shortly afterwards. Lester,[51] in 1916, by introducing still further experimental refinements, obtained very satisfactory agreement between the work functions determined by the two methods in the case of tungsten, molybdenum, tantalum and carbon, and Wilson,[101] in the following year, achieved equally satisfactory results with platinum wires coated with calcium, strontium and barium oxides. Further comparisons which have shown agreement between the work functions determined by the two methods have been made by Davisson and Germer,[14] Michel and Spanner,[52] and Rothe.[75] From the point of view of experimental technique, the work of Davisson and Germer is that which probably approaches most nearly to perfection.

The inverse effect, viz. the heating which accompanies the condensation of electrons in a conductor, has also been used for the determination of work functions, notably by Richardson and Cooke,[70] and more recently by Viohl.[91] It is, of course, necessary to allow for the energy with which the electrons enter the metal. Thus, if the electrons are derived thermionically from an emitter at a temperature T_e, from which they are emitted with a Maxwellian velocity distribution, and the potential of the conductor whose work function is to be determined is V above that of the emitter (including the contact difference of potential), then if λ' is the heat developed in the conductor per gram-molecule of electrons condensed in it, the work function χ must be given by

$$\frac{\chi}{k} = \mathrm{T}_{\chi} = \frac{\lambda'}{\mathrm{R}} - 2\mathrm{T}_{c} - \frac{e\mathrm{V}}{k}. \qquad (73)$$

This method would be particularly useful in its application to the less refractory metals whose work functions cannot easily be determined by the more direct methods.

Work functions have also been determined from the heat developed in an electrode in a gas discharge by Holst and Oisterhuis,[33] Penning,[59] Schottky [84] and v. Issendorff,[84, 36] and van Voorhis [92, 93] and Compton.[93] In view, however, of the complexity of the accompanying phenomena and of the many corrections that have, in consequence, to be applied, it seems doubtful whether the method is—at any rate in its present form—capable of yielding very accurate results.

Infra-Saturation Currents.—The only reason why infra-saturation thermionic currents are less than the saturation currents is that the electrons of the former have a greater potential hill to climb than those of the latter, the extra height of the hill being due to the space charge. For example, in the case of infinite plane parallel electrodes where the potential minimum due to the space charge is V_m below the potential of the cathode and the latter is at the temperature T, the velocity distribution of the electrons emitted from it being Maxwellian, the relationship between the infra-saturation current i_{A} and the emission i must be

$$i_{\mathrm{A}} = i\epsilon^{-e\mathrm{V}_m/k\mathrm{T}}. \qquad (74)$$

The corresponding formulæ for other geometrical arrangements will be of a similar type, but less simple. It is to be noted that except when i_{A}/i is very small indeed, V_m will be only a fraction of a volt. Thus, for example, if T is 2000°K., the value of V_m which makes $i_{\mathrm{A}}/i = \frac{1}{10}$ in (74) is 0·4 volt, and that which makes it $\frac{1}{100}$ is 0·8 volt.

The complete mathematical treatment of the infra-saturation problem is one of extraordinary complexity, and the best that has been achieved is an approximation to the complete solution—albeit a very close one—in a few geometrically simple cases.

A first approximation may be arrived at by neglecting both the initial velocities of ejection of the electrons and the height of the space-charge potential hill. This is equivalent to assuming that the velocities of the electrons are everywhere determined uniquely by the potential and that at the surface of the cathode the potential gradient vanishes. The relationship between space current and anode potential obtained in this way will be a good approximation to the truth for all infra-saturation anode potentials that are of a higher order than V_m. With the usual electrode dimensions, and emissions of at least some milliamperes, saturation is generally not attained under an anode potential of several volts, sometimes even not under a few tens or hundreds of volts. In such cases the solution obtained will be very nearly correct over the greater part of the infra-saturation anode voltage range.

As an illustration of the approximate treatment, let us consider the one-dimensional case of infinite parallel plane electrodes. The following are the conditions to be fulfilled :

$$\tfrac{1}{2}mv^2 = eV, \quad . \quad . \quad . \quad . \quad (75)$$

$$\nabla^2 V = \frac{d^2V}{dx^2} = 4\pi\rho_-, \quad . \quad . \quad . \quad (76)$$

and
$$V = 0, \ \frac{dV}{dx} = 0 \text{ where } x = 0, \quad . \quad . \quad (77)$$

where v is the velocity of the electrons, ρ_- the negative charge density, and V the (positive) potential with respect to the cathode at a distance x from it.

We wish to express the current i_A in terms of the potential V_A of the anode. By means of the relationship

$$i_A = v\rho_-, \quad . \quad . \quad . \quad . \quad (78)$$

we therefore eliminate v and ρ_- between the equations (75) and (76), obtaining

$$\frac{d^2V}{dx^2} = 2\pi i_A\sqrt{\frac{2m}{e}}V^{-1/2}. \quad . \quad . \quad . \quad (79)$$

To integrate, we multiply each side of this equation by dV/dx and, remembering the boundary condition for dV/dx in (77), obtain the integrated equation

$$\left(\frac{dV}{dx}\right)^2 = 8\pi i_A\sqrt{\frac{2m}{e}}V^{1/2}. \quad . \quad . \quad . \quad (80)$$

Integrating again, and making use of the boundary condition for V in (77), we finally obtain for i_A the value

$$i_A = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\,\frac{V^{3/2}}{x^2},$$

and if l is the distance between the electrodes we may write instead of this

$$i_A = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\,\frac{V_A^{3/2}}{l^2}. \quad . \quad . \quad . \quad (81)$$

The solution of this one-dimensional problem is due to J. J. Thomson * and C. D. Child.[9]

The infra-saturation problem for the case of coaxial cylinders has been solved by Langmuir.[43] The approximate solution is

$$i_A = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{V_A^{3/2}}{R\beta^2}, \quad . \quad . \quad . \quad (82)$$

where R is the radius of the outer cylinder and β is a constant depending on the ratio of the radii of the two cylinders which is very nearly equal to unity when the radius of the outer cylinder is great compared with that of the inner.

Finally, for concentric spherical electrodes, Langmuir and Blodgett [46] have obtained the approximate solution

$$i_A = \frac{4\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{V_A^{3/2}}{\alpha}, \quad . \quad . \quad . \quad (83)$$

where α is a function of the ratio of the two radii.

It will be observed that in all three formulæ the current is proportional to the square root of e/m and to the three-halves power of V_A. It is easily seen from the dimensions of eqns. (75), (76) and (78) that it must be so in all cases, irrespective of the electrode geometry. It is evident also that

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* See J. J. Thomson, "The Conduction of Electricity through Gases," Cambridge University Press, 2nd edition (1906), p. 223.

in the case of any particular electrode geometry it is possible to determine the ratio e/m to a high degree of precision by comparing the experimental i_A-V_A relationship with the theoretical. This has been done for example by S. Dushman,[17] employing cylindrical electrodes.

More rigorous solutions of the infra-saturation problem have been obtained for parallel plane electrodes by Schottky,[80] Epstein,[21] Fry [29] and Langmuir,[44] and for cylindrical electrodes by Langmuir [44] and by Langmuir and Blodgett.[47] In these, approximate corrections for the finite velocities of ejection of the electrons and the finite height of the space-charge potential hill have been made.

In none of these calculations is that part of the infra-saturation characteristic accounted for in which the rate of increase of space current becomes progressively less with increasing anode potential. This is mainly due, as B. S. Gossling has shown,* to the fact that the surface of the emitter is not absolutely smooth. The current from the projecting parts of the surface begins to saturate while that from the hollows is still space-charge limited, the area supplying saturated current growing at the expense of that supplying space-charge-limited current as the anode voltage is increased, until finally the current from the whole surface of the cathode is saturated. Gossling has been able to account quantitatively for the whole of the observed current-voltage characteristic in the case of a certain tungsten-filament valve by assuming the surface of the filament to have a sinusoidal corrugation, the ratio of the amplitude to the wave-length being 0·04. (Within wide limits the actual scale of the corrugation is immaterial.) While no actual surface will be of this simple geometrical form, the assumed order of roughness is by no means greater than that which we should expect to occur in nature.

In the case of certain cathodes, the $\frac{3}{2}$-power law is seriously departed from, even in the lower part of the infra-saturation characteristic. An example of such a cathode is imperfectly activated thoriated tungsten. In Fig. 10 are shown three thermionic current-voltage curves, all obtained with geometrically the same electrode system, the temperature of the

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* Unpublished work.

cathode having been adjusted to give about the same saturated current in each case. The cathode was either a pure or a thoriated tungsten wire. Curve I is that obtained with the pure tungsten cathode. Curve II was obtained with the thoriated cathode after a partial layer of thorium atoms had been "grown" on its surface. It will be observed that the lower infra-saturation ordinates of curve II are appreciably less than those of curve I, which accurately obeys the $\frac{3}{2}$-power law.

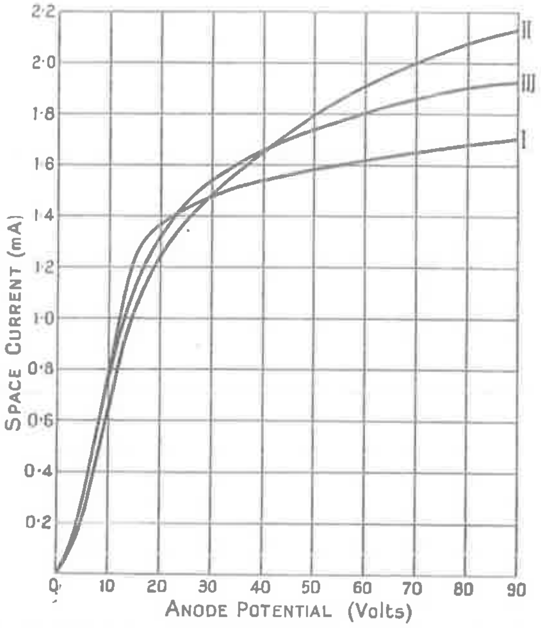

Fig. 10.—Showing the dependence of the infra-saturation thermionic current-voltage relationship on the state of the emitting surface.

Curve III was also obtained with the thoriated cathode, but only after the layer of thorium atoms on its surface had become complete. In the lower infra-saturation region this is indistinguishable from curve I. The departure from the theoretical $\frac{3}{2}$-power law in the case of the partially activated cathode is probably due to the existence of local fields near the surface associated with "patches" of different work functions.

A different kind of departure from the $\frac{3}{2}$-power characteristic that is sometimes observed is that due to the presence in the inter-electrode space of positive ions, either emitted with the electrons from the hot conductor or, in the case of a poor vacuum, produced by collisions of electrons with residual gas molecules. In either case the infra-saturation currents are greater than they would be in the absence of the positive ions. Owing to the relatively large mass of the ions, they can have an important effect in neutralizing the space charge and so indirectly enhancing the current even when their direct contribution to it is insignificant.

The Schottky Effect.—We have seen that thermionic currents never truly saturate ; an increase in anode potential is always accompanied by *some* increase in the current. One cause that always operates to bring about this result is a lowering of the work function due to the applied field. The quantitative theory of this effect is due to Schottky,[81] and it has been named after him the " Schottky effect."

The polarization field must effectively vanish at a distance of a very few atomic diameters from the surface. The image field, however, only becomes negligible, as we shall presently see, beyond a distance of the order of 10^{-6}–10^{-5} cm., i.e. something like a hundred atomic diameters from the surface. Thus the whole of the last, rising part of the potential hill up which an escaping electron has to climb is due to the image field, and its shape is therefore exactly known, from electrostatic laws. Hence, superposing the applied field on to the image field, it is easy to calculate where the negative slope of the former is exactly equal to the positive slope of the latter, i.e., at what distance the summit of the resultant hill is reached, and consequently, also, how much the work function is lowered by the applied field. It should perhaps be mentioned that there is no question of electrons going *through* the very wide potential hump resulting from the image and applied fields as there is in the case of the narrow humps formed by adsorbed monatomic electropositive films.

Let us first consider the image field alone. At a distance x from the surface of the emitter that is sufficiently great for the atomic structure of the surface to be disregarded, the force with which an electron ($-e$), if not moving too rapidly, is attracted by its electrical image ($+e$) in the surface is $e^2/4x^2$. The contribution to the work function of that part of the image field which lies between a distance x_0 and infinity is therefore

$$\int_{x_0}^{\infty} \frac{e^2}{4x^2} = \frac{e^2}{4x_0}. \quad . \quad . \quad . \quad (84)$$

From this we see, incidentally, that beyond a distance of 10^{-6}–10^{-5} cm. from the surface the contribution of the image force to the work function is negligible. Beyond 10^{-6} cm. it is

$$e \, . \, \frac{4{\cdot}77 \times 10^{-10}}{4 \times 10^{-6}} \times 300 = 0{\cdot}036 \text{ electron-volt,}$$

and beyond 10^{-5} cm. it is only 0·0036 electron-volt. The possible errors of even the most accurately determined work functions are greater than the latter quantity and those of only a very few are not also greater than the former.

If the summit of the potential hill resulting from the image and applied fields is at a distance x_0 from the surface, the work of exit of an electron is lowered not only by $e^2/4x_0$ on account of the summit being at x_0 instead of at infinity, but also by a further amount eEx_0, where E is the strength of the applied field, due to the diminution of the retarding field on the electron *up to* this distance. Thus the total reduction, $-\Delta\chi$, of the work function due to the applied field is

$$-\Delta\chi = \frac{e^2}{4x_0} + eEx_0. \quad . \quad . \quad . \quad (85)$$

The position of the summit is, of course, given by

$$eE = \frac{e^2}{4x_0^{\,2}}$$

or

$$x_0 = \frac{1}{2}\left(\frac{e}{E}\right)^{1/2}. \quad . \quad . \quad . \quad (86)$$

Thus substituting for eE or for x_0 in (85), we obtain

$$-\Delta\chi = \frac{e^2}{2x_0}$$

or

$$-\Delta\chi = e^{3/2}E^{1/2}. \quad . \quad . \quad . \quad (87)$$

Hence in the emission formula

$$i = AT^2\epsilon^{-\chi/kT}, \quad . \quad . \quad . \quad (2)$$

χ is given by

$$\chi = \chi_0 + \Delta\chi = \chi_0 - e^{3/2}E^{1/2}, \quad . \quad . \quad (88)$$

where χ_0 is the work function corresponding to zero field. Substituting for χ in (2) and writing i_0 for the emission at zero field, we thus have

$$i = i_0 \epsilon^{\frac{e^{3/2}E^{1/2}}{kT}}, \quad . \quad . \quad . \quad . \quad (89)$$

whence, taking logarithms and substituting for $e^{3/2}/k$ and $\log_{10}\epsilon$ their numerical values, we obtain

$$\log_{10} i = \log_{10} i_0 + \frac{1{\cdot}906\ E^{1/2},}{T} \quad . \quad . \quad (90)$$

where E is expressed in volts per cm.

The first to test the relation (90) was Schottky[81] himself, who found the slope of the line connecting log i with $E^{1/2}/T$ to be within about 20 per cent. of the theoretical value. Others who have since used the relation in order to calculate "zero-field" currents i_0 and hence zero-field work functions χ_0 of various metals (clean and contaminated) have generally found the observed slopes to exceed by anything up to 100 per cent. those calculated from the geometry of the electrode systems on the assumption of smooth cathode surfaces. Metal surfaces are, however, seldom truly smooth, and any roughness would give rise to excessive fields at the protruding points and so to a discrepancy in the direction found. According to Compton and Langmuir,[10] abnormally high slopes are found in the case of wires that have been subjected to positive ion bombardment, which probably results in a "pitting" of the surface, whereas "with clean tungsten wire of small crystal grain structure and flashed at a high temperature to smooth out surface inhomogeneities, eqn. (90) is satisfied as accurately as the measurements can be made, with the theoretical value of the slope." Excellent quantitative verification of Schottky's theory was obtained a few years ago by Pforte[61] and de Bruyne,[8] in both cases with tungsten filaments. Thus the mean of 20 slopes obtained by de Bruyne with filaments between 1580°K. and 2070°K. and exposed to fields up to more than 10^6 volts per cm. agreed well within 1 per cent. with the theoretical value. Incidentally, it is interesting to note that with a field strength at the surface of 10^6 volts per cm., x_0 is only 17·5Å. and the work function is reduced from 4·54 to 4·16 e.v.

Other Field Effects.—Certain composite emitters, such as thorium, cæsium, etc., on tungsten, exhibit an increase in emission with applied field which is greatly in excess of what can be accounted for by Schottky's theory alone, particularly at comparatively low field strengths. The effect is most marked where there is less than a full monatomic layer of adsorbed atoms on the surface. A theory which has been advanced to account for this is the "theory of patches," originally suggested by Langmuir,[45] and since developed by Richardson and Young,[71] Reynolds,[64] and Compton and Langmuir.[10] According to this theory, the adsorbed atoms do not spread themselves uniformly over the surface, but arrange themselves so that some areas (patches) have a greater, others a less surface concentration than the average. If the patches are not small enough to admit of the adsorbed atoms being regarded as "smeared out" over the surface, considerable local fields will be set up between them, due to differences in work function. The direction of the local field at the more active patches will be such as to suppress the emission, and it is to the gradual neutralization of these local fields by the applied field as the latter is increased that the abnormal growth of emission with applied field is supposed to be due. In the case of very strong applied fields the relative importance of the local fields should become less and the relationship between the current and applied field approach that predicted by Schottky's theory. This actually appears to be the case. It cannot be said, however, that there is yet a satisfactory *quantitative* theory of the effect of patches as there is of the pure Schottky effect.

Becker and Mueller [3] have advanced the hypothesis that while the field due to the adsorbed electropositive atoms (not necessarily grouped into patches) accelerates electrons very close to the metal, it retards them at greater distances, and that the reason why the current-voltage relationship is so different from that predicted by Schottky's theory is simply that the field due to the adsorbed atoms is not at all like the image field. Thus for the case of a partially activated thoriated tungsten filament they have calculated from the observed current-voltage relationship that the retarding field due to the adsorbed atoms attains its maximum strength at 75 atomic diameters from the surface. It is, however, not easy to see how such a picture can be reconciled with accepted ideas of adsorption and electric fields due to double layers.

A remarkable effect which was first observed by Lilienfeld many years ago is the emission of electrons from a metal at room temperature when a sufficiently intense electron-accelerating field (order of 10^8 volts per cm.) is applied to its surface. This was once thought to be an extreme case of the Schottky effect, but it is now known to be an essentially different phenomenon. If it were a Schottky effect, then the thermionic emission formula

$$i = \mathrm{A}\mathrm{T}^2\epsilon^{-\chi/k\mathrm{T}}, \quad . \quad . \quad . \quad (2)$$

in which χ represents the residual work function, would still hold, i.e. the emission at constant field would vary rapidly with the temperature. This is so far from being the case, however, that there has been a not inconsiderable amount of controversy as to whether "field currents," as they are called, are temperature-dependent at all. To at least a very close approximation they are not. On the other hand, the currents do vary exceedingly rapidly with the field, much as thermionic emissions do with the temperature, and may be satisfactorily represented by a formula of the type

$$i = f(\mathrm{E})\epsilon^{-\beta/\mathrm{E}}, \quad . \quad . \quad . \quad . \quad (91)$$

where f varies sufficiently less violently with E than does $\epsilon^{-\beta/\mathrm{E}}$. This is analogous to (1), E taking the place of T.

Attempts to explain this phenomenon on the basis of the classical electron theory have completely broken down. The strong variation of the current with the field suggests that there is still a finite residual work function, and if we assume that this is so, then the temperature independence of the emission at constant field is, on classical views, incomprehensible. In recent years, however, a successful wave-mechanical theory of field emissions has been worked out by Oppenheimer,[57] by Fowler and Nordheim,[28] and by Stern, Gossling and Fowler.[89] According to this theory, the field-current problem is essentially one of the transmission of electrons through the hump of a residual potential hill, this being of the form of Fig. 11. The horizontal dashed line represents the critical energy level of the Fermi distribution of the internal electrons.

The contribution to the emission of those few of the internal electrons which have energies much above this critical energy, and whose number varies rapidly with the temperature, is insignificant. Practically the whole of the current is derived from the electrons whose energies are not affected by the temperature. These are simply transmitted through the hump. As the field increases, the hump becomes lower and narrower, the transmission coefficient increases, and with it the current.

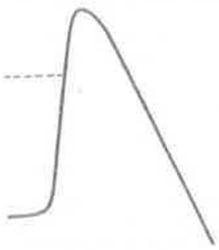

FIG. 11.

The Shot and Flicker Effects.—A thermionic current, consisting as it does of electrons in motion, is to be thought of as analogous rather to a hail of shot than to a stream of a continuous fluid. In consequence there must be a certain fluctuation of the current strength. This was first pointed out by W. Schottky [82] who worked out a quantitative theory of the effect and proposed for it the name "shot effect."

In Schottky's theory, the emission of each electron is assumed to be a perfectly random event, independent in time of the emission of any other, so that at certain instants the number of electrons passing must be above, at certain others below, the average. In any circuit coupled with that in which the thermionic current flows, secondary currents will therefore be induced, the time-average of whose energy dissipation will depend upon the current in the primary circuit, the closeness of coupling, and the natural frequency and impedance of the coupled circuit.

In observations of the effect it is usual to amplify the electromotive forces induced in the coupled circuit and to measure the effect produced in some final instrument, e.g. a pair of headphones or a thermo-couple. In a number of such experiments results have been obtained which agree to within the error of measurement with those predicted by the theory.

A current fluctuation, somewhat analogous to the above, but abnormally large at low frequencies, was observed in 1925 by Johnson.[37] This, which has been named the "flicker effect," is unlike the shot effect in that its magnitude varies not only with the thermionic current but also with the nature of the emitting body, being particularly large in the case of composite cathodes. Shortly after its discovery, Schottky suggested that the elementary event underlying the flicker effect might be, not the emission of a single electron as in the shot effect, but the arrival at or disappearance from the emitting surface of a single foreign atom which modifies the work function, and therefore the emission, in its immediate neighbourhood. On the basis of this assumption Schottky [83] has worked out a mathematical theory of the effect.

Thermal Emission of Positive and Negative Ions.—The typical emission from heated salts is ionic rather than electronic. The ions are more usually positive than negative and are of the same kind as those that carry the current in electrolysis. There is a very considerable literature dealing with the emission from heated salts, the older part of which has been reviewed, critically, and in some detail, by O. W. Richardson.* More recently, the researches of G. C. Schmidt and his students have done much to further increase our understanding of this subject, but it is as yet impossible to formulate anything approaching a complete theory of the various phenomena observed. The dependence of the ionic space current on the potential of the collector is governed by the same kind of law as applies for electrons, the only difference being that on account of the relatively larger mass of the carriers the importance of the space charge corresponding to any given current is greater. The variation of emission with temperature is, like that of electrons, adequately expressed by a formula of the type

$$i = f(\mathrm{T})\epsilon^{-\omega/k\mathrm{T}}, \quad . \quad . \quad . \quad (92)$$

in which the variation of f with T is sufficiently less violent than that of $\epsilon^{-\omega/k\mathrm{T}}$.

A positive "thermionic" emission of rather a different nature is that which occurs when certain metals are heated to incandescence in the presence of the more electropositive of the alkali metal vapours. Kingdon and Langmuir,[39] who were the first to observe this phenomenon, found that if the "electron affinity" (work function) of the hot metal surface

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* O. W. Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co., Chapter VIII.

exceeds that (the work of ionization) of the atoms of the vapour, then almost every atom that impinges on the surface of the hot filament loses an electron and evaporates as a positive ion. Thus a tungsten filament (work function = 4·54 e.v.) will ionize the vapours of cæsium, rubidium and potassium (works of ionization 3·87, 4·15 and 4·32 e.v. respectively) when heated therein.

Another positive emission, which was observed much earlier, and whose mechanism is probably similar, is that which commonly occurs from ordinary impure metals at quite moderate temperatures, sometimes even at far below a visible red heat. The temperature dependence of this emission is, like that of the emission from heated salts, represented by an equation of the form (92) and decreases with time according to a law similar to that of radioactive decay. The ions have been identified by mass spectrum analysis as mainly K^+ and to a much lesser extent Na^+. They must originate, therefore, from impurities of these metals or of their compounds present in the emitting body, which diffuse to its surface when it is heated. Impurity ions other than K^+ and Na^+ have also occasionally been observed. Thus Wahlin [94] has found that Th^+ ions are emitted from incandescent thoriated tungsten wires, and Smith [86] has detected Al^+ ions in the emission from impure tungsten and molybdenum wires heated to about 2000°K. Also Kunsman [41] has obtained Na^+, K^+, Rb^+, Cs^+, Mg^+, Ca^+, Sr^+ and Ba^+ ions from specially prepared metal emitters containing the oxides of the corresponding elements as impurities.

Finally, it has been shown in a series of researches by Smith,[87] Wahlin [95] and Barnes [2] that certain pure metals, such as tungsten, molybdenum, tantalum and rhodium, when heated to sufficiently high temperatures (e.g., 2300°K. in the case of Mo, 2500°K. in that of W) give appreciable positive ion emissions of their own material. As Compton and Langmuir [10] have pointed out, however, such emission represents but an insignificant fraction of the total evaporation of material at these temperatures. Thus in the case of tungsten at 2500°K., for every particle emitted as a positive ion about 2000 evaporate as neutral atoms.

LITERATURE.

1. O. v. Baeyer, *Phys. ZS.*, **10,** p. 168, 1909.
2. Le R. L. Barnes, *Phys. Rev.*, **40,** p. 1044, 1932 ; **42,** p. 487, 1932.
3. J. A. Becker and D. W. Mueller, *Phys. Rev.*, **31,** p. 341, 1928.
4. E. Becquerel, *Ann. de Chim. et de Phys.*, **39,** p. 355, 1853.
5. F. Bloch, *ZS. f. Phys.*, **52,** p. 555, 1928 ; **59,** p. 208, 1930.
6. R. Blondlot, *C.R.*, **92,** p. 870, 1881 ; **104,** p. 283, 1887.
7. E. Branly, *C.R.*, **114,** p. 1531, 1892.
8. N. A. de Bruyne, *Proc. Roy. Soc.* (*A*), **120,** p. 423, 1928.
9. C. D. Child, *Phys. Rev.*, **32,** p. 498, 1911.
10. K. T. Compton and I. Langmuir, *Rev. Mod. Phys.*, **2,** p. 123, 1930.
11. J. F. Congdon, *Phil. Mag.*, **47,** p. 458, 1924.
12. H. L. Cooke and O. W. Richardson, *Phil. Mag.*, **25,** p. 624, 1913 ; **26,** p. 472, 1913.
13. C. Davisson, *Phys. Rev.*, **25,** p. 808, 1925.
14. C. Davisson and L. H. Germer, *Phys. Rev.*, **20,** p. 300, 1922 ; **21,** p. 208, 1923 ; **24,** p. 666, 1924 ; **30,** p. 634, 1927.
15. A. Demski, *Phys. ZS.*, **30,** p. 291, 1929.
16. P. A. M. Dirac, *Proc. Roy. Soc.* (*A*), **112,** p. 661, 1926.
17. S. Dushman, *Phys. Rev.*, **4,** p. 121, 1914.
18. S. Dushman, H. N. Rowe, J. W. Ewald and C. A. Kidner, *Phys. Rev.*, **25,** p. 338, 1925.
19. T. A. Edison, *U.S. Patent Specification*, No. 307,031, filed Nov. 15, 1883, patented Oct. 21, 1884 ; also reported in *Engineering*, **38,** p. 553, 1884.
20. J. Elster and F. Geitel, *Ann. d. Phys.*, **16,** p. 193, 1882 ; **19,** p. 588, 1883 ; **22,** p. 123, 1884 ; **26,** p. 1, 1885 ; **31,** p. 109, 1887 ; **37,** p. 315, 1889 ; *Wien. Ber.*, **97,** p. 1175, 1889.
21. P. S. Epstein, *Verh. d. D. Phys. Ges.*, **21,** p. 85, 1919.
22. W. Espe, *Wiss. Veröff a. d. Siem. Konz.*, **5 (III),** p. 46, 1926.
23. H. E. Farnsworth, *Phys. Rev.*, **20,** p. 358, 1922.
24. E. Fermi, *ZS. f. Phys.*, **36,** p. 902, 1926.
25. J. A. Fleming, *Proc. Roy. Soc.*, **47,** p. 118, 1890 ; *Phil. Mag.*, **42,** p. 52, 1896.
26. R. H. Fowler, *Proc. Roy. Soc.* (*A*), **117,** p. 549, 1928.
27. R. H. Fowler, *Robert Boyle Lecture*, Oxford, 1929, p. 14.
28. R. H. Fowler and L. Nordheim, *Proc. Roy. Soc.* (*A*), **119,** p. 173, 1928.
29. T. C. Fry, *Phys. Rev.*, **17,** p. 441, 1921.
30. A. Gehrts, *Ann. d. Phys.*, **36,** p. 995, 1911.
31. L. H. Germer, *Phys. Rev.*, **25,** p. 795, 1925.
32. F. Guthrie, *Phil. Mag.*, **46,** p. 257, 1873.
33. G. Holst and E. Oisterhuis, *Physica*, **4,** p. 375, 1924.
34. A. W. Hull, *Phys. Rev.*, **7,** p. 1, 1916.
35. A. W. Hull, *Phys. Rev.*, **18,** p. 31, 1921.
36. J. v. Issendorff, *Wiss. Veröff. a. d. Siem. Konz.*, **4 (I)**, p. 124, 1925.
37. J. B. Johnson, *Phys. Rev.*, **26,** p. 71, 1925.
38. J. H. Jones, *Proc. Roy. Soc.* (*A*), **102,** p. 734, 1923.
39. K. H. Kingdon and I. Langmuir, *Phys. Rev.*, **21,** pp. 380 and 381, 1923.
40. L. R. Koller, *Phys. Rev.*, **25,** p. 671, 1925.
41. C. H. Kunsman, *Science*, **62,** p. 269, 1925 ; *J. Franklin Inst.*, **203,** p. 635, 1927.
42. I. Langmuir, *Phys. Rev.*, **8,** p. 171, 1916.

43. I. Langmuir, *Phys. Rev.*, **2**, p. 450, 1913.
44. I. Langmuir, *Phys. Rev.*, **21**, p. 419, 1923.
45. I. Langmuir, *Gen. El. Rev.*, **23**, p. 504, 1920.
46. I. Langmuir and K. B. Blodgett, *Phys. Rev.*, **24**, p. 49, 1924.
47. I. Langmuir and K. B. Blodgett, *Phys. Rev.*, **22**, p. 347, 1923.
48. I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc.* (*A*), **107**, p. 61, 1925.
49. M. v. Laue, *Jahrb. d. Rad. u. Elektronik*, **15**, pp. 205, 257 and 301, 1918.
50. M. v. Laue, *Ann. d. Phys.*, **58**, p. 695, 1919 ; *Phys. ZS.*, **20**, p. 202, 1919.
51. H. Lester, *Phil. Mag.*, **31**, p. 197, 1916.
52. S. Michel and H. J. Spanner, *ZS. f. Phys.*, **35**, p. 395, 1926.
53. H. G. Möller and F. Detels, *Jahrb. d. drahtl. Teleg. u. Teleph.*, **27**, p. 74, 1926.
54. L. Nordheim, *ZS. f. Phys.*, **46**, p. 833, 1927.
55. L. Nordheim, *Proc. Roy. Soc.* (*A*), **121**, p. 626, 1928.
56. W. B. Nottingham, *Phys. Rev.*, **41**, p. 793, 1932.
57. J. R. Oppenheimer, *Phys. Rev.*, **31**, p. 914, 1928 ; *Proc. Nat. Acad. Sci.*, **14**, p. 363, 1928.
58. W. Pauli, jr., *ZS. f. Phys.*, **41**, p. 81, 1927.
59. F. M. Penning, *Physica*, **5**, p. 211, 1925.
60. R. L. Petry, *Phys. Rev.*, **28**, p. 362, 1926.
61. W. S. Pforte, *ZS. f. Phys.*, **49**, p. 46, 1928.
62. H. E. Potter, *Phil. Mag.*, **46**, p. 768, 1923.
63. W. H. Preece, *Proc. Roy. Soc.*, **38**, p. 219, 1885.
64. N. B. Reynolds, *Phys. Rev.*, **35**, p. 158, 1930.
65. O. W. Richardson, *Proc. Cambr. Phil. Soc.*, **11**, p. 286, 1901.
66. O. W. Richardson, *Jahrb. d. Rad.*, **1**, p. 302, 1904 ; *Phil. Mag.*, **23**, pp. 601 and 619, 1912 ; **24**, p. 740, 1912 ; **28**, p. 633, 1914.
67. O. W. Richardson, *Phil. Mag.*, **16**, p. 890, 1908 ; **18**, p. 681, 1909.
68. O. W. Richardson, *Phil. Trans.* (*A*), **201**, p. 497, 1903.
69. O. W. Richardson and F. C. Brown, *Phil. Mag.*, **16**, p. 353, 1908.
70. O. W. Richardson and H. L. Cooke, *Phil. Mag.*, **20**, p. 173, 1910 ; **21**, p. 404, 1911.
71. O. W. Richardson and A. F. A. Young, *Proc. Roy. Soc.* (*A*), **107**, p. 377, 1925.
72. C. del Rosario, *Phys. Rev.*, **28**, p. 769, 1926.
73. M. Rössiger, *ZS. f. Phys.*, **19**, p. 167, 1923.
74. H. Rothe, *ZS. f. Phys.*, **37**, p. 414, 1926.
75. H. Rothe, *ZS. f. Phys.*, **36**, p. 737, 1926 ; **41**, p. 530, 1927.
76. H. Schneider, *Ann. d. Phys.*, **37**, p. 569, 1912.
77. W. Schottky, *ZS. f. Phys.*, **14**, p. 63, 1923.
78. W. Schottky, *Phys. ZS.*, **20**, pp. 49 and 220, 1919.
79. W. Schottky, *Ann. d. Phys.*, **44**, p. 1011, 1914.
80. W. Schottky, *Phys. ZS.*, **15**, pp. 526 and 624, 1914.
81. W. Schottky, *Phys. ZS.*, **15**, p. 872, 1914.
82. W. Schottky, *Ann. d. Phys.*, **57**, p. 541, 1918 ; **68**, p. 157, 1922.
83. W. Schottky, *Phys. Rev.*, **28**, p. 74, 1926.
84. W. Schottky and J. v. Issendorff, *ZS. f. Phys.*, **26**, p. 85, 1924.
85. Sih Ling Ting, *Proc. Roy. Soc.* (*A*), **98**, p. 374, 1921.
86. L. P. Smith, *Phys. Rev.*, **35**, p. 653, 1930.
87. L. P. Smith, *Phys. Rev.*, **33**, p. 279, 1929 ; **34**, p. 1496, 1929 ; **35**, p. 381, 1930.
88. A. Sommerfeld, *ZS. f. Phys.*, **47**, p. 1, 1928.
89. T. E. Stern, B. S. Gossling and R. H. Fowler, *Proc. Roy. Soc.* (*A*), **124**, p. 699, 1929.

90. J. J. Thomson, *Phil. Mag.*, **48**, p. 547, 1899.
91. A. Viohl, *Ann. d. Phys.*, **87**, p. 174, 1928.
92. C. C. van Voorhis, *Phys. Rev.*, **30**, p. 318, 1927.
93. C. C. van Voorhis and K. T. Compton, *Phys. Rev.*, **29**, p. 909, 1927 ; **36**, p. 1435, 1930.
94. H. B. Wahlin, *Phys. Rev.*, **35**, p. 653, 1930.
95. H. B. Wahlin, *Nature*, **123**, p. 912, 1929 ; *Phys. Rev.*, **34**, p. 164, 1929.
96. A. Wehnelt and F. Jentzsch, *Verh. d. D. Phys. Ges.*, **10**, p. 605, 1908 ; *Ann. d. Phys.*, **28**, p. 537, 1909.
97. A. Wehnelt and H. Liebreich, *Verh. d. D. Phys. Ges.*, **15**, p. 1057, 1913 ; *Phys. ZS.*, **15**, p. 548, 1914.
98. A. H. Wilson, *Proc. Roy. Soc.* (*A*), **133**, p. 458, 1931.
99. H. A. Wilson, *Phil. Trans.* (*A*), **197**, p. 429, 1901.
100. H. A. Wilson, *Phil. Trans.* (*A*), **202**, p. 258, 1904 ; *Phil. Mag.*, **24**, p. 196, 1912.
101. W. Wilson, *Proc. Nat. Acad. Sci.*, **3**, p. 426, 1917 ; *Phys. Rev.*, **10**, p. 79, 1917.

CHAPTER II.

ELECTRON EMISSION FROM CLEAN METALS.

We have seen how the work function of a conductor is related to the effective height of the potential barrier at its surface and how this barrier is due partly to the image field and partly to the surface polarization. In the case of clean metals the latter will depend mainly on the size of the atoms and the ease with which they are deformed or ionized, and probably to some extent also on their arrangement in the lattice. The distance from the surface at which there begins to be a true image force, and hence the image-force contribution to the work function, probably depends on the same things. In studying the thermionic properties of the clean metals, therefore, we shall expect to find that the work functions depend primarily on position in the periodic table, but in cases where a metal crystallizes in two or more different forms we shall also look for some change in the work function at the transition points.

From the orders of the experimentally determined emission constants A of the clean metals we shall also hope to gain some information concerning the existence of potential humps at their surfaces, and, in case they do exist, their magnitudes.

Thermionic and Photoelectric Work Functions.—The thermionic work function of a metal may be determined either by finding the slope of the Richardson line or by the calorimetric method. Of the two methods, the former is generally to be preferred on account of its superior accuracy. It is only applicable, however, in the case of metals that it is practicable to heat in a vacuum to temperatures at which they give an appreciable emission. With many of the more volatile or readily fusible metals this is not practicable, and in such cases the most satisfactory way of arriving at the work function is to determine it photoelectrically.

We shall see in Chapter V that the work function χ is equal to $C - \mu$, where C is the product of the inner potential and the electronic charge, and μ is the zero-temperature critical energy of the Fermi distribution of the internal electrons. Thus χ is the least energy which, if added to that already possessed by the fastest electrons in the metal at absolute zero, would enable them to escape.

We now know that electromagnetic radiation has some of the properties of particles as well as those of waves. The quasi-particles of radiation are known as "photons," and if the frequency of the radiation is ν, the energy ε of the photons is given by

$$\varepsilon = h\nu. \qquad (1)$$

This energy may be imparted to material or electrical particles. Thus if radiation whose frequency exceeds χ/h is incident on a metal at absolute zero, it will excite photoelectric emission from it. The critical frequency ν_0, equal to χ/h, below which photoelectric emission cannot be excited from a metal at absolute zero, is called the "threshold frequency," and if λ_0 is the corresponding wave-length, we have

$$\chi = \frac{hc}{\lambda_0},$$

where c is the velocity of light, and if λ_0 is expressed in Ångström units and χ in electron-volts, this becomes

$$\chi = \frac{12336}{\lambda_0}. \qquad (2)$$

Above the absolute zero of temperature a metal ceases, strictly speaking, to have a sharp threshold. The cut-off of the Fermi distribution becomes blurred, and the photoelectric response, instead of ceasing abruptly at λ_0, spreads to longer wave-lengths. At all ordinary temperatures, however, the Fermi energy distribution function still falls very steeply in the region of μ, and the photoelectric response dies away correspondingly rapidly near λ_0. Thus with such instruments as are commonly employed the photoelectric response ceases to be measurable at a wave length of exciting radiation very near λ_0 and the observed "threshold" gives an approximate measure of χ.

In a recent theory of photoelectric response due to Fowler,[28] the plausible assumption is made that the number of electrons emitted per given number of quanta of exciting radiation of frequency ν is proportional to the number of electrons per unit volume in the metal whose components of velocity normal to the surface exceed a critical value u_0, where

$$\tfrac{1}{2}mu_0^2 + h\nu = C. \qquad . \quad . \quad . \quad (3)$$

Now the velocity distribution of a Fermi gas is known in terms of the temperature, the molecular mass m, and the zero-temperature critical energy μ, and thus it is possible, on the basis of Fowler's assumption, to derive a theoretical relationship between the photoelectric response per unit intensity and ν for any given values of C, μ and the temperature. Fowler has shown that the observed photoelectric response curves for various metals obtained at different temperatures are of the theoretical form, and he has developed a method by which the value of $C - \mu$, i.e. of χ, may be derived from any such curve. He has shown that, while the longest wave-length at which a photoelectric response of a given metal can be detected increases quite appreciably with the temperature, the values of χ obtained by his method are practically the same (as they should be) at all temperatures. More recent analyses of photoelectric response data have shown equally satisfactory agreement with Fowler's theory, and in cases where the work function has also been determined thermionically it has been found to be in excellent agreement with that obtained photoelectrically by Fowler's method.

Experimental Conditions.—Metals cannot be regarded as "clean" for the purposes of thermionic or photoelectric measurements until their surfaces, as well as their interiors, have been substantially freed from contamination.

Surface contaminations on a metal may be of various kinds. Apart from oxides or other chemical compounds of the metal itself, they may consist of adsorbed atoms or molecules of a gas or of another metal. These may originate either from within the metal—almost all not specially treated metals contain occluded gases and traces of metallic impurities—or from without, i.e. from residual gases or vapours in the vacuum vessel or from the anode if this has not been properly outgassed. Whether or not an appreciable covering of a given contamination collects on the surface under any given set of conditions will depend on the relative rates of its evaporation from the surface and its replenishment by diffusion from within or condensation from without. If the contamination amounts to an appreciable fraction of a monomolecular layer of foreign material, the surface polarization and with it the work function (and possibly also the transmission coefficient) will be seriously affected, and the emission observed will not be that characteristic of the clean metal.

It must not be supposed that where the foreign material diffuses to the surface from within the metal, its concentration at the surface will necessarily be of the same order as that within. Actually this is very far from being the case. Thus (see Chapter III) a full monatomic layer of thorium may be " grown " on the surface of tungsten which contains less than 1 per cent. of thorium as an impurity. According to Langmuir, this is due to the fact that the surface energy of an adsorbed film of thorium is less than that of clean tungsten, so that diffusion of thorium to the surface is a thermodynamically irreversible process. In this, and a few similar cases, it is possible to determine the thermionic constants of the clean metal, in spite of continuous diffusion of foreign material to the surface, by confining observations of emission to temperatures so high that the foreign atoms evaporate almost immediately they reach the surface, and are in consequence unable to accumulate there sufficiently to form an appreciable fraction of a full monatomic layer. In other cases sufficient of the impurity may be " boiled out," by subjecting the metal to a prolonged heat treatment in a vacuum, for the same condition of practical freedom from contamination of the surface to be realized. Unfortunately, however, with many of the less refractory metals neither of these methods of obtaining a clean surface is applicable.

The formation of an appreciable surface concentration of adsorbed gas by condensation from without can be avoided by holding the metal at a sufficiently high temperature to ensure a short average " adsorption-life " of the foreign atoms or molecules, coupled with sufficient pains to secure a good vacuum. Obviously, the higher the temperatures at which observations are made the less perfect need the vacuum be, and *vice versa*.

The degree of vacuum attained does not depend only on the efficiency and speed of the pump and the length and width of the connecting tubing, important though these items are. It depends also on the amount of work the pumping system is given to perform, i.e. the rate at which gases and vapours are liberated within the vacuum vessel. Not only may these be given off from the metal whose thermionic or photoelectric properties are under investigation, but also from the glass walls and from the anode. All glass-work should be baked at a high temperature (e.g. 400°C. in the case of soda and lead glasses, 500°C. in that of pyrex) for at least several minutes while connected to the pump, to drive off water vapour, carbon monoxide and oxygen from its surface. As for the anode, this should be outgassed by a sufficiently intense heat-treatment (e.g. at 900°–1000°C. in the case of nickel) prior to use. The time that should be given to this varies with the material of the anode, its thickness, the temperature, and the degree of outgassing required. In some cases something of the order of a half-hour will suffice, in others many hours may be necessary. The outgassing may be carried out either in the vessel in which the anode is to be used, or, if more convenient, in a separate vessel, e.g. a vacuum furnace, before assembly. In the latter case it is highly desirable to supplement the main outgassing by a glowing of a few seconds' duration in the final vacuum, to liberate adsorbed gases from the surface. It is not necessarily enough that the temperature of this glowing be higher than any to which the anode will be raised in the subsequent experiments, for in these it will be subjected to electron bombardment, which, it has been found, frequently causes surface gases to be dislodged even when it is so mild that the increase in temperature to which it gives rise is negligible.

The most efficient pump to use when there is a strong ionizing discharge in the vacuum vessel is an active “ getter ” surface deposited on its walls. The best getters are such electropositive metals as magnesium, sodium, potassium, calcium and barium. The activities of these increase roughly in the order named. Their use constitutes somewhat of an art, however, whose difficulty increases in about the same order. Magnesium is quite a good "general purpose" getter and excellent vacua are obtainable with it when it is properly used. A small, clean, preferably previously outgassed piece should be either welded or otherwise attached to an outgassed metal carrier from which it may be volatilized after all the electrodes have had their outgassing treatment and either just before or just after sealing off from the pump. (It is best to seal off the vacuum vessel, to avoid "pumping the pump.") The piece of getter used should be large enough to give a good, generous deposit on the glass walls. It is questionable whether it is desirable to cool the getter film to a low temperature, e.g. by immersing the vacuum vessel in liquid air, during use, as this may hinder the diffusion of gettered gas into the interior of the film which tends to keep the surface clean and active. Also, if it can be avoided, the getter film should not be allowed to take up a positive potential with respect to the cathode; otherwise bombardment by stray electrons may dislodge from its surface certain kinds of already gettered gas. And finally, the greater the rate of formation of ions by the electron current, the more rapid, in general, is the gettering. In cases where the electron current obtained from the test specimen is weak it may be advantageous to supplement it by a current obtained from an auxiliary cathode, e.g. a hot tungsten filament.

In addition to thermal treatment of the cathode for the removal of adsorbed foreign material, a method that might prove useful in certain cases is that of bombardment of the surface by chemically inert positive ions, obtained from a gas which is pumped away before actual measurements are begun. Thus it has been found by Kingdon and Langmuir [39] that sufficiently fast ions of argon, neon and helium, *inter alia*, are capable of dislodging adsorbed thorium from the surface of cold tungsten. In the case of the first two, they began to observe the effect at about 50 e.v. energy of the incident ions. At 150 e.v. the number of incident ions per sputtered thorium atom was found to be 12 for argon, 45 for neon and 7000 for helium. Massive ions are in general more efficient sputterers than light ones.

In some cases it is not found possible to remove foreign material from an existing metallic surface. It is then necessary to form a new surface. If an appreciable rate of further contamination is unavoidable, the renewal of the surface should be made continuous. The new surface is best formed on the cathode by volatilization from an adjacent specimen of the test metal. Any unavoidable impurity in this specimen will probably be either more or less volatile than the metal. If it is more volatile it can be got rid of at an early stage, and if it is less volatile most of it will remain where it is. Thus in either case, serious surface contamination of the cathode may be avoided.

Thermionic and Photoelectric Data.—Let us now pass in review the more reliable of the experimental determinations that have been made of the thermionic and photoelectric properties of clean metals.

We have seen that a sharp photoelectric threshold exists only at absolute zero, and that at higher temperatures there is *some* photoelectric response well beyond the zero-temperature threshold λ_0. The only sound method we have of determining work functions photoelectrically at higher temperatures is that of Fowler, and a number of determinations by this method have recently been made. The earlier attempts to determine work functions by measuring supposed "thresholds" at higher temperatures can give us no accurate results, since the wavelengths beyond which no photoelectric response could be detected must have depended on the sensitivity of the current-measuring instrument used. Nevertheless the room-temperature determinations made by this faulty procedure have, in actual fact, yielded quite usable results, reliable to something like the nearest $\frac{1}{10}$ e.v. The photoelectric response falls away very rapidly beyond λ_0, and it so happens that the order of sensitivity of the experiments has not been sufficiently high for the measured "thresholds" at ordinary temperatures to differ very seriously from the zero-temperature λ_0. We shall therefore, in what follows, make use of such determinations where none better are available. Although, strictly speaking, no threshold exists above the absolute zero, we shall, in order to avoid circumlocution, employ the term "threshold" for the wave-length beyond which no photoelectric response could be detected experimentally.

(1) *The Alkali Metals.*—Although a considerable number of researches have been carried out with these metals, the data at present available are not, on the whole, very reliable. This is due to the difficulty of obtaining clean surfaces, for the metals are chemically very active and readily adsorb or chemically combine with residual gases. Actually the most reliable work function data we possess are those obtained photoelectrically.

No thermionic data appear to exist in the case of either lithium or rubidium. Various attempts have been made to determine the thermionic A and χ of sodium and potassium, but they have not met with much success. A good summary of this work has been given by Richardson and Young.[51] The most disturbing thing about the thermionic data obtained with sodium and potassium is that the Richardson lines which represent them are not straight, but show a decided concavity upwards.[66, 51] This has been ascribed by Richardson and Young to the existence on the metal surfaces of patches having different work functions, and they point out the possibility of these being due to contaminations. Further evidence of contaminations is that it was not found possible to repeat results quantitatively in successive "runs." It is doubtful whether really clean surfaces were ever obtained.

The only alkali metal for which even moderately trustworthy thermionic data seem to have been obtained is the most electropositive of all, viz. cæsium. From measurements of the emission from a pool of cæsium in the neighbourhood of 200°C., K. H. Kingdon [38] has found for the thermionic constants of this metal the values $A = 162$ amp./cm.^{2} deg.^{2}, $\chi = 1{\cdot}81$ e.v. He does not claim any great accuracy for these results, however, since he was not able entirely to eliminate the effects of adsorbed gases.

The photoelectric thresholds of the alkali metals have been observed by a number of workers, but here too, as with the thermionic data, there is a lack of consistency. This is due not only to the extraordinary sensitivity of these metals to gas contaminations, but also, as Ives and Johnsrud [35] have found, to an apparent dependence of the threshold upon the type of surface. Thus the thresholds found by Ives and Johnsrud for various kinds of surface, all fairly gas-free, of pure potassium are :

Matt surface	6100Å.
Molten pool	6000Å.
Specular layer on glass	5200Å.
Thin film on Pt	5100Å.

Millikan [48] has found for the thresholds of lithium and potassium, freshly cut in a vacuum, the values 5720Å. ($\chi = 2{\cdot}15$ e.v.) and 6800Å. ($\chi = 1{\cdot}82$ e.v.) respectively, but as Hughes and DuBridge * have pointed out, such surfaces are probably not free from gas contamination, on account of the large quantities of dissolved gases (with appreciable powers of diffusion) which they generally contain. According to Hughes and DuBridge, A. R. Olpin has found that "the most reliable and reproducible values of the thresholds of the alkali metals are obtained when thin films of the metal are allowed to deposit spontaneously at room temperature on the carefully outgassed surfaces of polished metal plates, all under extremely high vacuum conditions." Olpin's threshold values, obtained in this way, are 5400Å. ($\chi = 2{\cdot}28$ e.v.) for Li, 5000Å. ($\chi = 2{\cdot}46$ e.v.) for Na, 5500Å. ($\chi = 2{\cdot}24$ e.v.) for K, 5700Å. ($\chi = 2{\cdot}16$ e.v.) for Rb, and 6600Å. ($\chi = 1{\cdot}87$ e.v.) for Cs. Recently J. J. Brady [4] has measured the thresholds of potassium, rubidium and cæsium condensed in a vacuum on a metallic surface at liquid-air temperature and found for atomically thick films 5500Å. ($\chi = 2{\cdot}24$ e.v.) for K, 5900Å. ($\chi = 2{\cdot}19$ e.v.) for Rb, and 6300Å. ($\chi = 1{\cdot}96$ e.v.) for Cs. These results are in the order to be expected, except that for lithium, which we should have expected to have a higher, not a lower work function than sodium. The values found for cæsium are in fairly satisfactory agreement with Kingdon's thermionic value.

(2) *Magnesium.*—The photoelectric threshold of clean magnesium has recently been determined by Cashman and Huxford.[9] The experimental tube and all its metal parts were carefully outgassed and the magnesium slowly distilled, until a heavy mirror coating was formed upon the bulb. The distillation was repeated several times, and after each distillation a spectral response curve for the newly formed surface obtained. In all cases the measured thresholds were found to lie in the range 5000Å.–5200Å., and the most probable value

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* A. L. Hughes and L. A. DuBridge, "Photoelectric Phenomena," McGraw-Hill Book Company, Inc. (1932), p. 71.

of the true threshold for clean magnesium was estimated to be approximately 5100Å. This corresponds to a work function of 2·42 e.v. It is interesting to note that the vacua were so good that no changes could be detected in the thresholds after periods of rest up to as long as 50 hours.

(3) *Barium.*—Thermionic emission data for barium have been obtained by J. W. Ryde and N. L. Harris, by an experimental method the details of which will be given in Chapter III. It will be sufficient to state here that barium was distilled continuously from a heated source on to a tungsten filament, the rate of deposition on the latter being made greater than the rate of evaporation from it. The filament thus became covered with barium in bulk and gave an emission characteristic of this metal. From the emission-temperature data obtained, a Richardson line was plotted which gave values for χ and A of 2·1$_1$ e.v. and about 60 amp./cm.^{2} deg.^{2} respectively.

(4) *Rare Earth Metals.*—Measurements of the thermionic emission given by several of the rare earth metals have been made by Schumacher and Harris.[53] The metals cerium, lanthanum, praseodymium, neodymium and samarium were obtained very pure (> 99·8 per cent.), and a number of others in the form of aluminium alloys. The metals or their alloys were heated either in a tungsten boat or by being shaken in fine powder form on to a metal filament which served as a carrier. From observations of the emissions of the pure metals at various temperatures, Richardson lines were obtained whose slopes give the following work functions :

Lanthanum	3·3 e.v.
Cerium	2·6 ,,
Praseodymium	2·7 ,,
Neodymium	3·3 ,,
Samarium	3·2 ,,
Tungsten (empty boat)	6·9 ,,

Now the work function of tungsten is known to be only 4·5 e.v., so that the value found by Schumacher and Harris for this metal is seen to be much too high, and one might on this account hesitate to accept their results for the rare earth metals also. Probably, however, more reliance may be placed in these data than the result for tungsten indicates, since, at the higher of the test temperatures employed vigorous evaporation must have constantly renewed the surfaces of the metals, thereby tending to keep them uncontaminated.

With regard to the metals tested in the form of aluminium alloys, the data obtained probably give little indication of the thermionic properties of the pure metals. Thus for a cerium-aluminium alloy, the slope of the Richardson line corresponds to a work function of 5·75 e.v., which is almost certainly much too high.

(5) *Thorium, Hafnium and Zirconium.*—Wires of these three metals have been obtained by C. Zwikker,[67] and their thermionic constants determined by the temperature-variation method. The surfaces of the metals of this group, particularly those of zirconium and hafnium, are extremely difficult to free from their oxides, which are very stable at high temperatures. Presumably also adsorbed layers of oxygen would be difficult to remove. After flashing the wires to near their melting-points the results obtained were those of Table IV, but after subjecting the hafnium and zirconium wires to a prolonged ageing, their emission constants and work functions both fell to the values of Table V.[68] These last must be taken as the present-day best values for these metals.

TABLE IV.

THERMIONIC CONSTANTS OF FLASHED THORIUM, HAFNIUM AND ZIRCONIUM.

Metal.	A (amps./cm.^{2}deg.^{2}).	χ (electron-volts).
Thorium . . .	70	3·38
Hafnium . . .	55,000	5·12
Zirconium . .	3,000	4·50

(6) *Tantalum.*—Tantalum, being a very refractory metal (melting-point 3300°K.), may be taken to a very high outgassing temperature. It has, however, rather unfavourable chemical properties, its oxide being relatively non-volatile, and further-

more, at high temperatures it absorbs hydrogen. It is in consequence possible to obtain a clean surface only by subjecting the metal to a prolonged high-temperature ($\sim$ 2400°K.) treatment in a good vacuum.

TABLE V.

THERMIONIC CONSTANTS OF FLASHED AND AGED HAFNIUM AND ZIRCONIUM.

Metal.	A (amps./cm.^{2}deg.^{2}).	χ (electron-volts).
Hafnium . . .	14·5	3·53
Zirconium . .	330	4·12

Such thermionic data for tantalum as have been obtained under good or tolerably good vacuum conditions are given in Table VI. The mean of the values found for the work function is 4·15 volts. The most reliable determination is that of Dushman and associates. Probably 4·1 e.v. is within 1 or 2 per cent. of the true value.

TABLE VI.

THERMIONIC DATA FOR TANTALUM.

Observer.	Date.	A (amps./cm.^{2} deg.^{2}).	χ (electron-volts)—	
			From slope of Richardson line.	Calorimetric.
I. Langmuir[41] . .	1913	$\sim$30	$4{\cdot}0_5$	—
I. Langmuir[42] . .	1916	28	4·05	—
H. Lester[45] . . .	1916	—	—	4·44
H. J. Spanner[56] . .	1924	—	4·0	—
S. Dushman, H. N. Rowe, J. Ewald and C. A. Kidner[24] . . .	1925	60	4·12	—

The work function of tantalum has also been determined photoelectrically by A. B. Cardwell,[5] using Fowler's method. The specimen was outgassed for over 1000 hours in a good vacuum at temperatures up to 2500°K. The value of χ obtained was 4·11 e.v., which is in excellent agreement with the corresponding thermionic result of Dushman and associates.

(7) *Molybdenum.*—The melting-point of molybdenum is 2895°K., somewhat lower than that of tantalum, and it suffers from the same disability as the latter metal in the tenacity with which it holds surface contamination, adsorbed oxygen being particularly difficult to remove.

In Table VII are given the results of those thermionic measurements that have been made under relatively good experimental conditions.

TABLE VII.

THERMIONIC DATA FOR MOLYBDENUM.

Observer.	Date.	A (amps./cm.^{2} deg.^{2}).	χ (electron-volts)—	
			From slope of Richardson line.	Calorimetric.
I. Langmuir [41] . .	1913	~65	$4\cdot0_5$	—
I. Langmuir [42] . .	1916	52	4·05	—
H. Lester [45] . .	1916	—	—	4·53
S. Dushman, H. N. Rowe, J. Ewald and C. A. Kidner [24] . . .	1925	60*	4·44*	—
C. Zwikker [68] . .	1926	65	4·34	—
C. Zwikker [70] . .	1927	120†	4·44†	—
L. A. DuBridge and W. W. Roehr [18] .	1932	55	4·15	—

* Corrected by Dushman [22] for the revised temperature scale of A. G. Worthing.[65]

† These are the values which appear to fit most closely the emission and temperature data given.

Of these the most reliable determination is undoubtedly that of DuBridge and Roehr. These investigators observed not only the thermionic properties but also the photoelectric. They subjected their specimen to a 1600 hours' outgassing treatment at temperatures rising from 1750°K. to 2100°K. In order to obtain consistent thermionic and photoelectric emissions they found it necessary to seal off their vacuum vessel from the pump and use a getter. In this way the pressure was reduced to well below 10^{-7} mm.

During the first stages of outgassing, the photoelectric threshold was observed to move toward the red as far as about 3500Å. (3·5 e.v.), but then, as outgassing progressed, it moved back again toward the violet, to about 2800Å. (4·4 e.v.). This was before the tube was sealed off from the pump. After it was sealed off and the vacuum further improved by means of the getter, the threshold once more moved toward the red, and the final, stable values of the work function 4·14 e.v. and 4·16 e.v. found by Fowler's method for temperatures of the specimen of 303°K. and 940°K. respectively. The mean, 4·15 e.v., may be taken as the best value of the photoelectric work function of clean molybdenum. The possible error of this value was estimated to be of the order of 0·5 per cent. The photoelectric properties of the specimen could not be further changed by treatment at the highest temperatures.

It is interesting to compare these results with the values of the thermionic work function found by earlier observers. A fairly recent determination, one by Martin [47] in 1929, gave a value of 3·48 e.v. for the thermionic work function. At no time, however, was the temperature of Martin's specimen raised above about 1800°K., and considerably higher temperatures than this are needed to remove surface contaminations. For this reason, Martin's result has not been included in our list. It is noteworthy, however, that his value corresponds very closely to the extreme excursion of the photoelectric threshold toward the red observed by DuBridge and Roehr in the early stages of outgassing. On the other hand, the values of the work function obtained by Dushman and associates and by Zwikker for a surface which was certainly much cleaner corresponds to the extreme violet excursion of the threshold observed by DuBridge and Roehr when the outgassing had reached a more advanced but not yet final stage, before the vacuum vessel was sealed off from the pump. The intermediate values obtained several years earlier by Langmuir probably correspond to an intermediate stage of outgassing.

After the photoelectric properties had become stable, DuBridge and Roehr made four determinations of the thermionic work function at intervals during about six weeks, while the outgassing conditions were maintained. The values obtained were 4·15, 4·15, 4·17 and 4·14 e.v. The mean of these, 4·15 e.v., agrees beautifully with the mean value of the work function determined photoelectrically. The mean value found for A was approximately 55 amp./cm.^{2} deg.^{2}.

(8) *Tungsten.*—The thermionic properties of tungsten are known with greater accuracy than those of any other material. Not only has tungsten the very high melting-point of 3655°K., but the chemical compounds it forms with various gases and also adsorbed gas contaminations are much more volatile than are those of either tantalum or molybdenum. Thus their removal by "flashing" in a good vacuum presents little difficulty. Also the temperature of tungsten has been very accurately determined in terms of its electrical properties by Langmuir,[43] and more recently by Forsythe and Worthing,[27] and by Jones and Langmuir.[36] The data that have been published since 1913 are given in Table VIII.

TABLE VIII.

Thermionic Data for Tungsten.

Observer.	Date.	A (amps./cm.^{2} deg.^{2}).	χ (electron-volts)—	
			From slope of Richardson line.	Calorimetric.
H. L. Cooke and O. W. Richardson [10]	1913	—	—	4·19
I. Langmuir [41]	1913	~150	4·5	—
I. Langmuir [44]	1914	59	4·27	—
K. K. Smith [55]	1915	—	4·48	—
H. Lester [45]	1916	—	—	4·43
C. Davisson and L. H. Germer [12]	1922	—	4·55 *	4·52
S. Dushman and associates,[21, 23, 24, 25]	1923–25	60	4·53	—
H. J. Spanner [56]	1924	—	4·3	—
C. Zwikker [70]	1925	70	4·50	—
C. Zwikker [67]	1926	100	4·58	—
A. H. Warner [60]	1927	—	4·25	—

* This is the value obtained when $T_m/7740$, with $T_m = 2100°K.$, is subtracted from 4·82 e.v., the value found for the ϕ of the $T^{\frac{1}{2}}$ emission formula (see p. 30).

The mean of all the values of χ in this table is 4·425 e.v. and the A-values vary between 60 and 150 amp./cm.^{2}deg.^{2}. But it is not fair to assign equal weights to all the data, for it must be borne in mind that in some of the investigations much greater pains were taken to secure accuracy than in others. Undoubtedly the best determinations are those of Davisson and Germer, Dushman and his associates, and Zwikker. The mean of the values of χ found by these is 4·54 e.v. This may be taken as the present-day best value, the error probably not exceeding 1 per cent.

A. H. Warner [61] has recently determined by Fowler's method the photoelectric work function of a tungsten surface formed by evaporation after very careful outgassing. The value found was 4·54 e.v., which is in excellent agreement with the more reliable of the thermionic values.

(9) *Rhenium.*—The thermionic properties of this metal have been roughly determined by Alterthum.[1] Filaments having a rhenium surface were prepared by burning 0·03 mm. tungsten wires at about 2100°K. in a mixture of the gaseous rhenium chlorides. This caused the chlorides to decompose and a dense crystalline deposit of rhenium metal to form on the wires. The burning was usually continued until the wire diameter had grown to 0·2–0·3 mm.; 20 mm. lengths of this wire were then mounted as filaments in standard radio valves from which the grids had been removed, the emission-temperature relationship determined between 1900° and 2700°K., and the thermionic constants deduced from the corresponding Richardson line. The values found were

$$A = 200 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 5\cdot 1 \text{ e.v.}$$

There is good reason to believe that the emissions observed were those characteristic of clean rhenium. Microscopic examination of sections of the heat-treated wire showed the tungsten core to be distinct from the rhenium sheath, indicating that alloying had not occurred to any important extent. Also rhenium is a very refractory metal, melting only at 3440° ± 60°K., and thus it could be outgassed at a very high temperature. That the surface was in a gas-free condition when the emission measurements were made is indicated by the fact that no important change in the emission was found after five hours' further heat treatment in a vacuum at 2700°K.

At the same time, no very great accuracy can be claimed for the values of the constants obtained. The temperatures used for the Richardson plot were those found optically for the centre of the filament, assuming the absorption coefficient for a wave-length of 6500Å. to be 0·45. If, instead, the value of this quantity had been assumed to be 0·4, the temperature scale would have been about 30° higher, and if it had been assumed to be 0·5 the scale would have been 50° lower. But this was not the most serious of the possible sources of error. With such short, relatively thick filaments, the effect of the cool ends on the emission must have been important, and this was not properly allowed for. Finally, no correction was made for the Schottky effect.

The work function of rhenium has also recently been determined photoelectrically, by Engelmann.[26] After prolonged outgassing at temperatures up to 2300°K. the threshold was found to be in the neighbourhood of 2480Å. The corresponding value of the work function is 4·98 e.v.

(10) *Iron.*—The photoelectric threshold of iron after extended outgassing in a good vacuum has been found by Cardwell [6] to lie between 2580Å. and 2652Å. The corresponding value of the work function is 4·72 ± 0·07 e.v. More recently, G. N. Glasoe [30] has used Fowler's method to determine the photoelectric work function of electrolytic iron outgassed for several hundred hours at temperatures up to 1220°K. The value he found was 4·77 e.v.

Cardwell found the photoelectric sensitivity of his specimen to be considerably less after cooling *suddenly* than after cooling slowly from above 1180°K. (β-γ transition point). This he attributed to a retention in the former case of part of the γ form (face-centred cubic), this being the photoelectrically less sensitive. The β and α forms which are stable below 1180°K. are body-centred cubic crystals.

The corresponding thermionic properties of iron above and below the β-γ transition point have been studied by G. Siljeholm.[54] He found the Richardson line to consist of two parallel parts, with a discontinuity at the transition point. From the slope of this line for the specimens which had been most thoroughly outgassed the value 4·77 e.v. was obtained for the work function. This is in perfect agreement with Glasoe's photoelectric value.

(11) *Cobalt.*—Cobalt, like iron, crystallizes in two forms, one of which, the face-centred cubic, is stable above 1120°K., and the other, the hexagonal, below this temperature. It has been found by Cardwell [7] that a specimen suddenly cooled from above 1120°K., and which therefore retains the face-centred cubic structure, exhibits a markedly higher photoelectric sensitivity than a specimen which has been cooled slowly. Cardwell has recently [8] found for the photoelectric work functions 4·25 ± 0·08 and 4·12 ± 0·04 e.v. for the hexagonal and face-centred cubic forms respectively.

(12) *Nickel.*—No measurements of the thermionic properties of nickel have been made in which the experimental conditions were such as to ensure the necessary freedom from contamination of the surface.*

Recently G. N. Glasoe [30] has determined by Fowler's method the photoelectric work function of nickel outgassed for several hundred hours in a good vacuum at temperatures up to about 1370°K. After a final equilibrium state of the specimen had thus been reached its photoelectric work function was found to be 5·01 e.v. and its contact potential was 0·2 volts negative to outgassed iron. The observed contact potential difference thus agrees reasonably well with the difference (0·24 e.v.) between the photoelectric work functions of the two metals, as it should do.

(13) *Rhodium.*—This metal has been studied both thermionically and photoelectrically by E. H. Dixon.[14] The specimen, in the form of a ribbon, was subjected to an outgassing treatment of over 1000 hours' duration in a final vacuum of 10^{-8} mm. at temperatures rising from 1220°K. to 1720°K.

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* Since this was written, a paper has appeared in the *Physical Review*, Vol. **44**, p. 345, Sept. 1, 1933, by G. W. Fox and R. M. Bowie, giving the results of thermionic measurements on very carefully outgassed nickel. The values obtained for the thermionic constants were A = 1380 amp./cm.^{2} deg.^{2}, $\chi = 5{\cdot}03 \pm 0{\cdot}05$ e.v.

In the final condition the photoelectric work function measured at room temperature was found to be 4·92 e.v. As the temperature was raised the threshold appeared to shift toward the red, and did so abnormally rapidly at about 510°K. This might have been due to a change in the crystal structure occurring at this temperature. Between 510°K. and 920°K. the threshold corresponded to a work function of 4·57 ± 0·09 e.v.

The thermionic current showed a discontinuity (possibly also due to a structural change) at about 1370°K. The slope of the Richardson line beyond this point corresponded to a work function of 4·58 ± 0·09 e.v.

(14) *Palladium.*—The thermionic and photoelectric properties of pure palladium during an extended outgassing in high vacuum have recently been studied by L. A. DuBridge and W. W. Roehr.[19] Fowler's method was used for interpreting the photoelectric measurements and the photoelectric work function in the final, outgassed state was found to be 4·97 ± 0·01 e.v. For the corresponding thermionic work function the value 4·99 ± 0·04 e.v. was obtained, and for the emission constant about 60 amp./cm.^{2}deg.^{2}

(15) *Osmium.*—In 1913 H. L. Cooke and O. W. Richardson [11] found for the voltage equivalent of the latent heat of evaporation of electrons from osmium the value 5·0 e.v. After making allowance for the finite velocities of ejection of the electrons, the value 4·7 e.v. is obtained for the work function.

(16) *Platinum.*—Platinum is one of the more difficult metals to free of gaseous and other contaminations, and it is only in the last few years that consistent thermionic and photoelectric results have been obtained with it.

Among those who have used the photoelectric method to study the surface properties of platinum are Koppius,[40] Suhrmann,[57] Tucker,[59] Woodruff [64] and DuBridge.[15, 16] Koppius, after heating his specimen in a vacuum for some time at 1170°K., found the photoelectric threshold to be 2570Å., to which corresponds a work function of 4·8 e.v. Suhrmann, in his best approach to a gas-free condition, found for the threshold 2700Å. (4·57 e.v.). He also carried out thermionic emission measurements [58] and found from the slope of the

Richardson line a thermionic work function of 4·35 e.v. However, neither Koppius nor Suhrmann baked out their glass vessels at a high temperature, and unbaked glass is known to be a fruitful source of contaminating gases and vapours, particularly water vapour.

Much greater pains were taken to outgas their specimens by Tucker, Woodruff and DuBridge. Tucker found that after 8 hours' heating at 1170°K. in a residual gas pressure of the order of 10^{-6} mm. the photoelectric threshold of his specimen was about 2700Å., but that after subsequently heating it for two hours above 1670°K. it had become photoelectrically insensitive to his quartz-mercury-arc radiation. Woodruff found the same condition of insensitivity after 17 hours' heating at 1300°K. in a residual gas pressure of 10^{-6} mm. The shortest wave-length transmitted by quartz is about 1850Å., but this does not mean that in the final condition of Tucker's and Woodruff's specimens the threshold was necessarily of a shorter wave-length than this, for, as Woodruff has pointed out, the intensity of the mercury arc in this region is very feeble. Indeed, using an iron arc as his source of radiation, Woodruff was able to show that the threshold was somewhat above 1850Å.

By far the most exhaustive study of the photoelectric and thermionic properties of platinum as a function of outgassing treatment has been that made by DuBridge. Starting with specimens variously treated beforehand, he subjected them to prolonged heating at various temperatures in a well baked-out glass vessel connected to a good pump. The photoelectric sensitivity of the surface was found to vary at first in a somewhat erratic manner, but then to approach and finally attain a limiting value which was the same in all cases where the residual gas pressure was less than 10^{-6} mm. and the outgassing temperature higher than 1370°K. As one would expect, this condition was in general attained most quickly in the best vacua and with the highest outgassing temperatures, but in no case was it achieved in less than 10 hours. Further prolonged heating near the melting-point in the best attainable vacuum failed to further change the photoelectric condition of the surface. It seems reasonable to conclude, therefore, that the final condition of the specimen achieved by DuBridge was that of practically complete gas-freedom.

The photoelectric threshold found by DuBridge for the final condition was 1962Å. This corresponds to a work function of 6·30 e.v. For the thermionic work function DuBridge found by the temperature-variation method the value 6·27 e.v. ± 1 per cent., and for the emission constant 17,000 amp./cm.^{2} deg.^{2} ± 25 per cent. Whilst these are undoubtedly the most reliable data that have yet been obtained, it is not without interest to examine the results obtained also by other observers. The thermionic data obtained since 1913 are given in Table IX.

TABLE IX.

THERMIONIC DATA FOR PLATINUM.

Observer.	Date.	A (amps./cm.^{2}deg.^{2}).	χ (electron-volts).
I. Langmuir [41]	1913	$\sim 8 \times 10^6$	$6{\cdot}6_4$
L. L. Lockrow [46]	1922	$4{\cdot}46 \times 10^{-2}$	4·31
R. Suhrmann [58]	1923	30·1	4·18
H. J. Spanner [56]	1924	28·8	5·22
L. A. DuBridge [16]	1928	17,000 ± 25 °/₀	6·27 ± 1 °/₀

In view of the difficulty there would be in reconciling the extraordinarily large A found by DuBridge with theoretical requirements, it becomes important to consider any possibility there might conceivably be that, in spite of all the care taken to secure clean conditions, the experimental A is not the true A characteristic of platinum, but exceeds it by a large factor.

One such possibility has been discussed by R. H. Fowler.[29] It is, simply, that the true emitting surface area of the platinum in its final, outgassed condition is much greater than it appears to be. This, as Fowler has pointed out, is suggested by the work of Bowden and Rideal [3] on the overpotential of the hydrogen electrode, in which "they appear to have shown conclusively that silver may have a true surface . . . fifty times its apparent surface, nickel forty-five times and platinized platinum 1800 times. . . .

"In DuBridge's experiments the platinum was violently outgassed. It is necessary to dislodge the contamination (probably hydrogen) in a thickish surface layer, and this treatment inevitably tears up the metal surface. In view of Bowden and Rideal's result and the known power of platinum to form a metal sponge it is not unlikely that the true surface of the platinum emitter is very many times its apparent surface. One might even venture to attribute the whole extra factor in A to this effect if it were not that the greater part of such excessive areas must lie in deep cuttings or almost perfect enclosures into which the applied field which produces an apparently saturated current will not penetrate. Owing to this lack of penetration, large factors cannot be obtained in this way, but it is likely that much of the variation in A from specimen to specimen is due to this cause. Variations of this nature in the true emitting area probably occur for all metals, especially soft ones."

There is, perhaps, another possibility which should not be overlooked, viz. that even in its final condition the surface of DuBridge's platinum was not really clean, but had adsorbed on it some contamination, such as oxygen or hydrogen. Although a constant contamination cannot give rise to an abnormally high A, a varying one might. DuBridge's vacua were too good for it to be probable that any contamination condensed on the surface of the metal from outside. It might, however, have been held in solution in the metal and diffused to the surface. Diffusion to the surface of a dissolved impurity is known to occur in thoriated tungsten and similar systems. In such cases the amount of contamination present on the surface must, at each temperature at which its time-rate of change is unimportant, be such that the rate of its evaporation and the rate of arrival of fresh contamination from the interior at least very nearly balance each other. The amount of surface contamination determined by this condition will, in general, vary with the temperature, and in consequence there will be a temperature variation of χ. If χ decreases with rising temperature this must make the slope of the Richardson line too steep and so A too large. The supposed temperature variation of χ would not violate the thermodynamical theory of emission, since at no temperature would the system considered be in a state of true thermodynamical equilibrium.

Now if there is a variation of χ with T, it should be possible to detect and measure it photoelectrically. Indeed, DuBridge[17] has reported a temperature variation of the photoelectric threshold which is in the right direction and approaches the right magnitude to account for the observed high value of A. This was before the appearance of Fowler's photoelectric theory, however, and this theory puts rather a new complexion on the matter. According to Fowler's theory there is no true photoelectric threshold except at absolute zero, and at all higher temperatures the lowest frequency of exciting radiation which gives a measurable response depends merely on the sensitivity of the current-measuring instrument used. In particular this lowest frequency must decrease with rising temperature, and so the effect observed by DuBridge in the case of platinum is qualitatively accounted for. Even if it is assumed that the temperature variation of the threshold reported by DuBridge really corresponds, as it was at the time believed to do, to a variation of χ, its magnitude barely suffices to account for the observed value of A. And in the light of Fowler's theory, any temperature variation of χ that is reconciliable with the photoelectric observations must be still less.

Thus it does not appear that the abnormally high value of A found by DuBridge can be due either to any discrepancy between the real and apparent emitting areas or to a temperature variation of the work function brought about by a variation of surface contamination or, indeed, for that matter, in any other way.

(17) *Copper, Silver and Gold.*—In the only comparatively recent thermionic work on these metals, viz. that of Goetz,[31, 32] of Wehnelt and Seiliger,[62] and of Ameiser,[2] the immediate aim of the investigations was not so much to determine the thermionic properties of the solid metals as to find what *changes* in these properties are associated with change of phase at their melting-points. This rendered necessary an elaboration of experimental technique which could with advantage have been avoided (from the point of view of vacuum conditions), had the work been confined to the study of the solid phase.

The earlier results of Goetz are probably not very reliable, since in some respects they differ sharply from those he obtained later under greatly improved experimental conditions. The experimental conditions of Wehnelt and Seiliger, also, do not appear to have been such that, in the light of present-day knowledge, great reliance can be placed in their numerical results. Their specimens were contained in a quartz vessel and were raised to the requisite test temperatures, which were in the neighbourhood of 1300°K., by heating the quartz vessel in a furnace. At such temperatures, however, quartz gives off large quantities of gas, the evolution continuing at a rate sufficient to seriously impair the vacuum for many hours, or even days, and it is questionable, therefore, whether the surfaces of the specimens were free of contamination.

In the more recent work of Goetz [32] the experimental conditions appear to have been somewhat better, and a closer approach to freedom of the specimens from surface contaminations was probably achieved. The emissions were found to be very satisfactorily reproducible. The experimental conditions of Ameiser, too, appear to have been good, and she took some pains to secure gas-freedom of her electrodes. But unfortunately, with these low-melting-point metals it is difficult, even under the best of conditions, to be sure that the last traces of surface contamination have been removed. Even reproducibility of the results is no guarantee of this, for it may only mean that a constant state of contamination, e.g. that of a monomolecular adsorbed layer of some gas, has been reached.

Wehnelt and Seiliger found the emissions from both copper and silver to increase suddenly on fusion and the slopes of the Richardson lines to be a few per cent. less for the molten than for the solid metals. Goetz, in his more recent work, likewise found a sudden increase in the emission on fusion in the case of silver, but a *decrease* in the case of copper. He observed a discontinuity in the emission at the melting-point of gold also, the sign of which was, however, not always the same. Finally, Ameiser found a *decrease* in the emission and an *increase* in the slope of the Richardson line on fusion in the case of all three metals. Thus the observations of the three observers could not well have been more conflicting.

Wehnelt and Seiliger and also Ameiser found straight Richardson lines both below and above the melting-points of the metals. Goetz, however, obtained lines for the liquids which were decidedly curved, particularly close to the melting-points, being concave upwards. This was taken by Goetz to mean that the work functions of the liquids increase with rising temperature. It is, however, only possible to compute work functions from *straight* Richardson lines. As Ameiser remarks, the curvatures of the Richardson lines for the liquids obtained by Goetz may quite plausibly be interpreted in terms of variable gas contaminations, and she draws attention to Goetz's observation that the best vacua were obtained at the highest temperatures, possibly owing to the "gettering" of gases by volatilization and condensation of the metals, whilst at lower temperatures the vacua became so poor that ionization phenomena appeared.

The values of the thermionic constants found by Goetz for the solid metals and by Ameiser for the solid and liquid metals are given in Table X.

TABLE X.

THERMIONIC CONSTANTS FOR COPPER, SILVER AND GOLD.

Metal.	Observer.	A (amps./cm.^{2}deg.^{2}).	χ (electron-volts).
Solid Cu.	Goetz	65	4·33
,, ,,	Ameiser	4·6	4·26
Liquid Cu	,,	$2{\cdot}7 \times 10^{10}$	7·02
Solid Ag	,,	0·76	3·56
Liquid Ag	,,	$4{\cdot}4 \times 10^{3}$	4·54
Solid Au	Goetz	40	4·32

The changes in χ at the melting-points recorded by Ameiser are much too large to be plausible, particularly in the light of recent work by Randall and Rooksby [50] on the diffraction of X-rays by certain metals near their melting-points. It appears from this work that a metal really suffers no abrupt loss of its crystalline structure on fusion, but that a decided tendency of the molecules to group themselves in the crystalline structure still persists in the liquid. That being so, it is difficult to see what could bring about an abrupt change in thermionic properties on fusion, or if a change did occur, how it could be of any considerable magnitude. It is interesting to note that observations by Roller, Jordan and Woodward [52] on the photoelectric thresholds of solid and liquid mercury, which are not subject to the experimental uncertainties of the thermionic work on copper, silver and gold, do not reveal any change in the work function accompanying the change of state.

Ameiser's values for A are equally improbable, particularly that for liquid copper.

The photoelectric thresholds of outgassed silver and gold have been determined by Winch [63] and Morris [49] respectively. The silver was outgassed in a good vacuum for 800 hours at temperatures up to 870°K., after which the threshold was found to have reached a limiting value which suffered no change during a further 400 hours' heating at this temperature with occasional "flashings" at 1120°K. At the last-named temperature volatilization was very rapid. The gold was outgassed at 920°K. for 1800 hours, when it, too, was found to have reached a final state.

The data of Winch and Morris have been used by Fowler [28] to determine the true photoelectric work function by his method, each at three different temperatures. The results are given in Table XI.

TABLE XI.

Photoelectric Work Functions of Silver and Gold.

Metal.	Temp. (deg. K.).	χ(e.v.).	Metal.	Temp. (deg. K.).	χ(e.v.).
Ag	296	4·71	Au	296	4·86
,,	673	4·76	,,	733	4·92
,,	873	4·75	,,	1013	4·92

The mean values are 4·74 e.v. for silver and 4·90 e.v. for gold.

(18) *Zinc.*—The photoelectric properties of single-crystal and of polycrystalline zinc have been studied by Dillon.[13] After having been melted and outgassed in a high vacuum, the zinc was allowed to crystallize and then transferred to a photoelectric cell, where it was subjected to further outgassing treatment. Of course during its transference, involving exposure to air, its surface must have become contaminated by adsorbed

gas, and it is questionable whether this was subsequently entirely removed, for even after the outgassing in the photoelectric cell, the photo-currents were found to change spontaneously during exposure to ultraviolet light. This was thought to be possibly due to a photo-emission of adsorbed gas. After long exposure to light a steady state was reached, and the photoelectric thresholds of the single-crystal and polycrystalline surfaces were then found to be 3460Å. (3·57 e.v.) and 3720Å. (3·32 e.v.) respectively.

(19) *Mercury.*—The photoelectric threshold of mercury has been determined by Kazda,[37] Dunn,[20] Hales,[34] and Roller, Jordan and Woodward.[52] The first three employed essentially the same technique, but the vacuum conditions of Hales were much better than those of Kazda and Dunn. Freedom from surface contamination was ensured by working with the mercury in a good vacuum and causing it to flow while readings were being taken. Above a certain limiting rate of flow the threshold was found to be independent of the flow and of the nature of the residual gases present. Hales even observed the threshold to remain constant for a considerable time after the flow was stopped. All three obtained the same value for the threshold, viz. 2735 ± 10Å. The corresponding work function is 4·52 e.v.

Roller, Jordan and Woodward caused films of very pure mercury to deposit very slowly in a high vacuum on an oxidized iron plate maintained at liquid air temperature. The threshold found for an atomically thick layer of mercury was 2730 ± 15Å. This did not change when the mercury was allowed to melt, showing that the work functions of liquid and solid mercury are the same.

(20) *Carbon.*—The experimental data for this element are given in Table XII.

From this evidence it is impossible to be more precise than to say that the work function of carbon is probably in the neighbourhood of 4 e.v. In view of the wide differences between the values found for χ it would seem that the value of 5×10^{-4} amp./cm.^{2} deg.^{2} for A corresponding to the lowest of the χ-values is almost certainly far too low.

TABLE XII.

THERMIONIC DATA FOR CARBON.

Observer.	Date.	A (amp./cm.^{2} deg.^{2}).	χ (electron-volts)—	
			From slope of Richardson line.	Calorimetric.
I. Langmuir [41].	1913	$\sim 5 \times 10^{-4}$	2·5	—
I. Langmuir [42].	1916	—	3·88	—
H. Lester [45] .	1916	—	—	4·52

(21) *Tin.*—Photoelectric measurements on pure, carefully outgassed tin in the molten state and in two solid modifications have been made by Goetz,[33] and the true photoelectric work functions have been determined by Fowler,[28] using Goetz's data. The work functions thus found for the β, γ and liquid forms were 4·39, 4·28 and 4·17 e.v. respectively.

TABLE XIII.

THERMIONIC AND PHOTOELECTRIC DATA FOR CLEAN METALS.

Metal.	A (amps./cm.^{2} deg.^{2}).	χ (electron-volts)—		Metal.	A (amps./cm.^{2} deg.^{2}).	χ (electron-volts)—	
		Therm-ionic.	Photoelectric.			Therm-ionic.	Photo-electric.
Li . .	—	—	(2·28)	Co (hexag.) .	—	—	(4·28)
Na . .	—	—	(2·46)				
K . .	—	—	(2·24)	Co (face-centred cubic)	—	—	(4·12)
Rb . .	—	—	(2·16–2·19)	Ni . .	1380	5·03	5·01
Cs . .	162	1·81	(1·87–1·96)	Rh . .	—	4·58	(4·57)
Mg . .	—	—	(2·42)	Pd . .	60	4·99	4·97
Ba . .	60	2·11	—	Os . .	—	4·7	—
				Pt . .	17000	6·27	(6·30)
Rare Earth Metals	—	∼3	—	Ag . .	—	—	4·74
Zr . .	330	4·12	—	Au . .	—	—	4·90
Hf . .	14·5	3·53	—	Zn . .	—	—	(∼3·5)
Th . .	70	3·38	—				
Ta . .	60	4·12	4·11	Hg (liquid and solid)	—	—	(4·52)
Mo . .	55	4·15	4·15	C . .	—	∼ 4	—
W . .	60–100	4·54	4·54	Sn (β) .	—	—	4·39
Re . .	200	5·1	(4·98)	Sn (γ) .	—	—	4·28
Fe . .	—	4·77	4·77	Sn (liquid) .	—	—	4·17

The relatively more reliable of the above data are, for convenience of reference, tabulated in Table XIII. An estimate of their probable accuracy may be formed by referring to the foregoing discussions and also to the original literature. The photoelectric data not arrived at by Fowler's method are bracketed.

Concluding Remarks.—It is satisfactory to note that in the case of those metals (Ta, Mo, W, Fe, Pd)* for which the work functions have been determined both thermionically and photoelectrically by Fowler's method, the values obtained by the two methods are in excellent agreement. In this agreement we have confirmation of the validity both of Fowler's theory of photoelectric response for exciting wave-lengths near λ_0 and of the theory which leads to the T^2 thermionic emission formula.

Reliable work function data are now available for a sufficient number of metals for it to be possible to form a general picture of the relationship between work function and position in the periodic table. We see that, in general, χ, like the ionization potential for the isolated atoms, increases from left to right and, on the left-hand side, from bottom to top of the periodic table, thus exhibiting inverse correspondence with the chemical basicity of the elements.

Finally, we observe that in most cases the emission constant A has the same order of magnitude as the theoretical A_0, viz. 120 amp./cm.^{2}deg.^{2}, indicating little or no reflexion. Usually departures of experimental A-values from A_0 by a factor of 2 or less have little theoretical significance, in view of the great difficulty of determining A accurately. There are a few cases, however, where such departures probably cannot be wholly accounted for by experimental uncertainty. Such a case is that of tungsten, whose emission constant is almost certainly less than 120 amp./cm.^{2}deg.^{2}. It *may* be that this is due to the existence of a potential hump at the surface which projects slightly above the final image level and so gives rise to an appreciable reflexion of slow electrons. There is, however, a possible alternative explanation which

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* To this list nickel must now be added—see footnote on p. 89.

should not be overlooked. It will be remembered that the derivation of the emission formula

$$i = (1 - \bar{r})A_0T^2\epsilon^{-\chi/kT}, \tag{4}$$

in which χ is a constant, depends upon certain approximations, the most important of which is the neglect of c_p', the molecular heat of the condensed electrons. It will be shown in Chapter V that if c_p' is not neglected, the same formula (4) is obtained, but in it χ is no longer strictly constant, varying slightly with temperature. If c_p' is positive at all temperatures, χ must increase with rising temperature, and this has the effect of making the slope of the experimental Richardson line too small. In consequence, the A found experimentally will be less than $(1 - \bar{r})A_0$, where A_0 is 120 amp./cm.^{2} deg.^{2}, by a factor which may, in some cases, be as much as about 2.

LITERATURE.

1. C. Agte, H. Alterthum, K. Becker, G. Heyne and K. Moers, *Naturwiss.*, **19**, p. 108, 1931; *ZS. f. anorg. u. allgem. Chem.*, **196**, p. 129, 1931.
2. I. Ameiser, *ZS. f. Phys.*, **69**, p. 111, 1931.
3. F. P. Bowden and E. K. Rideal, *Proc. Roy. Soc.* (*A*), **120**, pp. 59 and 80, 1928.
4. J. J. Brady, *Phys. Rev.*, **41**, p. 613, 1932.
5. A. B. Cardwell, *Phys. Rev.*, **38**, p. 2041, 1931.
6. A. B. Cardwell, *Proc. Nat. Acad. Sci.*, **14**, p. 439, 1928.
7. A. B. Cardwell, *Proc. Nat Acad. Sci.*, **15**, p. 544, 1929.
8. A. B. Cardwell, *Phys. Rev.*, **38**, p. 2033, 1931.
9. R. J. Cashman and W. S. Huxford, *Phys. Rev.*, **43**, p. 811, 1933.
10. H. L. Cooke and O. W. Richardson, *Phil. Mag.*, **26**, p. 472, 1913.
11. H. L. Cooke and O. W. Richardson, *Phil. Mag.*, **25**, p. 624, 1913.
12. C. Davisson and L. H. Germer, *Phys. Rev.*, **20**, p. 300, 1922; **30**, p. 634, 1927.
13. J. H. Dillon, *Phys. Rev.*, **38**, p. 408, 1931.
14. E. H. Dixon, *Phys. Rev.*, **37**, p. 60, 1931.
15. L. A. DuBridge, *Phys. Rev.*, **29**, p. 451, 1927; **31**, p. 236, 1927.
16. L. A. DuBridge, *Phys. Rev.*, **32**, p. 961, 1928.
17. L. A. DuBridge, *Proc. Nat. Acad. Sci.*, **14**, p. 788, 1928.
18. L. A. DuBridge and W. W. Roehr, *Phys. Rev.*, **42**, p. 52, 1932.
19. L. A. DuBridge and W. W. Roehr, *Phys. Rev.*, **39**, p. 99, 1932.
20. H. K. Dunn, *Phys. Rev.*, **29**, p. 693, 1927.
21. S. Dushman, *Phys. Rev.*, **21**, p. 623, 1923.
22. S. Dushman, *Rev. Mod. Phys.*, **2**, p. 382, 1930.
23. S. Dushman and J. W. Ewald, *Gen. El. Rev.*, **26**, p. 154, 1923.
24. S. Dushman, H. N. Rowe, J. W. Ewald and C. A. Kidner, *Phys. Rev.*, **25**, p. 338, 1925.
25. S. Dushman, H. N. Rowe and C. A. Kidner, *Phys. Rev.*, **21**, p. 207, 1923.

26. A. Engelmann, *Ann. d. Phys.*, **17**, p. 185, 1933.
27. W. E. Forsythe and A. G. Worthing, *Astrophys. J.*, **61**, p. 126, 1925.
28. R. H. Fowler, *Phys. Rev.*, **38**, p. 45, 1931.
29. R. H. Fowler, *Proc. Roy. Soc.* (*A*), **122**, p. 36, 1929.
30. G. N. Glasoe, *Phys. Rev.*, **38**, p. 1490, 1931.
31. A. Goetz, *Phys. ZS.*, **24**, p. 377, 1923 ; **26**, p. 206, 1925.
32. A. Goetz, *ZS. f. Phys.*, **42**, p. 329, 1927 ; **43**, p. 531, 1927.
33. A. Goetz. *Phys. Rev.*, **33**, p. 373, 1929.
34. W. B. Hales, *Phys. Rev.*, **32**, p. 950, 1928.
35. H. E. Ives and A. L. Johnsrud, *Astrophys. J.*, **60**, p. 231, 1924.
36. H. A. Jones and I. Langmuir, *Gen. El. Rev.*, **30**, pp. 310, 354 and 408, 1927.
37. C. B. Kazda, *Phys. Rev.*, **26**, p. 643, 1925.
38. K. H. Kingdon, *Phys. Rev.*, **25**, p. 892, 1925.
39. K. H. Kingdon and I. Langmuir, *Phys. Rev.*, **22**, p. 148, 1923.
40. O. Koppius, *Phys. Rev.*, **18**, p. 443, 1921.
41. I. Langmuir, *Phys. Rev.*, **2**, p. 450, 1913.
42. I. Langmuir, *Trans. Am. Electrochem. Soc.*, **29**, p. 125, 1916.
43. I. Langmuir, *Phys. Rev.*, **7**, p. 302, 1916.
44. I. Langmuir, *Phys. ZS.*, **15**, p. 516, 1914.
45. H. Lester, *Phil. Mag.*, **31**, p. 197, 1916.
46. L. L. Lockrow, *Phys. Rev.*, **19**, p. 97, 1922.
47. M. J. Martin, *Phys. Rev.*, **33**, p. 991, 1929.
48. R. A. Millikan, *Phys. Rev.*, **7**, p. 380, 1916.
49. L. W. Morris, *Phys. Rev.*, **37**, p. 1263, 1931.
50. J. T. Randall and H. P. Rooksby, *Nature*, **130**, p. 473, 1932.
51. O. W. Richardson and A. F. A. Young, *Proc. Roy. Soc.* (*A*), **107**, p. 377, 1925.
52. D. Roller, W. H. Jordan and C. S. Woodward, *Phys. Rev.*, **38**, p. 396, 1931.
53. E. E. Schumacher and J. E. Harris, *J. Am. Chem. Soc.*, **48**, p. 3108, 1926.
54. G. Siljeholm, *Ann. d. Phys.*, **10**, p. 178, 1931.
55. K. K. Smith, *Phil. Mag.*, **29**, p. 802, 1915.
56. H. J. Spanner, *Ann. d. Phys.*, **75**, p. 609, 1924.
57. R. Suhrmann, *Ann. d. Phys.*, **67**, p. 43, 1922.
58. R. Suhrmann, *ZS. f. Phys.*, **13**, p. 17, 1923.
59. F. G. Tucker, *Phys. Rev.*, **22**, p. 574, 1923.
60. A. H. Warner, *Proc. Nat. Acad. Sci.*, **13**, p. 56, 1927.
61. A. H. Warner, *Phys. Rev.*, **38**, p. 1871, 1931.
62. A. Wehnelt and S. Seiliger, *ZS. f. Phys.*, **38**, p. 443, 1926.
63. R. P. Winch, *Phys. Rev.*, **37**, p. 1269, 1931.
64. A. E. Woodruff, *Phys. Rev.*, **26**, p. 655, 1925.
65. A. G. Worthing, *Phys. Rev.*, **25**, p. 846, 1925 ; **28**, p. 190, 1926.
66. A. F. A. Young, *Proc. Roy. Soc.* (*A*), **104**, p. 611, 1923.
67. C. Zwikker, *Proc. Amst. Acad. Sci.*, **29**, p. 792, 1926.
68. C. Zwikker, *Phys. ZS.*, **30**, p. 578, 1929.
69. C. Zwikker, *Physica*, **7**, p. 71, 1927.
70. C. Zwikker, *Physica*, **5**, p. 249, 1925.

Note on Constants for Platinum added in Proof.—H. L. van Velzer has recently shown (*Phys. Rev.*, **44**, p. 831, 1933) that the thermionic constants for platinum obtained by DuBridge probably do not correspond to a perfectly clean surface. For a specimen outgassed apparently even more completely than DuBridge's, van Velzer found

$$A = 170 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 5{\cdot}40 \text{ e.v.}$$

CHAPTER III.

ELECTRON EMISSION FROM CONTAMINATED METALS.

When the surface of a metal is contaminated with a film of foreign material only one or a very few atoms thick, the surface polarization is profoundly changed, and with it the work function and frequently also the transmission coefficient. While innumerable cases of such contaminated metals must occur in nature, there are only a few that have been the subject of detailed thermionic study. The most important of these are (1) thorium on tungsten (W-Th), (2) cæsium on tungsten (W-Cs) and on oxygenated tungsten (W-O-Cs), and (3) barium on tungsten (W-Ba) and on oxygenated tungsten (W-O-Ba). Of these cases W-Th, W-Cs and W-Ba may all be regarded as of one type and W-O-Cs and W-O-Ba of another. Instead of grouping them in this way for discussion, however, we shall find it more convenient to divide them into the groups (1), (2) and (3) above, where they are in the order in which they were first studied historically. These three groups will be treated in the first three sections of the present chapter. We shall then, in a fourth section, consider certain miscellaneous contaminations and questions of a general nature arising in connexion with contaminated metals.

It will be observed that in all five cases to be dealt with in the first three sections the contaminated metal is tungsten. This is the natural metal to choose in experimental investigations of the effects of contaminations, since it is so readily cleaned by flashing, and thus it is easy to avoid any other than the desired contamination.

SECTION I.

THORIUM ON TUNGSTEN.

In the early days of the tungsten filament lamp industry it was found that at the burning temperature the filaments grew very large crystals, and that when the lamps were burnt on alternating current these crystals became displaced relative to one another along their surfaces of contact, with consequent development of " hot spots " and early failure. It was found that this could be prevented by mixing with the tungsten a small quantity (something like 1 per cent.) of a refractory additive, which had the effect of keeping the crystals small, and that of all the additives tried the most suitable was thoria. Now in observations on the thermionic behaviour of such thoriated tungsten wires in 1913 by Langmuir and Rogers,[43] it was noticed that after proper thermal treatment in a good vacuum very much higher electron emissions could be obtained from them than from similar wires of pure tungsten at the same temperature. Since then the thermionic properties of thoriated tungsten have been the subject of very careful study and filaments of this material have come into wide use for the manufacture of " dull-emitting " thermionic valves.

The Main Phenomena.—The most important phenomena exhibited by thoriated tungsten were reported by Langmuir [30] in 1916, and again, in much greater detail, in 1923.[31]

The thermionic properties of thoriated tungsten are appreciably different from those of pure tungsten only after it has been properly " flashed " and " activated." In general a flash of about three minutes at 2800°K. is sufficient. If a lower flashing temperature is employed the time required is longer, but in no case should the temperature be below 2600°K. If now, after the flash, the filament is held at a temperature between about 1900°K. and 2200°K., the emission gradually increases from the value characteristic of clean tungsten to a much higher value. This lower range of temperatures is called the activating range.

The thermionic condition of the filament at any stage may be ascertained by measuring the emission from it at some suitable " testing " temperature. This should of course be chosen well below the activating range, so that the filament remains in a constant condition during the test. According to Langmuir, a convenient testing temperature is 1500°K. At this temperature the emission from clean tungsten is about 0·1 μA. per cm.^{2}, while that from a fully activated surface is about 18 mA. per cm.^{2}, and current densities between these limits from filaments of ordinary dimensions are easily measured with a galvanometer and universal shunt. The emission at the testing temperature may be called the " activity " of the filament.

It is found that the rate of growth of the activity increases with the activating temperature. With comparatively low activating temperatures the final activity reached is always about the same and is near the maximum attainable, but if the activating temperature is too high, say above 2200°K., the final activity falls appreciably short of this maximum. Also, if, after having been activated at a low temperature, the filament is heated above about 2200°K., a certain amount of deactivation occurs, and above 2300°K. the deactivation becomes practically complete. The range from about 2300°K. to 2600°K. (where reduction of thoria begins) is known as the deactivating range. The activity of a deactivated filament may be restored by again holding it for a sufficient length of time at an activating temperature.

The only reasonable explanation of these phenomena would appear to be that at the flashing temperature a certain amount of chemical reduction of thoria to metallic thorium occurs, and that the subsequent growth of activity at a lower temperature is due to the accumulation of some of this thorium at the emitting surface by diffusion from the interior of the wire at a greater rate than it evaporates. On the other hand, the loss of activity that occurs when the wire is heated to a deactivating temperature must be due to the rate of evaporation of surface thorium at this temperature exceeding that of its replenishment by diffusion.

From the fact that activation occurs at one temperature and deactivation at another, it follows that diffusion and evaporation must vary with temperature at different rates. Yet, as we have seen, the final activity is independent (or nearly so) of the activating temperature over the lower part of the activating range. The only plausible explanation of this would appear to be that over this range the rate of diffusion of thorium exceeds the rate of evaporation until the surface becomes completely covered with thorium. That this can occur in spite of the volume concentration of thorium in the wire being so small has been attributed by Langmuir to the smallness of the surface energy of thorium compared with that of tungsten, in consequence of which diffusion of thorium from the interior of the wire to the surface is a thermodynamically irreversible process.

Reduction of Thoria by Tungsten.—Although thoria has a greater heat of formation per atom of oxygen than any of the oxides of tungsten, the latter are so much more volatile than thoria that at sufficiently high temperatures some reduction of thoria by tungsten can occur, tungsten oxide being lost by evaporation in the process. And, as we have seen, it appears from the thermionic evidence obtained with thoriated tungsten wires that such reduction begins to occur at an appreciable rate at temperatures higher than about 2600°K.

Other evidence pointing to the same conclusion has also been obtained. Thus, some years ago, Smithells [57] examined the residues left after dissolving in a mixture of hydrofluoric and nitric acids a number of thoriated tungsten filaments which had been burnt at different temperatures for various lengths of time. He found that while the residues from unburnt filaments and from those that had been burnt for 24 hours at less than 2600°K. were white ThO_2, those that had been burnt for several hours above this temperature were of a different colour. As the temperature and time of burning were increased, the residue left after dissolving became green, blue, or grey, and it also diminished in volume. Similar observations have been made more recently by Geiss and van Liempt.[21] Although the chemical nature of these residues was not determined, the fact that they were different in appearance and quantity from those obtained from wires less severely heat-treated indicates that some chemical change must have occurred in the wires during their burning above 2600°K. It is difficult to see what this change could have been, primarily at least, other than a reduction of thoria.

A few years ago, Burgers and van Liempt [8] carried out X-ray analyses, by the Debye-Scherrer method, of a number of thoriated tungsten wires and of the residues left after dissolving the tungsten in a mixture of hydrofluoric and nitric acids. The spectra of the wires, whether they had been flashed at a high temperature or not, contained in addition to the tungsten lines only those of ThO_2. The non-appearance of thorium lines in the spectra of the flashed wires must, however, have been due merely to the smallness of the concentration of this metal in them, for the *residues* from wires which had been flashed for 10 minutes at 3200°K. showed distinct thorium lines besides those of ThO_2. The case of one such residue was exceptional in that its spectrum showed, in addition to the lines of ThO_2 certain other lines which probably came, not from metallic thorium, but from a solid solution of thorium in thoria.

The results of Burgers and van Liempt show that some, at least, of the reduced thorium exists in the form of crystalline inclusions of the metal in the tungsten or else is dissolved in included particles of thorium oxide. They leave open, however, the question as to whether some of the thorium may not also be dissolved in the tungsten. As a test for such solution, Geiss and van Liempt [21] measured the temperature coefficients of resistance of thoriated tungsten wires before and after flashing at 3450°K. for one hour in an inert gas, but were unable to detect any change. (The function of the inert gas was the same as in a gas-filled lamp, viz. to prevent the too rapid evaporation of metal.) On the other hand, Fonda, Young and Walker [19] recently did find an increase in resistivity of thoriated tungsten after a high-temperature flashing treatment in argon at 50 cm. pressure, indicating that some of the reduced thorium had gone into solution. Of course, even from the negative results of Geiss and van Liempt, it would be too much to infer that absolutely *none* of the thorium dissolved in the tungsten, particularly in view of the smallness of the total quantity of reduced thorium present in any case.

The Nature of the Surface Film of Thorium.—We may learn something concerning the thickness of the film of thorium that becomes adsorbed on tungsten from a closer study of the activation and deactivation phenomena. In Fig. 12, the curve OAB represents the growth with time of the emission, measured by Langmuir [31] at a testing temperature of 1500°K., from a filament during activation at 2100°K. The curve BD shows how the filament subsequently became deactivated when the temperature was raised from 2100°K. to 2250°K. The curve AC shows a similar deactivation of the same wire after activation had proceeded only as far as is represented by the point A. Both deactivation curves were found to be the same.

Now the suddenness with which the activity begins to fall when the filament is raised to a deactivating temperature, even long after the activity has ceased to increase, shows that when once the maximum activity has been attained there is no further growth in thickness of the adsorbed film of thorium. The final thickness of this film must therefore be something quite definite, say that of one, two or a very few atomic layers.

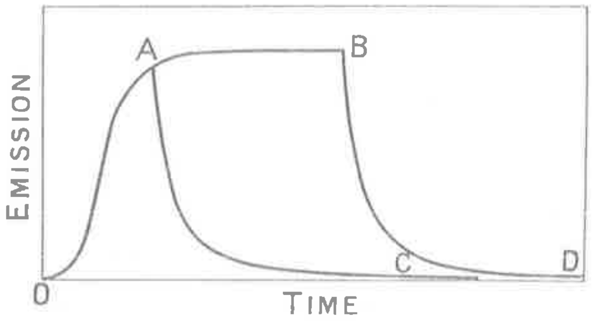

Fig. 12.—Activation and deactivation curves for thoriated tungsten.

That it is not many atoms thick also follows from the fact that the thermionic properties of fully activated thoriated tungsten are, as we shall see later, quite different from those of thorium in bulk.

There are at least two strong reasons for believing that the final film of thorium consists of only a single layer of atoms. The fact that the thorium film does not build up beyond a certain thickness can only be due to the rate of evaporation from a thick film being greater than that from a thin one. Now the rate of evaporation of a particular kind of atom at any given temperature must depend on the forces with which the surface atoms are held, and these, in turn, must be determined primarily by the nature of the underlying atoms. Thus we should expect an important difference between the rate of evaporation of thorium from a double atomic layer on tungsten and that from a single layer, a less important difference between the rate from a treble and that from a double layer, and so on, until the film is so thick that the effect of the tungsten vanishes. Only by virtue of such differences can the rate of evaporation just balance the rate of arrival of thorium at the surface and so the film be kept at a perfectly definite thickness *over a whole range of activating temperatures.** The one thickness that remains constant at all over a finite temperature range must be determined by the most important difference between the rates of evaporation just discussed. If, as we have seen there is reason to believe, this is the difference between the rates of evaporation from a single and from a double atomic layer of thorium, it must be a single layer that covers the tungsten when its activity is a maximum.

Again, we have seen what an important rôle polarization at the surface plays in determining the work function and transmission coefficient of an emitting body. And the polarization, like the volatility, must depend very much on the nature of the atoms immediately underneath those at the surface. Consequently, we should expect the thermionic activity of a thoriated tungsten filament to undergo a critical change at the point where the amount of thorium at the surface begins to exceed that in a single atomic layer. The activation curves obtained at all except the lowest temperatures show no sign of such a critical point having been gone through, however. It must be concluded, then, that normally the film does not grow to a thickness of more than a single atomic layer.

It is interesting to note that activation curves obtained by Nottingham[48] and by Brattain and Becker[6] at temperatures near the lower limit of the activating range differ in one important respect from those obtained at higher and more usually employed activating temperatures, and indicate that at these low temperatures rather more than a single layer of

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* Actually this is not strictly true. Even over the lower part of the activating temperature range there is a slight variation of the final activity with the temperature, and this can only be due to a corresponding temperature variation of the final film thickness. This is, however, only a second order effect, which we may ignore for the purpose of the present argument.

thorium atoms may be built up on the surface. Nottingham activated a thoriated tungsten filament containing a little carbon—this element is frequently introduced to counteract the "poisoning" effects of electronegative gases and vapours—at 1920°K., and found the activity to pass through a maximum before finally reaching an equilibrium value. On thereupon raising the temperature, he found the activity to increase again, reaching a new equilibrium value for each temperature. More recently, Nottingham [49] and Brattain and Becker have observed the same kind of thing with ordinary thoriated tungsten filaments (not containing carbon). Fig. 13 shows curves of the logarithm of the emission at 1549°K. plotted against time obtained by Brattain and Becker for activating temperatures of 1940° and 1845°K. It will be noted that both maxima are of the same height, but that the final activity is less at the lower temperature than at the higher. There can be little doubt that the maximum corresponds to the completion of the first atomic layer of thorium,

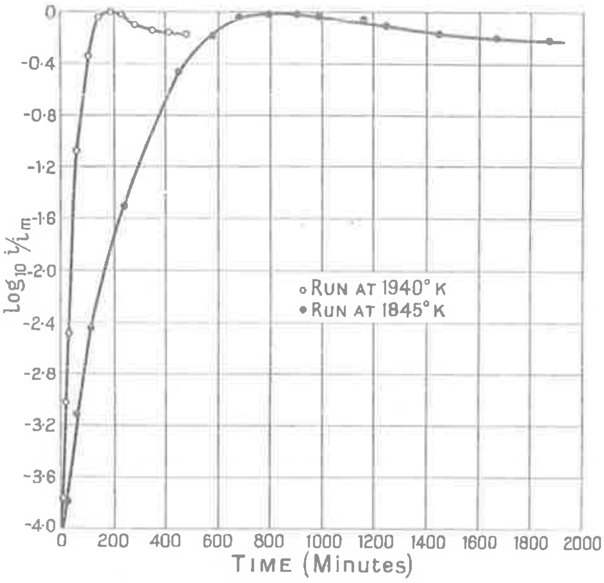

Fig. 13.—Time variation of the emission from initially inactive thoriated tungsten for two activating temperatures.

and that the lower the activating temperature the more thorium finally builds up on the surface beyond this quantity.

Curves very similar to those of Fig. 13 have also been obtained by Brattain and Becker by volatilizing thorium at a uniform rate from a thorium wire on to one face of an initially clean tungsten ribbon and observing the activity of the latter as a function of the time. One such curve is shown in Fig. 14. In order to avoid complications due to surface migration of thorium from the face of the ribbon on which it was deposited to the other face, the low testing temperature of 1274°K. was chosen. The points represent experimental values of log (i/i_m) as a function of t/t_m, where i is the emission observed after a time of deposition t, and i_m is the maximum emission, which occurred at the time t_m. The curve is that which perhaps goes most nearly through the points. It differs slightly from that given by Brattain and Becker (which represents an empirical formula) at low values of t/t_m.

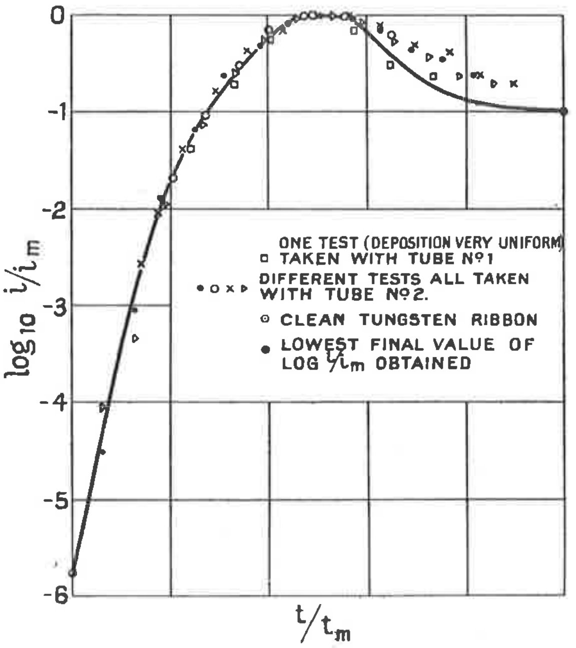

FIG. 14.—Dependence of the emission from initially clean tungsten on the quantity of thorium distilled on to it.

As regards the concentration of thorium atoms in a full monatomic layer, this was assumed by Langmuir[31] to be determined by the geometry of the underlying tungsten lattice. This lattice is body centred cubic, the side of a unit cube being 3·150Å. Langmuir found that the exposed crystal faces of tungsten that has been etched by heat treatment are exclusively those of the rhombic dodecahedron. These are (110) planes and are the faces which contain the greatest possible number of atoms ($1{\cdot}425 \times 10^{15}$ per cm.^{2}). Thorium, on the other hand, crystallizes in a face-centred cubic lattice, the side of a unit cube of which is 5·04Å., and from this Langmuir has calculated that the greatest possible number of thorium atoms that could be packed per cm.^{2} into a plane lattice is $0{\cdot}909 \times 10^{15}$, which is 64 per cent. of the number of tungsten atoms per cm.^{2} in the exposed surfaces.

Now there are two possibilities to be considered. Either the adsorbed thorium atoms take up some arrangement of their own (e.g. they may be close-packed), or else they arrange themselves in conformity with the underlying tungsten lattice. We have seen that thorium atoms evaporate much more readily from underlying thorium than from underlying tungsten. From this it would appear that the forces between thorium and tungsten atoms in adjacent positions are much greater than the forces between adjacent thorium atoms, and Langmuir has therefore concluded that the arrangement of the adsorbed thorium atoms conforms to the underlying tungsten lattice. The thorium atoms are, of course, too large for a one-to-one relationship between the thorium and tungsten concentrations. A one-to-two relationship would, however, be quite possible, and in that case there would be $0{\cdot}713 \times 10^{15}$ atoms of thorium per cm.^{2} on the exposed faces of the tungsten crystals.

Incidentally, a case where adsorbed atoms definitely do arrange themselves in conformity with the underlying lattice was found some years ago by Davisson and Germer.[11] In observing the diffraction of electron-waves reflected from a (111) face of a nickel crystal they found certain maxima which could not have been due to the nickel itself but must have come from a layer of adsorbed gas atoms. The lattice arrangement indicated by these maxima was similar to that of the nickel atoms in the surface, but with twice the scale factor.

Notwithstanding the tenacity with which thorium atoms are held to underlying tungsten, as shown by the slowness of their evaporation at temperatures in the neighbourhood of 2000°K., they can move *along the surface* of the tungsten, even at much lower temperatures than this, with comparative ease. This has been strikingly shown by an experiment of Brattain and Becker.[6] After depositing on one face of a tungsten ribbon 1·77 times as much thorium as that in a single complete layer of atoms, the ribbon was heated for $25\frac{1}{2}$ hours at 1535°K. and then for a further $8\frac{1}{3}$ hours at 1655°K. At the end of this time the activities of the front and back faces of the ribbon were found to correspond to the presence on them of 0·89 and 0·87 respectively of a complete single layer of thorium atoms. The sum of these quantities, 1·76 layers, agrees within the limits of the experimental uncertainty with the quantity originally deposited on the front face.* Thus the thorium had spread itself almost uniformly over the two faces of the ribbon without any measurable loss by evaporation having occurred in the process.

Incidentally, from the shape of the activity-time curve obtained for the front face at 1535°K., Brattain and Becker inferred that the coefficient of migration (surface diffusion) is not independent of the concentration, but that the rate of migration at a given temperature and for a given surface concentration gradient decreases as the concentration decreases. It does not appear, however, that the concentration gradient of the thorium film *as a whole* should necessarily be taken as the relevant quantity in the surface diffusion problem when the film is more than one atom thick. In view of the fact that thorium is held to underlying thorium much less tenaciously than to underlying tungsten, it might be expected that a second layer of thorium atoms would slide over the first more

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* The agreement between the quantity of thorium found after the heat treatment and that originally deposited is not really quite as good as these figures indicate, since, strictly, the spreading of thorium over the *edges* of the ribbon, as well as over the back face, should be taken into account. The edges of the ribbon used had an area $\frac{1}{10}$ that of the faces. When allowance is made for this, the quantity of thorium found after the heat treatment works out to about 5 per cent. more than that deposited. Judging by the spread of the points in Fig. 14, however, the two quantities still agree within the limits of experimental uncertainty.

easily than the first layer slides over tungsten. In that case the rate of migration for a given *total* concentration gradient would necessarily decrease as the quantity of thorium in the second layer of atoms decreases.

Further evidence of surface migration of adsorbed thorium, which is perhaps no less striking, is furnished by an experiment of Fonda, Young and Walker.[19] It is known that a thoriated tungsten wire of fine grain size is much easier to activate than one whose crystals are very large. Now Fonda, Young and Walker prepared a filament, in the form of a hairpin, of total length 15 cm., which, by suitable heat treatment, they caused to develop very long crystals (average length about 2 cm.) along a length 7 cm. from each support, while the remaining 1 cm. in the centre was left fine-grained. The filament was then activated in the usual way, and the emission measured at 1500°K. The final emission obtained at this temperature was 1780 μA. If the whole filament had become covered with the optimum amount of thorium its emission would have been 5000 μA., and if only the central 1 cm. which was fine-grained had become so covered it would have been only 334 μA. The fine-grained centre was then cut out and only the 7 cm. " legs " of the hairpin activated, the same temperature treatment being given as before. The maximum emission now obtainable was only 32 μA. Thus after the first activation at least $1780 - 334 = 1446$ μA. of the emission must have come from the legs, and of this at least $1446 - 32 = 1414$ μA. must have been due to thorium which migrated to the legs from the fine-grained centre.

Diffusion of Thorium through Tungsten.—The importance of grain size in determining the rate of diffusion of thorium from the interior of a tungsten wire to its surface has been strikingly demonstrated by Clausing [9] in experiments on the activation of thoriated tungsten wires enclosed in sheaths of pure tungsten. The method used for forming the sheaths was one due to van Arkel.[2] In this the wire to be covered is burnt at about 1600°K. in tungsten hexachloride vapour (WCl_6), whereupon the latter dissociates and a deposit of pure tungsten is formed on the wire. On making sections of wires so covered and examining them microscopically, Clausing found that the sheath is polycrystalline or consists of an apparently perfect single crystal according as the core on which it is formed is polycrystalline or monocrystalline.

Clausing's first experiments were made with uncovered monocrystalline and polycrystalline thoriated wires, and he found that as regards the ease with which they could be activated, deactivated and reactivated there was little to choose between them, although, if anything, the monocrystalline wire was rather easier to activate than the polycrystalline. This result may seem surprising, in view of what has been said regarding the importance of grain size in determining the rate of diffusion of thorium. Apparently, however, any imperfections in a monocrystalline wire, such as cracks, or even a disarrangement of the lattice along certain planes without the appearance of actual cracks, may cause it to behave very much as if it were made up of a number of separate crystals, differently orientated. Thus Fonda, Young and Walker [19] have observed an important effect on activation of the shattering of the lattice along certain planes caused by strain. They found that although an unstrained single-crystal wire failed to become appreciably activated at normal activating temperatures, presumably owing to its having been too perfect, a similar wire which had been coiled on a mandrel and then straightened again became fully activated under the same conditions, and at quite the normal rate. After this filament had been burnt for 550 hours at 2000°K., however, its rate of activation was found to have fallen considerably, owing, no doubt, to a partial healing of the lattice.

Clausing next studied the activation of single-crystal and polycrystalline wires which had had coverings of pure tungsten grown on them in the manner already described. The cores of these wires were 0·10 mm. in diameter and the thickness of the sheaths was 0·02 mm. The activation was now found to be totally different in the two cases. The rate of activation and the final activity of the covered polycrystalline wires were roughly the same as those of uncovered wires, although the time it was found necessary to flash at 2800°K. prior to activation was greater in the case of the covered than in that of the uncovered wires. The covered monocrystalline wires, however, did not exhibit any appreciable activity after having been given the same treatment. This shows that thorium must have diffused at a very much greater rate through the fine-grained sheath of the polycrystalline wire than through the single-crystal sheath of the monocrystalline wire. It must be concluded, therefore, that the diffusion of thorium from the interior of a wire to the surface takes place mainly along the grain boundaries.

There are, nevertheless, good reasons for believing that thorium can also diffuse to some extent through a tungsten crystal lattice. Even from a wire enclosed in a monocrystalline sheath of tungsten Clausing obtained *some* emission due to thorium—at 1700°K. it was of the order of 10^{-5} of the maximum emission obtained from a similarly treated wire enclosed in a polycrystalline sheath. Also Fonda, Young and Walker succeeded in completely activating a monocrystalline wire by holding it for 600 hours at 1750°K., a temperature at which evaporation is negligible, although they were unable to activate it appreciably by the normal treatment. It might of course, be objected that it is not certain that there were not in both cases some imperfections in the tungsten lattice which made diffusion of thorium possible, so this evidence is not absolutely conclusive. What does seem to be conclusive however, is the observation of Fonda, Young and Walker already referred to, that the resistivity of suitably heat-treated thoriated tungsten is slightly higher than that of pure tungsten indicating solution of some of the reduced thorium in the tungsten, in other words the diffusion of thorium atoms into the tungsten lattice. Of course, in the case of ordinary thoriated tungsten wires no very important effect on the resistivity can be expected, owing to the smallness of the amount of thorium produced. A wire made from a powdered mixture of tungsten with 1 per cent. of *metallic* thorium however, was found by Fonda, Young and Walker to have a temperature coefficient of resistance as much as 20 per cent below that of pure tungsten.

Still further evidence of the diffusion of thorium through the tungsten lattice is provided by an analysis by Fonda Young and Walker of activation data obtained with various fine-grained and coarse-grained wires. But before discussing this, it will be well first to consider briefly a theory of diffusion due to Langmuir.[31]

Langmuir assumed that the thorium diffuses only through the tungsten lattice and worked out the coefficient of diffusion D (in cm.^{2} sec.$^{-1}$) from his activation data on this assumption. Let us, for the present, accept this assumption as if it were correct. Now at sufficiently low temperatures, evaporation during at least the earlier stages of activation is negligible, and so the rate of growth of activity may be taken as a measure of the rate, Δ (in gm. cm.$^{-2}$ sec.$^{-1}$), at which thorium arrives at the surface by diffusion. It has been found that near the beginning of activation the logarithm of the emission, i, at the testing temperature always grows linearly with the time, t, and so it is convenient for graphical representation of the activation data to plot log i, rather than i itself, against t. It will be evident that the slope of any (log i)-t line in its linear part must be proportional to the corresponding value of Δ. The proportionality factor was calculated by Langmuir on the assumption that log i varies linearly with the amount of thorium at the surface throughout the whole course of activation and that at the surface of a completely activated filament there are just half as many thorium atoms as there are tungsten atoms. The proportionality factor so calculated is probably of the right order of magnitude even if neither of these assumptions is strictly true.

Now Δ is of course equal to the product DG, where D is the diffusion coefficient and G is the concentration gradient (in gm. cm.$^{-4}$) immediately underneath the surface. It is not an easy matter to determine these two quantities separately. Langmuir has, however, shown that it may be done by determining Δ from time to time during a prolonged heat treatment of the wire in which the value of G at the surface changes at a rate which depends on D. At a deactivating temperature which is not high enough for the wire to become *completely* deactivated, the value of D may also be derived from the shape of the last part of the deactivation curve, evaporation being taken into account. For the analysis, which is rather lengthy, the reader must be referred to Langmuir's article. The important thing to note, for what is now to follow, is that it yields, not D directly, but D/R^2, where R is the radius of the wire.

In view of the faultiness of Langmuir's assumption regarding the mechanism of the diffusion, it is hardly surprising to find, as we actually do, that it is not possible to obtain consistent values of D by either of his methods. This is shown in Table XIV, where values of D are given for different wire specimens at 2400°K. found by Fonda, Young and Walker, using Langmuir's second method. Sections of these wires were examined microscopically, and the effective grain size determined in each case by measuring the areas of about 400 grains and plotting the distribution. The point of mid-distribution was taken to give the effective grain radius r, determining the rate of diffusion of thorium to the surfaces of the grains.

TABLE XIV.

Relationship Between D and Effective Grain Radius r.

$r \times 10^4$ cm. .	4·0	4·8	5·3	6·2	6·3	6·9	7·3	8·2	8·6
$D \times 10^9$.	4·1	2·5	3·2	1·5	2·2	1·3	1·3	·09	1·0
$r^2D \times 10^{13}$.	65	58	90	58	87	62	69	61	74

The table shows that in general D diminishes as r increases, and that the product r^2D is roughly the same for all the wires. From this it must be inferred that the quantity yielded by Langmuir's analysis is not in reality D'/R^2 at all, where D' is now written for the *true* coefficient of diffusion through the tungsten lattice, but D'/r^2. Since all the wires used by Fonda, Young and Walker were of the same radius (0·005 cm.), D' is given approximately by the figures in the last row multiplied by $10^{-13}/R^2$, i.e. by 4×10^{-9}.

A mathematical theory of activation has recently been worked out by Gehrts,[20] on the assumption that the only diffusion of thorium that is of quantitative importance is that which takes place along the grain boundaries and then along the exposed surface of the wire, and that practically only such reduced thorium as is originally located in the grain boundaries can ultimately reach the emitting surface. The results of Fonda, Young and Walker show, however, that Langmuir's theory of the diffusion, although not correct in its original form, becomes valid when the unit considered is a single grain of tungsten instead of the whole wire, and that when once the thorium has reached a grain boundary its subsequent diffusion along it and spreading along the surface is too rapid at ordinary activating temperatures to be measurable.

By proper preliminary heat treatment of a filament, the concentration gradient, G, of thorium just underneath its crystal faces may be brought to substantially the same value at the beginning of each of a series of runs. To make sure that this has been achieved, one has merely to satisfy oneself that Δ maintains its value in successive runs carried out at the same temperature. By then carrying out activations at different temperatures it is easy to find the temperature dependence of Δ for a given G, and hence that of D′. In this way, Langmuir obtained data which show that D′ varies with temperature according to the law

$$D' \propto \epsilon^{-T_{D'}/T}, \quad . \quad . \quad . \quad . \quad (1)$$

where $T_{D'}$ is equal to 47,000 degrees. This value of $T_{D'}$ has since been confirmed by Fonda, Young and Walker for a number of different wire specimens.

Evaporation of Thorium.—After a full monatomic layer of thorium has been built up on the emitting surface at an activating temperature, no more thorium accumulates there, and so evaporation must exactly balance diffusion. And since for a whole range of activating temperatures the final state of the surface is practically independent of the temperature, we must conclude that when this state is reached either the evaporation adjusts itself to the diffusion or the diffusion adjusts itself to the evaporation.

If the diffusion adjusted itself to the evaporation, i.e. if after the completion of the layer of thorium atoms on the surface the rate of escape of thorium from the tungsten crystals fell to a much smaller value than it had at the beginning of activation, there would be a progressive accumulation of thorium underneath the surfaces of these crystals with continued burning of the filament at the activating temperature. If the adsorbed thorium were thereupon removed from the emitting surface by flashing at a high temperature for so short a time that the distribution of thorium within the tungsten crystals could not be appreciably affected, and the activating temperature were then re-established, Δ should be found to be much greater than before.

In an experiment designed to test for this, Langmuir flashed a filament for 23 seconds at 2800°K. in order to reduce some ThO_2 and then held it for 100 seconds at 2500°K. to allow irregularities in thorium concentration to become smoothed out. He then ran the filament for 187 minutes at an activating temperature of 2055°K., and measured the initial rate of activation, which was 0·00060 in certain units. After this treatment the filament was deactivated by flashing at 2800°K. for less than a second. This, other experiments showed, could not have appreciably affected the distribution of thorium in the tungsten. On now heating the filament at 2055°K. once more, the initial rate of activation was found to be only 0·00034. This showed that the very long previous activation, far from causing any accumulation of thorium under the surfaces of the crystals, had actually resulted in a considerable decrease in the thorium concentration there. Langmuir concluded that the diffusion of thorium goes on independently of the amount adsorbed, and that after the completion of activation the evaporation simply keeps pace with the diffusion.

It is convenient to think of this evaporation as made up of two parts. One is simply the evaporation from a monatomic film of thorium on tungsten at the temperature in question and has nothing to do with diffusion. This Langmuir has called the "normal evaporation." The other part is due to the constant tendency for a second layer of thorium atoms to be formed on top of the first, resulting from the undiminished rate of diffusion, and the relatively high volatility of these atoms. Evaporation from the incipient, but never appreciable, second layer has been called by Langmuir the "induced evaporation." Its rate is not directly dependent on the temperature but is simply given by the excess of diffusion over normal evaporation.

According to a theory advanced by Langmuir, induced evaporation occurs not only after a full single layer of thorium atoms has been formed on the surface, but also before. Langmuir supposed that a thorium atom, arriving at the surface, would increase the total amount of thorium there only if there were room for it at the point of its emergence. If, however, there were already a thorium atom adsorbed at this point, this would be " pushed off " by the new arrival, which latter would then take its place, and so the total number of thorium atoms on the surface would remain unchanged.

This theory was, however, based on the faulty assumption that the thorium diffuses only through the tungsten lattice and that its surface mobility is negligible. We now know that by far the greater part of the thorium that comes to the surface of an ordinary polycrystalline wire does so *via* the grain boundaries. Where these feed into the exposed surface the thorium merely has to turn round a corner to be on the latter, where it can affect the emission and whence it is possible for it to evaporate. And in view of the considerable surface mobility possessed by the thorium it would be surprising if there were any tendency for a second layer of atoms to be built up until after the completion, or practical completion, of the first layer.

That at low activating temperatures there is, in fact, no appreciable evaporation, either induced or normal, until the first layer of atoms is nearly complete, has now been shown by the work of Brattain and Becker.[6] By measuring the activity at intervals during the deposition of thorium at a uniform rate on one face of a clean tungsten ribbon in the manner already described, they first found how the activity depends on the quantity of thorium present on the surface. These measurements had, of course, to be made at a temperature sufficiently low for surface migration of thorium from one side of the ribbon to the other not to occur at an appreciable rate, but by means of subsidiary observations carried out with a filament over whose surface the distribution of thorium was uniform, they were easily able to convert activities measured at one temperature to those measured at any other. These results then enabled them to find the quantity of thorium present on the surface of an ordinary thoriated tungsten wire at any stage during its activation.

The quantity of thorium is conveniently expressed as the fraction, θ, of that in a full monatomic layer. As we have seen, this is almost certainly the quantity that is present on the surface when the activity is a maximum. Fig. 15 shows

θ-time curves for activating temperatures of 1940° and 1845°K. deduced in the manner indicated from experimental activity-time curves, the activities having been determined at a testing temperature of 1549°K. It is seen that θ increases linearly with time until it approaches the value 1. Incidentally it will be observed that θ was about 0·1 at the beginning, not zero as might have been expected. The explanation of this is that even though the filament becomes practically completely deactivated when it is flashed to a deactivating temperature,

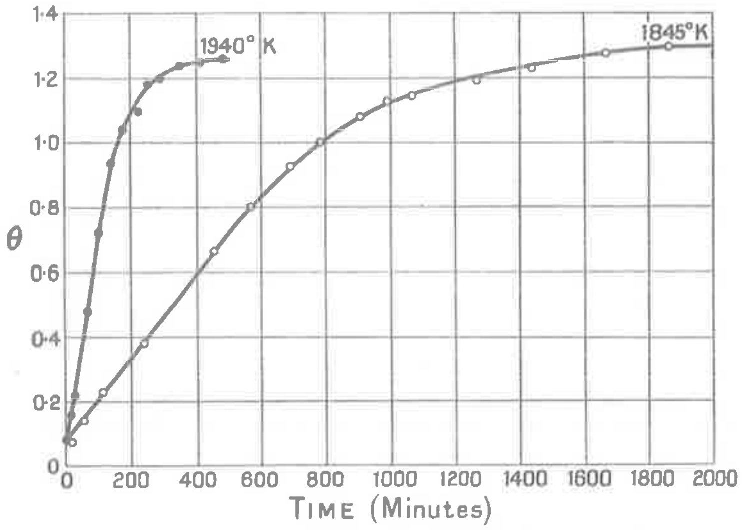

FIG. 15.—Growth with time of the θ of a thoriated tungsten filament at two activating temperatures.

it is impossible to avoid the occurrence of a certain amount of reactivation by diffusion while the filament is cooling down from this temperature to the testing temperature. This partial reactivation of a filament during cooling from a high flashing temperature has also been observed by Reynolds.[50]

The dependence of the rate of normal evaporation on θ was first calculated by Langmuir from the shape of his deactivation curves, after having made allowance for the diffusion of fresh thorium to the surface and for induced evaporation, and assuming that the logarithm of the emission, i, at the testing temperature is a linear function of θ. We now know, however, not only that Langmuir's assumption with regard to induced evaporation was incorrect, but also that log i does not vary linearly with θ, except, perhaps, for quite small values of θ (cf. Fig. 14). Andrews [1] has since redetermined the dependence of the rate of evaporation on θ from the observed deactivation of a pure tungsten wire covered with thorium by volatilization from a neighbouring thoriated tungsten wire or from a heated rod of metallic thorium. The necessity for making allowance for diffusion and possible induced evaporation was thus avoided.

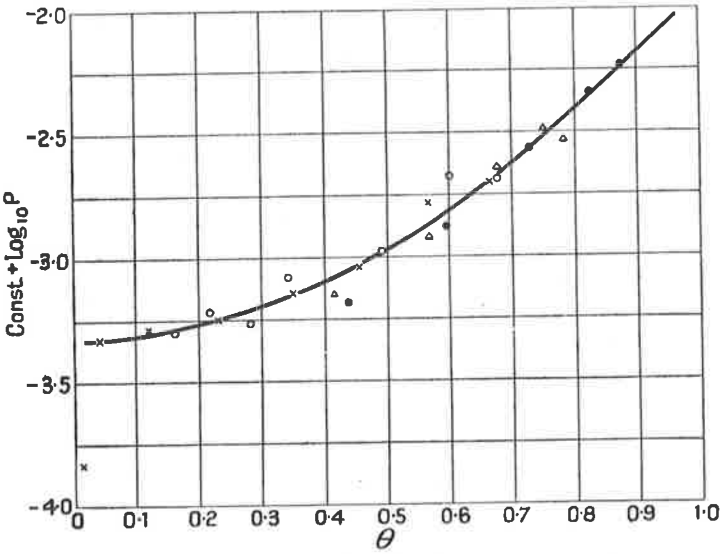

FIG. 16.—Increase with θ of the probability that any given adsorbed atom will evaporate.

The faulty assumption that log i varies linearly with θ was, however, still made use of.

The true relationship between the rate of evaporation at one temperature (2200°K.) and θ has been determined by Brattain and Becker [6] from observations of the deactivation of a pure tungsten ribbon covered with thorium. A quantity of thorium was first deposited on one side of the ribbon and then caused, by a suitable temperature treatment, to migrate and spread itself uniformly over the whole surface. The ribbon was now raised for successive short intervals to 2200°K., and after each such interval the activity was measured at some low testing temperature. From the activity-time curve the θ-time relationship was then deduced, and from this, in turn, the dependence of the rate of evaporation at 2200°K. on θ. The relationship, thus arrived at, between the logarithm of the probability P that any given atom will evaporate in a given second and θ is shown in Fig. 16. It is seen that this probability is about thirteen times as great when θ is 0·9 as it is when θ is only 0·1.

It is clear that, apart from a constant scale factor, the temperature variation of evaporation found experimentally to correspond to any given state of activity cannot be affected by the nature of the relationship assumed to hold between i and θ, and at high temperatures it will not even be much affected by any assumption made with regard to induced evaporation. The variation deduced by Langmuir from his deactivation data is

$$i_a \propto \epsilon^{-\mathrm{T}_a/\mathrm{T}} \quad . \quad . \quad . \quad . \quad (2)$$

for all values of θ, where i_a denotes the rate of evaporation * and T_a is a constant whose value is 102,500 degrees. This corresponds to a latent heat of evaporation of 204,000 calories per gram-atom. Andrews' data are also representable by a formula of the type (2), in which, however, T_a has the somewhat smaller value of 89,000 degrees for all values of θ. Both these values of T_a are roughly twice as great as that of $\mathrm{T}_{\mathrm{D}'}$, showing that evaporation varies much more violently with temperature than does diffusion.

Thermionic Properties.—In a hypothetical case of adsorbed particles where the effect of any one adsorbed particle in lowering the work function is independent of the presence or absence in its immediate neighbourhood of any other, we must have

$$\chi_0 - \chi = \theta(\chi_0 - \chi_1), \quad . \quad . \quad . \quad (3)$$

where χ is the actual work function, and χ_0 and χ_1 are the work functions corresponding to the states $\theta=0$ and $\theta=1$ respectively. If furthermore, either any variation of A with χ is unimportant

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* This rather unusual symbol is used for the atomic evaporation rate in order to conform to those used for the rates of evaporation of positive ions and electrons, viz. i_p (to be introduced in Chapter VI) and i respectively.

or else log A varies linearly with χ, it is a simple matter to derive from (3) the equation

$$\log i - \log i_0 = \theta(\log i_1 - \log i_0), \quad . \quad (4)$$

where i, i_0 and i_1 are the corresponding emissions at the test temperature, i.e. log i is a linear function of θ. This is what Langmuir assumed for the case of thoriated tungsten. We now know, of course (cf. Fig. 14), that eqn. (4) is not true for this case, and therefore one, at least, of the assumptions on which it is based must be false.

In the foregoing, we have disregarded the variation of i with applied field E. It has been found by Becker and Mueller,[5] and by Reynolds,[50] that while for high values of the applied field the i–E relationship is simply that required by Schottky's image theory, for low values of E it is something quite different. This is shown, for example, by the curve of Fig. 17, which is an experimental plot of log i against $\sqrt{E}$ obtained by Becker and Mueller with a partially activated thoriated tungsten filament at 1380°K. The dashed line represents the theoretical Schottky relationship. It is seen that in this case below about 20,000 volts per cm. the emission falls with applied field more steeply than it would if the Schottky law were obeyed. Similar results have been obtained by Reynolds with both partially

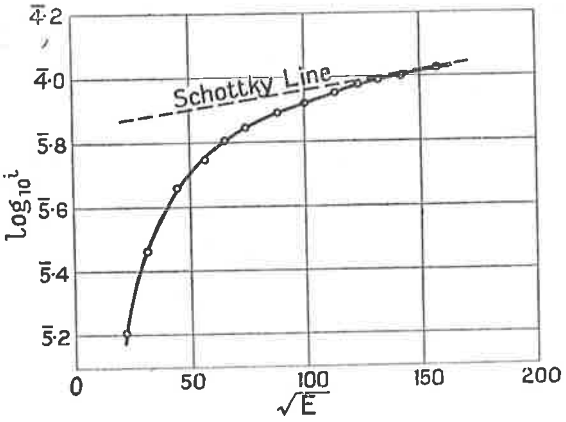

FIG. 17.—Showing departure from the Schottky law of the emission at moderate fields from partially activated thoriated tungsten.

and completely activated surfaces. The point of departure from the Schottky line was found to vary somewhat from run to run, the variation being attributable to the sputtering effect of positive-ion bombardment. Under the best vacuum conditions, however, the critical field was roughly constant at about 10,000 volts per cm. for all temperatures and degrees of activation. On the other hand, the *shape* of the $(\log i)$-$\sqrt{E}$ curve, where it departed from the Schottky line, was not found to be independent of the degree of activation. With decreasing θ the curve was observed to fall away from the Schottky line more and more steeply until θ became quite small and the emission approached that of clean tungsten.

It is thus evident that the shape of the $(\log i)$-θ curve must depend to some extent on the strength of the field applied to the cathode. The points through which the curve of Fig. 14 is drawn were obtained by Brattain and Becker with the anode held at a constant potential of 100 volts positive to the ribbon. The electrode geometry was not such as to make the field uniform over the surface of the ribbon, but its order of magnitude corresponding to this anode potential was 100 volts per cm. This is quite small, and corresponds to a point further to the left on the $(\log i)$-$\sqrt{E}$ curve than is shown in Fig. 17. The field was, in fact, so near to being effectively zero that a reduction in anode potential from 100 to 10 volts was found to cause i to fall by only 15 per cent. when θ was either 0 (clean tungsten) or 2·0, and by only 25 per cent. when θ was 0·7. Thus it appears that for zero applied field (the condition assumed in the thermodynamical theory of emission) the shape of the $(\log i)$-θ curve would be barely perceptibly different from that of Fig. 14. The work of Reynolds shows that for strong applied fields, however, the parts of the curve for fractional values of θ would be displaced upwards relatively more than those for $\theta = 0$ and $\theta = 1$.

The nature of the variation of A with χ as θ changes from 0 to 1 has been investigated by Kingdon,[25] by Dushman and Ewald,[16] and by Brattain and Becker.[6] Unfortunately the accuracy of such determinations when carried out with ordinary thoriated tungsten wires is not very high, since for fractional θ the range of temperatures which are sufficiently high for the emission to be measurable, and yet not so high that the state of the surface changes at an appreciable rate owing to diffusion, is rather limited, more particularly for small θ. Thus only relatively short Richardson lines can be obtained.

In Fig. 18 are plotted values of log A against those of χ obtained by Kingdon and by Dushman and Ewald. The points near the right-hand side of the figure, corresponding to small values of θ, are much less reliable than those further to the left. While Kingdon measured his emissions with a constant voltage applied to the anode, Dushman and Ewald extrapolated theirs to zero field, assuming the Schottky law to hold right down to the lowest fields. This, we now know, it does not do. Owing, however, to the relative slightness of the Schottky correction the results of Dushman and Ewald are probably not so very different from what they would have been if the measurements had been made at a constant, moderately high field, and are thus nearly comparable with Kingdon's.

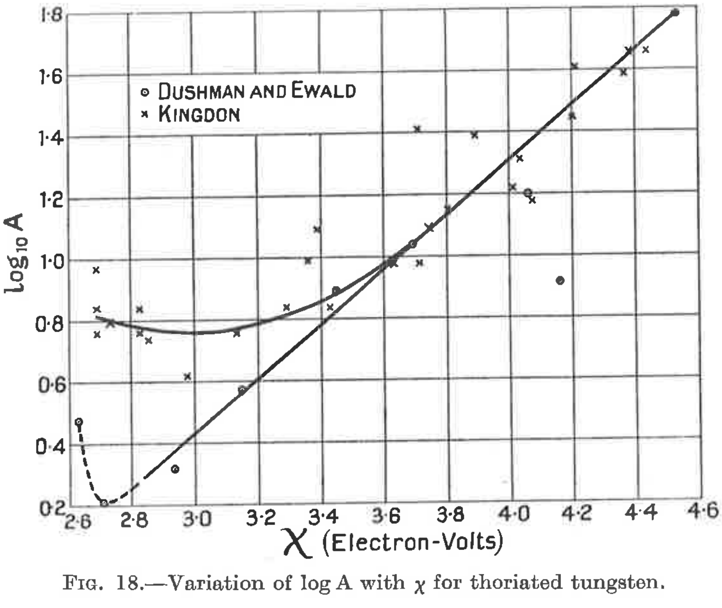

FIG. 18.—Variation of log A with χ for thoriated tungsten.

The spread of the points is such that any quantitative law deduced from them is subject to considerable uncertainty. They appear to indicate, however, that while for relatively small values of θ log A possibly varies linearly with χ, as θ increases the values of log A tend to become, if anything, higher than those corresponding to the linear law. If this conclusion is correct, the shape of the (log i)-θ curve cannot be explained by the departure from linearity of the (log A)-χ relationship, for this is in the wrong direction. It can then only be accounted for by supposing that the assumption underlying eqn. (3) is incorrect and that thorium atoms added to the surface lower the work function less when θ is large than when it is small.

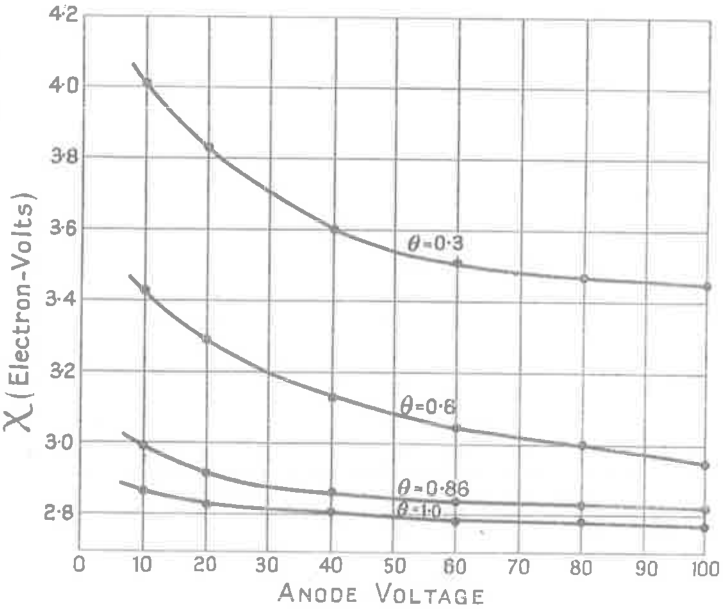

Fig. 19.—Dependence of χ on the applied field for thoriated tungsten at various stages of activation.

The dependence of χ and A on E for different values of θ has been determined by Brattain and Becker, and their results are shown in Figs. 19 and 20. It is seen that for all values of E, χ changes less and less rapidly with θ as θ increases. It is noteworthy that when θ is equal to 1, χ changes but little with applied field and A practically not at all.

According to Dushman and Ewald, the thermionic constants of fully activated thoriated tungsten are

$$A = 3\cdot0 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 2\cdot63 \text{ e.v.}$$

These figures, like those for values of θ less than 1, were arrived at by extrapolating the $(\log i)$-$\sqrt{E}$ lines obtained at high fields backwards, as if the Schottky linear law continued to hold for low fields, and taking the zero-field values of the currents so obtained for the calculation of the constants. In spite of the faultiness of this procedure, however, the results agree well with those obtained recently by Nottingham[49] for quite small E. With a constant accelerating potential of only 6 volts applied to the anode, which was just sufficient to comfortably avoid space-charge limitation of the thermionic currents, he obtained values of χ ranging from 2·38 to 2·83 e.v., while the corresponding values of A ranged from 0·56 to 10·2 amp./cm.^{2}deg.^{2} One of the best determinations gave

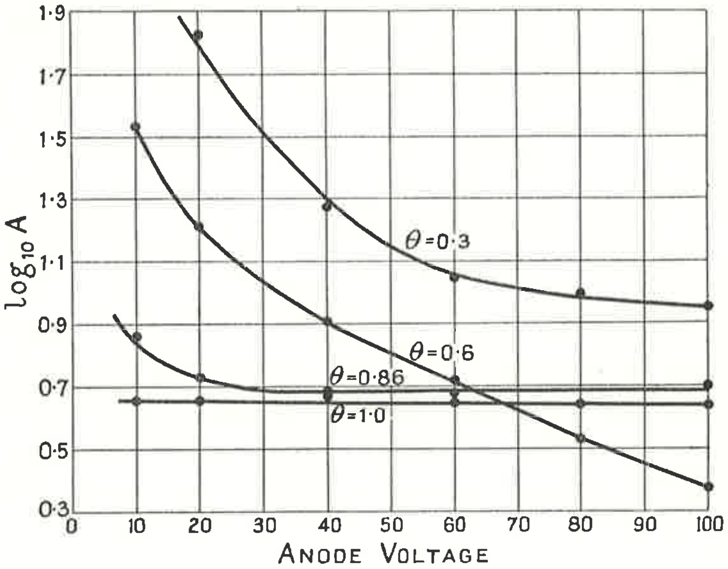

FIG. 20.—Dependence of log A on the applied field for thoriated tungsten at various stages of activation.

$$A = 3{\cdot}2 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 2{\cdot}64 \text{ e.v.}$$

The values extrapolated to zero field from the curves of Brattain and Becker for $\theta = 1$ are

$$A = 4{\cdot}5 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 2{\cdot}9 \text{ e.v.}$$

No great absolute accuracy was claimed for their data however.

We saw in Chapter I (p. 36) that the difference between the work functions, χ_1 and χ_2, of two emitters, 1 and 2, is related to their contact difference of potential, $V_1 - V_2$, at the temperature T by the equation

$$\chi_2 - \chi_1 = e(V_1 - V_2) + kT \log_e \frac{A_{02}}{A_{01}}, \quad . \quad . \quad (5)$$

where A_{01} and A_{02} are the two values of the constant A_0. Thus on the assumption that in the case of a thoriated tungsten filament the value of A_0 is independent of its condition, it is possible to find the change in work function accompanying any given change in the degree of activation by simply measuring the corresponding change in the contact difference of potential between it and some standard electrode.

Such a measurement has been carried out by Langmuir and Kingdon [38] with a thoriated tungsten filament first fully activated, then deactivated by high-temperature flashing. The standard electrode was a similar, fully activated filament separated by a short distance from the test filament. The standard filament was heated to an emitting temperature, and, with the test filament serving as anode, current-voltage characteristics observed with the test filament in each of the two conditions. The two characteristics differed from one another only in that one had a constant voltage displacement with respect to the other, and this was of course equal to the contact difference of potential between the fully activated test filament and the same filament after deactivation.

The contact difference of potential between the fully activated and the deactivated filament found in this way was 1·46 volts. The work function of clean tungsten is, as we have seen, 4·54 e.v. Thus on the assumption that the surface of the thoriated filament after deactivation was clean, we should obtain for the work function of fully activated thoriated tungsten the value 4·54 − 1·46 = 3·08 e.v. This does not agree at all well with the value of this quantity found directly from thermionic measurements, the discrepancy being well outside the possible experimental error. We do not have to look far for an explanation, however. It is that the surface of the filament after deactivation was almost certainly not clean, for it will be remembered that according to Reynolds and also Brattain and Becker it is practically impossible to obtain a completely deactivated condition of the surface by high-temperature flashing owing to the diffusion of fresh thorium to the surface of the filament while it is cooling. The exact amount of reactivation that occurs during cooling will of course depend on the diffusion characteristics of the filament and on its diameter. In the nearest approach to complete deactivation obtained by Brattain and Becker with a filament of 0·1 mm. diameter, θ was about 0·1, and to this, according to a table published by them, corresponds a work function of about 4·1 e.v. The test filament used by Langmuir and Kingdon was also

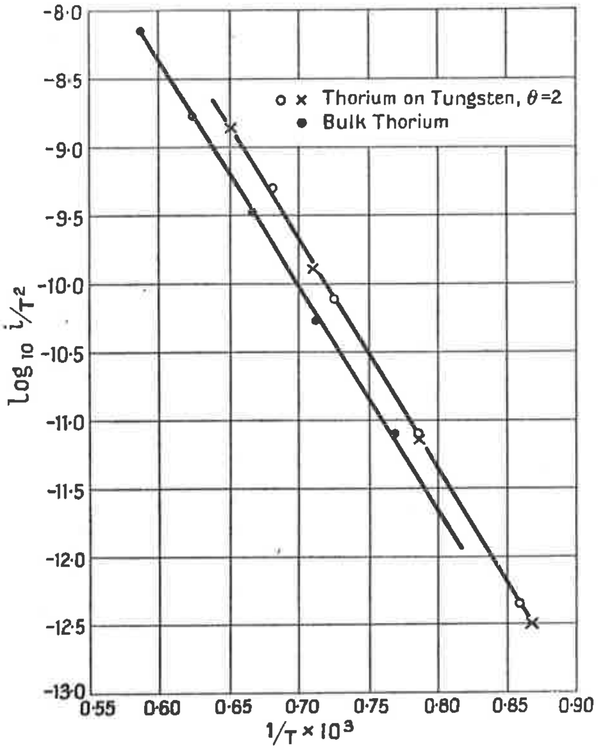

FIG. 21.—Richardson lines for tungsten covered with a double atomic layer of thorium and for thorium in bulk.

0·1 mm. in diameter, and if we assume that their minimum θ was roughly the same as that of Brattain and Becker and subtract 1·46 from about 4·1, instead of from 4·54 e.v., we obtain something like 2·6 or 2·7 e.v. for the work function of fully activated thoriated tungsten, and this agrees very satisfactorily with the values found thermionically.

We have seen that while the activity of a thorium-on-tungsten emitter increases with θ until θ is equal to 1, beyond this point it falls away again and finally approaches a steady value when θ is in the neighbourhood of 2. In Fig. 21 is shown a Richardson line for the condition $\theta = 2$ obtained by Brattain and Becker, together with the line for thorium in bulk obtained by Zwikker. Comparing them, we see that the thermionic properties of tungsten covered with a double layer of thorium are already so near those of thorium in bulk that the emission from the former is within a factor of only about 2 of that from the latter over the whole range of temperatures.

The Effects of Gases.—Thorium on tungsten, in common with other active composite emitters, is easily deactivated or "poisoned" by traces of electronegative gases such as oxygen,[30] and it is necessary to obtain the highest possible vacua if such poisoning is to be avoided.

On the other hand, Kingdon has reported a considerable enhancement of the emission from a fully activated filament due to exposure to nitrogen. At 1455°K. the emission was increased by a factor of 5. The nitrogen used was taken from a commercial tank and was not purified before reaching the experimental tube except by being passed through a vessel cooled by liquid air. It is therefore possible that the effect may have been due, not to the nitrogen itself but to some non-condensible impurity. After the gas had all been pumped out the emission slowly decreased again. At 1455°K. it took several minutes to fall to somewhere near the value characteristic of a thoriated surface.

An enhancement of the emission from a fully activated thoriated tungsten filament due to some unknown residual gas has also been observed by Nottingham.[49] At 1230°K. the emission was increased in this way by a factor of from 2 to 6.

An interesting effect which occurs when an oxygen-poisoned filament is exposed to methane has been reported by Langmuir.[30]

The methane momentarily causes the full thorium-on-tungsten emission to be restored, but it then falls away again. The explanation given by Langmuir is that the methane at first removes the oxygen adsorbed on top of the thorium film by chemical action, but that excess methane is then decomposed by the hot filament and the thorium becomes covered with carbon, and so the emission is again destroyed.

Not only may a film of thorium on tungsten be contaminated by chemically active gases, but it may also be removed by the sputtering action of ions derived from a chemically inactive gas or vapour. Thus Kingdon and Langmuir [26] have found that ions of argon, cæsium, mercury and neon all begin to sputter off thorium at about 50 e.v. energy. Helium ions also have an effect, which is, however, much smaller, owing, presumably, to the relative smallness of their mass. No effect was observed with hydrogen ions, even when their energies were as high as 600 e.v.

Other Emitters Similar to W-Th.—The emission, diffusion and evaporation phenomena exhibited by filaments of thoriated molybdenum have been investigated by Reynolds and Dushman.[14] Qualitatively the phenomena are similar to those characteristic of thoriated tungsten, but there are important quantitative differences. Thus on the assumption that the number of thorium atoms in a single complete surface layer is half as great as the number of molybdenum atoms, the rate of evaporation i_{a1} from a complete monatomic film at 2000°K. was computed to be $5{\cdot}4 \times 10^{12}$ atoms/cm.^{2}sec., as compared with only $1{\cdot}53 \times 10^9$ in the case of thorium on tungsten at the same temperature. Diffusion of thorium from the interior to the surface also occurs at a much greater rate in molybdenum than in tungsten, the value of D at 2000°K. having been found to be $1{\cdot}02 \times 10^{-6}$ cm.^{2} sec.$^{-1}$, while the corresponding value for thoriated tungsten obtained by Langmuir was only $5{\cdot}9 \times 10^{-11}$. Of course we now know that the grain structure of the wire is all-important in determining the rate of diffusion, and so these figures must not be accepted as applying to more than the particular specimens used. Since, however, the specimens were probably not very dissimilar as regards grain structure, the data given probably have a rough comparative value, and show that the rate of diffusion in molybdenum is in general very much higher than in tungsten at the same temperature. On account of the extremely large values of both D and i_{a1}, thoriated molybdenum must, of course, be worked at a much lower temperature than thoriated tungsten. Dushman [14] reports that θ decreases rapidly below unity for values of T greater than 1700°K.

The thermionic constants given by Reynolds and Dushman for a complete single layer of thorium on molybdenum are not very different from those of thorium on tungsten. They are

$$A = 1{\cdot}5 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 2{\cdot}58 \text{ e.v.}$$

These figures were presumably arrived at, like those for W-Th, by extrapolating emissions to zero applied field on the assumption of the validity of Schottky's law at low field strengths. This law probably applies no better in the case of Mo-Th than it does in that of W-Th. We have seen, however, that in the latter case it so happens that the values of the constants arrived at by this faulty procedure actually agree quite well with those obtained with very weak applied fields, and we should, by analogy, expect the same thing to be true in the case of Mo-Th. According to Dushman, the emission per watt obtained from thorium on molybdenum—this metal has a lower radiant emissivity than tungsten—is approximately the same as that from thorium on tungsten.

TABLE XV.

THERMIONIC, DIFFUSION AND EVAPORATION DATA FOR VARIOUS EMITTERS OF THORIUM-ON-TUNGSTEN TYPE.

Emitter.	A (amps./cm.^{2}deg.^{2}).	χ(e.v.).	$T_{D'}$(degs.).	D × 10^{11}(cm.^{2} sec.$^{-1}$).	i_{a1} × 10^{-9} (atoms cm^{-2} sec.$^{-1}$).
W-La .	8·0	2·71	—	—	—
W-Ce .	8·0	2·71	42,000	95	1450
W-Yt .	7·0	2·70	31,000	1820	—
W-Zr .	5·0	3·14	39,000	324	68
W-U .	3·2	2·84	50,000	1·3	> Th
W-Th .	3·0	2·63	47,000	5·9	1·53
Mo-Th .	1·5	2·58	26,000	102,000	5400

Dushman, Dennison and Reynolds [15] have also investigated the properties of tungsten filaments containing oxides other than that of thorium as an impurity. The values of the thermionic constants of $T_{D'}$, and of D and i_{a1} at 2000°K. found by them are given in Table XV. For comparison the corresponding data for thoriated tungsten obtained by Langmuir and those for thoriated molybdenum obtained by Reynolds and Dushman are also given. The thermionic data are in each case those for one complete atomic layer of the impurity metal on the tungsten or molybdenum.

SECTION II.

CÆSIUM ON TUNGSTEN AND ON OXYGENATED TUNGSTEN.

In 1923 it was observed by Kingdon and Langmuir [27] that in the presence of cæsium vapour tungsten will give an appreciable electron emission at temperatures far below a visible red. This emission has a maximum value at a certain temperature which depends on the cæsium vapour pressure. Thus when the cæsium vapour is saturated at 30°C. the maximum emission occurs at a filament temperature of 690°K. and has a value of about $8{\cdot}8 \times 10^{-5}$ amp./cm.[2, 28] There can be no doubt that the effect is due to contamination of the surface of the tungsten by cæsium. Beyond the optimum temperature cæsium distils off and the emission decreases until, at sufficiently high temperatures, it is practically that characteristic of clean tungsten.

At a temperature something like 100°–150° beyond the optimum for electron emission, positive ions begin to be given off from the filament. The infra-saturation positive-ion current varies with the potential difference between the filament and the collector according to the $\frac{3}{2}$-power law and the ratio of charge to mass deduced from the variation is that of singly charged cæsium ions.[39] At first the positive emission increases very rapidly with the filament temperature, but soon reaches a limit, and beyond the temperature where this occurs it remains absolutely constant. There is good reason to believe that for filament temperatures in the constant positive emission range, every cæsium particle that impinges on the filament becomes ionized, giving up an electron to the filament. From a study of the positive emission characteristics valuable information may be gained regarding the adsorption of cæsium on the filament surface. We shall consider the positive emission only very briefly in this section, reserving the fuller treatment for Chapter VI.

Qualitatively similar electron and positive-ion emission phenomena may be observed with filaments which, prior to exposure to cæsium vapour, have been treated with oxygen (" oxygenated ") in a certain manner which will be described later. Much higher electron emissions are obtainable from oxygenated than from non-oxygenated filaments exposed to cæsium. For example, in cæsium vapour saturated at 30°C. oxygenated tungsten gives a maximum emission as high as 0·35 amp./cm.^{2}. This occurs at a filament temperature of 1000°K.[28]

Similar phenomena are also exhibited in cases where certain other metals, e.g. molybdenum or tantalum, take the place of tungsten, and where rubidium, potassium or sodium are used instead of cæsium.

Electron Emission from Cæsium on Tungsten.—The variation, observed by Becker,[3] of the logarithm of the emission from a tungsten filament with the reciprocal of its temperature when exposed to cæsium vapour at a constant small pressure is shown by the curve marked " Cs on W " in Fig. 22. The line marked " Clean W " is the corresponding plot obtained in the absence of cæsium vapour. It is seen that at high temperatures the curve for Cs on W approaches the clean tungsten line. This is what we should expect, for at sufficiently high temperatures the equilibrium amount of cæsium adsorbed on the tungsten must be very small. As the temperature is lowered beyond a certain point, however, the emission begins to rise in spite of the fall in temperature. This can only be attributed to an increasing degree of contamination of the tungsten with adsorbed cæsium. This continues until at a certain quite low temperature the emission becomes a maximum, after which, with a further decrease in filament temperature, the emission falls sharply away again.

It is evident that when the emission is a maximum, the rate of increase of emission due to increasing thermionic activity as we proceed from the left to the right of the diagram is just balanced by the rate of decrease of emission due to the falling temperature. Thus the maximum thermionic activity must occur at a somewhat lower temperature than the maximum emission.

If the temperature is suddenly changed from a high value to a low or *vice versa*, interesting time changes occur, from which, as Becker has shown, it is possible to deduce just at what point the thermionic activity is a maximum. Thus on suddenly changing the temperature from its value at D to that at A, the emission, at first immeasurably small, is observed to grow to a maximum value indicated by the point A′ and then to fall to its equilibrium value at A. If now the temperature is suddenly increased again to its value at C, the emission quickly rises to a maximum at C′, then falls to its steady value at C. Thus both A′ and C′ must be points on the (log i)-1/T line corresponding to the maximum activity. This line touches the equilibrium line for Cs on W at B. We therefore infer that at this point on the curve the activity is a maximum. If the corresponding value of θ is θ_{opt}, then to the left of B θ must be less than θ_{opt}, while to the right of B it must be greater than θ_{opt}. Incidentally, the value of χ corresponding to the maximum activity indicated by the slope of the line A′C′ is about 1·54 e.v.

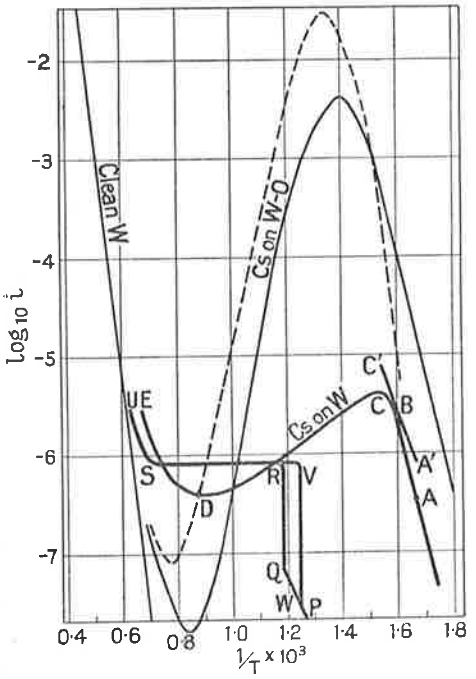

FIG. 22.—Emission-temperature characteristics obtained by Becker for plain and oxygenated tungsten in cæsium vapour.

Emission-temperature characteristics for a tungsten filament exposed to cæsium vapour saturated at a number of different temperatures, ranging from 0° to 80°C., have been determined by Langmuir and Kingdon.[59] These are shown

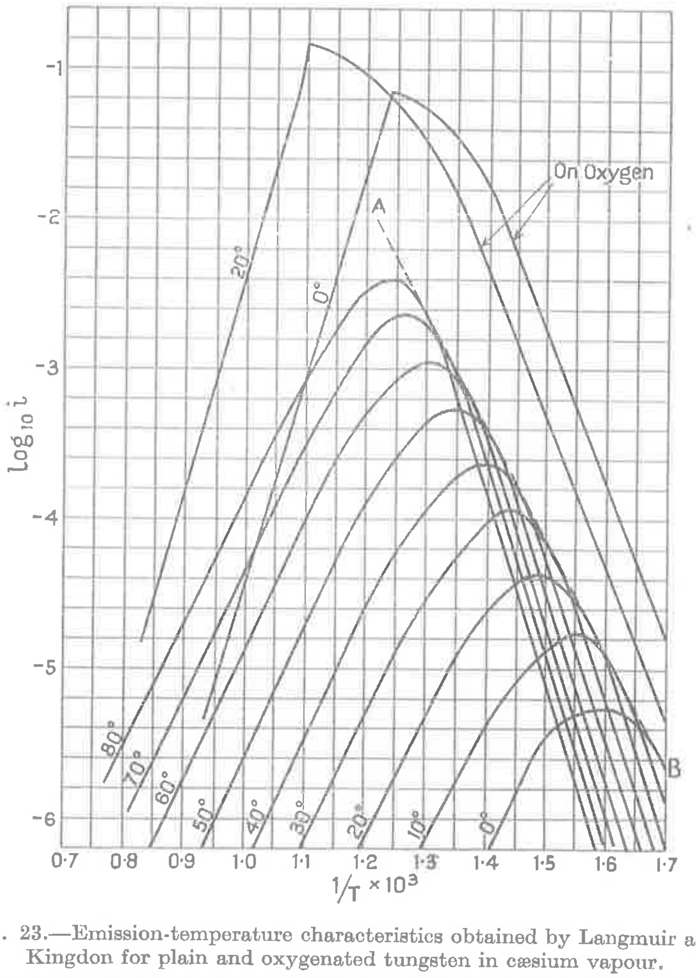

FIG. 23.—Emission-temperature characteristics obtained by Langmuir and Kingdon for plain and oxygenated tungsten in cæsium vapour.

in Fig. 23. The envelope of this family of curves is the straight line AB. Clearly, this must be the ($\log i$)-$1/T$ line for the state of maximum activity of the filament, corresponding, therefore, to the line A′C′ of Fig. 22. The values of the thermionic constants A and χ for the most active state derived from this line are

$$A = 3{\cdot}2 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 1{\cdot}36 \text{ e.v.}$$

This value of χ is nearly 0·2 e.v. less than that obtained from the line A′C′ in Fig. 22. It is not difficult to find a plausible reason for the discrepancy, however. The point A′ was obtained while condensation preponderated over evaporation, whereas the reverse was the case when the point C′ was obtained. Now evaporation must occur most rapidly from those parts where the concentration of adsorbed cæsium is greatest. On the other hand, the points of arrival of condensing particles are distributed entirely at random. Consequently the point A′ corresponds to a less uniform distribution of cæsium on the surface than does C′. As we shall presently see, there is good reason for believing that the less uniformly a given quantity (up to something beyond a single complete layer of atoms) of an electropositive contamination is distributed the less will be the thermionic activity of the emitter. Hence A′ must be too low relative to C′ and the slope of the line A′C′ must be too high.

The effect of the distribution of the adsorbed particles on the emission depends on the variation with θ of the mean contribution of each to the lowering of the work function. We have seen (p. 128) that experimental evidence in the case of thoriated tungsten leads to the conclusion that thorium atoms added to the surface lower the work function less when θ is large than when θ is small. It would be strange indeed if the same kind of thing were not true in the case of cæsium also. Now to see qualitatively what the effect of non-uniformity of distribution must be, we have only to consider the extreme case where the cæsium particles crowd themselves into little patches, leaving other patches free. In the patches occupied by the cæsium the concentration is higher than it would be if the cæsium were distributed uniformly over the surface, and so the contribution of each particle to the lowering of the work function * is less. Since the emission depends

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* The surface will still have only *one* work function, not two, in spite of the patches, if only the patches are small in comparison with the distance at which the applied field just neutralizes the image field. We may then

primarily upon the work function, we shall expect it to be less when the distribution of the adsorbed particles is non-uniform than when it is uniform.

It may be questioned whether the (log i)-θ curve obtained during the condensation of thorium atoms on one face of a tungsten strip, considered in the preceding section, might not have been affected to some extent by the random distribution of the points of arrival of the thorium atoms. While there might have been some effect of this nature, it was probably nothing like as important as in the case under discussion of cæsium condensing on tungsten, since the condensation of thorium was relatively very slow, and considerable readjustment of the distribution by surface migration would have had time to take place.

It will at once be evident that even the experimental maximum-activity points on the envelope of the equilibrium curves of Fig. 23 cannot be quite those for the optimum θ and a distribution of cæsium on the surface determined by the temperature alone. It is even possible that the departure from this ideal condition corresponding to points on the envelope may have varied slightly with the temperature. Thus the line AB in Fig. 23 can be no more than an approximation to the true (log i)-1/T line for an optimum adsorbed film of cæsium having a distribution determined solely by the temperature. It must, however, be a much closer approximation than A′C′ in Fig. 22. Indeed, in view of the smallness of the discrepancy between the χ-values derived from the two lines, it would be surprising if the χ and A determined from the line AB were as much in error as $\frac{1}{10}$ e.v. and a factor of 3 respectively.

The values of the thermionic constants determined from the line AB are, strictly speaking, valid only for the particular accelerating field applied to the surface of the filament in making the observations. Probably, however, as in the case of W-Th, these values do not differ greatly from those for zero field.

Measurements of the contact difference of potential between

(see Section IV of this chapter), as in the case of uniform distribution, think of all the charges at and near the surface of the emitter as smeared out into uniform sheets of charge parallel to the surface.

clean tungsten and tungsten covered with cæsium have been made by Langmuir and Kingdon.[38] The value found was 2·8 volts. On the assumption that A_0 had the same value for the contaminated as for the clean filaments, this means that the work function of the cæsium-covered filament must have been $4{\cdot}54 - 2{\cdot}8 = 1{\cdot}7_4$ e.v. This is much greater than the value of χ found from the slope of the line AB in Fig. 23. The two results are not really comparable, however, since the contaminated surface was prepared by simply letting cæsium condense on the clean, cold filament. In this way the filament must have become covered with more than a single layer of cæsium atoms and so its properties probably became those of bulk cæsium. Indeed, the χ found from the contact difference of potential agrees with that for bulk cæsium determined thermionically by Kingdon (see Chapter II) within less than 0·1 e.v.

Oxygenated Tungsten.—A process for oxygenating tungsten prior to exposure to cæsium vapour has been described by Kingdon.[25] After having been cleaned by flashing for a short time in a vacuum at 2700°K., the filament is exposed for a few seconds to oxygen at a pressure of about 0·02 mm., either cold or (preferably) heated to about 1900°K. The excess oxygen is then pumped out, with the filament cold. If cæsium vapour is now allowed to come into contact with the filament, only very small emissions are obtained. If, however, the filament is heated for a few seconds at from 1200° to 1600°K. and is then cooled to lower temperatures, very much higher emissions are obtained in cæsium vapour, e.g. about 0·35 amp./cm.^{2} with the filament at 1000°K. and the cæsium vapour saturated at 30°C. Kingdon supposes that the heating at from 1200° to 1600°K. probably frees the surface of the filament of excess oxygen and of adsorbed deleterious gases such as CO. The remaining oxygen is probably held to the filament as a monatomic adsorbed film.

Below about 1500°K. the electron emission from oxygenated tungsten is too small to be measurable. If the filament is heated to much above this temperature, however, the rate of evaporation from it becomes appreciable, so that it is impossible to determine how the emission varies with the temperature before the quantity of oxygen on the filament has changed.

Kingdon has, nevertheless, attempted to obtain a Richardson line for oxygenated tungsten by supplying oxygen to the experimental tube at a steady rate and allowing it to be consumed by the filament while the measurements were being made. In this way he obtained a Richardson plot which was a straight line, and from this he deduced for the thermionic constants of oxygenated tungsten the values

$$A = 5 \times 10^{11} \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 9{\cdot}2 \text{ e.v.}$$

It is, however, open to serious doubt whether the equilibrium amount of oxygen adsorbed on the filament remained constant over the whole temperature range employed for the observations. The value of A found is enormously greater than would be deemed possible according to present-day thermionic theory. Also the high value of χ cannot be reconciled with the value subsequently found by Langmuir and Kingdon [38] for the contact difference of potential between clean and oxygenated tungsten, which was a mere 0·8 volt. It might, perhaps, be objected that the oxygenation was not carried out in quite the same manner in the experiment of Langmuir and Kingdon as described above, the oxygen merely having been allowed to come into contact with the cleaned, cold filament. It does not appear likely, however, that this would have affected the order of magnitude of the result obtained.

Oxygen is not lost from oxygenated tungsten at an appreciable rate at temperatures below about 1550°K., even in the presence of cæsium vapour.[3] The adsorbed oxygen is apparently chemically quite indifferent to the cæsium, although, under ordinary circumstances, these two elements would combine with avidity.

Electron Emission from Cæsium on Oxygenated Tungsten.—An early attempt to determine the thermionic constants of cæsium on oxygenated tungsten was made by Kingdon.[25] After an oxygenated filament had been brought to a state of maximum activity in cæsium vapour, the bulb was cooled to liquid air temperature in order to prevent any more cæsium from condensing on the filament. It was then found that the rate of evaporation of cæsium from the filament up to temperatures of about 700°K. was so small that the activity did not change appreciably while data for a Richardson plot were being obtained. Unfortunately, however, the points representing these data lie on a slightly curved, rather than on a perfectly straight Richardson line, and numerical values of the thermionic constants derived from them cannot therefore be accepted without a certain amount of reserve. The values of the constants derived by Kingdon from the straight line that seemed best to represent the points were

$$A = 0{\cdot}003 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 0{\cdot}72 \text{ e.v.}$$

The equilibrium curves of log i plotted against $1/T$ for oxygenated tungsten in cæsium vapour at various pressures are of the same general shape as those for non-oxygenated tungsten. It would appear, then, that the common tangent to these curves should be the $(\log i)$-$1/T$ line for cæsium on oxygenated tungsten in or very near its state of maximum activity, and that, as in the case of Cs on W, one should be able to find the corresponding thermionic constants from this tangent. Two equilibrium curves for Cs on W-O, obtained by Langmuir and Kingdon, are shown in Fig. 23, and two obtained by Becker are shown in Fig. 22. It will at once be noticed that while the common tangent to the curves of Langmuir and Kingdon for Cs on W-O have a much lesser slope than that to the curves for Cs on W, indicating a correspondingly smaller work function, the reverse is the case with Becker's curves. The thermionic constants for Cs on W-O in its most active state derived from the curves of Langmuir and Kingdon are

$$A = 1{\cdot}5 \times 10^{-4} \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 0{\cdot}50 \text{ e.v.},$$

while those derived from Becker's curves are

$$A = 2{\cdot}7 \times 10^{8} \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 2{\cdot}24 \text{ e.v.}$$

These results are wildly at variance, not only with one another, but with those obtained by Kingdon using his method. The first value of χ is almost certainly too low, while the second is much too high. Also both values of A are most improbable. It is difficult to assign reasons for the want of agreement between the various determinations. Becker's curves were obtained at much lower vapour pressures than those of Langmuir and Kingdon.

If an oxygenated tungsten filament, initially free, or nearly free, of adsorbed cæsium, is exposed at a fairly low temperature to cæsium vapour at a constant pressure, interesting time changes of the emission from it may be observed. A series of curves obtained by Becker, showing the variation of log i with time of exposure for a number of different filament temperatures is reproduced in Fig. 24. Positive ions were first drawn with the filament at 1040°K. to rid it of practically the whole of its adsorbed cæsium. The temperature was then suddenly dropped and at the same time the plate voltage made positive with respect to the filament so as to draw electrons, after which the emission was observed as a function of time.

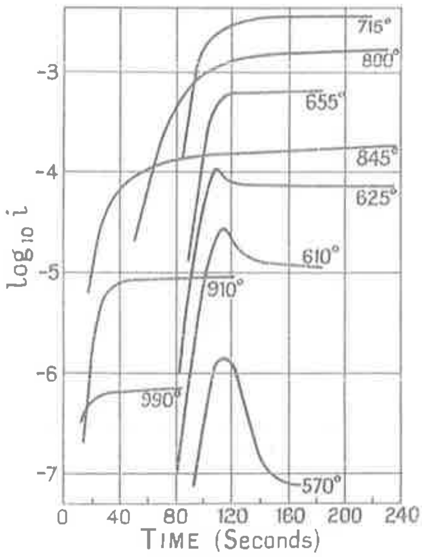

FIG. 24.

It will be observed that at the three lowest temperatures the emission first rose to a maximum and then fell away again, approaching asymptotically a final value. The final values attained at the various temperatures correspond, of course, to points on one of the equilibrium curves for Cs on W-O in Fig. 22. It will further be observed that all three maxima occurred after very nearly the same time t_m of exposure at the reduced temperature to the cæsium vapour. The most natural inference to draw from this is that up to the time t_m there was no important amount of re-evaporation of condensed cæsium from the filament and that at t_m θ had its optimum value for electron emission. We should therefore expect the three maxima to give three points on the Richardson line for W-O-Cs. Actually the three [log (i/T^2)]-1/T points corresponding to the maxima are not quite, though nearly collinear. From the straight line that oes most nearly through them we obtain the values of the hermionic constants

$$A = 2{\cdot}5 \times 10^7 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 2{\cdot}1 \text{ e.v.}$$

Although these values are in tolerable agreement with those derived from Becker's two equilibrium curves for Cs on W-O, they are both almost certainly much too high. The only reasonable explanation would appear to be that although at the time t_m approximately the optimum total amount of cæsium for electron emission may have been adsorbed on the filament at each of the three temperatures, the surface was nevertheless not in the same condition in each case. The respect in which the condition at the maximum differed in the three cases must have been the distribution of cæsium atoms on the surface. The higher the temperature and the more rapid, therefore, the surface migration, the more nearly uniform must the distribution of the atoms deposited at random on the surface become in a given time. The effect of this must be to make the Richardson line plotted from the maxima too steep and the values of both the A and χ derived from it too high.

Curves similar to those of Fig. 24 were also obtained by Becker when he exposed initially clean (non-oxygenated) tungsten to cæsium vapour. He found, however, that for a given cæsium vapour pressure t_m was always about 10 per cent. greater in the case of oxygenated than in that of plain tungsten. From this he inferred that the number of atoms per unit area in an optimum film of cæsium on oxygenated tungsten must be about 10 per cent. greater than the corresponding number on plain tungsten. He assumed this number to be the maximum that can be accommodated in a single layer in both cases. We shall see later, however, that there is a certain amount of evidence against this assumption.

The Generation of Positive Ions.—We have seen that when a plain or oxygenated tungsten filament is heated sufficiently strongly in cæsium vapour, a current of Cs^+ ions may be drawn from it whose saturation value is independent of the temperature.

Langmuir and Kingdon [27, 40, 41] have found that not only tungsten and oxygenated tungsten, but also molybdenum, tantalum, nickel and carbon filaments ionize cæsium when burnt at sufficiently high temperatures. They have found, moreover, that in cæsium vapour at a given pressure the positive-ion emission from all these filaments is the same. From this they have drawn what would appear to be the only reasonable conclusion, viz. that at high temperatures these filaments must ionize every cæsium atom that impinges on them. On the other hand, they have been unable to observe any appreciable ionization of cæsium by heated thorium or fully activated thoriated tungsten.

They have put forward a rough explanation of these observations in terms of "electron affinities." The electron affinity (work of ionization) of cæsium is 3·87 e.v. The electron affinities (work functions) of tungsten, molybdenum, tantalum, nickel and carbon are all greater than this, being 4·54, 4·15, 4·12, 5·01 and 4 e.v. respectively. On the other hand, the work functions of thorium and of fully activated thoriated tungsten are both less than the work of ionization of cæsium, being only 3·38 and 2·63 e.v. respectively. Thus it would appear that a surface will or will not ionize cæsium according as its electron affinity is greater or less than that of a cæsium atom.

A simple theoretical reasoning leads to the same conclusion. We may obtain a positive ion and an electron from a hot body either by extracting them separately as such or by first extracting a neutral atom and then ionizing it. In either case the same amount of work must be done. Hence if χ, χ_p and χ_a represent the reversible works of extraction of an electron, a positive cæsium ion and a neutral cæsium atom respectively, and U_i represents the energy required to ionize a cæsium atom, we must have

$$\chi + \chi_p = \chi_a + U_i,$$

or

$$\chi_a - \chi_p = \chi - U_i. \qquad (6)$$

This equation was first derived by Schottky [53] in 1920. It shows that according as χ is greater or less than U_i, more or less work has to be done to extract a neutral atom than to extract a positive ion. We should therefore naturally expect that in the former case adsorbed particles of cæsium would evaporate rather as ions than as atoms, while in the latter they would evaporate rather as atoms than as ions.

We shall consider a more rigorous theory in Chapter VI.

It will there be shown that there is really no sharp transition between a state of a surface that will ionize cæsium and one that will not, and that while it is true that most of the particles evaporate as ions when χ is greater than U_i and as atoms when χ is less than U_i, there must nevertheless be *some* evaporation of atoms when χ is slightly greater than U_i and some evaporation of ions when χ is slightly less than U_i.

Adsorption and Evaporation Characteristics.—We have seen that at a certain temperature of a tungsten filament exposed to cæsium vapour the θ for the cæsium adsorbed on it has an optimum value (θ_{opt}) for electron emission. At higher temperatures θ is, of course, less than θ_{opt}, and at lower temperatures it is greater.

An interesting method for determining relative values of the equilibrium θ at higher temperatures has been devised by Becker.[3] From the fact that the slopes of the lines A′C′ in Fig. 22 and AB in Fig. 23 are approximately the same, it is probably safe to infer that when the emission from a non-oxygenated filament on to which cæsium is being condensed at a low temperature passes through a maximum, θ is very nearly equal to θ_{opt}. Thus it would appear that in order to find the approximate relative equilibrium values of θ at various temperatures above that at which the equilibrium activity is a maximum, all that is necessary is, after the establishment of equilibrium at the higher temperature, to suddenly lower the filament temperature to a value at which evaporation of cæsium from it is negligible, and to note the times taken for the activity to reach a maximum. These times should be proportional (approximately) to $\theta_{\text{opt}} - \theta$.

The curves ABC and ABDEFGA in Fig. 25 show the θ-T relationships found by Becker, using this method, for plain tungsten exposed to cæsium vapour at a certain pressure. The curve ABC was obtained with an electron-accelerating field applied to the surface of the filament, while ABDEFGA was obtained with an ion-accelerating applied field. $A_0B_0C_0$ and $A_0B_0D_0E_0F_0G_0A_0$ are the corresponding curves obtained with oxygenated tungsten in cæsium vapour at the same pressure.

It will be noted that below a certain critical filament temperature T_{c1} the equilibrium value of θ is the same whether the applied field is electron-accelerating or ion-accelerating. On the other hand, above a certain higher critical temperature T_{c2} the equilibrium θ is always much smaller when ions are drawn than when electrons are drawn. At intermediate temperatures the value of θ that establishes itself when ions are drawn is either practically that characteristic of an electron-accelerating field or much less according as the temperature has been raised from below T_{c1} or lowered from above T_{c2}.

Let us now consider the explanation of these phenomena. Since the cæsium vapour pressure was kept constant, atoms arrived at the surface of the filament at a constant rate, and so the curves show for what value of θ at any temperature the evaporation rate under given field conditions was equal to this constant arrival rate. Thus, for example, the curve ABC, which was obtained under field conditions such that all evaporating ions were driven back to the filament, is the θ-T curve for a given rate of evaporation (equal to the arrival rate) of *atoms*.

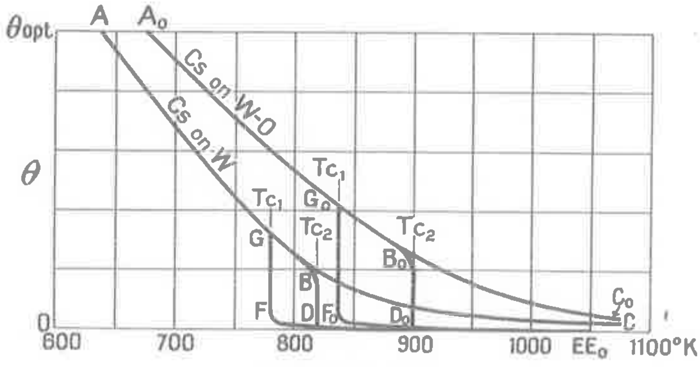

FIG. 25.

Suppose we start with the filament relatively cool and gradually increase its temperature while an ion-accelerating field is applied to its surface. When T is low, θ is high, $\chi - U_i$ is negative, and practically all the evaporating particles are atoms. Thus for low temperatures the θ-T relationship is the same when ions are drawn as it is when electrons are drawn. Just below a certain critical temperature T_{c2}, however, where χ approaches U_i, positive ions begin to evaporate at an appreciable rate, and so the equilibrium θ is less when ions are drawn than when electrons are drawn. At T_{c2} the increase in the rate of evaporation of ions brought about by a given decrease in θ becomes greater than the corresponding decrease in the rate of evaporation of atoms, and consequently at this temperature the filament spontaneously cleans itself, θ falling to a much lower value. This sudden evaporation, which is mainly ionic, has been observed by Becker to register itself as a ballistic throw of the galvanometer used for measuring thermionic currents. Beyond T_{c2} practically only ions evaporate, and so DE is the θ-T curve for the given rate of evaporation of *ions.*

Let the temperature now be decreased again. The curve BD will not be retraced, since the lower, vertical part of it does not represent equilibrium conditions. Instead, θ will remain low and the evaporating particles will continue to be practically only ions until a certain lower critical temperature T_{c1} is reached. Here a value of θ is attained, such that the tendency for the rate of evaporation of ions to increase with a further increase in the number of adsorbed particles is more than counterbalanced by the corresponding decrease in the probability of evaporation of any particular particle, due to the fall in $\chi - U_i$ as well as in T. A surface concentration of cæsium is then quickly reached, such that the evaporation of ions practically ceases entirely. At the same time θ is still too small for atoms to evaporate at an appreciable rate, and so practically every atom that strikes the surface sticks until θ approaches the equilibrium value which it has at this temperature when electrons are drawn. This value is presently attained and the θ-T relationship for temperatures below T_{c1} is represented by GA.

In Fig. 22, the curve PQRSUSVWP represents the logarithm of the current that may be drawn from a tungsten filament in cæsium vapour as a function of 1/T when an ion-accelerating field is applied to its surface. This shows the same hysteresis loop as the curve ABDEFGA in Fig. 25, and for any given cæsium vapour pressure the critical temperatures are the same in the two cases. The only part of the former curve that now calls for explanation is the rising part

SU which occurs at high filament temperatures. The rise is due, as Ives[22] has shown, to a photo and thermal emission of electrons from the plate and can be suppressed by means of a magnetic field parallel to the filament.

The number of adsorbed atoms that makes θ an optimum is obviously equal to the product of the time t_m taken by the initially clean (just flashed) filament kept at a low temperature to attain its maximum activity and the rate at which atoms condense on the filament surface. And to find the latter quantity one has merely to make use of the fact that at sufficiently high temperatures the filament converts every atom incident on it into an ion. Thus the arrival rate is simply equal to the maximum ion current obtainable divided by the ionic (= electronic) charge.

By multiplying the arrival rate found in this way by t_m, Becker obtained the figure $3{\cdot}9 \times 10^{14}$ for the number of atoms adsorbed per cm.^{2} of apparent filament surface corresponding to the optimum θ. He estimated this to be correct to within about 5 per cent. Of course the true surface must exceed the apparent surface. As we have already noted (p. 112), Langmuir[31] has shown that the exposed crystal faces of tungsten that has been etched by heat treatment are exclusively those of the rhombic dodecahedron. From this he deduced, by a faulty reasoning, that the "roughness factor," or ratio of true to apparent surface, for an etched tungsten wire must be 1·06. More recently, Tonks[58] has calculated that the roughness factor must be at least 1·225, and that it may be greater. This, in conjunction with Becker's result, gives us an upper limit for the concentration of cæsium on the exposed crystal faces corresponding to the optimum θ. This is, within about 5 per cent., $3{\cdot}2 \times 10^{14}$ atoms per cm.^{2}.

Now according to Simon and Vohsen,[56] cæsium crystallizes in a body-centred cubic lattice whose lattice constant at liquid-air temperature is 6·05Å., and thus at this temperature the shortest distance between atoms or the "effective diameter" of a cæsium atom is 5·24Å. If the effective diameter were the same in an adsorbed layer on tungsten at the temperatures of Becker's experiments and the atoms were close-packed, their surface concentration for $\theta = 1$ would be $4{\cdot}2 \times 10^{14}$ atoms per cm.^{2}. In the case of square packing the number vould be 3·6 × 10^{14} per cm.^{2}. It would, of course, be rather n extraordinary coincidence if the effective diameter of a æsium atom in a two-dimensional " crystal " adsorbed on ot tungsten happened to be exactly the same as that in a hree-dimensional crystal of cæsium at liquid-air temperature, nd so it would be going too far to draw any conclusions as o the precise arrangement of the adsorbed atoms and value f θ_{opt} from a comparison of these figures with that found xperimentally by Becker. Such a comparison does nevertheless show that the concentration of the atoms in the ptimum adsorbed film is of the order to be expected for a monatomic layer having some fairly close arrangement.

In addition to the two arrangements discussed, there is, of course, a third possibility that suggests itself, viz. that the cæsium atoms arrange themselves in conformity with the underlying tungsten lattice. Such an arrangement has been assumed by Langmuir.[32, 33] From the fact that cæsium and tungsten both crystallize in the same system (body-centred cubic) and that the lattice constant of cæsium is almost exactly double that of tungsten, considered in conjunction with the fact that the forces between cæsium and underlying tungsten atoms must be much greater than those between neighbouring cæsium atoms, Langmuir has argued that it may be asserted with considerable confidence that for $\theta = 1$ there must be just a quarter as many cæsium atoms on the surface as there are underlying tungsten atoms. If this is so, then the number of atoms in a full layer on hot tungsten must be 3·5 × 10^{14} per cm.^{2}, and so, according to Becker's result, θ_{opt} cannot be greater than 0·9.

A new method of determining concentrations of cæsium on tungsten has recently been developed by Langmuir [32] and by Langmuir and Taylor.[44] * When the concentration (σ) is low, practically every particle evaporates as an ion, and σ may therefore be found by simply flashing the filament at a high temperature while a cylinder surrounding it is held at a negative potential, and measuring the ballistic " throw " of

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* Full particulars of the work of Taylor and Langmuir on the properties of cæsium adsorbed on tungsten have recently been published by them —unfortunately too late for discussion in this section—in the *Physical Review*, Vol. **44**, p. 423, Sept. 15, 1933.

a galvanometer included in the space-current measuring circuit. When σ is high, however, atoms evaporate as well as ions. The method used for determining σ in this case was to measure the number of ions generated at the surface of a second, parallel filament which was kept at a high temperature and at whose surface an ion-accelerating field was maintained, while the first filament was flashed. The temperature at which the first filament was flashed was high enough to drive off the great majority of the adsorbed particles, but on account of an ion-retarding field maintained at its surface none were allowed to leave it permanently as ions. Incidentally, this method has also been developed for measuring the rate of evaporation of atoms (i_a) and of positive ions (i_p) separately.

Langmuir[33] reports that "Taylor's experiments have shown that at low temperatures and high cæsium pressures, the surface concentration approaches a definite limiting value of $4{\cdot}8 \times 10^{14}$ atoms per cm.^{2} of apparent surface corresponding to $\theta = 1$." (The order of temperatures and pressures referred to is unfortunately not stated. Of course at *sufficiently* low filament temperatures and high cæsium vapour pressures, cæsium in bulk would be formed on the filament surface.) This exceeds Langmuir's theoretical maximum concentration for a single layer adsorbed on the face of a dodecahedral crystal by a factor of between about 1·35 and 1·37—the exact figure depends on the temperature of the filament, whose thermal expansion should be taken account of. This factor was therefore assumed to be the actual roughness factor of the filament surface. It is to be noted that the value found for it exceeds, as we might have expected it to do, the minimum possible value of the roughness factor (1·225) calculated by Tonks.

Langmuir further reports that according to Taylor's data the optimum electron emission occurs at $\theta = 0{\cdot}67$, corresponding to $\sigma = 2{\cdot}4 \times 10^{14}$ atoms per cm.^{2}. This means that the number of atoms per cm.^{2} of *apparent* surface found to give the maximum emission must have been $3{\cdot}2 \times 10^{14}$ (Langmuir took 1·347 to be the roughness factor). This is to be compared with Becker's $3{\cdot}9 \times 10^{14}$. Perhaps in view of the experimental uncertainties involved in both determinations the agreement between the two figures may be regarded as tolerable. At the same time, however, the discrepancy between them serves as a warning that the precise numerical results obtained from these experiments cannot be accepted without a certain amount of reserve.

The fact that both Becker's and Taylor's experiments indicate that θ_{opt} is less than 1 is highly interesting. That it should be so is perfectly feasible, as Langmuir has pointed out. The lowering of the work function by the adsorbed atoms must be due to their formation, with the underlying tungsten, of electric dipoles, of which the positive poles are on the outside. These must have a certain depolarizing action on one another. Thus it may well be that when σ has reached a certain value the rate of weakening of the average dipole strength with progressive crowding of the adsorbed particles is such that the electric moment per unit area no longer increases with θ. This is the theory that has been advanced by Langmuir. It should be borne in mind, however, that while the optimum θ may well be less than 1 in the case of cæsium on tungsten, it by no means necessarily follows that it is also less than 1 in other cases of adsorbed electropositive atoms. Where the optimum θ occurs in any particular case will depend entirely on the importance of the mutual depolarizing action of the adsorbed particles. The only generalization that can be made from the existence of this mutual depolarizing action is that as θ increases the effectiveness of additional adsorbed particles in lowering the work function must become progressively less.

Independent evidence of the mutual depolarization of neighbouring adsorbed atoms is provided by evaporation data. With progressive depolarization we should expect the tenacity with which an atom of cæsium is held to underlying tungsten or oxygenated tungsten to become less and less, and if crowding results in mutual depolarization we should thus expect the rate of evaporation of cæsium per unit surface concentration to increase rapidly with θ. This is, in fact, just what has been found. Becker [4] has reported that as a first approximation the logarithm of the rate of evaporation of cæsium from oxygenated tungsten varies linearly with θ. And Langmuir [33] has reported that at 800°K. the rate of evaporation of cæsium from plain tungsten divided by θ has been found to increase about 10^{10}-fold as θ increases from 0 to 1.

Adsorbed atoms of cæsium, like those of thorium, have been found to have a quite appreciable mobility along the surface of tungsten, and measurements of the coefficient of surface diffusion η have been made by Langmuir and Taylor.[44]

A straight tungsten filament was stretched along the axis of three cylinders placed end to end and separated by short gaps. A cæsium film was allowed to form on the filament, the cæsium vapour was frozen out by immersing the bulb in liquid air, and σ was thereupon reduced to a very small value ($< 3{\cdot}6 \times 10^{13}$ atoms per cm.^{2}) by heating the filament to a suitable temperature. From a film of such small concentration practically only ions evaporate. This fact was made use of to establish a known non-uniform distribution of cæsium along the filament. The filament was heated to such a temperature that the atom evaporation rate was quite negligible, but not so the rate of evaporation of ions. At the same time, by making the central cylinder negative and the end cylinders positive to the filament, the field at the surface of the filament was made ion-accelerating along a definite central portion, but ion-retarding nearer the ends. In consequence, almost the whole of the cæsium was removed (in the form of ions) from the central part of the filament, but practically none from the ends. The ion current to the central cylinder was measured during the removal and the current-time integral gave the total amount of cæsium removed, and from this and the known length of filament from which this cæsium came the original concentration on the central portion and the still existing (equal) concentration on the ends could be calculated.

The filament was now raised to a certain temperature for a certain length of time while all evaporating ions were driven back by an ion-retarding field. During this time a certain migration of cæsium from the end sections to the central section took place. The number that had migrated was then measured by flashing the filament with all three cylinders at a negative potential, and measuring the quantity of ions collected by the central cylinder.

From the data obtained in this way the coefficient of surface diffusion η was calculated, assuming η to be independent of σ. It was found, however, that the values obtained varied with the original concentration on the uncleaned ends, increasing with the latter. Thus at 812°K. the value of η increased from $1{\cdot}4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ to $3{\cdot}4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ when σ for the ends was increased from $1{\cdot}74 \times 10^{13}$ to $2{\cdot}73 \times 10^{13}$ atoms per cm.^{2}. Thus the assumption that η is independent of σ is not justified and the values of η obtained can only be regarded as a kind of average for the range of values of σ involved.

The temperature dependence of η for a given σ was found to be expressed by

$$\eta \propto \epsilon^{-\mathrm{T}_\eta/\mathrm{T}}, \quad . \quad . \quad . \quad . \quad (7)$$

where T_η is a constant whose value is 7050 degrees. The form of this indicates that the adsorbed atoms move along the surface by a succession of jumps from one position of equilibrium (definite arrangement with respect to the underlying tungsten lattice ?) to a neighbouring one. Dividing T_η by 11,600 we obtain 0·61 e.v. for the energy required for the jump.

In cases where σ is so large that the rate of evaporation of atoms is no longer negligible relative to that of ions, the above method of determining η ceases to be applicable, and so a new method has been devised for such cases by Langmuir and Taylor.[44] This depends on the fact that when an ion-accelerating field is applied to a tungsten filament in cæsium vapour the adsorbed cæsium can, at certain filament temperatures, exist in two phases, which have been called the α and β phase, the α phase being the more and the β the less concentrated. Particles from the α phase evaporate, as we have seen, as atoms, while from the β phase they evaporate as ions. Both evaporation rates are, of course, equal to the arrival rate from the vapour. By suitably manipulating the potentials of the three cylinders it is not difficult to establish both phases at the same time, separated by a definite boundary. At the boundary, where there is a sharp concentration gradient, there is, of course, a continuous diffusion of cæsium out of the α into the β phase, but under equilibrium conditions this is balanced by differences between the rates of evaporation into and arrival from the vapour, and so the boundary remains stationary. If, however, the vapour pressure is changed, the boundary will move with a definite velocity in either one or the other direction, depending on whether the pressure has been increased or decreased. Langmuir and Taylor have shown that this velocity is a definite function both of the change in pressure and of the coefficient of diffusion η, and by measuring the velocity associated with a given change in pressure, they have, using the theoretical relationship between the three quantities, been able to determine η. For a concentration of $7{\cdot}3 \times 10^{13}$ atoms per cm.^{2} in the α phase they have found η at 967°K. to be 6×10^{-4} cm.^{2} sec.$^{-1}$. Extrapolating the η-T relationship found by the first method for a concentration on the end portions of the filament of $2{\cdot}73 \times 10^{13}$ atoms per cm.^{2} they have calculated for this concentration and a temperature of 967°K. a value of $1{\cdot}1 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ for η. They attribute the higher value of η found experimentally by the second method to the higher concentration.

The explanation for the increase of η with σ given by Langmuir and Taylor is that the diffusion is not due merely to random heat motions, but also to the existence of a definite "spreading force," associated with the mutual repulsions of the dipoles, and that the importance of these repulsions increases with σ.

Other Cases of Alkali Metal Contaminations.—The electron and positive-ion emission characteristics of tungsten and of oxygenated tungsten exposed to the vapours of rubidium and of potassium at various pressures have been studied by Killian,[24] and those of tungsten exposed to cæsium, rubidium, potassium and sodium vapours by Ives.[22]

For the electron emissions in both rubidium and potassium vapours, families of $(\log i)$-$1/\mathrm{T}$ curves have been obtained by Killian which are quite similar to those of Langmuir and Kingdon obtained with cæsium vapour, except that Killian's curves for oxygenated tungsten have not the peculiar kink shown by the corresponding curves of Langmuir and Kingdon.

The envelopes to Killian's families of curves for plain tungsten in the two different vapours are straight lines, and if we assume that they represent the constant, most active conditions of the filament, we obtain for the thermionic constants of W-Rb the values

$$\mathrm{A} = 0{\cdot}0022 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 1{\cdot}14 \text{ e.v.}$$

and for those of W-K

$$A = 0{\cdot}25 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 1{\cdot}71 \text{ e.v.}$$

We have no means of estimating the accuracy of these figures. The apparent value of χ for W-Rb is certainly remarkable n being less than that obtained from the measurements of Langmuir and Kingdon on W-Cs, instead of greater, as we should have expected. And hardly less remarkable is the smallness of the apparent A for W-Rb.

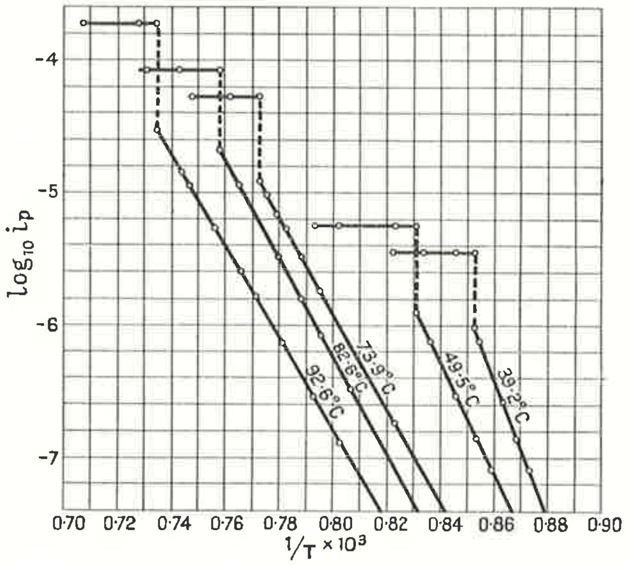

FIG. 26.—Temperature variation of positive-ion emission from tungsten exposed to rubidium vapour at various pressures.

In Fig. 26 is reproduced a family of curves obtained by Killian showing the variation with 1/T of the logarithm of the positive emission from a plain tungsten filament exposed to rubidium vapour saturated at various temperatures. A quite similar family was obtained when potassium vapour was substituted for rubidium. These show the same sudden ncrease at a critical filament temperature and the same constancy at high temperatures as do the corresponding curves for tungsten in cæsium vapour. Also, it will be noted, the magnitude of the constant, high-temperature positive emission increases with the alkali vapour pressure, as it should do.

Just as Langmuir and Kingdon found the carriers of the positive emission in cæsium vapour to be singly charged cæsium atoms, so Killian found those in the vapours of rubidium and potassium at all pressures studied to be singly charged rubidium and potassium atoms respectively. Ives on the other hand, found the currents in the three vapours to be carried by Cs^+, Rb^+ and K^+ particles only at the higher vapour pressures. At low pressures he observed current voltage relationships indicating a higher average mass of the carriers than the atomic. In the case of sodium vapour, too Ives found the average mass of the ions to be greater at low than at high pressures. Here, however, the mass found at the highest pressures was not that of a single sodium atom but of two atoms. It would appear, then, that hot tungsten is unable to ionize single atoms of sodium. It is interesting to note that while the works of ionization of cæsium, rubidium and potassium (3·87, 4·15 and 4·32 e.v. respectively) are less than the work function of tungsten (4·54 e.v.), that of sodium (5·11 e.v.) is greater.

The negative and positive emissions from the metals tungsten, molybdenum and tantalum in potassium vapour saturated at various pressures have been studied by Meyer.[4 While for the negative emission, (log i)-1/T curves were obtained whose general character agreed with that of the curves of Langmuir and Kingdon and of Becker for tungsten in cæsium and of Killian for tungsten in rubidium and potassium they differed from these in one important respect, viz. that the maxima all occurred at the same temperature. The positive emission curves, too, differed from those of Becker and of Killian in showing no discontinuity in the rapidly rising parts. These differences may have been due, at least in part, to the non-uniformity of the temperatures of the filaments along their lengths, which, with the dimensions employed (lengths 6–8 cm., diameter 0·1 mm.), must have been rather serious.

De Bruyne [7] has reported an effect on the electron emission from tungsten in cæsium vapour due to the presence of nitrogen. The emission-temperature relationship for the tungsten in cæsium vapour alone showed the single maximum at a low temperature observed by Langmuir and Kingdon. When, however, nitrogen was also present and the electrons were accelerated to something between 4 and 9 volts, a secondary peak appeared at a somewhat higher temperature. There was no secondary peak when lower accelerating voltages were used. Its appearance must therefore have depended in some way on the formation of " activated " nitrogen.

It was at one time believed that nitrogen forms an adsorbed layer on tungsten when a discharge is passed through it, depressing the emission. It has since been established by Langmuir,[34] however, that this effect is not really due to nitrogen, as such, but to *oxygen*. Metastable molecules of nitrogen, which begin to be formed at something like 9 volts, on coming into contact with the walls of the tube (however well baked out) and the surfaces of the electrodes, decompose adsorbed water molecules or metallic oxides, which are almost always present, liberating oxygen, probably in the atomic form. This then reacts with the filament.

It would appear, then, that the phenomena observed by de Bruyne were probably due to the formation of a partial adsorbed film of oxygen on the tungsten, on which cæsium could remain adsorbed at a higher temperature than on plain tungsten.

SECTION III.

BARIUM ON TUNGSTEN AND ON OXYGENATED TUNGSTEN.

An exhaustive study of the thermionic properties of monatomic films of barium on tungsten and on oxygenated tungsten, and also of multiple layers of barium and oxygen on tungsten, was made some years ago at the Research Laboratories of the General Electric Co., Wembley, by Messrs. J. W. Ryde and N. L. Harris, who have now very kindly placed their unpublished results at the author's disposal. Where not otherwise stated it is to be understood that it is this work that is referred to in the following discussion. Researches in the same field have also been carried out by Eglin,[18] Becker,[4] and Nelson,[47] short reports of which have appeared in the literature.

The Experimental Tube.—The electrode arrangement employed by Ryde and Harris consisted essentially of two equal, straight tungsten filaments, one of which served as the cathode and the other as a comparison wire for the purposes of temperature measurement, and three barium-coated cylindrical spirals placed end to end and separated by short gaps, which served as the anode. The tungsten filaments were stretched parallel and close to the common axis of the three spirals. On passing a heating current through the spirals in series, barium could be distilled from them on to the test filament, whereby the thermionic activity of the latter was increased. The electrons emitted from this filament were collected by the spirals, which were kept at a positive potential with respect to it, but only the centre spiral was included in the thermionic current measuring circuit, the end spirals merely functioning as " guard rings."

The spirals were of 0·4 mm. vacuum-furnaced nickel wire, wound on an 8 mm. " former " to a pitch of 2·5 mm. The centre spiral was 1·5 cm. long and the end ones were either of the same length or longer. The filaments were 0·0249 mm. in diameter and 12 cm. or more in length.

Before being coated, the spirals were given a final outgassing by mounting them in separate bulbs and heating them in a vacuum for several minutes to a bright yellow by means of a current. The bulbs were then broken open and the spirals coated to a thickness of about 0·2 mm. with barium azide (BaN_6) by being dipped several times in succession into a creamy suspension of the azide in distilled water and dried between dips in a current of air at about 80°C. They were then ready for assembly. The azide was decomposed (at about 160°C.) on the pump, the bulk of the nitrogen being pumped away and a black residue of finely divided barium remaining on the wire. The barium residue still contained some nitrogen in an occluded form, but most of this was got rid of in a subsequent operation before the tube was used.

To the bulb, which was of lime-soda glass, was attached a short length of wide tubing of the same material, continuous *via* a graded seal, with a hard-glass tube, closed at the end. The hard-glass tube contained outgassed charcoal which could be cooled by liquid air and thus made to act as a very efficient pump. In addition, four previously outgassed nickel discs, to each of which was attached a small piece of outgassed magnesium, were supported by the filament leads. These could be heated by high-frequency induction and the magnesium " dispersed " from them so that it should act as a " getter " for the clean-up of residual gases not dealt with by the charcoal. Incidentally, barium, a plenteous deposit of which was always formed on the glass walls, is also a very efficient getter—in fact much more efficient, as is now known, than magnesium. All the electrode supports, as well as the electrodes themselves, were outgassed before assembly.

For the supply of small doses of oxygen to the bulb, a long piece of narrow tubing was attached to it and closed at the end remote from the bulb. This contained near the closed end several small grains of potassium permanganate from which oxygen could be liberated by heating the tube locally with a small flame. Condensible gases evolved from the glass were prevented from reaching the bulb by a " trap " immersed in liquid air between the permanganate and the bulb. In some cases arrangements were made for the supply to the bulb of gases other than oxygen, also through a trap cooled by liquid air.

The operations carried out on the pump were usually as follows : The charcoal was outgassed for some hours at 550°C. and the side tube containing the potassium permanganate thoroughly " torched " with a flame, the permanganate crystals being moved about as required, i.e. away from the part of the tube that was being heated, by tapping. An electrically heated cylindrical oven was then lowered over the bulb and charcoal tube. The apparatus was first baked for ten minutes at 120°C. to dry the azide and incidentally drive off much of the moisture held by the glass walls. The temperature was then raised to 160°C. to decompose the azide and held there until no more nitrogen was evolved. Finally the temperature was raised to 300°C., where it was kept for at least two hours. The reason why a higher temperature, e.g. 400°C., was not employed was that baking temperatures much in excess of 300° were found to result in a chemical attack of the barium by the gases evolved. The long bake at 300° was certainly adequate in the present instance, since the bulb never became hot in operation and in any case eventually became completely covered on the inside with a film of barium, which has a strong gettering action for moisture and for various gases. After the bake, magnesium was dispersed from the discs by high-frequency induction heating. The spirals were then heated in turn to just below visible redness to drive off occluded nitrogen, the bulb becoming coated in the process with a thin transparent film of barium. The tungsten filaments were thereupon "flashed" at 2900°K. for two minutes, and the apparatus sealed off. Finally, the charcoal tube and trap for condensable gases were immersed in liquid air for at least an hour before experimental work was begun.

No systematic measurements of vacuum were carried out, but that the vacuum must have been very good indeed is indicated by the fact that after the test filament had been given a certain barium covering it could be left cold for days (during which time the charcoal tube was kept immersed in liquid air) without the occurrence of any appreciable change in its thermionic activity.

The Main Phenomena.—A typical emission-time curve obtained during and after the condensation of barium on tungsten is shown in Fig. 27. The curves obtained with barium on oxygenated tungsten were qualitatively similar. With the spirals hot and supplying barium, the test filament was kept at a temperature sufficiently high to keep it practically free of barium. The filament temperature was then suddenly dropped to a much lower value, so that an appreciable covering of barium could form on the surface, and the emission measured as a function of time. The emission at first remained immeasurably small, and then rose rapidly to a maximum at A, after which it fell away

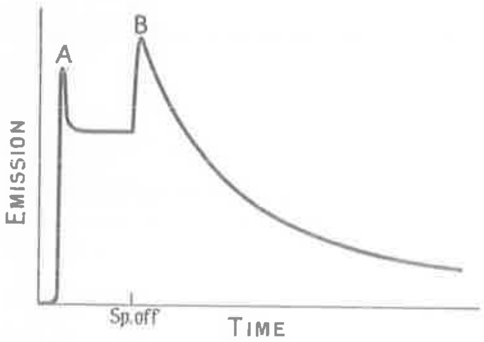

FIG. 27.

to a lower, steady value. The current through the spirals was then suddenly switched off, allowing them to cool. This caused the emission to rise to a second maximum at B. Finally it again fell away at a more or less rapid rate, depending on the filament temperature.

The explanation of these phenomena in general terms is not difficult. The first maximum at A corresponds to a quantity and arrangement of barium on the filament surface very near the optimum for electron emission. As in the case of cæsium condensing on tungsten or on oxygenated tungsten, however, it was not quite the optimum, owing to the random distribution of the points of arrival of the barium atoms and the finiteness of their surface mobility. Beyond A the quantity of barium continued to increase until so much had collected on the filament that its rate of evaporation was equal to the rate of arrival. The emission then became steady. When the supply of barium was cut off, barium was lost by evaporation from the filament, more particularly from the regions where the concentration was greatest or where a second layer had begun to form, and during this evaporation the optimum condition for electron emission was again nearly passed through at B—in general, more nearly than at A, just as the point C′ in Fig. 22 represents a more nearly ideal covering of cæsium on tungsten than does A′. Thus the second maximum was usually higher than the first.

The exact shape of the curves varied with the temperature of the spirals with respect to that of the filament in a way that is easily understood. With a given filament temperature, the higher the temperature of the spirals, and the greater, therefore, the rate of supply of barium, the sooner was the first maximum reached, and, owing to the increased importance of condensation relative to evaporation, the less nearly did the corresponding state of the filament approach the optimum. Also, of course, the higher the spiral temperature, the more the emission was depressed by the presence of excess of barium between the two maxima. On the other hand, the lower the spiral temperature, the less pronounced did the maxima become, until, with sufficiently low spiral temperatures, they disappeared altogether, the first tending to do so before the second.

In cases where the filament temperature was sufficiently low, it was found that while the emission rose at an appreciable rate to the second maximum, its rate of fall beyond this maximum was relatively very small indeed. The suddenness with which, in these cases, the evaporation practically ceased when the second maximum was attained indicates that at this point some very definite condition of the surface must have been reached, and strongly suggests that this condition was different *in kind* from that obtaining just before the maximum, when the evaporation was relatively rapid. If the condition corresponding to the second maximum was that of the adsorption of just one complete layer of barium atoms this is quite understandable, for we should naturally expect the rate of evaporation of second-layer atoms to be of a higher order than that of first-layer atoms. It would, however, be difficult to account for if θ_{opt} were less (or greater) than 1.

Thermionic Properties.—Use was made of the relative stability of the condition for maximum emission in determining the corresponding thermionic constants. After sufficient barium had been deposited on the filament to make θ greater than θ_{opt}, the spirals were allowed to cool and the filament was heated to a temperature such that while the excess of barium evaporated reasonably rapidly, the evaporation practically ceased entirely as soon as θ_{opt} was reached. The filament temperature was then varied while observations were taken for the plotting of a Richardson line. Plots obtained in this way for W-Ba and W-O-Ba are reproduced (with others) in Fig. 28.

The values of the thermionic constants found for W-Ba were

$$A = 1{\cdot}5 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 1{\cdot}56 \text{ e.v.}$$

Those found by Eglin[18] for the same system were

$$A = 2{\cdot}5 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 1{\cdot}66 \text{ e.v.}$$

The values found by Ryde and Harris for W-O-Ba were not always the same, χ, for example, varying between 1·34 and 1·44 e.v. There is, however, as we shall see later, reason to believe that the cases in which values of χ higher than the lower limit, viz. 1·34 e.v., were obtained were those in which the layer of oxygen underlying the barium was not quite complete. For what appeared to be complete layers of oxygen and barium the constants obtained were

$$A = 0{\cdot}18 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 1{\cdot}34 \text{ e.v.}$$

Values were also obtained for the thermionic constants of tungsten with two layers of adsorbed barium and of barium in bulk. We have seen that with a given filament temperature, the higher the temperature of the spirals the less was the equilibrium emission between the two maxima. On plotting this equilibrium emission for the barium-on-tungsten case against spiral current, curves like that of Fig. 29 were obtained over a certain range of filament temperatures. This, it will be observed, has a fairly well-defined kink at C. This kink must correspond to the passage through some critical condition of the surface of the filament, and since in the building up of a barium film on the filament the stage where there is one complete layer of adsorbed barium atoms has already been passed through, it is natural to suppose that the kink at C must correspond to the stage where there are just two layers of adsorbed atoms. Of course we should not expect the double layer of barium atoms ever to be perfect. There is probably considerably less difference between the rates of

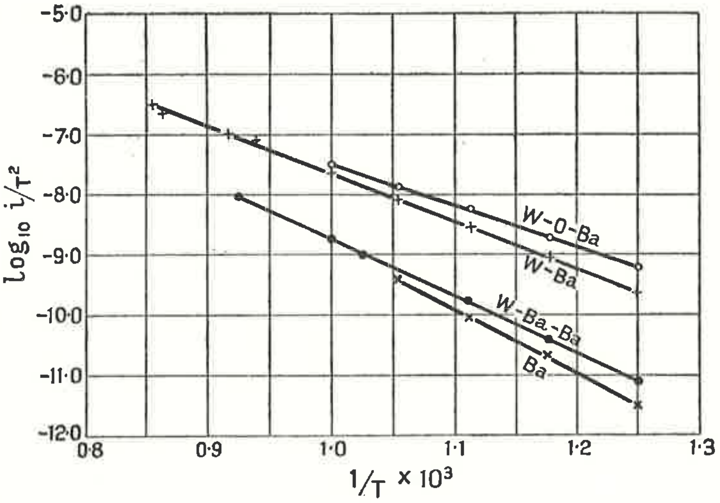

FIG. 28.—Richardson lines for W-Ba, W-O-Ba, tungsten covered with a double atomic layer of barium, and barium in bulk.

evaporation of second and third layer atoms than between those of first and second layer atoms, and so we should expect an appreciable amount of third layer to begin to form before the second is complete. Nevertheless, we might reasonably hope that a Richardson line corresponding to the C-kinks obtained at various temperatures would give some sort of approximation to the correct values of A and χ for two layers. Such a line is shown in Fig. 28, labelled W-Ba-Ba, and the values of the constants obtained from it are

$$A = 4{\cdot}1 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 1{\cdot}86 \text{ e.v.}$$

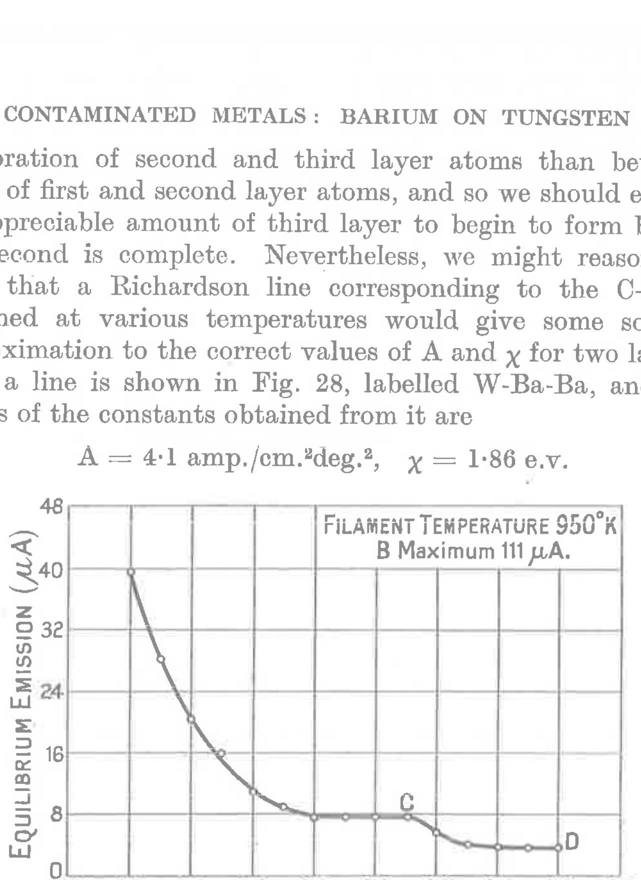

FIG. 29.

At sufficiently high spiral temperatures, e.g. in the region of D in Fig. 29, the emission was found no longer to vary with the temperature of the spirals. This can only mean that the rate of supply of barium to the emitting filament was sufficient to keep it covered with an atomically thick film of this metal. The Richardson line representing the emission-temperature relationship for this condition is shown in Fig. 28, marked Ba. The thermionic constants derived from this line, which must be those for barium in bulk, are

$$A = 60 \text{ amp./cm.}^2\text{deg.}^2, \quad \chi = 2{\cdot}11 \text{ e.v.}$$

The values of the temperatures used for making the various Richardson plots were calculated from the filament currents on the basis of the tables given by Jones and Langmuir,[23] assuming the radiation from the filament not to be affected by the presence on it of a contamination of a mere monatomic order of thickness. There can hardly be any question regarding the validity of this assumption. Apart from possible errors due to end cooling and thermal effects associated with the passage of the space current, the temperatures so determined were estimated to be accurate to within 1 per cent.

By measuring the distribution of thermionic current between the centre and end spirals in the case of barium-activated filaments of different lengths at various temperatures, it was ascertained that over the whole range of temperatures employed the part of the filament in the centre whose temperature was sensibly uniform was longer than the centre spiral. Also it was readily calculated that below a certain temperature in the case of each contamination the combined effect on the filament temperature of the cooling associated with the latent heat of evaporation of the electrons and of the heating due to the passage of the thermionic current along the filament was negligible. At the higher temperatures, where it was no longer negligible, the centre part of the test filament was matched by eye against that of the comparison filament from which no space current was taken. After a little practice, this could be done very accurately, the possible error of matching never being greater than 2 per cent.

On considering all the possible sources of error in temperature measurement and taking into account the " spread " in the thermionic constants obtained in separate runs and with different tubes, the values given above for the work functions of W-Ba and W-O-Ba were estimated to be accurate to within 3 per cent., and the corresponding values of the emission constants to within a factor of about 2. The constants obtained for W-Ba-Ba and for barium in bulk are probably less accurate.

The values obtained for the thermionic constants in the various cases are, of course, valid only for the particular accelerating field used. The emission readings were all taken with the spirals at 30 volts positive to the test filament. This, while sufficient to avoid space charge limitation of the thermionic current, corresponded to only a very weak accelerating field at the surface of the filament. The constants obtained may therefore be taken to be very nearly those for zero field.

The variation of log i with θ for barium on tungsten at 1100°K. has been determined by Becker,[4] and is shown by the curve in Fig. 30. The data for this curve were obtained by distilling barium at a uniform rate from an alloy filament on to one face of a tungsten ribbon which was kept at a low temperature except when readings were being taken, and observing the emission from the tungsten filament as a function of time. The value of θ was assumed to be 1 when the emission was a maximum.

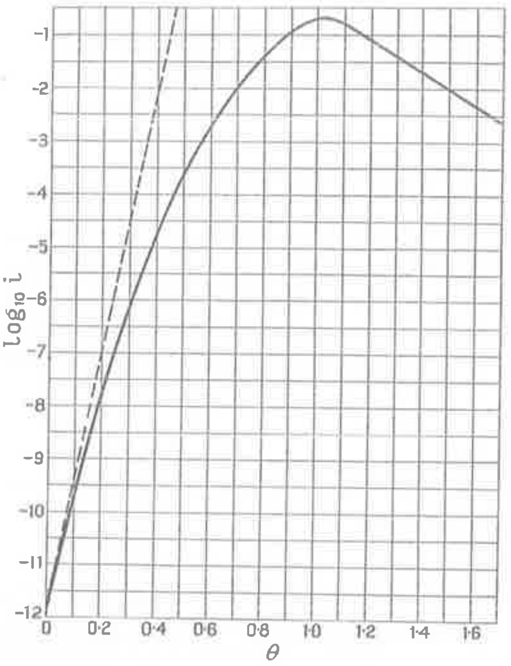

Fig. 30.—Relationship between log i and θ for barium on tungsten at 1100°K.

Adsorption and Evaporation Characteristics.—Evidence of surface migration of barium on tungsten has been obtained by Becker [4] as follows: After a certain quantity of barium, not sufficient to form a full monatomic layer, had been deposited on the front face of a tungsten ribbon, the temperature of the ribbon was raised to about 900°K., and it was found that the emission from the front face thereupon decreased while that from the back face increased. Finally a steady state was reached when the emission was the same from both faces. The amount of barium on each face could then be calculated from the previously determined relationship between log i and θ. Thus in a case where 80 per cent. of a full monatomic layer had originally been deposited on one face, the amount of barium found on each face after the heat treatment was 40 per cent. of a full layer. The barium must, therefore, have migrated from one face to the other without any appreciable loss by evaporation.

In the course of some experiments the author once had occasion to carry out in parallel with those of Ryde and Harris, he observed that if a plain tungsten filament that has been covered with a complete layer of barium atoms is " poisoned " by oxygen and is then heat-treated at a temperature rather above 1000°K., the emission gradually recovers, ultimately reaching a value and exhibiting a stability of the same order as that from W-O-Ba. If the properties of the filament are not practically those of a perfect W-O-Ba system after the first poisoning and recovery, one or more further poisonings and recoveries will generally make them so. This phenomenon can only be accounted for by supposing that the poisoned system W-Ba-O is transformed by the thermal treatment into the system W-O-Ba, the layers of barium and oxygen changing places without any appreciable loss of barium.

Subsequent further study of the phenomenon by Ryde and Harris showed that the less complete the poisoning, the more readily does the " reversal " occur. Indeed, if oxygen reaches the barium-activated filament sufficiently slowly, the reversal appears to be practically instantaneous, the rate of decay at high temperatures (due to the evaporation of barium) changing abruptly, without the occurrence of any appreciable poisoning. On the other hand, a filament that has been sufficiently completely poisoned at a low temperature normally shows no tendency to recover. It is as if vacant places in the poisoning oxygen layer were necessary to give the barium and oxygen atoms room to change places.

It was found that with successive poisoning and recovery treatments, χ showed a tendency to decrease, approaching a limit which was about the same as the lower limit of the

χ-values obtained in the case of W-O-Ba formed in the more orthodox manner. From this it seems that the lowest values of χ correspond to the most complete layers of oxygen underlying the barium.

Reversal of Ba-O on tungsten may in any given case be accelerated by nitrogen which, acting on the hot filament, removes oxygen from it. Small amounts of nitrogen remove small amounts of oxygen and a normal reversal ensues. On the other hand, if large doses of nitrogen are admitted, the bulk of the oxygen may be "stripped off" before reversal has had time to occur, and then repeated oxygen poisonings and recoveries are necessary in order to establish anything like a perfect W-O-Ba system.

There is evidence that nitrogen is able to remove oxygen from tungsten itself at 1600°K.

By noting the rates of decay at different temperatures of the thermionic activity of plain tungsten filaments covered with various amounts of barium, Ryde and Harris have found that for any given condition of the filament the temperature variation of the atom evaporation rate i_a may be expressed by a formula of the type

$$i_a \propto \epsilon^{-\omega_a/kT}, \quad . \quad . \quad . \quad . \quad (8)$$

where ω_a is a constant. This constant cannot be very different from the reversible work of evaporation of an atom. The various conditions of the filament surface were defined by the quantity

$$\Theta = \frac{\log i - \log i_0}{\log i_1 - \log i_0}, \quad . \quad . \quad . \quad (9)$$

where i is the electron emission from the filament at a certain temperature and i_0 and i_1 are the corresponding emissions for $\theta = 0$ and $\theta = 1$ respectively. Now by means of Becker's curve shown in Fig. 30 we may find the values of θ corresponding to each Θ. In Table XVI the experimental values of ω_a are given for a number of values of Θ, and also the corresponding values of θ according to Becker's curve. We see that there is an important decrease in ω_a as θ increases. This is further evidence of the mutual depolarization of neighbouring adsorbed atoms.

The evaporation of barium from oxygenated tungsten was always found to be much slower than from plain tungsten. Thus, while at 1250°K. it took only about thirty seconds for the emission from barium on plain tungsten to fall to half value after the passage of the B peak, it took many hours at the same temperature in the case of barium on oxygenated tungsten. Incidentally, in the latter case the oxygen layer was left practically complete after the evaporation of the barium.

TABLE XVI.

RELATIONSHIP BETWEEN Θ, θ AND ω_a.

Θ	θ	ω_a (electron-volts).
0·5	0·29	5·8
0·6	0·37	5·4
0·7	0·46	5·1
0·8	0·58	4·9
0·9	0·73	4·7

Multiple Atomic Layers of Barium and Oxygen on Tungsten.—Ryde and Harris have investigated the properties not only of the systems W-Ba and W-O-Ba, but also of W-Ba-O and of the systems in which several atomic layers of oxygen and barium were adsorbed on the tungsten filament. While, in view of the experimental difficulties, they claim no great quantitative accuracy for the values of χ and A arrived at in the various cases, they do feel justified in claiming that the manner in which they found these quantities to change with changes in the contaminating layers is qualitatively correct.

We have seen how the systems W-Ba and W-O-Ba were formed. Beginning with these, the two systems which were probably W-Ba, W-Ba-O, W-Ba-O-Ba, . . ., and W-O-Ba, W-O-Ba-O, W-O-Ba-O-Ba, . . ., respectively, were built up. This was done as follows : In order to add one complete layer of barium atoms to a system which had last been treated with oxygen, barium was condensed on to it until the emission had passed through a maximum, and then, by careful heat treatment, the excess was evaporated off in the manner already described for W-Ba and W-O-Ba. And in order to add full monatomic layer of oxygen to a system ending with B successive doses of oxygen were admitted, with the filamen either cold or held at 800°K., until no further depression the emission, measured at 800°K., occurred. The measurin temperature was too low for reversal to occur at an appreciabl rate. At the same time, it was probably high enough for an second and further layers which might have condensed on to of the first layer added to be driven off. The constancy the emission beyond a certain number of oxygen doses admitte was taken to be a criterion that some perfectly definite state probably that of the addition to the previous system of jus one complete layer of oxygen atoms, had been achieved.

It was found that the building up of a given multiatomi contamination could in the simpler cases be reversed step b step by evaporating off the barium layers and either also evaporating off the oxygen or else stripping it off with nitrogen. rather striking example of this process by the pure evaporatio method carried out at 1250°K. with W-O-Ba-O-Ba is give in Table XVII.

TABLE XVII.

VARIATION OF EMISSION DURING EVAPORATION AT 1250°K. FROM W-O-Ba-O-Ba.

System.	Time (hours).	Emission (*m*A).
W-O-Ba		0·935
W-O-Ba-O		0·00725
W-O-Ba-O-Ba	0	0·70
	$10\frac{1}{2}$	0·15 (min.)
	$27\frac{1}{2}$	0·4
	$35\frac{1}{2}$	0·55
W-O-Ba (probably)	$56\frac{1}{2}$	0·94 (max.)
	76	0·19
	83	0·004

It is seen that the emission measured under given conditions after passing through a minimum, reached a maximum at $56\frac{1}{2}$ hours which agreed very closely with the emission obtained from W-O-Ba during the building up. It thereupon decayed again, owing to the evaporation of barium. The minimum rst passed through did not agree with the value obtained r the emission from W-O-Ba-O, presumably because oxygen egan to evaporate, exposing underlying barium, before the vaporation of the outermost layer of barium atoms was mplete.

The thermionic properties of the members of the two series ere determined by observing their emissions at various mperatures and plotting their Richardson lines. In the ases where barium formed the last layer the thermionic ctivity was always much higher, and so much longer and more

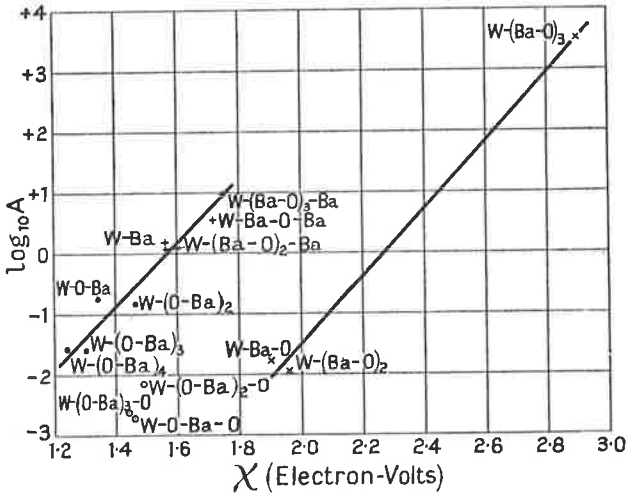

FIG. 31.

ccurate Richardson lines could be obtained than in the cases here the last layer consisted of oxygen. Even in the latter ases, however, results which were of *some* quantitative value ould be obtained by using a sufficiently sensitive galvanometer or measuring the thermionic currents. Typical sets of values f log A and χ obtained for the two series are plotted in ig. 31. A shortened notation has been used for labelling the oints whose meaning will be obvious. W-(Ba-O)$_3$-Ba, for xample, stands for W-Ba-O-Ba-O-Ba-O-Ba.

It will be observed that, according to these data, log A s roughly a linear function of χ for all the completed systems n which barium forms the last layer, irrespective of whether

Ba or O is next to the tungsten. On the other hand, th points representing systems ending with oxygen do not al lie near any one straight line. Possibly all the points repre senting systems of the type W-$(Ba\text{-}O)_n$, where n is a whol number, lie near one straight line and those representin systems of the type W-$(O\text{-}Ba)_n$-O lie near another, but sinc only three points were obtained corresponding to each type of which two are very close to one another in the former cas and all three in the latter, this has not been establishe experimentally. It is interesting to note that the straigh line which passes most nearly through the W-$(Ba\text{-}O)_n$ points is roughly parallel to that representing the systems ending with Ba.

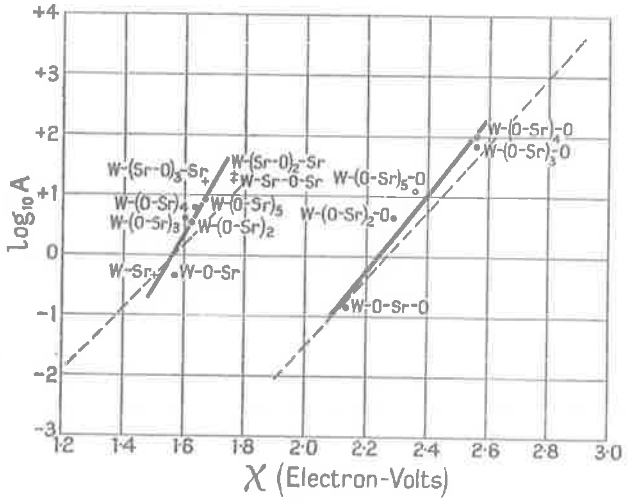

FIG. 32.

In certain experiments strontium took the place of barium, and the two series of systems W-Sr, W-Sr-O, W-Sr-O-Sr, . . . and W-O-Sr, W-O-Sr-O, W-O-Sr-O-Sr, . . . were built up. Sets of (log A)-χ points corresponding to members of both series, with the exception of those of the type W-$(Sr\text{-}O)_n$, for which the experimental data were not very accurate, are plotted in Fig. 32. It will be noted that the points corresponding to all the systems ending with Sr lie close to one straight line, irrespective of whether Sr or O is next to the tungsten, ust as do the points for all the systems ending with Ba. The oints corresponding to the five first systems of the type V-(O-Sr)$_n$-O all lie close to another straight line. In addition o these two lines, those of Fig. 31 are re-drawn, dashed, in ig. 32 for comparison. It will be observed that the line or systems ending with Sr is very close to that for systems nding with Ba. The other two lines are also, as it happens, lose together, although the types of systems they represent re not really comparable.

It is to be noted that while the work functions of the sysems ending with O are all higher than those of the systems nding with Ba or Sr, they are still very much less than the vork function of clean tungsten, viz. 4·5 e.v. Thus an overying layer of oxygen must fall considerably short of neutralzing the whole of the beneficial effect of the Ba or Sr on the hermionic activity.

As for the emission constant, this, it will be noted, is in every ase except that of W-(Ba-O)$_3$ less than 120 amp./cm.^{2}deg.^{2}. he A found for this system was 3500, which is greater than he theoretical A_0 by a factor of nearly 30. This is, perhaps, ot greater than the factor of uncertainty for systems ending vith oxygen.

In the case of the series of systems containing strontium, pair of layers added to a given contamination was generally ound to increase both χ and A. An increase of both constants n the addition of a pair of layers was also frequently observed n the case of the systems containing barium. The increase n A must, according to the modern theory which will be iscussed in Chapter V, be due to a decrease in the effectiveess of the resultant potential hump which reflects electrons. he electron-reflecting hump is that part of the potential hill vhich projects above the final image level. The hump can ardly increase in thickness as more layers are added and yet ecome less effective in reflecting electrons. Possibly the only rojecting part of the hill is that in the region of the first trontium or barium layer.

It is a remarkable thing that the A of W-Ba-O was actually ound to be less than that of W-Ba, in spite of the raising of he final image level due to the addition of oxygen. According o the modern theory this must mean that oxygen, adsorbed on top of the barium, somehow increases the height and/o thickness of the projecting hump although this is, presumably underneath the barium.

The manner in which log A varies with χ as an additiona layer is gradually built up on a given contamination has als been investigated. An example of this, in which the origina system was W-Ba and the added layer oxygen, is illustrate in Fig. 33. Only very small doses of oxygen were admitted a a time and the thermionic constants determined after eac

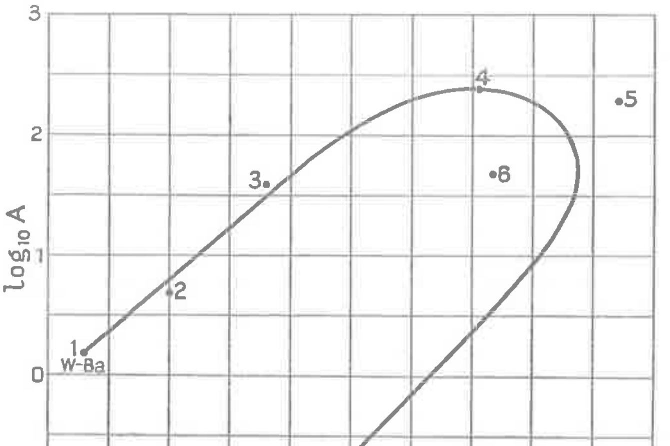

Fig. 33.

one. Emission readings for the plotting of a Richardson lin were in each case confined to temperatures sufficiently low to avoid "reversal" of the barium and oxygen layers. Th various (log A)-χ points in Fig. 33 are numbered in the orde in which they were obtained. The decided loop which represents these data is in striking contrast to the straight line representing those for the various series of completed systems

A qualitatively similar (log A)-χ loop was found in the cas of the transition from W-Ba-O to W-O-Ba by reversal, only of course, in this case the points were obtained in the revers order.

SECTION IV.

GENERAL.

Miscellaneous Contaminations.—In addition to the ases of contaminated metals discussed at length in the receding sections, there are a number of others (all, incident- lly, cases of gas contaminations) which have been studied n a general way and which we shall now briefly consider.

Hydrogen, when it has any effect at all, usually enhances he emission from metals. A beneficial effect of hydrogen n the thermionic emission from platinum, for example, has een reported in much of the earlier literature.* More ecently, DuBridge[12] has observed a large increase also in he photoelectric emission from platinum after heat treat- nent in hydrogen. In this case the platinum had had a very horough outgassing prior to exposure. The emission sub- equently decreased to the value characteristic of clean latinum when the specimen was heated for a short time in vacuum. Lockrow,[45] on the other hand, has reported that he effect of hydrogen on the thermionic emission from pure latinum is probably nil. There is reason to believe, however, see Chapter II), that the final surface of Lockrow's specimen vas less clean than that of DuBridge's.

According to Simon,[54] hydrogen will, in a comparatively hort space of time, increase the emission from tantalum eated in it to a value which is very close to that obtained in he absence of hydrogen only after a very prolonged and severe utgassing treatment. Probably in this case the hydrogen imply helps to remove adsorbed oxygen, perhaps in a manner imilar to that in which nitrogen removes oxygen from barium n tungsten and apparently also from plain tungsten.

The opposite effect, viz. a depression of the emission due o hydrogen, was observed many years ago by Langmuir.[35] This was found to be only an indirect effect, however. Glowing ungsten causes hydrogen molecules that come into contact

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* For a comprehensive survey of this and other early observations on he effects of gases on thermionic emission, see O. W. Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co., 2nd edition 1921), Chapter IV.

with it to break up into atoms,[42, 36] and the atomic hydroge is a very powerful reducing agent for metallic oxides, such a tungsten oxide condensed on the walls of the bulb or film of oxide present on the lead-in wires. The resulting wate vapour, coming into contact with the hot filament, oxidize it, with liberation of hydrogen. While the bulk of the oxid formed on the filament surface immediately evaporates, monatomic film of oxygen will, except at the highest tem peratures, remain behind, depressing the emission. Langmui found the emission to remain depressed, even after the hydroge had been pumped away. When, however, the bulb containin hydrogen was immersed in liquid air, evaporation of wate vapour from its walls being thus prevented, the emissio obtained from the filament after flashing at a high temperatur was that characteristic of clean tungsten, the hydrogen n longer having any effect on it.

In contrast to Langmuir's results, Simon [55] has reporte that hydrogen enhances the emission from tungsten. N appreciable time-lag was found in his experiments, th emission returning to the value it had before admission of th hydrogen shortly after it was pumped away.

An effect of hydrogen on the emission from potassium wa observed a few years ago by Laird.[29] Observations of th thermionic activity after successive cleansings of a potassiu surface by distillation, followed by contaminations of th surface by hydrogen, led to the conclusion that the larg thermionic currents frequently obtained from potassium ar due to hydrogen contamination.

Oxygen has almost invariably been found to have a depres sing effect on thermionic and photoelectric activity. Wit the case of oxygenated tungsten we have already deal DuBridge [12] has also observed a depression of the photoelectri emission from platinum after heating in dry air. The activ constituent of the air was presumably oxygen. These tw cases are but examples of what probably occurs to a greate or lesser extent with all metals.

Water vapour, also, has generally been found to poiso the emission from metals. It is mainly for this reason tha it is so necessary to bake out all glass work at a high tempera ture in a good vacuum before thermionic or photoelectri measurements are made, for otherwise water vapour will be given off from the glass at an appreciable rate for almost indefinite periods. Probably in most cases the water vapour simply oxidizes the surface of the metal, its effect thus being the same as that of oxygen. The oxides of carbon have also been observed to have an effect similar to that of oxygen.

A depression of the emission from tungsten due to nitrogen has been reported by Langmuir.[35] There was no effect, however, until the accelerating voltage applied to the anode exceeded a certain minimum value. Langmuir has recently shown [34] that, as in the case of hydrogen, this effect is an ndirect one, and is in reality due to oxygen poisoning. When the energy of the electrons exceeds a certain value, metastable molecules of nitrogen (" active " nitrogen) are formed, and when these come into contact with oxidized electrode surfaces or with the glass walls (no matter how well these may have been baked out) reduce the metallic oxides or adsorbed moisture, liberating oxygen, which then poisons the emitter.

A remarkable empirical relationship has been found by Wilson,[59] Richardson [51] and others to hold between the A and χ of metals contaminated with various kinds and quantities of gases. This is

$$\log \mathrm{A} = \xi + \eta\chi, \quad . \quad . \quad . \quad (10)$$

where ξ and η are constants, η being positive. Examples of this are shown in Fig. 34, where the values of log A and χ ound by Langmuir,[35] DuBridge,[13] and Richardson and Young[52] or variously contaminated tungsten, platinum and potassium espectively are plotted. We have seen that the same kind of relationship holds for certain definite groups of the various cases of completed single and alternating multiple layers of barium and oxygen on tungsten investigated by Ryde and Harris.

A possible theory of such a variation of A with χ for cases f atomically thick contaminations will be considered in Chapter V. In this, the A found experimentally is assumed o be the true A, i.e. it is identified with $(1 - \bar{r})\mathrm{A}_0$. While, owever, this theory might well account for the potassium data represented in Fig. 34, if we disregard the highest point, t is certainly not possible to apply it to the corresponding data for tungsten and platinum and at the same time take A_0 to have its theoretical value, viz. 120 amp./cm.^{2}deg.^{2} since most of the values of A found for these metals exceed the theoretical A_0 by large factors. There is as yet no theory by means of which these data could be accounted for.

While, empirically, eqn. (10) describes the variation of A with χ in a large number of cases, it by no means always does so. Thus, as we have seen, when the surface concentration of barium or oxygen forming the outside of a multiple-layer

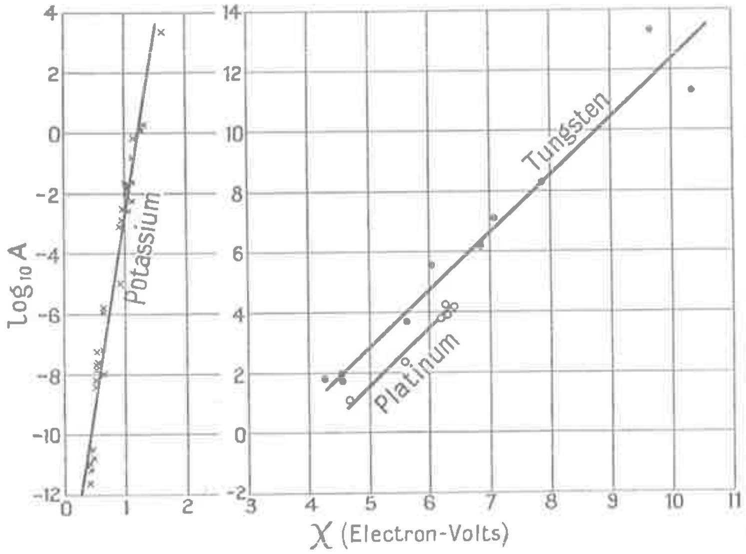

FIG. 34.—Showing approximately linear relationship between log A and χ for potassium, tungsten and platinum, variously contaminated.

contamination on tungsten is varied, log A does not var linearly with χ. For the somewhat analogous case of variations in the surface concentration of a single layer of foreig atoms adsorbed on a metal we have unfortunately not ye any very accurate experimental data.

The Condition of the Adsorbed Particles.—We hav seen that the particles at the surface of an emitter, bein subjected to asymmetric forces, must be distorted, and tha the associated polarization is an important factor contributin to the surface potential hill. This must be true whether th surface particles are of the bulk metal or are those of an adsorbed foreign material. In the latter case, the more electropositive the particles, the more we shall expect them to be distorted, and the question naturally arises whether some or all of them may not be ionized.

Now when the metal is at a high temperature, the adsorbed particles will naturally not all be in exactly the same condition at any moment, and it is perfectly feasible that some might be atoms and others ions. And from the observed fact that when adsorbed electropositive particles like cæsium evaporate, some do so as neutral atoms while others evaporate as positive ions, Becker [4] has argued that both kinds of particle must, in fact, be represented in the adsorbed film, and for one case, that of barium on tungsten, he has attempted to calculate what proportion of the particles is ionized.

This calculation is as follows : It is assumed that an adsorbed atom has no effect on the work function, the observed depression of this quantity by the contamination being due entirely to those particles that are ionized. Let the number of these per unit area be N_p. The positive charges in the plane occupied by the ions may be thought of as smeared out into a uniform sheet of charge, whose surface density is $N_p.e$. There will be an equal sheet of charge, but of opposite sign, induced on the " surface " of the metal underneath and the field E between these sheets must, therefore, by well-known electrostatic principles, be given by

$$E = 300 \,.\, 4\pi N_p \, e \text{ volts/cm.} \quad . \quad . \quad (11)$$

If the distance between the sheets of charge is l, the lowering of the work function by the positive ions must be

$$-\Delta\chi = eEl = 300 \,.\, 4\pi N_p \, e^2 l \text{ electron-volts,} \quad . \quad (12)$$

and by equating this to the observed lowering of the work function due to the contamination one may determine the value of $N_p \, l$. Hence, finally, if one knows the total number of adsorbed particles per unit area and the distance l, the fraction of the adsorbed particles that are ionized can at once be found.

We have seen that $-\Delta\chi$ for an optimum film of barium atoms on tungsten is $4{\cdot}54 - 1{\cdot}5_6 = 3{\cdot}0$ e.v. For l, Becker assumed the value $1{\cdot}53 \times 10^{-8}$ cm., which is the radius of a Ba^+ ion in a polar compound. Substituting these values in eqn. (11) one obtains $1{\cdot}1 \times 10^{14}$ for N_p. Becker took $-\Delta\chi$ to be 2·8 instead of 3·0 e.v., and this would make N_p only $1{\cdot}02 \times 10^{14}$ instead of $1{\cdot}1 \times 10^{14}$, but the difference is not important. For the maximum number of barium ions that could be packed in a square or close-packed two-dimensional lattice per unit area Becker calculated from X-ray data $1{\cdot}06 \times 10^{15}$ and $1{\cdot}22 \times 10^{15}$ respectively, i.e. something of the order of ten times the value found for N_p. Hence he concluded that roughly 10 per cent. of the adsorbed particles in a full layer are ions and the remainder atoms. And since, as the curve of Fig. 30 indicates, each barium particle is on the average about twice as effective in reducing the work function when θ is small as it is when θ is equal to 1, Becker further concluded that when the surface is sparsely covered something like 20 per cent. of the adsorbed particles are ionized. He seems, however, to have overlooked the fact that if most of the adsorbed particles are atoms, the maximum number in a single layer must be less than the maximum number of *ions*, and that therefore the proportion of particles that are ions must, for full and for sparse covering, be somewhat greater than 10 and 20 per cent. respectively.

Becker's theory is open to certain criticisms, quite apart from this slip, however. It may in the first place be questioned whether the maximum number of particles of either kind that can be adsorbed in a single layer is uniquely determined, as Becker supposed it to be, by the effective diameters of barium ions and atoms as determined from X-ray data, or whether the adsorbed particles arrange themselves, as Langmuir has assumed in the case of thorium and of cæsium on tungsten, in conformity with the underlying tungsten lattice. According to Ebert and Hartmann,[17] barium crystallizes in a body-centred cubic lattice, the lattice constant being 5·01Å. And tungsten, as we have seen, is also body-centred cubic, with a lattice constant of 3·15Å. Thus the shortest distance between barium atoms in a crystal of barium is 4·34Å., while the length of a diagonal of a face of a tungsten unit cell is 4·45Å., i.e. slightly greater. Hence if the adsorbed barium conforms to the underlying tungsten lattice there would probably be just half as many barium atoms in a full layer as there are underlying surface tungsten atoms, i.e. $7{\cdot}13 \times 10^{14}$ per cm.^{2}.

It also seems questionable whether l should really be taken as small as the effective radius of a Ba^+ ion in a polar salt. If it is assumed that an adsorbed barium particle is robbed of an electron, then, surely, this electron must revolve about the underlying tungsten nucleus, making the tungsten particle a negative ion. This negative ion will then be the "induced charge." And if it is further assumed, as tacitly it is in Becker's theory, that the barium ion is undistorted, the same assumption ought logically to be made also for the tungsten ion. Thus it would appear that the effective distance between the two sheets of charge should be taken as the sum of the radii of the barium and tungsten ions, rather than the radius of the former alone. This would make l a round 3Å. instead of the assumed 1·5Å. Taking this value for l and assuming one adsorbed barium particle to every two underlying surface tungsten particles, one finds by Becker's method that about 8 per cent. of the adsorbed particles in a full layer are ionized. It so happens that this result is not very different from Becker's.

Finally, there is the more general criticism that Becker's theory is too simple. On the one hand, an adsorbed atom, being subjected to strong asymmetric forces (strong enough to keep it adsorbed) must certainly be distorted, or, on the average, polarized, and must therefore have some effect on the work function. On the other hand, an adsorbed ion must also be distorted, and will therefore by no means be the same thing as an isolated ion in space. It is easily seen that in this case the distortion must be in such a sense as to tend to neutralize its ionization. Thus an adsorbed atom contributes more than the assumed nothing to the lowering of the work function, while an adsorbed ion contributes less than the amount assumed. And since we do not know how much more, in the one case, or how much less, in the other, the problem becomes indeterminate. It seems, then, that little, if any, useful distinction can be made between the two kinds of adsorbed particles. It would probably be more correct to say that each particle is, on the average, about one-twelfth ionized, than to say that at any moment one-twelfth of the particles are ionized.

Field Effects.—It has been known for a long time tha for relatively weak applied fields the emission from a meta having a monatomic surface contamination does not saturat nearly so well as does that from a clean metal, particularl if the contaminating layer of atoms is incomplete. This i shown, for example, by the curves of Fig. 10 and again by tha of Fig. 17. Various attempts, already briefly referred to i Chapter I, have been made to explain this phenomenon, bu so far none of them have been very successful quantitatively.

The only theory that in any way meets the case i Langmuir's "patch" theory.[37] It is assumed that most o the contamination collects into more or less definite patches the surface concentration on the remaining areas being relatively small. Let us suppose, in order to fix the ideas, tha only two surface concentrations are represented and tha the contamination is electropositive with respect to the bul metal. If the emitter is in equilibrium with an externa electron gas, the amount of work that must be done on a electron in the interior of the metal to extract it must be th same whether it makes its exit through a patch where th surface concentration is great (a "more active" patch) o through one where it is small (a "less active" patch). Thi can only be so if there are local fields which retard the exi of electrons from the more active patches and accelerate then from the less active ones, the line-integral of the field betweer the two kinds of patches being equal to their contact potentia difference. If now the equilibrium is upset by the applicatior of an electron-accelerating field, the exit of electrons from th more active patches will be greatly facilitated by the gradua neutralization of the local electron-retarding fields, while tha from the less active patches will be relatively little affected since the fields there are already electron-accelerating. Th abnormal growth of emission with field will go on until th electron-retarding fields at the more active patches ar entirely neutralized. Thereafter, the emission-field relationship will follow approximately the Schottky law. This qualitatively, is precisely what is actually observed.

A few years ago, Compton and Langmuir[10] carried out quantitative investigation of the effects of certain kinds o patches, but were unable to make their theoretical curve imitate those observed except above a certain lower limit of field strength and with assumed patches of quite improbable dimensions. Their view of the matter was substantially as follows: To each value of the applied field there corresponds, as we saw in Chapter I, a certain distance x_0 from the surface where the applied and image fields just balance one another, and this distance increases as the applied field is made weaker. Thus in the case of sufficiently weak applied fields, x_0 will be greater than the greatest distance at which the local fields due to any given system of patches are appreciable. All the charges at and near the surface may then be thought of as smeared out into uniform sheets of charge and the emitter must behave as if there were no patches, giving a normal Schottky effect. On the other hand, when the applied field is so strong that x_0 is of a lesser order than the linear dimensions of the patches, we shall again have a normal Schottky effect. The Schottky line for strong fields must, of course, lie appreciably higher than that for weak fields, as will be obvious on consideration of the changes with applied field of the resultant potential hills in the regions of the two kinds of patches. At intermediate applied fields there must be a transition from the lower to the upper Schottky line. Thus if AB and CD in Fig. 35 are these two lines, we shall expect the $(\log i)$-$\sqrt{E}$ relationship for the patchy surface to be represented by a curve qualitatively like AGHKD. We see that the part HKD of this curve is similar to the experimental curve of Fig. 17.

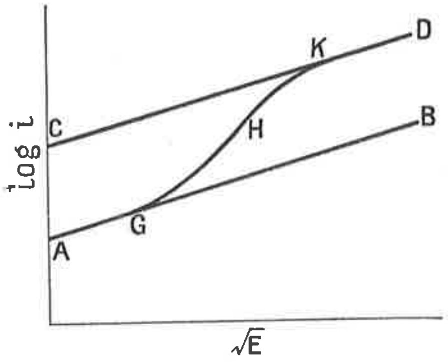

Fig. 35.—Theoretical relationship between $\log i$ and $\sqrt{E}$ for a patchy surface.

The curve of Fig. 17, which is typical of those obtained with partially covered surfaces, coincides with the Schottky line for applied field strengths above about 20,000 volts per cm. For this E, the value of x_0 is, by eqn. (79) of Chapter I, about $1 \cdot 3 \times 10^{-6}$ cm., and since, according to the above theory, this must be small compared with the linear dimensions of the patches, we may take these to be something like 10^{-5} cm. across and each to contain, therefore, something like 10^5, or at the very least 10^4, adsorbed atoms. This is a serious difficulty of the theory, for the spontaneous formation of two-dimensional " crystals " of such a size seems hardly reconcilable with the repulsions between neighbouring adsorbed atoms for which, as we have seen, there is a certain amount of evidence.

Now let us consider the lower part of the theoretical curve of Fig. 32. With patches of the assumed size the field strength corresponding to the point G on this curve can hardly be greater than 500 volts per cm. and it may perhaps be as small as 100 volts per cm. In the case of ordinary electrode dimensions these fields would, if there were no space charge, occur at the very low anode potentials of about 10 volts and 2 volts respectively. On account of space charge the corresponding anode potentials will in general be somewhat higher. In any case, however, owing to the complications arising out of space charge and, as we saw in Chapter I, also surface roughness, it would be a matter of some difficulty to determine the precise nature of the $(\log i)$-$\sqrt{\mathrm{E}}$ relationship for these low fields. While a relationship such as is indicated by the part AGH of the theoretical curve has never actually been observed, it has also not, so far as the author is aware, been established experimentally that such a relationship does not exist. Thus the large scale it is necessary to assume for the patchwork, although a serious difficulty of the theory, is, so far as we know, also the only difficulty.

LITERATURE.

1. M. R. Andrews, *Phys. Rev.*, **33,** p. 454, 1929.
2. A. E. van Arkel, *Physica*, **3,** p. 76, 1923.
3. J. A. Becker, *Phys. Rev.*, **28,** p. 341, 1926.
4. J. A. Becker, *Trans. Am. Electrochem. Soc.*, **55,** p. 153, 1929.
5. J. A. Becker and D. W. Mueller, *Phys. Rev.*, **31,** p. 431, 1928.
6. W. H. Brattain and J. A. Becker, *Phys. Rev.*, **43,** p. 428, 1933.
7. N. A. de Bruyne, *Proc. Cambr. Phil. Soc.*, **25,** p. 347, 1929.
8. W. G. Burgers and J. A. M. van Liempt, *ZS. f. anorg. u. allgem. Chem.*, **193,** p. 144, 1930.
9. P. Clausing, *Physica*, **7,** p. 193, 1927.
10. K. T. Compton and I. Langmuir, *Rev. Mod. Phys.*, **2,** p. 123, 1930.

1. C. Davisson and L. H. Germer, *Phys. Rev.*, **30**, p. 705, 1927.
2. L. A. DuBridge, *Phys. Rev.*, **29**, p. 451, 1927.
3. L. A. DuBridge, *Phys. Rev.*, **31**, pp. 236 and 912, 1928 ; *Proc. Nat. Acad. Sci.*, **14**, p. 788, 1928.
14. S. Dushman, *Rev. Mod. Phys.*, **2**, p. 311, 1930.
15. S. Dushman, D. Dennison and N. B. Reynolds, *Phys. Rev.*, **29**, p. 903, 1927.
16. S. Dushman and J. W. Ewald, *Phys. Rev.*, **29**, p. 857, 1927.
17. F. Ebert and H. Hartmann, *ZS. f. anorg. u. allgem. Chem.*, **179**, p. 418, 1929.
18. J. M. Eglin, *Phys. Rev.*, **31**, p. 1127, 1928.
19. G. R. Fonda, A. H. Young and A. Walker, *Physics*, **4**, p. 1, 1933.
20. A. Gehrts, *ZS. f. techn. Phys.*, **12**, p. 66, 1931.
21. W. Geiss and J. A. M. van Liempt, *ZS. f. anorg. u. allgem. Chem.*, **168**, p. 107, 1927.
22. H. E. Ives, *J. Franklin Inst.*, **201**, p. 47, 1926.
23. H. A. Jones and I. Langmuir, *Gen. El. Rev.*, **30**, pp. 310, 354 and 408, 1927.
24. T. J. Killian, *Phys. Rev.*, **27**, p. 578, 1926.
25. K. H. Kingdon, *Phys. Rev.*, **24**, p. 510, 1924.
26. K. H. Kingdon and I. Langmuir, *Phys. Rev.*, **22**, p. 148, 1923.
27. K. H. Kingdon and I. Langmuir, *Phys. Rev.*, **21**, p. 380, 1923.
28. K. H. Kingdon and I. Langmuir, *Phys. Rev.*, **23**, p. 112, 1924.
29. H. R. Laird, *Phys. Rev.*, **34**, p. 463, 1929.
30. I. Langmuir, *J. Am. Chem. Soc.*, **38**, p. 2221, 1916.
31. I. Langmuir, *Phys. Rev.*, **22**, p. 357, 1923.
32. I. Langmuir, *J. Am. Chem. Soc.*, **54**, p. 1252, 1932.
33. I. Langmuir, *J. Am. Chem. Soc.*, **54**, p. 2798, 1932.
34. I. Langmuir, *Phys. Rev.*, **37**, p. 1006, 1931.
35. I. Langmuir, *Phys. Rev.*, **2**, p. 450, 1913.
36. I. Langmuir, *J. Am. Chem. Soc.*, **37**, p. 417, 1915 ; **38**, p. 1145, 1916.
37. I. Langmuir, *Gen. El. Rev.*, **23**, pp. 503 and 589, 1920.
38. I. Langmuir and K. H. Kingdon, *Phys. Rev.*, **34**, p. 129, 1929.
39. I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc.* (*A*), **107**, p. 61, 1925.
40. I. Langmuir and K. H. Kingdon, *Phys. Rev.*, **21**, p. 381, 1923.
41. I. Langmuir and K. H. Kingdon, *Science*, **57**, p. 58, 1923.
42. I. Langmuir and G. M. J. Mackay, *J. Am. Chem. Soc.*, **36**, p. 1708, 1914.
43. I. Langmuir and W. Rogers, *Phys. Rev.*, **4**, p. 544, 1914.
44. I. Langmuir and J. B. Taylor, *Phys. Rev.*, **40**, p. 463, 1932.
45. L. L. Lockrow, *Phys. Rev.*, **19**, p. 97, 1922.
46. E. Meyer, *Ann. d. Phys.*, **4**, p. 357, 1930.
47. H. Nelson, *Physics*, **1**, p. 84, 1931.
48. W. B. Nottingham, *Phys. Rev.*, **35**, p. 1128, 1930.
49. W. B. Nottingham, *Phys. Rev.*, **41**, p. 793, 1932.
50. N. B. Reynolds, *Phys. Rev.*, **35**, p. 158, 1930.
51. O. W. Richardson, *Proc. Roy. Soc.* (*A*), **91**, p. 524, 1915.
52. O. W. Richardson and A. F. A. Young, *Proc. Roy. Soc.* (*A*), **107**, p. 377, 1925.
53. W. Schottky, *Ann. d. Phys.*, **62**, p. 142, 1920.
54. H. Simon, *ZS. f. techn. Phys.*, **8**, p. 434, 1927.
55. H. Simon, *ZS. f. techn. Phys.*, **5**, p. 221, 1924.
56. F. Simon and E. Vohsen, *ZS. f. phys. Chem.*, **133**, p. 165, 1928.
57. C. J. Smithells, *J. Chem. Soc.*, **121**, p. 2236, 1922.
58. L. Tonks, *Phys. Rev.*, **38**, p. 1030, 1931.
59. H. A. Wilson, *Phil. Trans.* (*A*), **208**, p. 247, 1908.

CHAPTER IV.

OXIDE CATHODES.

An oxide cathode may be defined as the system that results when a metal is coated with one or more of the alkaline earth oxides and the whole is then subjected to a suitable "activating" or "forming" treatment.

Oxide cathodes are remarkable both for their high thermionic activity and for their variability. Thus, for example, one whose coating consists largely or entirely of barium oxide will, under the most favourable conditions, give as much as $\frac{1}{10}$–1 amp./$cm.^2$ emission at a barely visible red heat.[49, 50] But the emission is very sensitive both to the residual gases to which the cathode is exposed and to its past history. The phenomena exhibited by these cathodes are so complex, that although they have been the object of serious study since their discovery by Wehnelt [51] in 1903, it is only quite recently that anything approaching a complete theory of their action has been worked out.

The variation of the emission of oxide cathodes with temperature is of the same type as that of other thermionic emitters, obeying Richardson's formula. There is, however, little approach to agreement regarding the values of the thermionic constants. These undoubtedly vary considerably with the physical condition as well as with the chemical nature of the constituent parts of the cathodes. The earliest published values of the work functions obtained with the oxides coated on platinum or platinum-iridium cores were all of the order of 3—4 e.v.[51, 32, 13, 46] Recently, however, much lower values have been obtained. For example, those found by Espe [16] in very careful measurements made in 1926 were 0·99 e.v. for BaO, 1·27 e.v. for SrO and 1·77 e.v. for CaO, all on a platinum-iridium core. One of the main reasons for this change is undoubtedly the great advance made in vacuum technique in the intervening period.[24] The sensitivity of oxide cathodes to vacuum conditions is well illustrated by an experiment of Koller,[36] in which, by merely exposing an activated coated filament to oxygen at 1/200 mm. pressure for a short time, he changed the work function from 1·04 to 3·10 e.v.

Another condition with which the thermionic properties of an oxide cathode may vary is the temperature.[11, 17] Davisson and Germer [11] found the sudden change of emission accompanying an alteration in temperature to be followed by a " creep " to a new equilibrium value. This is illustrated by the curve of Fig. 36, which was obtained by them. After the emission from a filament heated by a current of 1·01 amp. had become steady, the heating current was suddenly lowered to 0·81 amp. The emission thereupon gradually increased from an initial value at the new temperature in the neighbourhood of 0·285 mA. to a final steady value of 0·485 mA. The curve shows all but the last part of this increase. Davisson and Germer also found that the Richardson line representing the initial emissions after sudden changes from a given temperature differed in slope from that representing the final emissions sometimes by as much as 25 per cent. That the former gave the true work function is indicated by the fact that

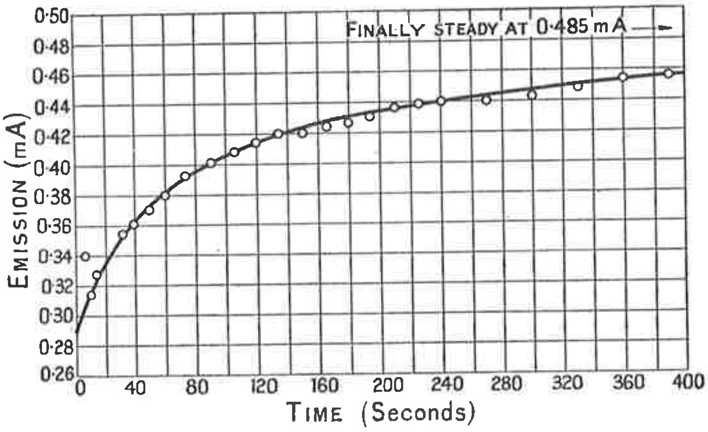

FIG. 36.—Gradual change in thermionic activity of an oxide cathode following a change in temperature.

it agreed perfectly with the value determined calorimetrically at the same temperature. Recent calorimetric measurements by Heinze [27] also point to a temperature dependence of the condition of oxide cathodes, the measured work functions having been found to increase quite appreciably with temperature.

Preparation of Oxide Cathodes.—The efficiency of a cathode of given chemical ingredients seems to depend to some extent on the method by which the coating has been applied to the core. For a full description of the various methods employed the reader should consult an article by Statz.[49] We shall confine ourselves here to a brief sketch.

The core wire or ribbon may be drawn through or dipped into the coating material in the form of alkaline earth carbonate, hydroxide, nitrate, peroxide or oxide, or a mixture of two or more of these, held either in suspension or in solution in a suitable "carrier," e.g. water or amyl acetate. Alternatively, the coating material, together with a "binder," may be sprayed on to the core. If the compound chosen is the nitrate, the carrier is sometimes dispensed with, the core being simply drawn through a bath of the molten salt. If the core metal is such that it is not easily oxidized, a length of it may be kept red-hot in air by passing a current through it and a crystal of nitrate or finely divided alkaline earth material contained in a stick of paraffin wax, sealing wax or resin drawn along it.

If the coating material is first applied to the core in a form other than the oxide it is necessary to break it down to the oxide subsequently by a suitable heat treatment, whereupon, incidentally, any remaining carrier or binder material is driven off and the coating is rendered firmly adherent to the core. This operation is known as "sintering." In the case of an easily oxidizable core metal this must, of course, be carried out either in a vacuum or in a non-oxidizing atmosphere. If the coated wire is to be exposed to air for any length of time after sintering it is best to sinter in carbon dioxide and subsequently break down the resulting carbonate in the vessel in which the cathode is to be used while this is being pumped. For the preparation of cathodes on a small scale a convenient method is to dip the wire once or several times in a water suspension of a finely divided (ball-milled) alkaline earth carbonate, drying after each dip. The wire is then given a final dip into molten paraffin wax, which, on solidifying, protects the coating from mechanical injury. The cathode is now ready for mounting. The wax all disappears in the " bake " on the pump, and when the wire is heated to dull redness the carbonate decomposes, leaving the oxide as a hard, tenacious coating.

Arnold[2] has found that if, in the process of coating a platinum-iridium core with barium oxide, the sintering is done in air, there is formed next to the core " a firmly adhering layer . . . due to chemical reactions between the coating and the core." Analysis showed the compound present in largest amount in this layer to be barium platinate ($BaPtO_3$). Becker[4] states that these compounds are decomposed when the cathode is subsequently heated to a high temperature in a vacuum and that " this leaves a finely dispersed metal mixed with the oxides and gives the filaments a greyish appearance."

While coatings prepared in the above manner are usually of the order of 10,000 to 50,000 molecules thick, it is important to note that there is no fundamental virtue in having so great a thickness. A film of oxide distilled on to a clean wire from a neighbouring coated wire and consisting of only a single closely packed layer of molecules, or even less, has been found to give an emission by no means inferior to that obtainable from " bulk " coatings.[12]

A technique for the preparation of oxide cathodes which is quite different from those discussed above is that usually known as the " barium-vapour process." The filament, which is of tungsten, is not provided with any alkaline earth material at all before it is mounted in its bulb with the other electrodes, but is, instead, superficially oxidized. One of the other electrodes, usually the anode, is coated on the side facing the filament with barium azide (BaN_6). This decomposes during the early part of the bake (as soon as its temperature reaches about 160°C.), giving off nitrogen, which is pumped away, and leaving behind a black mass of finely divided metallic barium. At this stage the barium generally still contains a considerable quantity of nitrogen in an occluded form, most of which is, however, readily driven off by heating the anode to dull redness for a few seconds, after which the tube may be sealed off from the pump. By now keeping the anode at or just below a visible red heat, and simultaneously heating the filament to bright redness, its coating of tungsten oxide is reduced by barium vapour, barium oxide being formed in its place. This is intimately mixed with finely divided reduced tungsten, which gives it a black or greyish appearance. The anode may be kept hot during the reduction either by high-frequency induction or by electron bombardment from the filament.

The thermionic constants of barium-vapour-process cathodes have been determined by Espe.[18] The results of two such determinations were $A = 1 \cdot 1 \times 10^{-1}$ amp./cm.^{2}deg.^{2}, $\chi = 1 \cdot 09$ e.v. and $A = 3 \cdot 0 \times 10^{-1}$ amp./cm.^{2}deg.^{2}, $\chi = 1 \cdot 10$ e.v. These constants represent a much higher emission than those obtained earlier by Espe for a barium oxide on platinum-iridium "paste" cathode, viz. $A = 3 \times 10^{-4}$ amp./cm.^{2}deg.^{2}, $\chi = 0 \cdot 99$ e.v. During the last few years, however, "paste" cathodes have been very considerably improved, and the emissions now obtained from them are in no way inferior to those of vapour-process cathodes.

Activation and Deactivation.—To activate or "form" an oxide cathode it is sometimes sufficient to heat it to bright redness for a minute or two.[22, 26, 39, 36] This is particularly effective if the core is alloyed with a small percentage of some reducing metal. In general, however, a much better activation is secured by drawing a strong electron current from the cathode simultaneously with heating it.[4, 17, 43, 45] The time necessary to develop the full emission depends upon the temperature, the space current taken, the thickness of the coating and the residual gases to which the cathode is exposed. It may be as short as a few minutes or as long as several hours, or even days. It is most rapid in the case of thinly coated cathodes held at a relatively high temperature in a good vacuum whilst a vigorous electron current is drawn. The dependence of the growth of the emission (measured under given conditions) on the temperature and the space current taken is well illustrated by the curve of Fig. 37 obtained by Espe.[17] This represents the emission as a function of time as the temperature and anode potential are changed in steps.

There is some want of agreement as to whether the growth of emission is due to a change in the emission constant, or in the work function, or both together. Richardson lines plotted by Espe[17] at various stages of activation are all parallel, indicating that A alone changes. On the other hand, Detels[14] and Huxford[31] have found that activation is accompanied by a steady decrease of both constants, there being, in the case of Huxford's data, a not quite linear relationship between log A and χ.

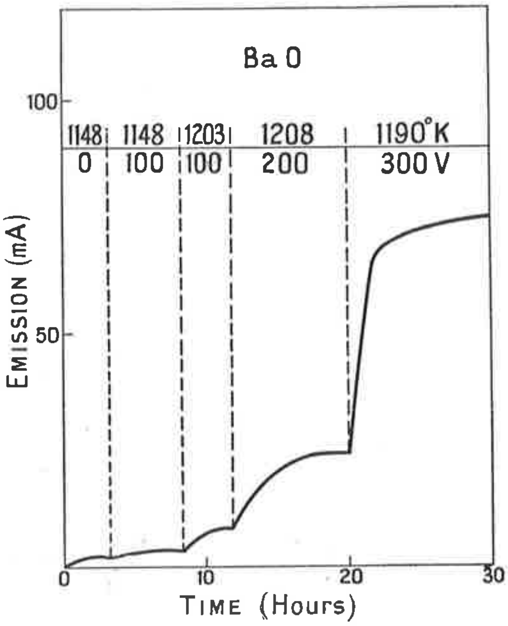

FIG. 37.—Time changes in the activity of an oxide cathode resulting from changes in its temperature and in the anode potential.

In the early stages of activation with space current, gas is evolved from the cathode which Detels[14] has succeeded in identifying spectroscopically as oxygen. Its initial rate of evolution has been observed by Horton[29] to be within 8 per cent. of that required by Faraday's law on the assumption that the coating conducts the thermionic current electrolytically. The oxygen yield falls off as activation proceeds, however, and finally becomes quite negligible. According to Becker,[4] a well-aged cathode can be made to evolve oxygen only by drawing a strong electron current from it at not too low a temperature. If the temperature is also not too high (not much more than about 800°K.) the oxygen comes off *alone*, i.e. unaccompanied by alkaline earth metal.

From the fact that oxygen is lost by a cathode during activation, it is to be inferred that an activated cathode must differ from an unactivated one in being relatively richer in alkaline earth metal. It has, indeed, been shown by Becker that if a well-activated cathode whose coating consists of mixture of barium and strontium oxides is " flashed " at abou 1250°K., barium evaporates from it, but that none is obtainable at the same temperature from an unactivated cathode (Incidentally, Gehrts [23] has recently confirmed that bariur practically unaccompanied by strontium evaporates from a over-heated active mixed BaO-SrO-coated cathode by observing spectroscopically the glow produced in the vaporize metal by an electric discharge.) And such high-temperatur flashing has been observed by a number of investigators t result in a loss of activity.

An active cathode may be deactivated not only by flashing but also by exposing it to an electronegative gas, such a oxygen. During such exposure the excess alkaline eart metal must necessarily become oxidized and the cathode revert at least chemically, to its original, inactive condition.

The Free Barium Theory.—We have seen that an activ cathode differs from an inactive one in the possession o excess barium * and that if this excess is destroyed, either b evaporation or by oxidation, the activity is lost. The onl natural conclusion to draw from these facts is that it is to th presence of the excess barium that the activity is due. Thi theory was first advanced by Koller [36] and is now generall accepted. Further items of evidence supporting it are th following: (1) Barium, distilled on to an inactive cathode activates it.[4] (2) Barium has been detected spectroscopicall in the cores of activated, but not of unactivated filaments. (3) Higher emissions and longer lives are obtainable fron coated nickel alloyed with barium than from pure nicke similarly coated.[7]

The barium obviously cannot be present in the cathod in ordinary bulk form, for then it would have a vapour pressur in the normal operating range of temperatures of the orde of some centimetres of mercury. The actual barium vapou pressure is, of course, of a much lower order than this. I is, in fact, so low that the useful lives of oxide cathodes unde normal operating conditions are of the order of hundreds o

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* In what follows barium will be written for short where barium and/o strontium and/or calcium is meant.

ousands of hours. In what form can the excess barium be, en ? It has been suggested that it combines chemically ith the original oxide, forming a suboxide.[41] Careful X-ray nalysis of an active cathode fails to support this suggestion, owever ; the only lines that appear are those of the core nd of the normal monoxide.[8] There remain one or more of he following possibilities : (1) The barium may be dissolved the core ; (2) it may be dissolved in the coating ; (3) it ay be adsorbed as a film of a monatomic order of thickness n the surface of the core and/or coating. That barium ay be dissolved in the core is, as we have seen, indicated y spectroscopic analysis. The question of its solution in he coating will be discussed later. And its existence as a onatomic adsorbed film, at least on the surface of the coating, is the natural explanation of the high thermionic activity f cathodes containing free barium. We shall see presently hat there is strong evidence in favour of this in the dependnce of the emission from an initially inactive cathode on the uantity of barium distilled on to it from an external source.

Now let us consider the question of how much barium there ay be in the adsorbed form. The barium is first formed rom the oxide by chemical reduction * and in general subequently also by electrolysis, first making its appearance at he core/coating interface and thence diffusing to the outside f the coating. In the equilibrium condition, then, there must e adsorbed barium on all the free faces of all the crystals of he coating, and the core metal surface may perhaps be imilarly covered. Thus it is plain that the total quantity of dsorbed barium may greatly exceed that which would suffice to cover the macroscopic superficial area of the cathode. Unfortunately we have no very definite knowledge concerning the sizes of the oxide crystals or of their relation to one another.

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* It has also been suggested [22] that barium may be produced in the athode by thermal dissociation of the oxide. S. Dushman [16] has pointed ut, however, that it is highly improbable that this can occur below the melting-point of nickel (a core metal in common use), calculations having shown that " with the most favourable assumptions the dissociation pressure at $T = 1000°K$. would be less than 10^{-40} atm. On the other hand, it is probable that there is a reduction of BaO by the metal of the core, which would be analogous to the reduction of ThO_2 in tungsten filaments by the tungsten atoms. It would not be necessary to have the reaction occur to any greater extent than the reduction of a very small fraction of the barium oxide present."

It has, however, been shown by X-ray analysis of an activ coating[8] that no important fraction of the crystals have linea dimensions less than 10^{-5} cm. or greater than 10^{-3} cm. Thu remembering that each crystal has six faces and assuming tha each face is a freely exposed surface, it may readily be ca culated that of all the barium atoms (combined and u combined) in the coating the proportion adsorbed on crysta faces must be between 0·05 and 0·0005 per cent. If not a the crystal faces are free, the proportion may be less. In an case, 0·05 per cent. must be regarded as the upper limit.

Becker has found that the quantity of barium that coul be distilled from a well-activated filament whose coating wa about 20,000 molecular layers thick without appreciabl affecting its emission was as much as hundreds of times tha which would have covered the macroscopic surface area wit a single layer of atoms, that is to say, several per cent. of th quantity originally present (combined with oxygen) in th coating. Unless there was a continual formation by reductio of fresh barium during the flashing—which is, of course, possibility—this can only mean that in addition to the adsorbed barium there must have been a considerable " reservoir " of dissolved barium in the core and/or coating from whic the surface barium was replenished as it evaporated. Th existence of such a " reservoir " would account for a phenomenon reported by Koller[36] and Espe,[17] viz. that the emissio from a cathode which has been deactivated by excessiv flashing may often be recovered subsequently by holding th cathode for some time at a much lower temperature. Th probable explanation is that at the lower temperature fres barium diffuses to the emitting surface to take the place o that removed by flashing, just as thorium does in the cas of thoriated tungsten.

The dependence of the emission of an initially rather inactive coated filament upon the quantity of barium distille on to it has been studied by Becker.[4] The filament was firs glowed for several minutes at about 1300°K. in order to partially deactivate it. It was then held at a much lower temperature, viz. 600°K., and exposed to a constant supply o barium from a neighbouring active filament heated to 1460°K The emission from the test filament was observed as a function f time. The kind of relationship found is shown in the part B of the curve in Fig. 38. Upon the supply of barium now eing stopped and the filament held at the temperatures 25°, 710°, 800° and 890°K. in succession the further dependnce of the emission on the time was found to be represented y the parts of the curve BC, CD, DE and EF respectively.

It will be noted that the general form of this curve is similar that of Fig. 27, which shows the analogous case of tungsten xposed to a source of barium. It undoubtedly also has a milar explanation, except in this one particular, that whereas the barium-on-tungsten experiments the time changes ccurring after the cut-off of the barium supply were due to e evaporation of barium, in the present case the temperares were far too low for appreciable evaporation to have ccurred. The corresponding time changes must therefore ave been due, as Becker has shown, to the removal of barium om the emitting surface by diffusion. The exact mechanism the diffusion is open to question. It may be a mere spreadg of the barium over the crystal surfaces or a diffusion of

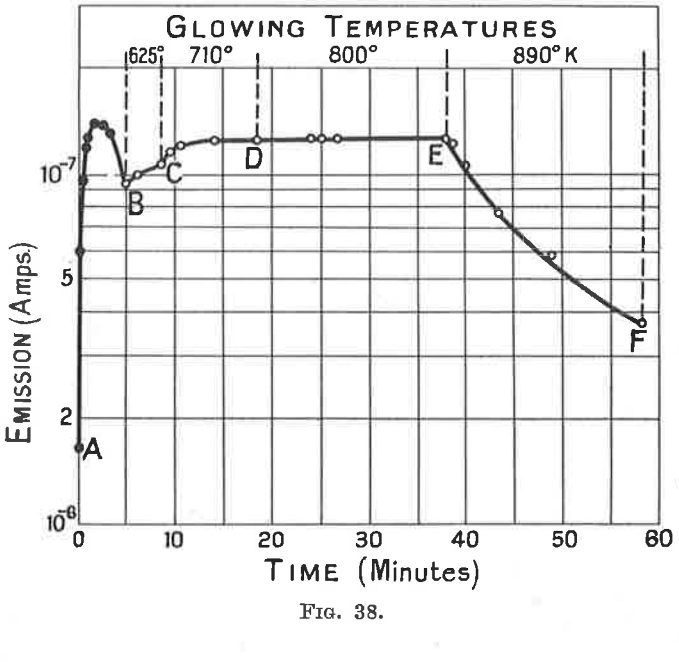

FIG. 38.

the surface barium into the interior of the oxide crystals and/c core.

A rather surprising quantitative result is that the amour of barium received by the filament up to the time of the firs maximum was only about $\frac{1}{14}$ that which would have bee necessary to cover the macroscopic surface area with on complete layer of atoms, and consequently an even lesse fraction of what would have been required to completely cove the microscopic area. As Becker has pointed out, this surel can only mean that in the initial, comparatively inactive stat the emitting surface was already *almost* completely covere

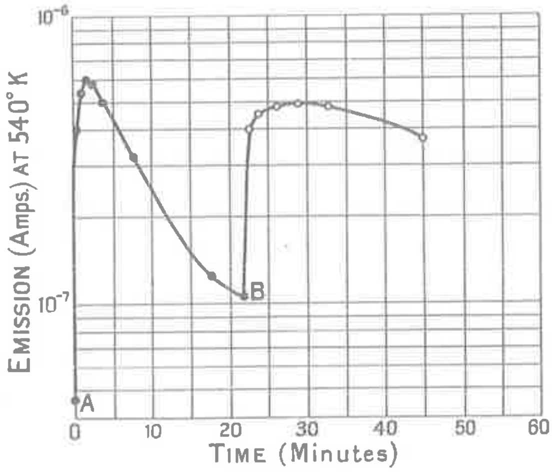

Fig. 39.

with barium. The result is instructive in that it indicat that the emission must be extraordinarily sensitive (at an rate at low temperatures) to slight changes in the surfac concentration of barium. The difficulty of greatly diminishir the concentration of surface barium by flashing would be e plained by the existence of an equilibrium relationship betwee this concentration and that in the reservoir, such that th former is not very sensitive to changes in the latter.

Barium may be brought to the emitting surface not onl by distillation from an external source but also by electrolysi In Fig. 39 are shown the results of an experiment by Beck in which this was done. The test filament was coated wit mixture of barium and strontium oxides and held at a low emperature while electrons were sent into it from an external ource, the outside of the coating thus being the electrolytic athode. The activity was found thereby to rise to a sharp naximum and then to fall to a much lower value. This is hown by the part AB of the curve. Upon now stopping the upply of electrons and raising the filament temperature to 300°K., the activity rose to a second maximum, after which t slowly diminished again. Thus qualitatively we have once more the type of behaviour shown by tungsten exposed to a ource of barium. Unfortunately here, as in the condensation experiment, the filament was initially in a not very inactive condition. But from a similar experiment performed with a strontium-oxide coated filament which was initially almost completely inactive, Becker found that in order to establish the maximum activity roughly 200 times as many electrons had to be sent into the filament as would, according to Faraday's law, have electrolytically liberated sufficient strontium to cover the macroscopic surface area of the coating with a complete layer of strontium atoms. From this result he has concluded that Faraday's law does not apply to the conduction of electricity through the alkaline earth oxides, only a relatively insignificant fraction (about $\frac{1}{200}$ in the present case) of the current being carried by ions, and the remainder by electrons.

Life.—After a certain time of burning, an activated oxide cathode begins progressively to lose emission. The variation with burning temperature of the rate of loss of the emission measured at a given test temperature is extremely rapid. Thus in the case of a filament coated with barium and strontium oxides in about equal proportions the rate of loss is roughly doubled for every 2 per cent. increase in the temperature.

We have already seen that high-temperature flashing causes some of the free barium, to which the thermionic activity is due, to evaporate. Evaporation is a process whose speed always varies very strongly with temperature, and, as the same thing is true of the life of oxide cathodes, it is natural to suppose that the loss of emission during life is due simply to the loss by evaporation of barium. On this assumption we should expect a cathode which has lost emission on account of thermal treatment, but which still retains the bulk of its coating, to be in the same condition as an unformed or only partially formed cathode, so that it should be possible to fully restore the emission by re-forming. It has in fact been found by Benjamin and Rooksby [8] that the emission from a filament coated either with BaO or with SrO may be repeatedly restored by this means after its loss due to high-temperature flashing.

It has long been known, however, that in the case of the cathodes in most widespread commercial use, viz. those coated with a mixture of barium and strontium oxides, the emission cannot be restored by re-forming after normal life failure. Also, if the emission of such a cathode has been destroyed by high-temperature flashing, it can, in general, be only partially restored by repeating the forming process, and if it is flashed several times in succession the recoverable emission is found to be less and less after each flashing. It would appear, then, that in the case of mixed oxide coatings something other occurs than mere evaporation of barium.

The problem of the irreversibility of the loss of emission from mixed-oxide cathodes has been studied by Benjamin and Rooksby.[8] X-ray examination of these oxides by the Debye-Scherrer powder method reveals the fact that when derived by decomposition from a sintered mixture of finely divided carbonates they generally form a solid solution in one another, for the diffraction pattern is of the same type as for either oxide alone, but the positions of the lines are intermediate between those for barium oxide and those for strontium oxide.* The lines move continuously from the positions characteristic of pure barium oxide to those characteristic of pure strontium oxide as the proportion of strontium oxide is increased from 0 to 100 per cent. Thus if the law connecting the positions of the lines with the proportions of BaO and SrO in the coating is known, the measurement of the former is a convenient method of determining the latter. Assuming the position of any given line to be a linear function of the molecular proportion of either oxide in the coating, Benjamin and Rooksby have used this method for the examination of filaments before and after activation and also after irreversible loss of emission

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* It has been found [9] that a sufficient, though not a necessary condition for the formation of a solid solution of oxides is their derivation from a solid solution of carbonates.

due to flashing. In an independent paper, Burgers[10] has shown that the law connecting line positions with molecular proportions of BaO and SrO is indeed linear.

Whilst Benjamin and Rooksby could detect no appreciable difference between the X-ray patterns of activated and of unactivated filaments, they found that flashed filaments had relatively less barium oxide in their coatings than comparable filaments that had not been flashed. The same preferential loss of barium oxide from the coating was found in the case of a filament which had been run for several hundred hours at 1100°K. Burgers,[10] in observations on coatings about 40 times as thick as those of Benjamin and Rooksby, found a similar loss by evaporation of BaO from the outermost parts of the coating, but, owing to the slowness of diffusion, not from the more deep-seated parts.

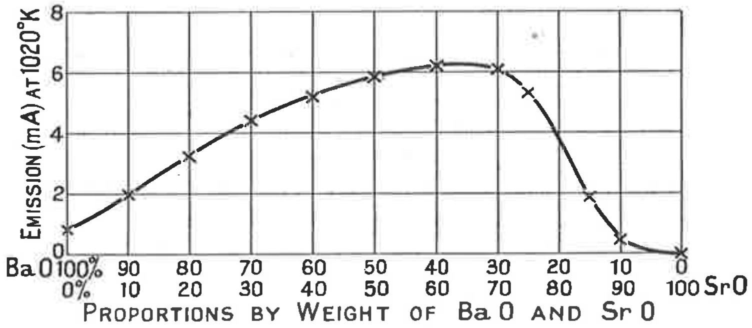

Fig. 40.—Variation with coating composition of the emission from a BaO-SrO coated cathode.

Quantitatively, the preferential loss of barium oxide from the coating is such that it probably accounts for the whole of the observed irreversible loss of emission. Benjamin and Rooksby have measured the emissions at 1020°K. (the usual running temperature) obtained after forming from a number of nickel filaments, of 0·044 mm. diameter, 20 mm. length, coated along the central 10 mm. to a thickness of about 4μ with BaO and SrO in various proportions. Their results are plotted in Fig. 40.* It is seen that there is a fairly flat maximum

* The curve published by Messrs. Benjamin and Rooksby was for 68 mm. filaments. The corresponding curve of Fig. 40, which is for 20 mm. filaments de-coated at the ends, has been plotted from data since supplied by them to the author.

at about 40%BaO-60%SrO by weight. A filament having the above dimensions and coated with 43%BaO-57%SrO by weight gave 7 mA. after forming and was then flashed for several one-minute intervals at 1600°K., being re-formed and tested for emission after each flash. Finally it gave only 0·2 mA. at the testing temperature and the composition of its coating was then redetermined by the X-ray method. The result obtained was 9%BaO-91%SrO by weight. According to the curve of Fig. 40, the composition corresponding to 0·2 mA. emission is 7%BaO-93%SrO. This differs from that found by X-ray analysis by less than the possible combined error of the latter and of the emission curve.

Benjamin and Rooksby have also found that when a filament initially having a coating of 80%BaO-20%SrO loses BaO through heat treatment, its emission does not immediately begin to fall, but first rises to a maximum. From the known relationship between emission and coating composition, this is precisely what one would expect.

It is interesting to note that a comparison between the losses in weight of coating suffered by filaments during flashing and the corresponding changes in the relative proportions of BaO and SrO showed that practically only BaO was lost. Of course at sufficiently high flashing temperatures there must be an appreciable evaporation of SrO also.

In a more recent publication,[9] Benjamin and Rooksby have shown that in certain cases where the oxides are obtained by decomposition of simple mixtures of the carbonates, the final oxide coating may consist, not of a single solid solution of BaO and SrO in one another, but of two such solutions, one relatively richer in BaO than the other. Such coatings gave lower emissions than they would have done had they consisted of a single solid solution. This is, of course, what was to be expected, in view of the fact that except at the extreme ends, the curve of Fig. 40 is everywhere convex upwards. By suitable heat treatment the two solutions may be converted into a single one, and Benjamin and Rooksby have shown that when not too much BaO is lost in the process, this gives rise to an increase in the emission, as it should do.

Effects of Gases.—The effects of various gases on the emission from oxide cathodes have been investigated by

Fredenhagen,[20] Germershausen,[25] Arnold,[2] Koller,[36] Rothe,[45] Macnabb,[40] Reimann and Murgoci,[43] and Benjamin and Rooksby.[8] Arnold found the commoner gases to bring about quite large changes in the emission at pressures of the order of $\frac{1}{1000}$ mm. One of the most harmful of these is oxygen, particularly if the cathode is heated during its exposure, when it may be difficult or impossible subsequently to recover the emission in a good vacuum. Water vapour also depresses the emission. Carbon dioxide is reported by Arnold to "poison" the emission, but Koller and Macnabb both state that bombardment of the cathode by positive ions produced in carbon dioxide is actually beneficial. The ions produced from carbon monoxide, hydrogen and argon are, according to Koller, similarly beneficial, sometimes permanently enhancing the emission by a factor of 10–100. On the other hand, the author has observed that whilst a short bombardment by the ions produced from carbon monoxide frequently enhances the emission somewhat, a long-continued bombardment invariably results in deactivation. Possibly this is at least partially due to oxygen poisoning, for a certain amount of disintegration of carbon monoxide molecules into their constituent atoms is known to take place in an ionizing discharge.[28] With regard to hydrogen, the majority of investigators are agreed that it tends to enhance the emission. Both Fredenhagen and Arnold have observed that a small quantity of hydrogen in contact with a cathode of abnormally low emission (e.g. one that has been partially poisoned) may have the effect of restoring it to a normal condition. The same has been found by the author to be true of nitrogen. Nevertheless, long-continued bombardment by the ions of either of these gases ultimately results in partial poisoning. In addition, bombardment by the ions of mercury and of the inert gases when their velocity exceeds 20–25 volts has been found by Hull[30] to destroy the emission. Probably here the action is simply one of sputtering of the emitting barium film.

From these results it appears that some gases may either increase or decrease the emission, according to the state of the cathode and the conditions of exposure. It should be mentioned that no treatment with a gas has been found that will make a cathode more active than when correctly activated and used in the best possible vacuum. The only effect (if any) that a gas can have on such a cathode is to lower the emission. The effect is not always chemical. Sufficiently fast positive ions, however chemically indifferent, must have the effect of sputtering off the film of barium at the emitting surface, and so of deactivating the cathode. On the other hand, if the cathode has been activated and operated under such imperfect conditions that it is partially poisoned, positive-ion bombardment may well have the effect of sputtering off the harmful contamination and so bring about an increase in activity. This would appear to be the explanation of the beneficial action of the passage of an ionizing discharge in carbon monoxide, carbon dioxide, hydrogen and argon observed by Koller. Finally, it seems not improbable that the enhancement of the emission from a partially poisoned cathode obtained on exposure (without bombardment) to nitrogen or hydrogen is due to the same thing as in the case of oxygen-poisoned W-Ba exposed to nitrogen, viz. a stripping off by the gas of the poisoning oxygen layer.

In many cases a poisoned cathode may have its activity completely restored by normal re-forming in a good vacuum. In the case of poisoning by oxygen, however, recovery by this means is not always possible. If the exposure to oxygen has lasted only a very short time the emission may, perhaps, be recoverable by ordinary re-forming once or a few times after successive poisonings, but not an unlimited number of times.

It may seem strange that a badly oxygen-poisoned cathode cannot be re-formed in the ordinary way, for one would naturally suppose that such a cathode would, after all, only be in the same condition as one that had never been formed. Apparently, however, this is not the case. The most natural inference is that there is on the surface of the poisoned cathode a film of adsorbed oxygen which, like adsorbed oxygen on tungsten, is extremely difficult to remove. If this is the case, it should be possible to dislodge the oxygen either by very drastic heat treatment or by sputtering. Actually, Benjamin and Rooksby [8] have found both these agencies to be effective. By heating an oxygen-poisoned filament coated with a single oxide to near the melting-point of nickel and then giving it the ordinary forming treatment they were able to completely recover the emission. In the case of a filament coated with a mixture of barium and strontium oxides this method is, of course, inapplicable, since it would result in the loss by evaporation of most of the barium oxide. The emission from such a filament has, however, been shown by Benjamin and Rooksby to be completely recoverable by substituting bombardment by argon ions for the high-temperature flashing. They also tried bombardment by ions of mercury instead of argon and succeeded in recovering most, though not the whole of the emission. Their failure to *completely* recover the emission in this case was presumably due merely to the fact that, in order to drive the mercury out of their vacuum vessel after bombardment, it was necessary to re-bake it and so expose the filament to fresh poisoning.

The author has found that an oxide cathode may suffer partial poisoning during activation by its own gas (oxygen) which is given off in this operation. This effect may be observed by mounting several similar independent coated filaments side by side within the same anode. If each in turn is given a short forming treatment, a definite cycle being followed, it is found that between successive formings of the same filament it loses an appreciable part of its emission, due, undoubtedly, to the poisoning action of the oxygen given off by the others. With each repetition of the cycle, the poisoning becomes less and less—a result that is in harmony with Becker's observation of the diminution in the rate of oxygen evolution as activation proceeds. It may also be observed that if all the filaments are formed together in parallel, the system then being equivalent to a single large cathode, complete activation takes longer and the final emission per filament may be less than in the case of any one of the filaments formed alone.

Miscellaneous Peculiarities of Oxide Cathodes.—A peculiarity of oxide cathodes which has already been referred to in Chapter I is the poorness of saturation of their emission. This seems to be true of all cathodes of this type, irrespective of the materials of the core and coating.

One cause that sometimes operates to make oxide cathodes appear to saturate badly is the heating of the coating due to the passage of the space current radially through it. This heating is particularly important when the coating is relatively thick or has a poor electrical conductivity, and it may then considerably outweigh the cooling associated with the evaporation of the electrons. Rothe,[45] for example, has reported a case in which the effect was so great that even when the filament-heating current was switched off the filament did not grow cold or cease to emit.

Poorness of the apparent saturation due to this cause is, however, of no really fundamental interest, since it arises merely from failure to maintain the emitting surface at a constant temperature. The effect may be avoided, as Espe[17] has pointed out and confirmed experimentally, by working with sufficiently thin coatings. It may also be avoided by taking readings only at low temperatures. This follows from certain results of Reimann and Murgoci.[43] It has been found by these that the apparent conductivity c[*] of a formed coating varies with the temperature T according to the formula

$$c = \alpha\epsilon^{-\beta/\mathrm{T}}, \quad . \quad . \quad . \quad . \quad (1)$$

where α and β are constants. We may also, with negligible error, express the temperature dependence of thermionic emission by the similar formula

$$i = a\epsilon^{-b/\mathrm{T}}, \quad . \quad . \quad . \quad . \quad (2)$$

in which a and b are other constants. The energy dissipated in the coating when saturated[†] space current passes is therefore given by

$$w = \frac{a^2}{\alpha}\epsilon^{-\frac{2b-\beta}{\mathrm{T}}}. \quad . \quad . \quad . \quad . \quad (3)$$

Now it has been found[43, 44] that for a well-activated cathode $2b - \beta$ is a positive quantity of the same order as b. Hence the energy dissipation must fall off very rapidly as the temperature is lowered. In spite of this, the saturation has been found by Reimann and Treloar[44] actually to become poorer with decreasing temperature, and at very low temperatures they

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[*] This, as we shall see later, is probably not the true conductivity. It is, however, the quantity that determines the energy dissipation in the coating when a current passes through it.

[†] There is generally some approach to saturation, and we are here dealing merely with orders of magnitude.

ound no sign of saturation at all. Obviously, then, we must ook for some other cause of poor saturation than mere energy dissipation in the coating.

We have already considered two causes of genuine poorness of saturation. These are the Schottky effect and the "local-ield" effect, due to patches of unequal work functions in the surface of the cathode. The emitting surface of an oxide cathode is rough and probably contains many sharp edges and points. At these there may be very intense fields, sufficient to produce a large Schottky effect even with quite moderate anode voltages. And since the emission is due to the presence of an adsorbed film of barium, any sufficiently large-scale lack of uniformity of the film would manifest itself as patches of different work functions. Thus it seems possible that either or both of these two causes of poor saturation may operate in the case of oxide cathodes.

Another peculiarity of oxide cathodes is a certain instability of the emission that is sometimes observed. The activity may apparently be changed by the current taken from a cathode even after careful forming and ageing. Espe [17] has observed that the taking of a large current enhances the activity, but that when subsequently a smaller current is taken at the same temperature the activity falls off again. Becker,[4] and Kniepkamp and Nebel,[35] on the other hand, have reported the opposite effect, large space currents causing the emission to fall. An oxide cathode is so complex a system that such contradictions can hardly cause surprise. The fact that the taking of a space current may change the emission is, of course, due to the fact that the current electrolyses the coating. In the electrolysis, oxygen is liberated on the emitting side of the coating, and the barium already there must move into the coating. We should therefore naturally expect the emission to be decreased. But at certain temperatures these electrolytic effects may conceivably be completely nullified by diffusion, and since the passage of a large space current causes a cathode to lose oxygen it is also quite understandable that the emission should be increased.

A few observers have reported the emission of ions from oxide cathodes. By a magnetic dispersion method, Barton [3] found the emission of electrons from a well-formed and aged cathode to be accompanied by that of singly negatively charged oxygen molecules. He was able to observe these at even lowe temperatures than he could the electron emission. The temperature variation of the ion current was found to conform to a law of the Richardson type. From certain other considerations, however, it must be concluded that the ion current cannot in general be more than a quite insignificant fraction of the total negative emission. During a normal life of an oxide cathode the number of electrons collected may be of the order of 10^6 or even more times the number of oxygen atoms originally present (combined with barium) in the oxide coating And in general only a small fraction of the oxide is lost during life. On the supposition that this evaporates as oxygen and barium separately and not as oxide, the number of electrons evaporating per oxygen molecule would be at least of the order of 10^7. But Becker has found that no appreciable fraction of the oxygen given off from his cathodes at high anode potentials could have been electrically charged. We may therefore set the upper limit of oxygen-ion current at something like 10^{-9} of the electron emission. It would seem that Barton's cathodes must have been in some rather unusual condition.

Glass,[26] on the other hand, has reported an emission of positive ions from a platinum-iridium wire coated with barium and strontium oxides at temperatures exceeding about 1400°K. Whether these were charged alkaline earth metal atoms or those of some impurity, such as sodium or potassium, was not determined. Kozanowski and Williams [37] have also presented evidence of positive ion emission from an oxide cathode in the form of certain abnormalities in the shot effect. For reasons similar to those just discussed in connexion with negative ions, however, the positive-ion emission from the cathode cannot be more than an insignificant fraction of the electron emission. Of course, under ordinary operating conditions in a valve, positive ions, even if emitted, could not escape from the region of the cathode *as such.* They would swing about the surface of minimum potential due to the space charge until either re-absorbed by the cathode or until they captured an electron. It does not seem unlikely that a large proportion would do the latter and so be able finally to escape.

Dependence of Thermionic Properties on Materials f Core and Coating.—Qualitatively the behaviour of cathodes ated with all three alkaline earth oxides is similar. Those ated with barium oxide, however, give a much higher emission an similarly treated cathodes with strontium oxide at the me temperature, and strontium oxide cathodes, in turn, ve a higher emission than those coated with calcium oxide. his is reflected in the order of the work functions of the ree oxides, as measured, for example, by Espe.[16]

From this it might be expected that a mixture of barium nd strontium oxides would give a lower emission than arium oxide alone. We have seen, however (p. 201), that is is not found to be the case. A coating consisting of a lid solution of about 40 per cent. BaO and 60 per cent. SrO n nickel is capable of giving about eight times as much nission at 1020°K. as is obtainable from BaO alone, also n nickel.

Although we have no definite knowledge of what this is ue to, it is not, when we consider it, after all very surprising. rom the fact, already noted,[4, 23] that barium with only a ery slight admixture of strontium evaporates at high temeratures from a well-activated 50%BaO-50%SrO-coated athode, we may, perhaps, infer that until the proportion of aO in a BaO-SrO mixed coating becomes very small, the dsorbed alkaline earth metal is almost entirely barium. his we may attribute to the fact that the heat of formation f SrO is greater than that of BaO and that therefore the eaction

$$BaO + Sr \rightleftharpoons SrO + Ba$$

oes more readily in the direction from left to right than from ight to left. And we have seen that the thermionic properties f a composite emitter are determined not only by the outerost layer of atoms but to some extent also by those undereath. There is no apparent reason why the emission from arium on a solid solution of barium and strontium oxides hould not be greater than that from barium on barium oxide.

According to Spanner,[48] compounds of the alkaline earth etals other than the oxides give a high electron emission. rom measurements with the sulphides, arsenides, carbides,

fluorides and hydrides, he came to the rather surprising co
clusion that the emission from all except the hydrides is abo
the same as that from the oxides, the thermionic properti
being a function merely of the electropositive (metalli
constituent of the coating. The emission from the hydrid
was found to be greater than that from the other compound
a result which was attributed by Spanner to the relati
electropositiveness of hydrogen.

Spanner has also measured the electron emissions fro
cathodes coated with the oxides of the related metals, ma
nesium and beryllium, finding that magnesium oxide (pr
sumably activated) has a higher work function than calciu
oxide, and beryllium oxide the highest of all in this grou
In addition, he has studied the thermionic properties of t
oxides of the elements of the third and fourth columns of t
periodic table. A systematic study of the properties of
very large number of oxides was made much earlier (190
by Jentzsch.[32] Owing to the relative poorness of the vacu
obtainable in those days, however, but little reliance can
placed in the results. Thus the values found by him for t
work functions of the alkaline earth oxides were of quite
different order (> 3 e.v.) from those obtained more recent
under really good vacuum conditions.

Until comparatively recently, very little consideration wa
given to the possible effect of the core metal on the behavio
of oxide cathodes. One reason for this is that Deininger,
as early as 1908, presented what seemed like convincing ev
dence that the rôle of the core metal is nil. The emissio
obtained from platinum, carbon, tantalum and nickel, coate
with lime, were found to be representable as a function
temperature by points, all of which lay on a single Richardso
line. Recently, however, the results of similar experimen
performed by Lowry [39] under far superior vacuum conditio
have pointed just as convincingly to the opposite conclusio
Lowry found that an alloy of Pt-10%Ir, coated with t
usual BaO-SrO mixture, has to be raised to a temperatu
150°–200° higher than that of an alloy of nickel, cobalt, iro
and titanium similarly coated in order to give the sam
emission. Experience accumulated at Wembley also sho
definitely that the nature of the core has an important effe

n the emission, and also on the time changes of the activity hich accompany the taking of emission.

The Seat of the Emission.—It is natural to assume in he absence of evidence to the contrary that the thermionic ctivity of an oxide cathode is determined solely by the condition of the outer surface of the coating. Recently, however, eimann and Murgoci[43] and also Lowry[39] have suggested hat the seat of the observed emission might well be the arium-contaminated surface of the core metal rather than hat of the coating.

The evidence advanced by Lowry in favour of this view as the observed dependence of the emission on the material f the core. He supposed the electrons, emitted at the surface f the core, to simply diffuse through the gaps between the xide particles and so to find their way into the vacuum. eimann and Murgoci, on the other hand, observed a remarkble parallelism between the current-voltage characteristics f a system in which current passes between two metal ectrodes separated by a formed alkaline earth oxide and hose of an ordinary oxide-coated-filament diode valve. From his they inferred that there is really no difference between he two systems save one of relative geometrical dimensions, e. that there is a finite gap between each metal electrode and he oxide in both cases. They pictured the current as passing hermionically across the gap between the core and coating nd again thermionically from the external surface of the oating to the anode. Now in such a case, as many electrons ust condense on the inside of the coating as evaporate om the outside. Therefore the work function as measured alorimetrically must be that of the barium-contaminated ore. Hence, from the known agreement of this with the alue of the work function calculated from the slope of the ichardson line it was argued that the *observed* emission is robably that of the core. In the system imagined this could e so only if of the two surfaces in series that of the core had he lesser emission and so limited the space current.

The view that the observed emission is that of the core now no longer tenable, however. It has been shown by ecker and Sears[6] that bringing barium to the outer surface f the coating of a cold, relatively inactive cathode either by electrolysis or by depositing it there from an outside sour changes the emission in the same kind of way as we ha already noted on pages 197 and 198. The emission w tested at intervals at 500°K., a temperature at which no tim changes in activity could be observed, and at which, therefor presumably no appreciable diffusion of barium toward t core occurred.

Becker and Sears also succeeded in removing, by mea of a mechanical shock, the whole of the coating of one of the cathodes. After this the emission at the testing temperatu was found to have decreased by a factor of 6000.

In another experiment, Becker and Sears found that t emission was not affected by a change in the effective area the core, that of the coating remaining constant. After first coating had been applied to a metal cylinder, a ribb of the same metal was wound helically about it and t whole then covered over with a second coat of oxide. It w found that at a given temperature the emission was the sa whether the cylinder alone, the ribbon alone, or both togeth were connected in circuit and made the negative metal electrod Had the currents been limited at the core surface they woul of course, have been proportional to the area of metal electr cally connected and thus have been very different in the thr cases.

Thus we may definitely conclude that the emission is n limited at the core. The rôle of the core metal in determinin thermionic behaviour must, then, be an indirect one. T material of the core probably affects the equilibrium quantit of free barium present in the coating.

Conduction in the Coating.—There is considerab evidence for the occurrence of electrolysis when a curre passes through an oxide coating. Thus we have seen th an oxide cathode may in general be activated much mo easily by drawing a strong electron current from it simu taneously with heating it than by thermal treatment alon and that during activation with space current oxygen is evolve We have also seen that oxygen may be obtained from a wel aged cathode provided a sufficiently strong thermionic curre is drawn from it. And finally, polarization effects in forme cathodes have been observed both by Becker [5] and by Mey nd Schmidt.[41] There can be no doubt, therefore, that both formed and in unformed cathodes at least a part of the current rough the coating is carried by ions.

An apparent objection to the picture of an appreciable nic conduction is that during the life of an oxide cathode mething like 10^7 times as many electrons may be drawn om the coating as there are oxygen atoms lost from it. There re, however, strong reasons for believing that the products f electrolysis may continually recombine without evaporating, nd in view of this the long life ceases to be a difficulty. We now that in an activated cathode there must be a film of arium covering the whole of the emitting surface. We should herefore naturally expect oxygen appearing there electrotically to recombine with this barium instead of simply vaporating. Of course this can go on only if the barium so sed up is continually replaced by fresh barium diffusing from he inner surface of the oxide where it is electrolytically iberated. Such diffusion is, however, already required by ur theory of forming.

The diffusion of material in an outward direction must e compensated for by an equal transfer of material inwards f the coating is to remain on the core. What more natural han to suppose that the latter is of barium ions ? We have hus the picture of " barium circulation " proposed by Reimann nd Murgoci.[43] We do not need to postulate any movement f oxygen ions, for in view of the unipolarity of most solid lectrolytes it appears not improbable that the oxygen ions ake no active part in the electrolysis.

Incidentally, it should be noted that the theory of barium irculation appears to provide a natural explanation of the volution of oxygen from a well-aged cathode which occurs when a strong electron current is drawn. For a strong current means vigorous circulation, the diffusion part of which requires a correspondingly strong barium concentration gradient across the coating. It is only what we should expect, therefore, that the drawing of a sufficiently strong current might cause the film of adsorbed barium at the emitting surface to become so depleted that some of the oxygen appearing there electrolytically would evaporate before having had a chance to recombine with barium.

Employing the picture of barium circulation, it is possib to compute the average life of a particle of barium at th emitting surface in terms of the electrolytic current. Thu Reimann and Murgoci have shown that in the case of a electrolytic current of $\frac{1}{3}$ amp./cm.^{2} the mean "adsorptio life" of a barium particle would be about 10^{-3} second. No $\frac{1}{3}$ amp./cm.^{2} is a fairly good representative figure for the orde of thermionic emission generally obtained from oxide cathode at normal operating temperatures. And 10^{-3} second happen to be just the order of adsorption life of a barium particle cal culated by Schottky[47] from the magnitude of the flicke effect in an oxide cathode as observed by Johnson.[33] On is thus tempted to infer that an important part, if not th whole of the thermionic current is carried through the coatin by ions. Perhaps in view of the uncertainty of the theor of the flicker effect, however, this should not be taken as logically necessary conclusion from the evidence.

Evidence of a different kind bearing on the question o the nature of the conduction has been advanced by William and Huxford.[52] They have reported that the conductivity o an oxide coating falls with increasing frequency of alternatin potential applied across it in such a way as to "indicate transfer of electrical charges through the coating by ioni conduction, the process being inhibited at the higher frequencies." Meyer and Schmidt[41] have been unable to confirm this result, however, finding no dependence of the conductivity on the frequency either with formed or with unformed oxides.

Becker[4] has reported that in order to form a monatomic film of strontium on the emitting surface of an initially inactive strontium-oxide cathode by electrolysis he was obliged to send into the coating about 200 times as many electrons as would have been necessary, had the conduction been purely ionic This figure was based on the assumption that the emitting area was equal to the macroscopic surface area of the cathode. Although part of the factor of 200 was probably due to a discrepancy between the real and assumed emitting areas, it might not be possible to account for the whole of it in this way. Becker inferred that by far the greater part of the current must have been carried through the coating by electrons.

actors of the order of 200 were also obtained with barium xide and mixed barium and strontium oxide cathodes.

It may be questioned what rôle barium circulation could ave played in Becker's experiments ; for it must be reembered that barium and/or oxygen circulation is a necessary art of any picture of conduction in which more than about 0^{-7} of the current is carried by ions, and according to Becker's esults at least something like 1/200 must actually have been o carried. Obviously, if the barium circulated freely it might e possible to account for the whole factor of 200 without aving to suppose that any of the current was carried by lectrons. It is probable, however, that at the low temperature t which Becker carried out his electrolysis diffusion was inppreciable. The part AB of the curve of Fig. 39 was obtained uring electrolysis. The part of the curve beyond B was btained by subsequently glowing the filament at 800°K. he changes in activity brought about by the glowing can nly be attributed to diffusion. If, however, there was already arium circulation at the (lower) temperature of the electroysis, how could the activity subsequently change at 800°K. n account of diffusion ? There would appear to be only one way in which this might occur, viz. if there were at 800°K. a *volume* diffusion (from the crystal surfaces into the oxide attice) which was inappreciable at the temperature of the electrolysis, the only important diffusion at the lower temperature being that along crystal faces. In the absence of positive evidence for these two kinds of diffusion at the two temperatures, however, the more natural inference to draw from Becker's observations is that, unless the real surface of his specimen was about 200 times the apparent surface, the conduction in it at the temperature of the electrolysis was mainly electronic.

There remains to be accounted for Horton's result, referred to on page 193, viz. that the rate of evolution of oxygen from a coated cathode at the beginning of forming is within 8 per cent. of that required by Faraday's law. If we may take this result at its face value we must conclude than an unformed coating conducts entirely, or at least mainly, ionically. Yet Becker's result also applies to a coating which was, at least initially, "inactive." However, Becker's vacuum conditions were so much superior to Horton's that his cathode, eve initially, was perhaps only *relatively* inactive. The mere heating in contact with the core metal to which the oxide wa subjected before the experiment was carried out might hav produced an appreciable amount of free barium which wa not subsequently oxidized.

Can it be, then, that the conductivity of a formed coatin is different from that of an unformed coating ? From certai experiments of Reimann and Murgoci it appears that it i at least quantitatively different. In these experiments, tw coated wires were twisted together and a fresh coating the applied over the whole. Observations were made both o the currents that passed through the oxide when variou potential differences were maintained between the wires an of the thermionic currents obtained from the system whe the two wires were connected together and potential differences applied between them and a neighbouring anode. Th observations were carried out both at different temperatures and for different states of activation of the oxide. A remarkable parallelism was found to exist between the slope, c, of the conduction current-voltage curve at the origin at any given temperature and the thermionic emission, also at a given temperature. Both quantities were observed to grow by orders of magnitude during the forming process, and it was also found that anything that subsequently reduced the emission (e.g. gas poisoning) also reduced c. Later investigations of Krokzek and Lübke,[38] Albricht,[1] and Meyer and Schmidt [41] confirm these results. If, as seems likely, c is related to the conductivity of the oxide, we must conclude that the conductivity depends on the same thing as the thermionic emission, viz. the presence of free barium in the coating. This could hardly be the case unless there were barium metal dissolved in the oxide crystals, for, as we have already seen, X-ray analysis fails to reveal any bulk material in formed coatings that is not present in unformed coatings. Thus the combined evidence (including that of Horton and Becker) suggests that the presence of dissolved barium in the oxide lattice causes a strong electronic conductivity to be superimposed on an already existent weak electrolytic conductivity.

This suggestion is strongly supported by some recent theoretical investigations of Wilson,[53] and of Fowler and Wilson.[19] Wilson has shown how the conductivity of electronic semi-conductors might be accounted for by the presence in the lattice of foreign atoms of an impurity of the right kind. Fowler and Wilson have further shown that the general features of observed current-voltage curves for formed alkaline-earth-oxide coatings at not too low temperatures are capable of explanation on the assumption that the formed oxides are " impurity conductors " of this type. There can be little doubt that the impurity is free barium.

We saw in Chapter I that in an insulator in which there is no thermal excitation all the allowed energy bands up to a certain one are completely " filled " with electrons, and the next higher allowed band, which is empty, is separated from the last filled band by a considerable interval. Wilson has discussed the combined effects of thermal excitation and applied field in such a case, and has shown that if the energy interval between the highest filled band and the lowest unoccupied band is ΔW, the electronic conductivity σ must vary with the temperature according to the law,

$$\sigma = \sigma_0 \, \epsilon^{-\Delta W/2kT}, \quad . \quad . \quad . \quad (4)$$

where σ_0 is a constant.

This result is remarkable for the occurrence of $\frac{1}{2}\Delta W$ in the exponential factor, instead of simply ΔW, as might, at first sight, have been expected. The reason for the occurrence of a quantity less than ΔW is that before an electron that has been excited into the higher band can return to the lower one, it has, so to speak, first to find a " hole " in the latter. The difficulty of return gives rise to a heaping up of electrons in the upper band so that the equilibrium number present in it is much greater than it would be if return were easy.

A very simple derivation of eqn. (4) is the following : * On any theory of conduction the conductivity σ must obey the relationship

$$\sigma \propto nl, \quad . \quad . \quad . \quad . \quad (5)$$

where n is the number of conducting electrons per unit volume and l is the mean free path. There is no important

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* For this the author is indebted to Prof. R. H. Fowler.

variation in l at ordinary temperatures, and so we have, very nearly,

$$\sigma \propto n. \qquad . \quad . \quad . \quad . \quad (6)$$

Now n is the (small) number of electrons in the upper band, maintained there by thermal excitation, and is also the number of holes in the lower (nearly full) band. The situation is one of dissociative equilibrium, the dissociated elements being a free electron and a hole and the combined substance a bound electron. The ordinary laws of dissociative equilibrium will apply, and these always yield an expression of the form

$$\frac{n_1 n_2}{n_{12}} = \mathrm{K(T)}, \qquad . \quad . \quad . \quad . \quad (7)$$

where

$$\frac{d \log \mathrm{K}}{d\mathrm{T}} = \frac{\Delta \mathrm{W}}{k\mathrm{T}^2}. \qquad . \quad . \quad . \quad . \quad (8)$$

Here $n_1 = n_2 = n$, and n_{12}, the number of bound electrons, is practically a constant, so that

$$n^2 \propto \epsilon^{-\Delta \mathrm{W}/k\mathrm{T}}, \qquad . \quad . \quad . \quad . \quad (9)$$

and hence, substituting for n in (6),

$$\sigma = \sigma_0 \, \epsilon^{-\frac{1}{2}\Delta \mathrm{W}/k\mathrm{T}}. \qquad . \quad . \quad . \quad (4)$$

Now according to Wilson, ΔW is probably always of the order of a few electron-volts, except, of course, in the case of metals, for which it is zero, and he points out that "if this is true, then no pure non-metallic solid can ever have a significant natural electronic conductivity at ordinary temperatures, and the observed conductivity of semi-conductors must be due to the presence of impurities."

He then discusses the case of a lattice containing atoms of an impurity, each of which possesses a single electron in a discrete state of energy W_1, where W_1 lies between the lower limit W_2 of the lowest unoccupied allowed band and the upper limit of the next lower, full band. The impurity electrons cannot fall into this lower band, since it contains no unoccupied energy levels. They may, however, be thermally excited into the upper band and thus become conducting electrons. They will make this transition more easily than the electrons occupying the highest filled band, since $\mathrm{W}_2 - \mathrm{W}_1$

is less than ΔW, and, as Wilson has shown, the conductivity due to the impurity is given by

$$\sigma = \sigma_0{}' \, T^{-3/4} \epsilon^{-\frac{W_2 - W_1}{2kT}}, \quad . \quad . \quad . \quad (10)$$

where $\sigma_0{}'$ is a constant which is proportional to the square root of the concentration of the impurity. The temperature variation of σ in (10) is dominated by the exponential factor and could not be distinguished experimentally from one of the type

$$\sigma = \sigma_0{}'' \epsilon^{-w/kT}, \quad . \quad . \quad . \quad (11)$$

where $\sigma_0{}''$ and w are new constants. The constant w is not very different from $\frac{1}{2}(W_2 - W_1)$.

Wilson's theory of impurity semi-conductors has recently been experimentally verified in a most striking manner by Jusé and Kurtschatow [34] in observations of the temperature dependence of conductivity of a number of specimens of cuprous oxide containing various amounts of oxygen as an impurity. The quantities of oxygen were found by chemical analysis. The $(\log_{10} \sigma)$-$1/T$ curves representing their results are plotted in Fig. 41, each curve being marked with the atomic percentage of oxygen impurity in the corresponding specimen.

It will be observed that at low temperatures the curves are linear, and all have practically the same (negative) slope, but that—except for the case of the specimen containing 0·47 per cent. of oxygen—the conductivity at a given temperature increases with the amount of impurity. This is as it should be according to the theory. As the temperature is increased, however, each curve presently bends sharply upwards and again becomes linear with a much steeper slope than for low temperatures. Also the conductivity at high temperatures no longer depends upon the amount of impurity, the upper parts of the curves coinciding, within the limits of experimental uncertainty, with the line for pure Cu_2O. This again is what the theory would lead us to expect, for although ΔW is greater than $W_2 - W_1$, there are far more electrons available for excitation in the highest full band than there are at the impurity level, and so as the temperature is increased the conductivity due to the impurity must eventually be swamped by the intrinsic conductivity of the material. From the slopes at high and low temperatures the values 0·73 e.v. and 0·14 e.v. are obtained for $\frac{1}{2}\Delta W$ and w respectively. The corresponding value of $\frac{1}{2}(W_2 - W_1)$ is 0·17 e.v.

The apparent anomaly in the case of the specimen containing 0·47 per cent. of oxygen impurity is due, as Jusé and Kurtschatow have explained, to the fact that the impurity was not uniformly distributed in this specimen as it was in the others, so that the *effective* concentration of the impurity was less than that given by chemical analysis. That the distribution was not uniform was shown by the presence of little crystals of CuO. These were visible under a microscope.

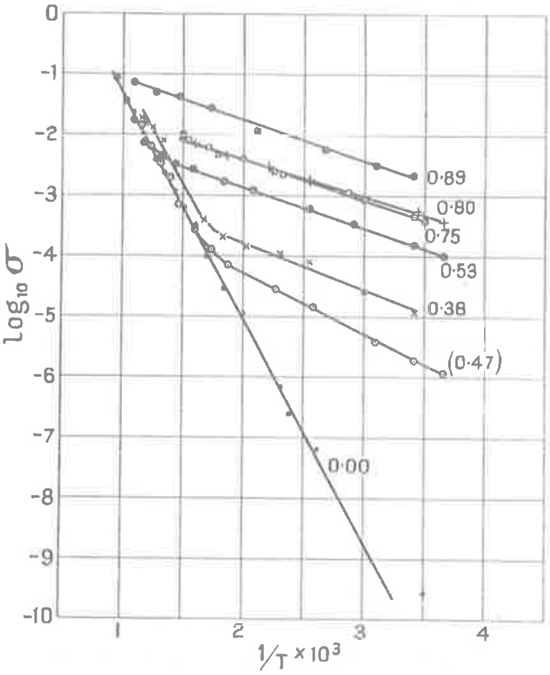

FIG. 41.—Relationship between log σ and 1/T for specimens of Cu_2O containing various proportions of oxygen impurity.

Now Reimann and Murgoci have found that for a formed alkaline-earth-oxide coating the quantity c, defined on page 216, varies with the temperature according to a law

$$c = \alpha\epsilon^{-\beta/T}, \quad . \quad . \quad . \quad . \quad (1)$$

where α and β are constants. This is of the same form as (11). Thus if c represents the conductivity of the coating, the observed nature of its temperature dependence is not in conflict with the supposition that the conductivity is electronic. We cannot go further than this, for a temperature dependence of conductivity of the type represented by (11) is known to be characteristic of solid electrolytes as well as of electronic semi-conductors. The observed dependence of c on the state of activation of the coating is also in qualitative agreement with Wilson's theory, on the assumption that c represents the conductivity and that dissolved barium is the relevant impurity, for, as we have seen, σ_0' in (10) becomes greater with increasing concentration of impurity.

Becker,[5] working at rather lower temperatures than Reimann and Murgoci, found that in order to represent his results on the temperature variation of c he required two terms on the right-hand side instead of one, thus :

$$c = \alpha_1 \epsilon^{-\beta_1/T} + \alpha_2 \epsilon^{-\beta_2/T}. \quad . \quad . \quad . \quad (12)$$

This he supposed to be due to the existence of a mixed conduction, the electronic current being represented by one term, and the ionic by the other. If we assume this interpretation to be correct we must conclude that the conduction is mainly electronic at high temperatures (where c varies with the barium content of the coating) and mainly ionic at low.

It is natural to assume that the potential difference between two metal electrodes separated by a mass of alkaline earth oxide is the same as the potential drop across the oxide. This assumption leads to a difficulty, however. According to all that is known the conductivity of solid electrolytes is ohmic, and the same should, according to Wilson's theory, be true of electronic semi-conductors. Yet current-voltage relationships have been observed by Reimann and Murgoci,[43] and by Reimann and Treloar,[44] which are certainly not ohmic. According to Reimann and Treloar the non-linear relationships are characteristic of the higher temperatures. A typical curve obtained by them at a relatively high temperature (922°K.) is reproduced in Fig. 42. It will be observed that the curve is linear for low voltages, but that as the voltage is increased it presently bends toward the voltage axis and then, finally, bends away from it again.

Now Fowler and Wilson[19] have recently shown that a current-voltage relationship of just this nature is to be expected on the basis of Wilson's theory of electronic semiconductors when account is taken of the rectifying properties of semi-conductor/metal contacts and of the consequent potential falls across these.

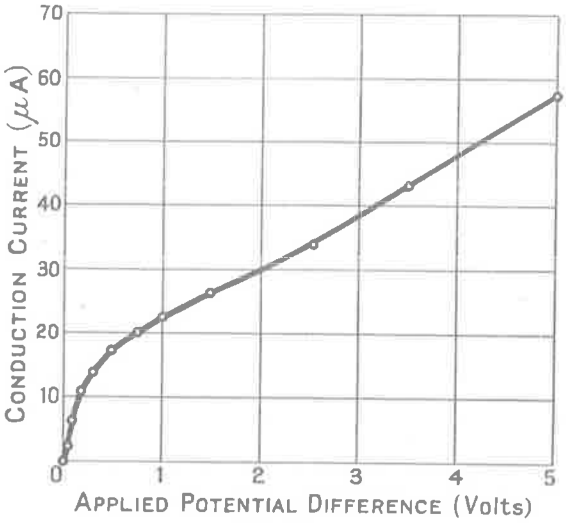

Fig. 42.

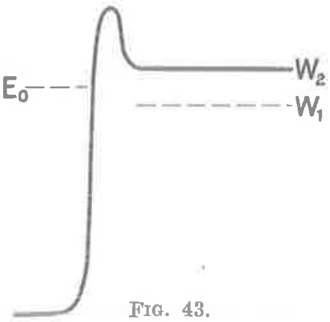

Fig. 43.

The theory of semi-conductor/metal rectifiers has been worked out by Wilson,[54] Frenkel and Joffé,[21] and Nordheim.[42] The region of the boundary between the metal and the semi-conductor is pictured as in Fig. 43. The continuous curve represents the potential energy of conduction electrons, the left-hand and right-hand horizontal portions corresponding to the potential energies in the metal and semi-conductor respectively. At the boundary between the two, a hump occurs. The level E_0 in the metal corresponds to the critical energy of the Fermi distribution and the level W_2 in the semiconductor is that of the lower limit of the first unoccupied allowed band. W_1 is the energy level of the unexcited impurity electrons. For electrons to pass from the metal to the semi-conductor, they must acquire kinetic energies corresponding to the normal velocity component not less than W_2. And for electrons to pass from the semi-conductor to the metal they must also be raised by thermal excitation to the level W_2, for otherwise they cannot become conduction electrons in the semi-conductor. In the semi-conductor, electrons are raised twice as high at any given temperature as they are in the metal, and it may be shown that when an equal number of electrons flows in either direction (the equilibrium "no-field" condition), the potential of the metal has adjusted itself relative to that of the semi-conductor so that E_0 is just about half-way between W_1 and W_2. The hump has the same transmission coefficient for either direction of travel and may be ignored in a rough qualitative discussion.

Let us denote the equilibrium current in either direction when there is no applied field by I_0. Now suppose the potential of the metal to be raised by the small quantity $V\ (< W_2 - E_0)$. The current from right to left will still be I_0, but that from left to right will now be $I_0\epsilon^{eV/kT}$, and so the net current from left to right must be $I_0(\epsilon^{eV/kT} - 1)$. If, on the other hand, the potential of the metal is lowered by the small quantity V, it is easily seen that the resultant net current from right to left must be $I_0(1 - \epsilon^{-eV/kT})$.

We have so far neglected the effect of the applied voltage on the hump and so on the transmission coefficient. We have also not considered the effect of the temperature on I_0. It may be shown that on account of the former effect the current from left to right must be multiplied by ϵ^{-eV/kT_0} and that from right to left by ϵ^{eV/kT_0}. The quantity T_0 is a constant and is in general great compared with T. Also it may be shown that the effect of the temperature is to make I_0 proportional to $\epsilon^{-w/kT}$, where w is nearly equal to $\frac{1}{2}(W_2 - W_1)$. More accurate expressions contain factors of small powers of T, but for the sake of simplicity these have been neglected here, being of but small importance compared with the exponential factors.

Now let us consider the application of all this to the case of a current flowing from one metal electrode, through a semi-conducting oxide, to another metal electrode. There are, as

Fowler and Wilson have pointed out, three separate voltage drops to be taken account of, the sum of which makes up the potential difference between the metal electrodes. These are (1) that across the metal/oxide contact, V_1, (2) that across the oxide, V_2, and (3) that across the oxide/metal contact, V_3. The total voltage drop is

$$V_0 = V_1 + V_2 + V_3, \quad . \quad . \quad . \quad (13)$$

and if there is a current I flowing, we have

$$I = G\epsilon^{-w/kT}(\epsilon^{eV_1/kT} - 1)\epsilon^{-eV_1/kT_0} \text{ (metal/oxide)}, \quad . \quad (14)$$

$$I = H\epsilon^{-w/kT}V_2 \text{ (Ohm's law in oxide)}, \quad . \quad . \quad (15)$$

and

$$I = G\epsilon^{-w/kT}(1 - \epsilon^{-eV_3/kT})\epsilon^{eV_3/kT_0} \text{ (oxide/metal)}, \quad . \quad (16)$$

where G and H are constants.

It is easily seen that for sufficiently small currents (and therefore voltages), eqns. (14) and (16) both approximate to the form

$$I = G\epsilon^{-w/kT}\epsilon^{eV/kT_0}, \quad . \quad . \quad . \quad (17)$$

and for $eV \ll kT_0$ such a relationship between I and V must be linear. And since in (15) I also varies linearly with V, it follows that the slope of this curve in its linear part, which we have denoted by c, must vary with the temperature like $\epsilon^{-w/kT}$. Thus if the theory applies to the case of a formed alkaline-earth oxide between two metal electrodes, we may identify w/k with β in (1), so that the temperature dependence of c is the same as that of the conductivity σ of the oxide.

Let us now consider the case where I is so large that $\epsilon^{eV_1/kT}$ is great compared with 1. For this case, comparing (14) with (16), we easily see that the voltage V_1 dropped across the metal/oxide contact becomes relatively unimportant and may be left out of consideration. The shape of the current-voltage curve for the whole system is then essentially that represented by (16) with all the voltages increased by an amount proportional to the current on account of the ohmic resistance of the oxide expressed by (15).

It is obvious by inspection of (16) that the current at first tends to saturate at $G\epsilon^{-w/kT}$ and later increases again owing to the increased transmissibility represented by the last factor. The shape of the high-temperature current-voltage curves found by Reimann and Treloar is thus qualitatively accounted for. For a quantitative comparison we should, of course, need to know the values of the parameters. Of these, w enters into all three equations (14)–(16) in the same way and merely gives the common scale factor $\epsilon^{-w/kT}$. The actual " character " of the curves, on the other hand, is determined by the ratio G/H and by T_0. The independent parameters are $G\epsilon^{-w/kT}$, G/H and T_0.

In Fig. 44, currents are plotted to an arbitrary scale against the corresponding applied voltages V_0 for various assumed values of T_0 and G/H, and for a temperature of 922°K. These all show the initial linear rise and the tendency to saturate, followed later by a further increase. For comparison, the experimental curve of Fig. 42, which is for 922°K., is also shown. It is seen that except for a too rapid increase at higher voltages (~ 5 V.) it is possible to imitate very well the observed curve by choosing appropriate parameters. We need not be unduly disturbed by the want of agreement at the higher voltages, for this, according to Fowler and Wilson, is due merely to the faulty approximations used in the theory.

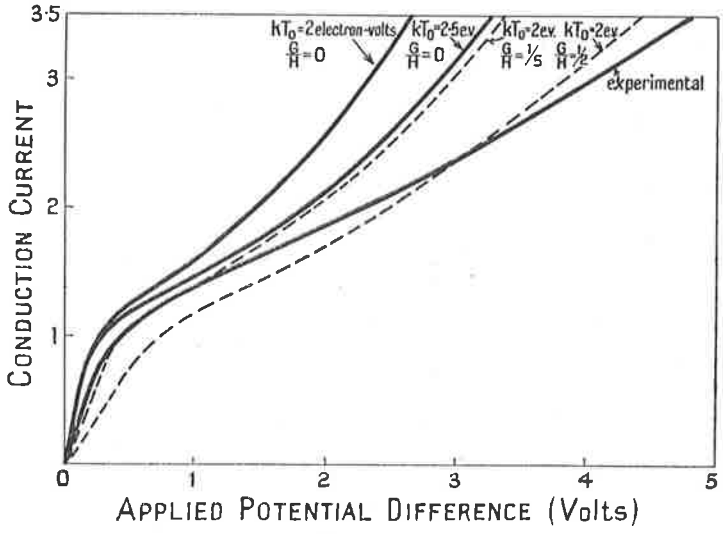

Fig. 44.

It is readily seen that beyond an I corresponding to a V_3

that makes $\epsilon^{-eV_3/kT} \ll 1$, the theoretical curves given by any set of parameters must be the same for all temperatures except for the scale factor $\epsilon^{-w/kT}$. Actually, however, there is no approach to similarity of shape between the experimental high-temperature and low-temperature curves. As the temperature is lowered, the " character " which is such a marked feature of the high-temperature curves is gradually lost, and the curves for the lowest temperatures are, when time changes are allowed for, probably linear. From this it must be inferred that the nature of the conduction at low temperatures is essentially different from that at high temperatures. Since the conduction appears to be mainly electronic at high temperatures it is probably mainly ionic at low temperatures. Indeed, it follows from the time changes observed at low temperatures, quite apart from the shapes of the curves, that at least a part of the low-temperature currents must be ionic.

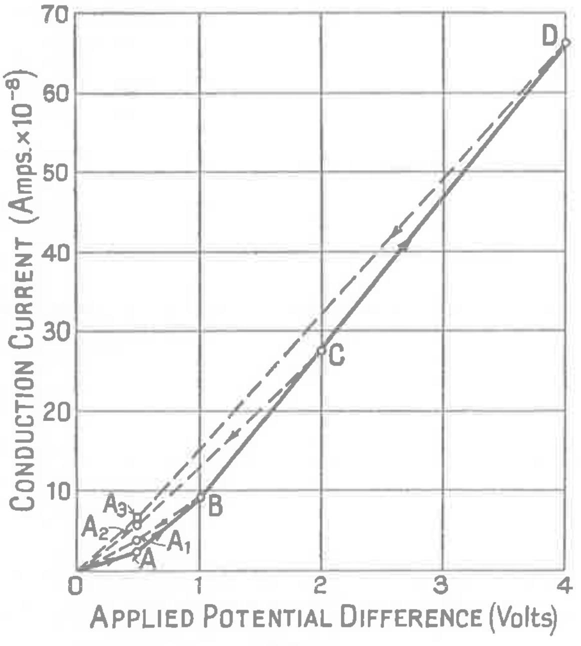

FIG. 45.

The nature of the time changes observed at low temperatures may be seen from Fig. 45. In this the full curve represents he relationship between the final equilibrium current and the applied voltage found by Reimann and Treloar for one of heir specimens held at a temperature of 572°K. If, now, tarting from the conditions represented by the points B, C and D on this equilibrium curve, the voltage was suddenly reduced to 0·5, the points A_1, A_2 and A_3, respectively, were obtained immediately after the change, and then the current ell gradually to the value represented by A. The points A_1, A_2 and A_3 lie nearly on the straight lines joining the origin to the points B, C and D respectively. Thus the "instantaneous" I-V relationships corresponding to equilibrium conditions at these points are probably linear, or very nearly so.

Fowler and Wilson have, with some reserve, proposed the following possible explanation of these time changes: When a current passes, Ba^{++} ions travel to the cathode surface and O^{--} to the anode. If the ions form layers of dipoles at these surfaces they must modify the potentials in such a way as to encourage the passage of electrons both from metal to oxide at the cathode interface and from oxide to metal at the anode interface. Thus the electronic part of the current, originally perhaps a small or even an insignificant part of the whole, is greatly increased and eventually it may actually outweigh the ion current. If this is the true explanation of the time changes, the linearity of the instantaneous I-V curves must be due to V_1 and V_3 both being small compared with kT/e within the range covered by the observations.

The Mechanism of the Emission.—Let us now consider the energy changes suffered by the emitted electrons in their passage from the core metal, through the oxide, into the vacuum. Suppose the continuous line in Fig. 46 to represent the potential energy of the electrons carrying the current in the core metal, oxide, and free space. There will be a potential hump at the boundary between the metal and the oxide (cf. p. 222) and probably another at the outer surface of the oxide, associated with the surface polarization due to the adsorbed barium. In free space the potential energy is asymptotic to W_∞. Let its value in the oxide be W_2 and let W_1 and E_0 be the energy level of the impurity electrons in the oxide and the critical energy of the Fermi distribution respectively. At absolute zero E_0 would be exactly midway between W_1

and W_2, and at higher temperatures it is still very nearly midway between these values :

$$E_0 = \tfrac{1}{2}(W_1 + W_2). \qquad . \qquad . \qquad . \quad (18)$$

Neglecting small powers of T, we have for the number n_0 per unit volume of electrons thermally excited from the impurity level W_1 to the conduction level W_2 :

$$n_0 \propto \epsilon^{-\frac{W_2 - W_1}{2kT}}. \quad . \qquad . \qquad . \qquad . \quad (19)$$

The concentration of electrons at the conduction level is slight

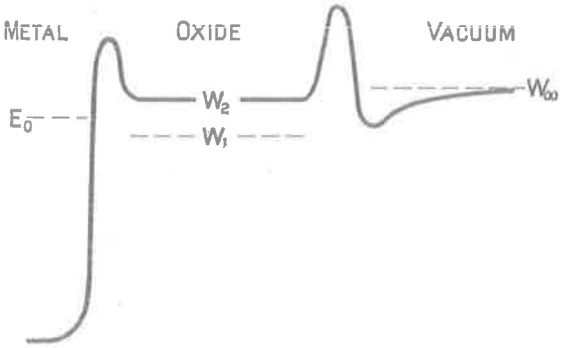

FIG. 46.

and their distribution is therefore Maxwellian. Hence for the thermionic emission we have

$$i \propto n_0 \epsilon^{-\frac{W_\infty - W_2}{kT}}, \qquad . \qquad . \qquad . \quad (20)$$

which, on account of (18) and (19), reduces to

$$i \propto \epsilon^{-\frac{W_\infty - E_0}{kT}}. \qquad . \qquad . \qquad . \quad (21)$$

This is the emission formula without the power-of-T factor.

It is interesting to note that the expression $W_\infty - E_0$ for the work function does not directly involve energy levels in the oxide, although, of course, it does so indirectly, since the potential of the metal must adjust itself so that E_0 is nearly midway between W_1 and W_2. This is as it should be, for otherwise the metal and the oxide could not be in equilibrium both with one another and with an external electron gas.

According to our picture the work function $W_\infty - E_0$ nust be greater than $\frac{1}{2}(W_2 - W_1)$ and therefore log i should vary more rapidly with 1/T than does log σ or (cf. p. 224) log c. Actually it has been found by Reimann and Treloar that the lopes of experimental (log i)-1/T plots always are steeper than those of the corresponding (log c)-1/T plots, but not very much steeper—the slope ratios found by them varied between 1·12 and 1·28. Hence it must be concluded that, or their specimens at least, $W_\infty - W_2$ was never a very mportant part of the total work function.

Since the emission is the result of a two-stage excitation, the heat effect associated with it must also be made up of two parts. There is a direct cooling due to the emission of electrons rom the conduction level at the outer surface of the oxide, but this only represents a part—and not necessarily an important part—of the work function. The drawing-off of electrons from the conduction level at the emitting surface nust be balanced by a supply of electrons to this level at the surface of the metal. Thus a part of the cooling which accompanies the drawing of electrons takes place at the metal/oxide interface. Of course there will be a continual flow of electrons rom the impurity level to the conduction level also, but in any particular part of the oxide this will be balanced by an equal flow in the opposite direction, and so there will be no net current between the two levels.

It might be thought that the emission constant A of an oxide cathode, in addition to being affected by the shape of he potential hill at the surface of the oxide, should be proportional to the concentration n_0 of conducting electrons, which in turn increases the concentration of dissolved barium. with/ This is not the case, however, and is only suggested by he approximations we have made. When no emission current is taken, the metal and the vacuum, both being in equilibrium with the oxide, must also be in equilibrium with one another, and so the ordinary thermodynamical theory of he emission applies just as in the case where there is no oxide. The A_0 for the oxide cathode must therefore be the same as or the uncoated core metal, and A must be equal to the product of A_0 and $1 - \bar{r}$, where $\bar{r}$ is the mean reflexion coefficient for the surface of the oxide.

The emission from an oxide cathode at a given temperatur does nevertheless depend on the concentration of dissolve barium as well as on the state of affairs at the oxide surface. This has been observed experimentally by Becker and Sears, and is accounted for very simply by our theory. Let u suppose for simplicity that the potential step and the shap of the potential hill at the surface of the oxide both remai constant while the concentration of dissolved barium increase from zero. When there is no dissolved barium, E_0 will be abou half-way between W_2 and the upper limit of the highest fille band in the oxide. On the other hand, when the concentratio of dissolved barium is high, E_0 is about half-way betwee W_2 and W_1. Thus, as the amount of dissolved barium i increased from zero, E_0 rises, the work function $W_\infty - E$ becomes less, and the emission increases.

LITERATURE.

1. W. Albricht, *Physica*, **11**, p. 146, 1931.
2. H. D. Arnold, *Phys. Rev.*, **16**, p. 70, 1920.
3. H. A. Barton, *Phys. Rev.*, **26**, p. 360, 1925.
4. J. A. Becker, *Phys. Rev.*, **34**, p. 1323, 1929.
5. J. A. Becker, *Trans. Am. Electrochem. Soc.*, **59**, p. 207, 1931.
6. J. A. Becker and R. W. Sears, *Phys. Rev.*, **38**, p. 2193, 1931.
7. N. C. Beese, *Phys. Rev.*, **36**, p. 1309, 1930.
8. M. Benjamin and H. P. Rooksby, *Phil. Mag.*, **15**, p. 810, 1933.
9. M. Benjamin and H. P. Rooksby, *Phil. Mag.*, **16**, p. 519, 1933.
10. W. G. Burgers, *ZS. f. Phys.*, **80**, p. 352, 1933.
11. C. Davisson and L. H. Germer, *Phys. Rev.*, **24**, p. 666, 1924.
12. C. Davisson and H. A. Pidgeon, *Phys. Rev.*, **15**, p. 553, 1920.
13. F. Deininger, *Ann. d. Phys.*, **25**, p. 285, 1908.
14. F. Detels, *Jahrb. d. drahtl. Telegr. u. Teleph.*, **30**, pp. 10 and 52, 1927.
15. S. Dushman, *Rev. Mod. Phys.*, **2**, p. 381, 1930.
16. W. Espe, *Wiss. Veröff. a. d. Siem. Konz.*, **5 (III)**, p. 46, 1926.
17. W. Espe, *Wiss. Veröff. a. d. Siem. Konz.*, **5 (III)**, p. 29, 1926.
18. W. Espe, *ZS. f. techn. Phys.*, **10**, p. 489, 1929.
19. R. H. Fowler and A. H. Wilson, *Proc. Roy. Soc. (A)*, **137**, p. 503, 193
20. K. Fredenhagen, *Phys. ZS.*, **15**, p. 19, 1914.
21. J. Frenkel and A. Joffé, *Sow. Phys.*, **1**, p. 60, 1932.
22. A. Gehrts, *Verh. d. D. Phys. Ges.*, **15**, p. 1047, 1913.
23. A. Gehrts, *Naturwiss.*, **20**, p. 732, 1932.
24. W. Germershausen, *Phys. ZS.*, **16**, p. 104, 1915.
25. W Germershausen, *Ann. d. Phys.*, **51**, pp. 705 and 847, 1916.
26. M. S. Glass, *Phys. Rev.*, **28**, p. 521, 1926.
27. W. Heinze, *Ann. d. Phys.*, **16**, p. 41, 1933.
28. T. R. Hogness and R. W. Harkness, *Phys. Rev.*, **32**, p. 936, 1928.
29. F. Horton, *Phil. Mag.*, **11**, p. 505, 1906.
30. A. W. Hull, *Gen. El. Rev.*, **32**, p. 213, 1929.

31. W. S. Huxford, *Phys. Rev.*, **38**, p. 379, 1931.
32. F. Jentzsch, *Ann. d. Phys.*, **27**, p. 129, 1908.
33. J. B. Johnson, *Phys. Rev.*, **26**, p. 71, 1925.
34. W. P. Jusé and B. W. Kurtschatow, *Sow. Phys.*, **2**, p. 453, 1932.
35. H. Kniepkamp and C. Nebel, *Wiss. Veröff. a. d. Siem. Konz.*, **11 (II)**, p. 75, 1932.
36. L. R. Koller, *Phys. Rev.*, **25**, p. 671, 1925.
37. H. N. Kozanowski and N. H. Williams, *Phys. Rev.*, **36**, p. 1314, 1930.
38. J. Krokzek and E. Lübke, *Wiss. Veröff. a. d. Siem. Konz.*, **9 (II)**, p. 252, 1930.
39. E. F. Lowry, *Phys. Rev.*, **35**, p. 1367, 1930.
40. V. C. Macnabb, *J. Opt. Soc. Amer.*, **19**, p. 33, 1929.
41. W. Meyer and A. Schmidt, *ZS. f. techn. Phys.*, **13**, p. 137, 1932.
42. L. Nordheim, *ZS. f. Phys.*, **75**, p. 434, 1932.
43. A. L. Reimann and R. Murgoci, *Phil. Mag.*, **9**, p. 440, 1930.
44. A. L. Reimann and L. R. G. Treloar, *Phil. Mag.*, **12**, p. 1073, 1931.
45. H. Rothe, *ZS. f. Phys.*, **36**, p. 737, 1926.
46. H. Schneider, *Ann. d. Phys.*, **37**, p. 569, 1912.
47. W. Schottky, *Phys. Rev.*, **28**, p. 74, 1926.
48. H. J. Spanner, *Ann. d. Phys.*, **75**, p. 609, 1924.
49. W. Statz, *ZS. f. techn. Phys.*, **8**, p. 451, 1927.
50. B. J. Thomson, *Phys. Rev.*, **36**, p. 1415, 1930.
51. A. Wehnelt, *Verh. d. D. Phys. Ges.*, **5**, pp. 255 and 423, 1903 ; *Ann. d. Phys.*, **14**, p. 425, 1904.
52. N. H. Williams and W. S. Huxford, *Phys. Rev.*, **37**, p. 463, 1931.
53. A. H. Wilson, *Proc. Roy. Soc.* (*A*), **133**, p. 458, 1931 ; **134**, p. 277, 1931.
54. A. H. Wilson, *Proc. Roy. Soc.* (*A*), **136**, p. 487, 1932.

CHAPTER V.

MODERN GENERAL THEORY OF ELECTRON EMISSION.

THE older theory of thermal electron emission, whilst satisfactory so far as it goes, raises three important questions to which it provides no answers. These are : (1) What is the absolute magnitude of the quantity A_0 which we must expect to approach to universal constancy ? (2) On what physical factors does the mean reflexion coefficient $\bar{r}$ depend ? and (3) What energy distribution of the free internal electrons can it be that makes the emission obey the T^2 formula ? It is with these questions that the more recent theoretical developments mainly deal.

The Constant A_0.—Thermodynamics alone gives us no information concerning the absolute magnitude of A_0. For this it is necessary to appeal to quantum statistical reasoning. The first to attempt a theoretical evaluation of A_0 by means of the quantum theory was O. W. Richardson [30] in 1914, and he succeeded in obtaining a value approaching the right order. A much closer approach to the correct value was found by S. Dushman [13] in 1923, although this had also appeared somewhat earlier in a series of papers by M. v. Laue.[24] Dushman based his derivation on the value of the vapour pressure constant * for monatomic gases as found by Sackur [34] and Tetrode.[36] As was later pointed out by R. H. Fowler,[19] however, Dushman's value was in error by a factor of $\frac{1}{2}$ on account of his not having taken into account the (then unknown) electron spin.

The condition of equilibrium at constant temperature and pressure between an electron-emitting body and an external electron gas is

$$\delta\Phi = 0, \quad . \quad . \quad . \quad . \quad (1)$$

---

* This is the new name now coming into use for what was formerly known as the " chemical constant."

here $\delta\Phi$ is the variation of the characteristic function Φ lefined in Chapter I) of the system accompanying a virtual ansference of electrons from the condensed to the gaseous hase or *vice versa*. This condition is fulfilled only when the haracteristic function per gram-molecule of electrons in the aseous phase, ϕ,* is equal to that in the condensed phase, ϕ' :

$$\phi = \phi'. \qquad (2)$$

Let u, v, c_v, c_p, s and w $(= u + pv)$ represent the internal nergy, volume, heat capacity at constant volume, heat apacity at constant pressure, entropy and heat function at onstant pressure respectively per gram-molecule of electrons the gaseous phase, and let the same symbols dashed represent ne corresponding quantities per gram-molecule of electrons in ne condensed phase. Then by definition,

$$\phi = s - \frac{w}{T} = s - \frac{u + pv}{T}. \qquad (3)$$

or a gas,

$$u = c_v T + b, \qquad (4)$$

here b is a constant, and

$$pv = RT, \qquad (5)$$

that (3) becomes

$$\phi = s - c_v - R - \frac{b}{T} = s - c_p - \frac{b}{T}, \qquad (6)$$

nd since the entropy of a perfect gas is given by

$$s = c_p \log T - R \log p + \kappa, \qquad (7)$$

here κ is a constant, we have, finally,

$$\phi = c_p \log T - R \log p + \kappa - c_p - \frac{b}{T}. \qquad (8)$$

For electrons in the condensed phase, we have

$$\phi' = s' - \frac{w'}{T}. \qquad (9)$$

or the entropy, s', of the condensed electrons, we may write

$$s' = s_0' + \int_0^T \frac{c_p'}{T} dT, \qquad (10)$$

---

* This must, of course, not be confused with the constant of the empirical emission formula for which the same symbol was used in Chapter I.

where s_0' is the value we choose to assign to the entropy absolute zero. The heat function, w', is obviously given by

$$w' = w - l, \quad . \quad . \quad . \quad . \quad \text{(1}$$

where l is the latent heat of vaporization of one gram-molecu of electrons, and, as in Chapter I,

$$l = l_0 + \int_0^T (c_p - c_p')dT = l_0 + c_pT - \int_0^T c_p'dT, \quad . \quad \text{(1}$$

where l_0 is the latent heat at absolute zero. Thus, substitu ing (10), (11) and (12) in (9), and substituting for w its valu on account of (4) and (5), we obtain

$$\phi' = s_0' + \int_0^T \frac{c_p'}{T}dT - \frac{1}{T}\int_0^T c_p'dT + \frac{l_0}{T} - \frac{b}{T} \cdot \quad . \quad \text{(1}$$

Our condition (2) now becomes

$$c_p \log T - R \log p + \kappa - c_p = s_0' + \int_0^T \frac{c_p'}{T}dT - \frac{1}{T}\int_0^T c_p'dT + \frac{l_0}{T}, \quad \text{(1}$$

or

$$\log p = \frac{c_p}{R}\log T + \frac{\kappa - c_p - s_0'}{R} + \frac{1}{R}\left(\frac{1}{T}\int_0^T c_p'dT - \int_0^T \frac{c_p'}{T}dT\right) - \frac{l_0}{RT} \cdot \quad \text{(1}$$

Neglecting c_p' as in Chapter I, and substituting for c_p its val for a monatomic gas, viz. $\frac{5}{2}R$, we have

$$\log p = \frac{5}{2}\log T + \left(\frac{\kappa - s_0'}{R} - \frac{5}{2}\right) - \frac{l_0}{RT}, \quad . \quad \text{(1}$$

and hence

$$p = \epsilon^{\frac{\kappa - s_0'}{R} - \frac{5}{2}} T^{5/2} \epsilon^{-\frac{l_0}{RT}}. \quad . \quad . \quad . \quad \text{(1}$$

The emission current, i, may be expressed in terms of th pressure, the temperature, the electronic charge and mass, an the mean reflexion coefficient thus :

$$i = (1 - \bar{r})e\frac{p}{\sqrt{2\pi mkT}} \cdot \quad . \quad . \quad . \quad \text{(1}$$

Combining (17) and (18), we obtain, therefore, the emission formula

$$i = (1 - \bar{r}) \frac{e\epsilon^{\frac{\kappa - s_0'}{R} - \frac{5}{2}}}{\sqrt{2\pi m k}} T^2 \epsilon^{-\frac{l_0}{RT}}. \quad . \quad . \quad (19)$$

Comparing this with formula (31) of Chapter I, we see that A_0 must be given by

$$A_0 = \frac{e\epsilon^{\frac{\kappa - s_0'}{R} - \frac{5}{2}}}{\sqrt{2\pi m k}}. \quad . \quad . \quad . \quad (20)$$

The quantity

$$\frac{\kappa - s_0'}{R} - \frac{5}{2}$$

is the so-called "vapour pressure constant" of our gas. Its value in terms of known quantities may be found by comparing the thermodynamical expression for the entropy of the gas, viz.,

$$s = c_p \log T - R \log p + \kappa, \quad . \quad . \quad (7)$$

with the value of s derived statistically from Boltzmann's hypothesis, which may be written

$$s - s_0' = k \log \frac{W}{W_0'}, \quad . \quad . \quad . \quad (21)$$

where W and W_0' are the so-called "thermodynamic probabilities" for one gram-molecule of the gas at the temperature T and at absolute zero respectively.

The thermodynamic probability may be defined as the number of different complexions of the gas molecules consistent with their total energy. Perhaps the simplest derivation of this quantity for a monatomic gas that has yet been given is one due to Brody,[5] which we shall reproduce below, taking account of the fact that the particular molecules with which we are concerned are electrons having a spin of angular momentum $h/4\pi$, where h is Planck's quantum of action.

Let us consider a gram-molecule of gas enclosed within a cubical box of side l, whose faces are perfectly smooth and elastic, so that at every collision of a molecule with a face, the two velocity components parallel to the face are unaffected, while that perpendicular to the face is reversed. The motion of each molecule is then "conditionally periodic," and the quantum conditions applying to the three components of momentum are

$$\left.\begin{aligned}\int mv_x dx &= n'h\\ \int mv_y dy &= n''h\\ \text{and}\qquad \int mv_z d_z &= n'''h\end{aligned}\right\}, \qquad (22)$$

where the integrals are taken along a side and back again, i.e. over a complete period. In these equations m represents the mass of a molecule, v_x, v_y; and v_z the three velocity components, and n', n'', and n''' positive whole numbers.

From the equations (22) we have at once

$$\left.\begin{aligned}|v_x| &= \frac{n'h}{2ml}\\ |v_y| &= \frac{n''h}{2ml}\\ \text{and}\qquad |v_z| &= \frac{n'''h}{2ml}\end{aligned}\right\}. \qquad (23)$$

Hence the energy of a molecule is

$$\tfrac{1}{2}m\,(v_x^2 + v_y^2 + v_z^2) = \frac{h^2}{8ml^2}(n'^2 + n''^2 + n'''^2), \qquad (24)$$

and the energy of the whole gas is

$$\mathrm{E} = \frac{h^2}{8ml^2}\sum_{r=1}^{\mathrm{N}}(n_r'^2 + n_r''^2 + n_r'''^2), \qquad (25)$$

where N is Loschmidt's number, i.e. the number of molecules in a gram-molecule.

The thermodynamic probability W is related to the number of different sets of values of the positive whole numbers n_1', n_1'', n_1''', n_2', . . ., n_{N}''' which satisfy equation (25), or rather, since in general no single set of values of the n can be found to satisfy it, $1/d\mathrm{E}$ of the number of sets of values corresponding to energies between E and E + dE. This latter number of sets may be arrived at as follows. Consider n_1',

n_1'', . . ., n_N''' as the rectangular co-ordinates of a point in a 3N-dimensional space. Then the number we seek is the number of points in this space whose co-ordinates are all positive whole numbers and which lie between the surfaces of the 3N-dimensional spheres of radii

$$\sqrt{\frac{8ml^2E}{h^2}},$$

and

$$\sqrt{\frac{8ml^2(E + dE)}{h^2}}.$$

Since the part of the 3N-dimensional space in which all the co-ordinates are positive is the 2^{-3N} fraction of the whole, the number we seek is

$$\frac{1}{2^{3N}}\frac{dV_{3N}}{dE}\,dE,$$

where V_{3N} is the volume of the 3N-dimensional sphere, and the probability W is related to the coefficient of dE, viz.,

$$W^{\times} = \frac{1}{2^{3N}}\frac{dV_{3N}}{dE}. \qquad . \qquad . \qquad . \qquad (26)$$

The next question to decide is that of the relationship between $W^{\times}$ and W. One thing that makes these two quantities differ from one another is the fact, now well established, that an electron has a definite spin and may be in either of two quantum states associated with this spin. In order not to interrupt unduly our present line of reasoning, let us now take this statement for granted, postponing its justification until later. Since there are two possible spin arrangements of each electron, there must be 2^N spin arrangements of the N electrons. The number of complexions is therefore greater than $W^{\times}$ by this factor on account of the spin, quite apart from anything else.

If we suppose an individuality to be assignable to the electrons, this is the only factor that differentiates W from $W^{\times}$, and we have

$$W = 2^N W^{\times}. \qquad . \qquad . \qquad . \qquad . \qquad (27)$$

If, on the other hand, we suppose this to be impossible, the mere interchange of two identical electrons will not introduce a new complexion, and W must be less than the value given it in (27) by the factor N !, the number of ways of arranging N different things. We shall cater for either assumption by putting N ! in the equation

$$W = \frac{2^{N}}{(N\,!)} W^{\times}, \qquad . \quad . \quad . \quad (28)$$

in brackets. N ! is to be thought of as present or absent in (28) and in the equations immediately to follow where it is bracketed, according as individuality is not or is assignable to the electrons.

On now eliminating $W^{\times}$ between (26) and (28) we have

$$W = \frac{1}{2^{2N}(N\,!)} \frac{dV_{3N}}{dE}. \qquad . \quad . \quad . \quad (29)$$

It may be shown by the aid of Dirichlet's multiple-integration formula that the volume of a sphere of radius r in $2n$-dimensional space is

$$\frac{\pi^{n}}{n\,!} r^{2n}.$$

Hence, if 3N is even,

$$V_{3N} = \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!}\left(\frac{8ml^{2}}{h^{2}}E\right)^{\frac{3N}{2}}, \qquad . \quad . \quad . \quad (30)$$

and substituting this in (29) we have

$$W = \frac{1}{2^{2N}(N\,!)} \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!}\left(\frac{8ml^{2}}{h^{2}}E\right)^{\frac{3N}{2}-1} \cdot \frac{3N}{2} \cdot \frac{8ml^{2}}{h^{2}}. \qquad . \quad (31)$$

Now let us consider the quantity $W_0{}'$, the thermodynamic probability for the condensed electrons at absolute zero. As the temperature of any system falls, its W decreases, and at the absolute zero it has reached the lowest value it ever can. If we assume that individuality is not assignable to the molecules, the lowest mathematical limit to W is unity, and we should expect this to be attained at absolute zero. On the other hand, in the supposed alternative case where individuality is assignable to the molecules we should expect

$_0'$, the value of W at absolute zero, to be N !. Thus, in either se, dividing (31) by W_0' we obtain

$$\frac{W}{W_0'} = \frac{1}{2^{2N}N\,!}\,\frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}\,!}\left(\frac{8ml^2}{h^2}E\right)^{\frac{3N}{2}-1}\cdot\frac{3N}{2}\cdot\frac{8ml^2}{h^2}. \qquad (32)$$

It might be thought that the condensed electrons at solute zero would be capable of as many spin arrangements those in the gaseous phase. Actually this is not so, how-er, as we shall see later when dealing with the theory of etals. The spin arrangements as well as the states of linear otion of the condensed electrons are " frozen " into a unique stem. It will be necessary, for the present, to accept this atement on trust.

We may now simplify (32) by neglecting small factors hich we are entitled to do, since we are not interested in /W_0' directly, but only in its logarithm) and applying irling's formula for the factorials of large numbers, viz.,

$$n\,! = n^n\epsilon^{-n}, \qquad (33)$$

d so obtain the equation

$$\frac{W}{W_0'} = 2^N\left(\frac{4\pi mE}{3h^2}\right)^{\frac{3N}{2}} l^{3N}\left(\frac{\epsilon}{N}\right)^{\frac{5N}{2}}, \qquad (34)$$

hence, eliminating l, N and E by means of

$$l^3 = \frac{RT}{p}, \qquad (35)$$

$$N = \frac{R}{k}, \qquad (36)$$

d

$$E = \tfrac{3}{2}RT \qquad (37)$$

spectively, taking logarithms, and substituting in (21), we nd for s the expression

$$= s_0' + \tfrac{5}{2}R\log T - R\log p + R\log\left\{\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\right\} + \tfrac{5}{2}R + R\log 2. \qquad (38)$$

n comparing this with

$$s = \tfrac{5}{2}R\log T - R\log p + \kappa, \qquad (7)$$

e see that

$$\kappa - s_0' = R\log\left\{\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\right\} + \frac{5}{2}R + R\log 2, \qquad (39)$$

and so, finally, we find for the vapour pressure constant tl value

$$\frac{\kappa - s_0'}{R} - \frac{5}{2} = \log\left\{\frac{2(2\pi m)^{3/2}k^{5/2}}{h^3}\right\}, \quad . \quad . \quad (4$$

which, substituted in (20), gives us

$$A_0 = \frac{4\pi mek^2}{h^3}, \quad . \quad . \quad . \quad (4$$

or, if we substitute for the constants their numerical value viz. $m=8{\cdot}99\times10^{-28}$ gm., $e=4{\cdot}77\times10^{-10}$ e.s.u., $k=1{\cdot}371\times10^{-}$ erg./deg., and $h = 6{\cdot}55 \times 10^{-27}$ erg. sec.,

$$A_0 = 3{\cdot}60 \times 10^{11}\ \text{e.s.u./cm.}^2\text{deg.}^2 = 120\ \text{amp/cm.}^2\text{deg.}^2. \quad (4$$

This, then, is the upper theoretical limit for the emission co stant A of an emitter whose c_p' is zero.

The Energy Distribution of the Free Interna Electrons.—In Chapter I a brief, qualitative sketch wa given of classical and modern statistical theories and of the application to the electron theory of metals. We shall no supplement this by a somewhat more detailed, quantitativ discussion.

In the statistical treatment of a monatomic gas, phas space, having six dimensions, three (x, y, z) of position and thre (ξ, η, ζ) of momentum, is divided into equal phase cells, an the various *different, possible* arrangements of the representativ points of the molecules among these cells are considere Each different arrangement is called a "complexion," an the normal, or most probable "statistical state" of the gas i assumed to be that which embraces the largest number o complexions. Characteristic of this statistical state is th so-called "distribution function" f, which gives the mos probable number dN of representative points in a sma portion $dx\,dy\,dz\,d\xi\,d\eta\,d\zeta$ of phase space about the point $(x, y, z$ $\xi, \eta, \zeta)$ by means of the equation

$$dN = f(x, y, z, \xi, \eta, \zeta)\,dx\,dy\,dz\,d\xi\,d\eta\,d\zeta. \quad . \quad (43$$

If the gas is not subjected to any field of force, f will be a function of the momenta ξ, η, ζ only, and in this case it ma easily be shown by a discussion involving merely three imensional "momentum space" that the number dN of olecules having (kinetic) energies between ε and $\varepsilon + d\varepsilon$ is iven by the following equation involving the "energy disribution function" $F(\varepsilon)$:

$$dN = F(\varepsilon)d\varepsilon, \quad . \quad . \quad . \quad . \quad (44)$$

here

$$F = 2\pi V(2m)^{3/2}\varepsilon^{1/2}f, \quad . \quad . \quad . \quad (45)$$

and m representing the volume of the gas and the mass f a molecule respectively. On the assumptions made as to hich complexions are possible and different from one another he forms of the functions f and F will depend.

In the classical statistics, all those complexions are taken o be possible ones for which the mass, energy and volume of he system as a whole are conserved, and the molecules are hought of as having individuality, so that an interchange of he representative points of two molecules between two phase ells gives a new complexion. On the basis of these assumptions he energy distribution function F takes the well-known axwellian form

$$F(\varepsilon) = \frac{2N}{\pi^{1/2}(kT)^{3/2}}\varepsilon^{1/2}\epsilon^{-\frac{\varepsilon}{kT}}, \quad . \quad . \quad . \quad (46)$$

here N is the total number of molecules.

In 1924 Bose[2] succeeded in treating statistically the adiation corpuscles, or photons, contained within a uniformemperature enclosure and in deriving by this method Planck's ell-known black-radiation formula. It is now well established hat the energy and momentum of a photon are respectively ν and $h\nu/c$, where ν is the frequency of the radiation, c is the elocity of light, and h is Planck's quantum of action. There s nothing corresponding to a conservation of the identity of photon with a change of momentum (or of frequency), so ose abandoned all attempt to attribute individuality to photons n any circumstances. He asserted that no new complexion ould be introduced by an interchange of photons (supposing hat such could be imagined) between two cells. This was ne important departure from the classical statistical method. nother, quite as important, was the assignment of a definite agnitude, viz. h^3, to the phase cells. This was to bring he new statistics into line with quantum principles.

It then occurred to Einstein [16] that if, as indicated by th success of the new method in deriving Planck's radiatio formula, Bose's assumptions are valid for radiation corpuscle they might well be valid for material particles also, for th parallelism between the properties of radiation and of materia particles was at this time becoming increasingly eviden If no individuality is assigned to the molecules of a monatomi gas in complexion-counting and the cells into which phas space is divided are each of magnitude h^3, the energy dis tribution function becomes

$$F(\varepsilon) = \frac{2\pi V(2m)^{3/2}\varepsilon^{1/2}}{h^3(\epsilon^{\lambda+\varepsilon/kT} - 1)}, \quad . \quad . \quad . \quad (47$$

where λ is a quantity which involves the temperature bu is independent of ε. It may be evaluated by equating th integral of $F(\varepsilon)d\varepsilon$ from 0 to ∞ to the total number o particles N.

Shortly after the development of the statistics of Bose an Einstein, Fermi,[18] and independently, Dirac,[10] proposed a important modification to their assumptions. This consiste in the extension to the statistics of material particles of Pauli' exclusion principle, which had hitherto proved very fruitfu in the realm of atomic structural physics. According to thi principle, no two electrons in any given atom may simul taneously be defined by the same set of four quantun numbers. As extended to the statistics of a gaseous systen the principle may be stated thus : No phase cell of magnitud h^3 may contain at any instant more than a single representa tive point of any one kind of molecule. The incorporation o this restriction into the Bose-Einstein statistics makes th distribution function

$$f(x, y, z, \xi, \eta, \zeta) = \frac{1}{h^3(\epsilon^{\lambda+\varepsilon/kT} + 1)}, \quad . \quad . \quad (48$$

and the energy distribution function

$$F(\epsilon) = \frac{2\pi V\,(2m)^{3/2}\epsilon^{1/2}}{h^3(\epsilon^{\lambda+\varepsilon/kT} + 1)}, \quad . \quad . \quad . \quad (49$$

where λ is again independent of ε. Thus the mathematica expressions of the Fermi-Dirac differ from those of the Bose Einstein statistics in the replacement of the -1 by $+1$ i the denominators.

For material gases at almost all temperatures and con-entrations realizable in the laboratory, both the Bose-Einstein nd Fermi-Dirac distributions are, as we shall now see, ndistinguishable from the Maxwellian.

It is easily seen that all three distributions must be the ame when

$$\epsilon^{\lambda+\varepsilon/kT} \gg 1, \quad . \quad . \quad . \quad . \quad (50)$$

r F(ε) is then the same kind of function of ε in (47) and 9) as it is in (46). Its integration over all ε-values for any iven temperature can give the same total number N of olecules in all three cases (as it must) only when

$$\frac{2\pi V\,(2m)^{3/2}\epsilon^{-\lambda}}{h^3} = \frac{2N}{\pi^{1/2}(kT)^{3/2}},$$

e. when

$$\epsilon^{-\lambda} = \frac{nh^3}{(2\pi mkT)^{3/2}}, \quad . \quad . \quad . \quad . \quad (51)$$

here n represents the number of molecules in unit volume. hus, bearing in mind that $\epsilon^{\varepsilon/kT}$ is not a very large quantity, being of the same order as kT, we see that the condition (50) r the practical equivalence of the three distributions may be ritten

$$\frac{nh^3}{(2\pi mkT)^{3/2}} \ll 1. \quad . \quad . \quad . \quad . \quad (52)$$

Let us consider, for example, the case of the monatomic as helium at normal temperature and pressure. It is easily alculated that for this case the left-hand side of (52) is only bout 4×10^{-6}. It would be possible to cool this gas to such low temperature and subject it to such a high pressure that he condition (52) would no longer be fulfilled, and one might hen hope to test experimentally which of the three distributions really has. All other gases, however, would liquefy long efore the distributions became appreciably different.

Now let us take the case of the densest external electron as that is ever likely to interest us—that which is supposed, our thermodynamical discussions, to be in equilibrium ith tungsten at its melting-point, 3655°K. (The high tempera-ure is unfavourable to the fulfilment of (52), since n increases uch faster than $T^{3/2}$.) Assuming the reflexion coefficient to be $\frac{1}{2}$, as is perhaps indicated by the fact that experimenta values of the emission constant of tungsten as low as abou $\frac{1}{2}A_0$ have been obtained, and giving the emission at 3655°K its value of 480 amp./cm.^{2}, we find for the left-hand sid of (52) a value of only $1{\cdot}2 \times 10^{-6}$. Thus there would be n noticeable departure of this gas from the classical distributio and our earlier assumption of this distribution is justified.

The case of the internal electron gas is, however, profoundl different. We shall not expect to be wrong in order of magnitude if we assume that the number of free internal electron is equal to the number of atoms. On this assumption, th number of free electrons in a cubic centimetre of tungster for example, would be $6{\cdot}4 \times 10^{22}$. For a gas of this concentration whose molecules have the small mass of electron the left-hand side of (52) would no longer be small compare with 1, even at the highest temperatures. Thus at 3655°K it would be about 120. The Fermi-Dirac and Bose-Einstei distributions would therefore no longer be equivalent to th Maxwellian or to one another.

But now it may be asked: Are we in any case entitled t treat the system of internal electrons as a gas? Can we ignor the forces exerted by the electrons on one another and thos between the electrons and the ions of the metal? Doubtles the assumption that we can do so is somewhat crude. W are, nevertheless, encouraged to neglect these forces at leas for the purposes of a first approximation when we remembe that (1) slow electrons are sometimes observed to go righ through atoms as if these were non-existent, and (2) electron behave not only as particles, but also as waves, and a wave train can travel through a system of obstacles, each of whic by itself would give rise to a dispersion, if these are arrange in a regular lattice whose spacing is smaller than the wavelength. This last-named condition is always fulfilled by a the electrons in which we are interested. The trial of treatin the internal free electrons as the molecules of a gas with Fermi distribution has, in fact, succeeded so well in explainin many of the properties of metals that the assumption seem to be amply justified.

Let us now consider the justification of the statemen made on page 237 concerning the electron spin. A spin of th lectron was first postulated in 1921 by A. H. Compton,[6] but he suggestion seems to have failed to attract the attention it leserved. In 1925 Uhlenbeck and Goudsmit [39] independently ut forward the same hypothesis in order to provide a physical nterpretation of the hitherto mysterious fourth quantum umber in the theory of spectra. In order to explain the eeman effect it is necessary to ascribe to the spinning electron n angular momentum of $\frac{1}{2}h/2\pi$ and a magnetic moment $eh/4\pi mc$. he new concept has not only proved very fruitful in the field f spectroscopy, but it has enabled the theoretical magnitude f the magneto-mechanical (Einstein and de Haas) effect to e reconciled with the experimental value, and furthermore, auli [29] has shown that by means of it the magnetic properties f the alkali metals can be satisfactorily accounted for.

In a magnetic field (which we may, if we like, take to be anishingly small), an electron will have its least potential nergy when its spin-vector is parallel to the field and its reatest when it is anti-parallel. According to the quantum heory, these are the only two orientations possible, since the ngular momentum about the direction of the field can change nly by an integral multiple of $h/2\pi$, and this is just twice he angular momentum associated with the spin. And since lectrons with opposite spins are necessarily in different quantum tates, their representative points may occupy the same cell f six-dimensional phase space without violating the extended auli exclusion principle. It is as if we had two different and ndependent electron gases, the parallel and the anti-parallel, he distribution of each being unaffected by the presence of he other. Thus the Fermi energy distribution function for he " mixed " electron gas is

$$F(\varepsilon) = G \cdot \frac{2\pi V(2m)^{3/2}\varepsilon^{1/2}}{h^3(\epsilon^{\lambda+\varepsilon/kT}+1)}, \quad . \quad . \quad . \quad (53)$$

vhere G, the " statistical weight " for an electron, is equal to 2.

As stated on page 242, λ may be evaluated by integrating he energy distribution function with respect to the variable over all ε-values from 0 to ∞ and equating the integral to N. Sommerfeld [35] has shown that where $\epsilon^{-\lambda}$ is large the integral may be expressed in the form of a convergent series, hus :

$$\int_0^\infty \mathrm{F}(\epsilon)d\epsilon = \mathrm{N} = \frac{\mathrm{GV}}{h^3}\cdot\frac{4\pi}{3}(2mk\mathrm{T}\alpha)^{3/2}\left(1+\frac{\pi^2}{8}\alpha^{-2}+\ .\ .\ .\right), \quad (54$$

where for convenience α is written for $-\lambda$. Let us assum for a moment that α is so large that we may without seriou error neglect all but the first term of the series. Then, writin n for N/V as before, we have

$$\alpha = \frac{h^2}{2mk\mathrm{T}}\left(\frac{3n}{4\pi\mathrm{G}}\right)^{2/3}. \quad .\quad .\quad .\quad (55$$

Assuming n to be equal to the number of atoms of metal pe cm.^{3}, we should have for the α of a Fermi free electron gas i tungsten at 3655°K. the value 5·95 and of course higher value at lower temperatures. The corresponding value of $\frac{\pi^2}{8}\alpha^{-2}$ i 0·035 at 3655°K. and less at lower temperatures. Thus ou neglect of the second and further terms in the series appear to be justified.

If we now write

$$\alpha k\mathrm{T} = \frac{h^2}{2m}\left(\frac{3n}{4\pi\mathrm{G}}\right)^{2/3} = \mu, \quad .\quad .\quad .\quad (56$$

the functions f and F become respectively

$$f(x, y, z, \xi, \eta, \zeta) = \frac{\mathrm{G}}{h^3\left(\epsilon^{\frac{\varepsilon-\mu}{k\mathrm{T}}}+1\right)} \quad .\quad .\quad (57$$

and

$$\mathrm{F}(\epsilon) = \mathrm{G}\,.\,\frac{2\pi\mathrm{V}(2m)^{3/2}\epsilon^{1/2}}{h^3\left(\epsilon^{\frac{\varepsilon-\mu}{k\mathrm{T}}}+1\right)}. \quad .\quad .\quad (58$$

This distribution is patently very different from th Maxwellian. Thus at absolute zero (where, incidentally (55 ceases to be merely an approximation),

$$f = \frac{\mathrm{G}}{h^3} \text{ or } 0$$

and

$$\mathrm{F} = \mathrm{G}\,.\,\frac{2\pi\mathrm{V}(2m)^{3/2}\epsilon^{1/2}}{h^3} \text{ or } 0$$

according as ϵ is less or greater than μ. Each phase cell t whose position in phase space corresponds an energy less tha μ contains the representative points of just two electrons (c pposite spins), whilst all cells beyond are empty. Thus the ero-temperature distribution function for nickel, which has wo free electrons per atom and for which μ is equal to 11·7 e.v., s shown in its dependence upon ε by the full line in Fig. 47. As the temperature is raised, the sharp corners become rounded ff and the curve approaches the ε-axis asymptotically. In fact, as ε becomes sufficiently greater than μ for the 1 in the denominator to be negligible in comparison with $\epsilon^{(\varepsilon-\mu)/kT}$, the distribution actually merges into the Maxwellian. The dashed curve shows the distribution in nickel at 1500°K.

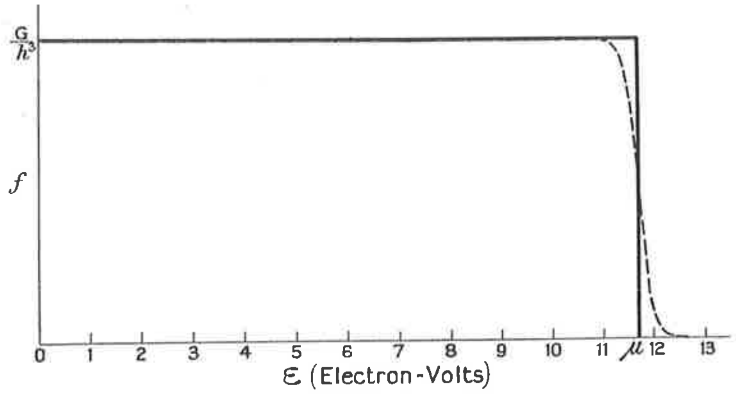

FIG. 47.—Relationship between the distribution function f and the energy ε of the free electrons in nickel at 0°K. and at 1500°K.

The Escape of a Fermi Electron Gas through a Potential Barrier.—The problem of the passage of electrons through the potential barrier at the surface of a metal is of a two-fold nature. First it is necessary to find the function N(W) by means of which we may express the number N(W)dW of electrons having kinetic energies corresponding to their normal velocity components between W and W + dW which impinge internally on unit area of the surface in unit time. Next we must find the transmission coefficient D(W) of these electrons through the barrier. The electron emission is then expressed simply by

$$i = e\int_0^\infty \mathrm{N(W)D(W)}d\mathrm{W},$$

or, since D(W) must vanish for all values of W less than C, b

$$i = e\int_{C}^{\infty} N(W)D(W)dW. \quad . \quad . \quad . \quad (59$$

For a gas whose molecules are not acted upon by an externa field of force, eqn. (43) may evidently be replaced by

$$dn = f(\xi, \eta, \zeta)\, d\xi\, d\eta\, d\zeta, \quad . \quad . \quad (60$$

where dn represents the number of molecules per unit volume having components of momentum between ξ, η, ζ and $\xi + d\xi$ $\eta + d\eta$, $\zeta + d\zeta$. The number of molecules $n(\xi)d\xi$ having a normal component of momentum between ξ and $\xi + d\xi$ is

$$n(\xi)d\xi = d\xi\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} f\,.\,d\eta d\zeta, \quad . \quad . \quad (61)$$

and the number passing in the positive direction through a unit of area of a surface $x =$ const. is therefore

$$\frac{\xi}{m}\,n(\xi)d\xi = \frac{\xi d\xi}{m}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} f\,.\,d\eta d\zeta. \quad . \quad . \quad (62)$$

On changing the variable from ξ to W, where $W = \xi^2/2m$, this becomes

$$N(W)dW = dW\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} f\,.\,d\eta d\zeta. \quad . \quad . \quad (63)$$

According to the modern electron theory of metals the free paths of the internal electrons are of the order of hundreds of atomic diameters. We may therefore take it that the emission is determined directly by the distribution of the electrons right in the interior of the metal rather than by any modified distribution there may be in the immediate neighbourhood of the surface. Taking for f the Fermi distribution function, Nordheim [25] has integrated the right-hand side of (63) and thus found for N(W) the expression

$$N(W) = \frac{2\pi G m k T}{h^3}\log\left(1 + \epsilon^{-\frac{W-\mu}{kT}}\right),. \quad . \quad (64)$$

with the following approximations :

$$N(W) = \frac{2\pi G m}{h^3}(\mu - W) \text{ for } \frac{W - \mu}{kT} \ll 0, \quad . \quad (64a)$$

$$N(W) = \frac{2\pi G m k T}{h^3} \text{ for } W \sim \mu, \quad . \quad . \quad . \quad (64b)$$

and $$N(W) = \frac{2\pi G m k T}{h^3} \epsilon^{-\frac{W-\mu}{kT}} \text{ for } \frac{W-\mu}{kT} \gg 0. \quad . \quad (64c)$$

This function is represented by the dashed curve in Fig. 48. The straight line represents the function at absolute zero.

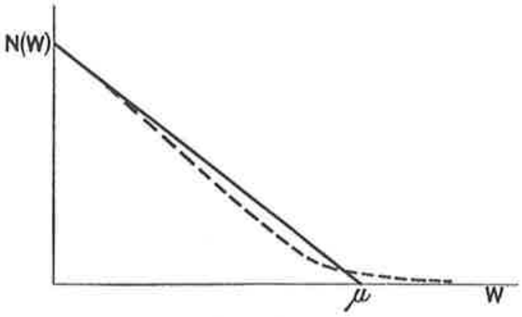

FIG. 48.

For our emission problem, however, it is unnecessary to work out the complete expression N(W), for the function only interests us for $W > C$. But, as we shall see in a moment, for $W > C$, $\epsilon^{(\varepsilon-\mu)/kT} \gg 1$, so that the distribution function reduces to the simple Maxwellian form (so far as ε is concerned ; not, of course, as regards temperature variation) :

$$f_{W>C} = \frac{G}{h^3}\epsilon^{-\frac{\varepsilon-\mu}{kT}}. \quad . \quad . \quad . \quad (65)$$

The integration of (63) thus becomes a perfectly simple matter.

That $\epsilon^{(\varepsilon-\mu)/kT} \gg 1$ for $W > C$ is evident from the following considerations. From (58) we see that at absolute zero, for $0 < \varepsilon < \mu$, the energy distribution function $F(\varepsilon)$ of an electron gas depends on ε only, and that beyond μ it is zero. There is an abrupt " cut-off " at $\varepsilon = \mu$, and since, according to (56), μ depends directly on n, so does the position of the cut-off. Consequently, the energy gained or lost by the metal when an infinitesimal quantity of electrons is condensed or evaporated at absolute zero is μ per electron. Thus we may identify $C - \mu$ with the latent heat of evaporation per electron at absolute zero, i.e. with the work function χ. The lower the work function of an emitter, the lower are in general also the temperatures at which the emission is commonly observed, and thus $\frac{C - \mu}{kT}$ or χ/kT is a quantity of a fairly constant order. It is, in fact, something like 10–30. Clearly, therefore, $\epsilon^{(C-\mu)/kT} \gg 1$.

In order, then, to obtain the expression for N(W) for this case, all we have to do is to neglect the 1 in the denominator of the Fermi distribution function and integrate. Thus from (63)

$$N(W)_{W>C} = \frac{G}{h^3}\epsilon^{\mu/kT}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\epsilon^{-\varepsilon/kT}d\eta d\zeta, \quad . \quad (66)$$

or, since
$$\varepsilon = \frac{\xi^2 + \eta^2 + \zeta^2}{2m}$$

and
$$\frac{\xi^2}{2m} = W,$$

$$N(W)_{W>C} = \frac{G}{h^3}\epsilon^{-\frac{W-\mu}{kT}}\int_{-\infty}^{+\infty}\epsilon^{-\frac{\eta^2}{2mkT}}d\eta\int_{-\infty}^{+\infty}\epsilon^{-\frac{\zeta^2}{2mkT}}d\zeta$$
$$= \frac{G}{h^3} \cdot 2\pi mkT \cdot \epsilon^{-\frac{W-\mu}{kT}}. \quad . \quad . \quad . \quad (67)$$

Incidentally, it is important to note that if the transmission coefficient D(W) is independent of W for all values of W greater than C, the normal velocity distribution of the electrons that get through the surface must still be Maxwellian after emergence. This is at once evident from the form of (67).

The expression (59) for the emission now becomes

$$i = \frac{4\pi mekT}{h^3}\int_{C}^{\infty}D(W)\epsilon^{-\frac{W-\mu}{kT}}dW, \quad . \quad . \quad (68)$$

G having been given its value of 2. Obviously the integral in this equation may be replaced by

$$\overline{D}\int_{C}^{\infty}\epsilon^{-\frac{W-\mu}{kT}}dW,$$

where $\overline{D}$ is the mean transmission coefficient at the temperature T for all the electrons whose W lies between C and ∞.

Thus, substituting this for the integral in (68) and integrating, we obtain for the emission the formula

$$i = \overline{\mathrm{D}} \cdot \frac{4\pi mek^2}{h^3}\mathrm{T}^2\epsilon^{-\frac{\mathrm{C}-\mu}{k\mathrm{T}}}, \quad . \quad . \quad . \quad (69)$$

which, if we may identify $\overline{\mathrm{D}}$ with $1 - \bar{r}$, may be written

$$i = (1 - \bar{r})\mathrm{A}_0\mathrm{T}^2\epsilon^{-\frac{\mathrm{C}-\mu}{k\mathrm{T}}}, \quad . \quad . \quad (70)$$

where A_0 has the same value as in (42), viz. 120 amp./cm.^{2}deg.^{2}.

The rate of escape of a Fermi electron gas through a plane potential barrier was first calculated by L. Nordheim,[26] and independently, without, however, taking into account the possibility of a finite internal reflexion or of the electron spin, by A. Sommerfeld.[35] The emission formula arrived at in this way is remarkable in that it not only agrees in form with that derived thermodynamically, but the maximum emission constant of which it allows is identical with that obtained by v. Laue and Dushman, corrected for the electron spin, from consideration of the vapour pressure constant of an ideal external electron gas.

According to this theory C, the inner potential of a metal multiplied by the electronic charge, must exceed the work function χ by μ, the maximum kinetic energy of the electrons in the cold metal. In the case of tungsten, for example, the value of μ would be 5·8, 9·2, . . . e.v. according to the number (1, 2, . . .) of free electrons per atom, and since χ for tungsten is 4·5 e.v., the corresponding values of C would be 10·3, 13·7, . . . e.v. In the case of nickel, μ for one electron per atom would be 7·4 e.v., and for two it would be 11·7 e.v. The work function of nickel is 5·0 e.v., so that the corresponding values of C would be 12·4 and 16·7 e.v. respectively. There is good reason to believe that the number of valency electrons in nickel is two per atom, so we should expect the actual value of C for this metal to be 16·7 e.v., or that of the inner potential to be 16·7 volts.

Now fortunately there is a method for determining the inner potential of a metal which is independent of any thermionic of photoelectric measurements. When electrons are reflected by a metal single crystal, well-defined reflexion maxima occur corresponding to certain angles of incidence. This is due to the penetration of the electron waves to several atomic diameters beneath the surface and their interference after reflexion from different net planes. Thus if the geometry of the crystal lattice is known, it is possible from the positions of the maxima to calculate the wave-length of the electrons in the metal, and hence, by means of the well-known de Broglie relation

$$\lambda = \frac{h}{mv} \qquad . \qquad . \qquad . \qquad . \qquad (71)$$

connecting the wave-length λ with the electron velocity v, their kinetic energy. This must exceed the kinetic energy possessed by the electrons before they enter the metal by C.[32]

The metal for which the most reliable electron diffraction data are available is nickel. The first observations with this metal were made by Davisson and Germer[8] in 1927, and interpreted by Bethe[1] and by Eckart.[15] According to the data of Davisson and Germer the inner potential of nickel is 18 volts. Later results with this and a number of other metals have been obtained by Rupp.[33] The experiments are rather difficult and it is not always possible to be sure of the accuracy of the results to within less than 2 or 3 volts. Rupp's best value for nickel is 16·5 volts. This, as well as the 18 volts obtained by Davisson and Germer is in very satisfactory agreement with the value we should have expected for this metal. The values of inner potential obtained from electron diffraction data for other metals are also generally of the order to be expected according to the new theory.

The Transmission Coefficient.—The mean transmission coefficient $\overline{\mathrm{D}}$ is, of course, the same as $1 - \bar{r}$, where $\bar{r}$ is the mean coefficient of internal reflexion for the electrons whose normal velocity is sufficient to enable them to escape.

It is important to note at the outset that the reflexion coefficient is the same for both directions of travel of the electrons, into and out of the metal. More precisely stated, the coefficient of external reflexion averaged over a certain incident velocity range is equal to that of internal reflexion for the electrons whose velocities would be spread over the same range after emergence. For if it were not so, the equilibrium of an external electron gas with a condensed phase could not be expressed, as thermodynamically it must be, simply by eqn. (15), which takes no account of reflexion coefficients. The equality of the two reflexion coefficients has also been proved directly by Nordheim [26] on the basis of the laws of reflexion.

The reflexion of electron waves incident on a plane potential discontinuity or hill has been theoretically investigated by Nordheim [26, 27] and by Fowler and Nordheim,[21] and expressions for $\overline{\mathrm{D}}$ derived for a number of different cases.

By combining the de Broglie relation (71) with the equation

$$\frac{\partial^2 \mathrm{S}}{\partial t^2} = \frac{\lambda^2}{\tau^2}\nabla^2\mathrm{S}, \qquad . \quad . \quad . \quad (72)$$

describing the wave propagation of a sine-function S of the time t whose period is τ, the well-known Schrödinger wave equation

$$\nabla^2\mathrm{S} + \frac{8\pi^2 m}{h^2}(\mathrm{E} - \mathrm{U})\mathrm{S} = 0 \qquad . \quad . \quad (73)$$

is obtained, in which E and U represent the total and potential energies respectively of the particle.

For the case of electrons approaching a plane potential barrier whose plane is perpendicular to the x-direction, the substitution in (73) of

$$\mathrm{S} = \psi(x)\epsilon^{\frac{2\pi\iota}{h}(yk_y + zk_z)} \qquad . \quad . \quad . \quad (74)$$

in which k_y and k_z are constants (obviously having the dimensions of momentum), and ι is written for $\sqrt{-1}$,* gives us

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}\left(\mathrm{E} - \frac{k_y{}^2 + k_z{}^2}{2m} - \mathrm{U}\right)\psi = 0,$$

or, writing $\varkappa^2$ for $\frac{8\pi^2 m}{h^2}$ and W for $\mathrm{E} - \frac{k_y{}^2 + k_z{}^2}{2m}$, i.e. for the total energy apart from that associated with the components of velocity in the y and z directions,

$$\frac{d^2\psi}{dx^2} + \varkappa^2(\mathrm{W} - \mathrm{U})\psi = 0. \; . \qquad . \quad . \quad (75)$$

Thus our problem is reduced to one in a single dimension.

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* This symbol is used instead of the more usual i, as the latter is already in use to denote electron emission.

In this equation, the square of the absolute magnitude of the wave function ψ (i.e. the kind of quantity that would represent the energy of a wave in classical physics) in any particular region is, according to the wave-mechanical theory, proportional to the " probability-density " of a particle's being in that region. Thus the relative probability that the position of an electron is in an element dx is $|\psi|^2 dx$.

Let us consider, first of all, regions of constant potential, and therefore of constant W — U. For such regions the solution of eqn. (75) is

$$\psi = c\epsilon^{-\iota\varkappa(\mathrm{W}-\mathrm{U})^{1/2}x} + c'\epsilon^{\iota\varkappa(\mathrm{W}-\mathrm{U})^{1/2}x}. \qquad (76)$$

The constants c and c' correspond to the electrons travelling with speeds $v = \sqrt{\frac{2(\mathrm{W}-\mathrm{U})}{m}}$ in the positive and negative x-directions respectively. The density ($\propto$ probability) of the electrons travelling in the positive direction is proportional to $|c|^2$ and the current, therefore, to $|c|^2$ multiplied by the velocity, i.e. to $|c|^2(\mathrm{W}-\mathrm{U})^{1/2}$. Similarly, the negative current is proportional to $|c'|^2(\mathrm{W}-\mathrm{U})^{1/2}$. Let us write $c(\mathrm{W}-\mathrm{U})^{1/4} = a$ and $c'(\mathrm{W}-\mathrm{U})^{1/4} = a'$. Then eqn. (76) may be written

$$\psi = \frac{a}{(\mathrm{W}-\mathrm{U})^{1/4}}\epsilon^{-\iota\varkappa(\mathrm{W}-\mathrm{U})^{1/2}x} + \frac{a'}{(\mathrm{W}-\mathrm{U})^{1/4}}\epsilon^{\iota\varkappa(\mathrm{W}-\mathrm{U})^{1/2}x}. \qquad (77)$$

These substitutions are convenient, for now $|a|^2$ and $|a'|^2$ are proportional directly to the positive and negative *currents* respectively. The constants a and a' are, of course, in general complex.

Now it has been found by Nordheim,[26] employing a mathematical method due to Jeffreys,[23] that under certain conditions the solution for regions of variable potential may be expressed in an analogous form. The quantity $\varkappa$ is very large, its numerical value being 4×10^{13}, and so Nordheim sought to develop $\psi(x)$ in a series of falling powers of $\varkappa$, thus :

$$\psi(x) = \varphi(x)\epsilon^{\iota\varkappa\omega}\left(1 + \frac{f_1}{\varkappa} + \frac{f_2}{\varkappa^2} + \ldots\right). \qquad (78)$$

Substituting this in (75) and equating the coefficients of the various powers of $\varkappa$ to zero (which must be their value for the substitution to be valid), we obtain

$$\left.\begin{aligned}&(a)\quad \left(\frac{d\omega}{dx}\right)^2 = \mathrm{W}-\mathrm{U},\\ &(b)\quad \frac{\frac{d\varphi}{dx}}{\varphi} = -\frac{\frac{d^2\omega}{dx^2}}{2\frac{d\omega}{dx}},\\ &(c)\quad \frac{df_1}{dx} = \frac{\iota\frac{d^2\varphi}{dx^2}}{2\varphi\frac{d\omega}{dx}}\\ &\qquad + \text{terms in } f_2 \text{ etc.,}\\ &\qquad \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\end{aligned}\right\} \quad . \quad . \quad (79)$$

whence

$$\left.\begin{aligned}&(a)\quad \omega = \pm\int(\mathrm{W}-\mathrm{U})^{1/2}dx,\\ &(b)\quad \varphi = \left(\frac{d\omega}{dx}\right)^{-1/2} = (\mathrm{W}-\mathrm{U})^{-1/4},\end{aligned}\right\} \quad . \quad . \quad (80)$$

and therefore, where the series in (78) sufficiently strongly converges, we have for an approximate solution of (75)

$$\psi = (\mathrm{W}-\mathrm{U})^{-1/4}\epsilon^{\pm\iota\varkappa\int^{x}(\mathrm{W}-\mathrm{U})^{1/2}dx}, \quad . \quad . \quad (81)$$

and for the most general solution

$$\psi = \frac{a}{(\mathrm{W}-\mathrm{U})^{1/4}}\epsilon^{-\iota\varkappa\int_{x_0}^{x}(\mathrm{W}-\mathrm{U})^{1/2}dx} + \frac{a'}{(\mathrm{W}-\mathrm{U})^{1/4}}\epsilon^{\iota\varkappa\int_{x_0}^{x}(\mathrm{W}-\mathrm{U})^{1/2}dx}, \quad (82)$$

with the condition that ψ has the value $\dfrac{a+a'}{(\mathrm{W}-\mathrm{U})^{1/4}}$ at $x=x_0$.

Obviously in (82), as in (77), $|\,a\,|^2$ and $|\,a'\,|^2$ are proportional to the positive and negative electron current, respectively, and thus it is seen that wherever (82) is a solution the currents in the two directions are constant with regard to x, i.e. there is no reflexion.

This conclusion can no longer be drawn, however, when

(81) is not a sufficiently good approximation to a solution of (75), i.e. when the condition

$$\frac{f_1}{\varkappa} + \frac{f_2}{\varkappa^2} + \ldots \ll 1 \quad . \quad . \quad . \quad (83)$$

is not fulfilled. From (79*c*) and (80) we find that

$$\frac{1}{\varkappa}\frac{df_1}{dx} = \frac{\iota}{8\varkappa}(\mathrm{W} - \mathrm{U})^{-3/2}\left[\frac{d^2\mathrm{U}}{dx^2} + \frac{5}{4}(\mathrm{W} - \mathrm{U})^{-1}\left(\frac{d\mathrm{U}}{dx}\right)^2\right]$$
$$+ \text{ terms in } f_2 \text{ etc.,} \quad . \quad . \quad . \quad (84)$$

and so, if we may assume the order of magnitude of the left-hand side of (83) to be given by its first term, we have for our condition that (81) shall be an acceptable solution of (75),

$$\frac{1}{8\varkappa}\int_{x_0}^{x}(\mathrm{W} - \mathrm{U})^{-3/2}\left[\frac{d^2\mathrm{U}}{dx^2} + \frac{5}{4}\,(\mathrm{W} - \mathrm{U})^{-1}\left(\frac{d\mathrm{U}}{dx}\right)^2\right]dx \ll 1. \quad (85)$$

It is at once evident on inspection that this condition will not be fulfilled, and therefore the reflexion may become appreciable, in regions where either $\frac{d^2\mathrm{U}}{dx^2}$ or $\frac{d\mathrm{U}}{dx}$ is sufficiently large, or where W − U is sufficiently small. On the whole, the more gentle the transition from the potential inside the metal to that outside the less shall we expect the reflexion to be.

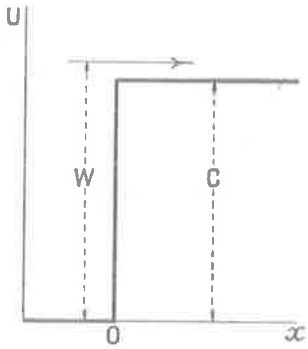

Fig. 49.

Nordheim[26] has investigated the reflexion at a potential discontinuity, such as is depicted in Fig. 49. This case is interesting, being that in which the potential change is the most abrupt conceivable and which we should therefore expect to give the greatest reflexion possible where there is no hump.

Let the potential discontinuity be at $x = 0$. On each side of the U-axis, then, the potential is constant, and the wave equations may be written

$$\psi = \frac{a}{\mathrm{W}^{1/4}}\epsilon^{-\iota\varkappa\sqrt{\mathrm{W}}\,.\,x} + \frac{a'}{\mathrm{W}^{1/4}}\epsilon^{\iota\varkappa\sqrt{\mathrm{W}}\,.\,x} \quad . \quad . \quad (86)$$

or $x < 0$ and

$$\psi = \frac{b}{(W - C)^{1/4}}\epsilon^{-\iota\varkappa\sqrt{W-C}\,.\,x} + \frac{b'}{(W - C)^{1/4}}\epsilon^{\iota\varkappa\sqrt{W-C}\,.\,x} \qquad (87)$$

or $x > 0$.

Now it may be shown (as it has been, for example, by Faxén and Holtsmark[17]) that both ψ and $\frac{d\psi}{dx}$ must be everywhere continuous. The condition that ψ shall be continuous at $x = 0$ is

$$a + a' = (b + b')\left(\frac{W}{W - C}\right)^{1/4}, \quad . \quad . \quad (88)$$

and the condition that $\frac{d\psi}{dx}$ shall be continuous is

$$a - a' = (b - b')\left(\frac{W - C}{W}\right)^{1/4}. \quad . \quad . \quad (89)$$

If, in particular, there are no electrons impinging on the discontinuity from the right, b' must be zero, and the transmission coefficient is expressed by

$$D(W) = \frac{b^2}{a^2} = \frac{4\sqrt{W}\sqrt{W - C}}{(\sqrt{W} + \sqrt{W - C})^2}. \quad . \quad . \quad (90)$$

It is seen from this that D(W) increases from 0 to 1 as W ncreases from C to infinity. Furthermore, it is evident from the symmetry of the formula that D(W) for electrons impinging on the discontinuity from the left is equal to D(W — C) for those impinging from the right.

For the mean transmission coefficient defined on page 250 we have

$$\bar{D} = \frac{\int_C^\infty D(W)\epsilon^{-\frac{W-\mu}{kT}}dW}{\int_C^\infty \epsilon^{-\frac{W-\mu}{kT}}dW} = \frac{\int_C^\infty D(W)\epsilon^{-\frac{W}{kT}}dW}{\int_C^\infty \epsilon^{-\frac{W}{kT}}dW} \quad . \quad (91)$$

The problem of evaluating this quantity is appreciably simplified if we now make use of the fact just stated that D(W) for electrons travelling from left to right is the same as

D(W − C) for those travelling in the reverse direction. Writing x for $\dfrac{W - C}{kT}$ we then have

$$\bar{D} = \int_0^\infty D(kTx)\epsilon^{-x}dx, \quad . \quad . \quad . \quad (92)$$

and substituting (90) in (92), changing − C to + C on account of the change in the direction of motion of the electrons considered, we obtain finally

$$\bar{D} = \int_0^\infty \frac{4\sqrt{kTx}\sqrt{kTx + C}}{(\sqrt{kTx} + \sqrt{kTx + C})^2}\epsilon^{-x}dx. \quad . \quad (93)$$

We need not consider the electrons which approach the metal with energies kTx greater than C, for on account of the exponential factor those with relatively large energies make no appreciable contribution to the integral in (93). Thus we may develop the factor under the integration sign with which $\epsilon^{-x}\,dx$ is multiplied in a converging series of powers of $\sqrt{\dfrac{kTx}{C}}$, obtaining

$$\bar{D} = 4\sqrt{\frac{kT}{C}}\int_0^\infty \sqrt{x}\left(1 - 4\sqrt{\frac{kTx}{C}} + \frac{17}{2}\frac{kTx}{C} - + \dots\right)\epsilon^{-x}dx$$
$$= 4\sqrt{\frac{kT}{C}}\left(\frac{1}{2}\sqrt{\pi} - 4\sqrt{\frac{kT}{C}} + \frac{51}{16}\sqrt{\pi}\frac{kT}{C} - + \dots\right). \quad . \quad (94)$$

Since the series alternates, it seems safe to assume that the error incurred by cutting it off short at a certain point will not be greater than the last term considered. Thus

for $\dfrac{kT}{C} = \dfrac{1}{50}$, $\bar{D} = 0{\cdot}24 \pm 0{\cdot}08$,

and for $\dfrac{kT}{C} = \dfrac{1}{100}$, $\bar{D} = 0{\cdot}18 \pm 0{\cdot}02$.

In the case of tungsten, for example, on the assumption that C is 10·3 e.v. (corresponding to one free electron per atom) kT/C would be $\frac{1}{50}$ and $\frac{1}{100}$ at the temperatures 2400° and 1200°K. respectively. Thus it is seen that the temperature dependence of $\bar{D}$ is not very important.

By an analogous reasoning, straightforward but rather borious, Nordheim [26] * has found the transmission coefficient

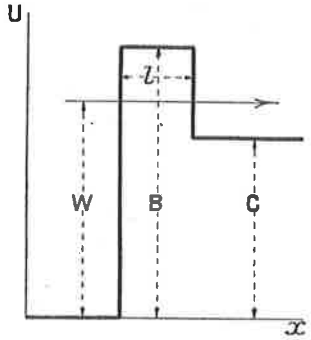

FIG. 50.

electrons of energy W through the square-shouldered potenal hump of Fig. 50 to be expressed by

;)

$$\mathrm{D(W)} = 0 \text{ for } \mathrm{W} < \mathrm{C},$$

)

$$\mathrm{D(W)} = \frac{8\left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}}\right)^{1/2}}{\left[\frac{\mathrm{B(B-C)}}{\mathrm{W(B-W)}} \cosh (2\varkappa \mathrm{B} - \mathrm{W})^{1/2} l + \left\{1 + \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}}\right)^{1/2}\right\}^2 - \left\{\left(\frac{\mathrm{B}-\mathrm{W}}{\mathrm{W}}\right)^{1/2} - \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{B}-\mathrm{W}}\right)^{1/2}\right\}^2\right]}$$

$$\text{for } \mathrm{C} < \mathrm{W} < \mathrm{B}, \qquad (95)$$

nd

)

$$\mathrm{D(W)} = \frac{8\left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}}\right)^{1/2}}{\left[\frac{\mathrm{B(C-B)}}{\mathrm{W(W-B)}} \cos 2\varkappa\, (\mathrm{W} - \mathrm{B})^{1/2} l + \left\{1 + \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}}\right)^{1/2}\right\}^2 + \left\{\left(\frac{\mathrm{W}-\mathrm{B}}{\mathrm{W}}\right)^{1/2} + \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}-\mathrm{B}}\right)^{1/2}\right\}^2\right]}$$

$$\text{for } \mathrm{W} > \mathrm{B}.$$

(W) is shown graphically as a function of W in Fig. 51. owler [19] has found that provided the hump is not too wide

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* An algebraical slip which appeared in Nordheim's paper was subseently corrected by Fowler.[19]

in relation to its height, the mean transmission coefficient approximately

$$\bar{D} = 8\sqrt{\pi}\frac{(kTC)^{1/2}}{B}\epsilon^{-2\kappa l(B-C)^{1/2}}. \qquad (9$$

A particularly interesting thing about these results is tha the transmission of electrons becomes finite before the energy has attained the value B. Classically this would b impossible.

Of course, no such sharp corners as are depicted in Fig 49 and 50 can actually occur in nature, and, as the discussio on page 256 would lead us to expect, their rounding off bring with it an important increase in the transmission.

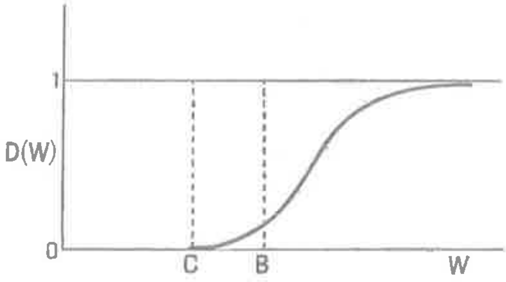

Fig. 51.

Thus, in the case where there is no hump, the upper par of the potential step must be of the shape determined by th image force. If we again take C to be the energy correspondin to the total height of the step, the shape of its upper portio is given by

$$U = C - \frac{e^2}{4x}, \qquad (97$$

where x is the distance from the surface of the metal, an thus

$$\frac{dU}{dx} = \frac{e^2}{4x^2} \qquad (98$$

and

$$\frac{d^2U}{dx^2} = -\frac{e^2}{2x^3}. \qquad (99$$

The kinetic energy with which the electrons that contribut the bulk of the thermionic current emerge from the metal i only a small fraction of an electron-volt, whereas C is generally of the order of 10–15 e.v. Neglecting the difference between C and W, then, we have by (97)

$$W - U = \frac{e^2}{4x}. \quad . \quad . \quad . \quad (100)$$

Hence from (98), (99) and (100) we find that both terms under he integral sign in (85) are of the same order and vary as $x^{-3/2}$. We are thus led to expect that the bulk of the reflexion occurring in the image-force part of the potential step will do so at its lower portion. Incidentally, we have here *à postiori* justification for our identification, for purposes of approximation, of W with C.

We do not know what proportion of the total potential step is due to the image force. If it were the whole, we should have a hill of the form of the full line n Fig. 52, the potential rise commencing abruptly at $x = x_0$, where $x_0 = e^2/4C$. Thus if C were 12 e.v., x_0 would be 0·30Å. But this is much less than the distance between adjacent atoms, and it is difficult to see how there can be a true mage force until a distance of at least one or two atomic diameters from the surface has been passed through. The real shape of the ower part of the potential step might be something like that of the dashed curve, for which both terms under the integration sign in (85) would be comparatively small.

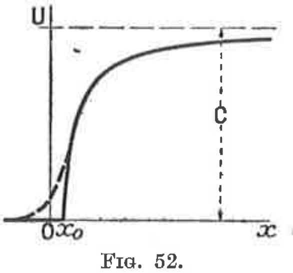

FIG. 52.

For a pure image-force step of height 12 volts, Nordheim [27] has found, by a process which is rather too involved to be conveniently reproduced here, that the transmission coefficient s 0·93, the reflexion thus being only 7 per cent. For an actual step we should expect from the foregoing discussion that the reflexion would be considerably less still, i.e. for practical purposes negligible. The emission constant would then be equal to the theoretical A_0, viz. about 120 amp./cm.^{2}deg.^{2}. From the fact that the experimentally determined emission constants of the majority of clean metals are of this order,*

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* As we shall see later, departures of experimental values of A for clean metals from 120 amp./cm.^{2}deg.^{2} by factors up to about 2 may possibly be due to the finiteness of c_p'.

it would appear probable that the potential barriers at the surfaces are of the type represented by the dashed curve Fig. 52.

Now let us consider the passage of electrons of energy through a potential barrier with a hump such as is depicte in Fig. 53, the potential energy B corresponding to who highest point is greater than W. The last, asymptotic ri in which the potential energy approaches the value C is du to the image force. Let the potential gradient be nowhe steep enough or its rate of change rapid enough to render (8 invalid, except for regions withi a certain distance of the points and d where the classical kinet energy of the electrons vanishe Apart from these regions, the (82) must be a solution of (75 Sufficiently near c and d, howeve the condition (85) will not be fu filled, for as U approaches W th quantity under the integration sig diverges. It is therefore not legit mate to take (82) as a solution fo regions near these points. Nevertheless, the absence of an obvious physical reason why a particularly important reflexio should be associated with the passage of the waves throug these critical regions encourages us to hope that by proceedin as if (82) were a solution for the whole potential barrier, onl avoiding any attempt to attach a meaning to ψ for the region near c and d, we might arrive at a value for D(W) which woul be at least approximately correct. According to Nordheim, a rigorous mathematical discussion, in which the critical region are treated specially, justifies this procedure, and shows tha the result to which it leads is a very good approximatio indeed to the correct value of D(W).

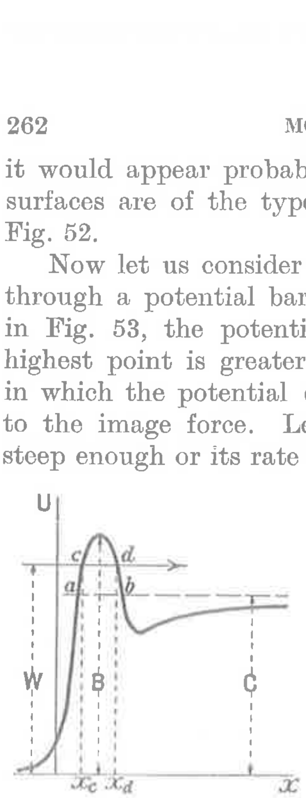

FIG. 53.

For that part of the potential barrier to the left of c, U i less than W, and, as we saw on page 255, $|a|^2$ and $|a'|^2$ i (82) are proportional to the positive and negative current respectively, so that there is no reflexion. For values of between x_c and x_d, however, U is greater than W, and i consequence the exponents in (82) become real. The equation may therefore be written

$$\psi = \frac{a\epsilon^{-\varkappa\int_{x_c}^{x}(\mathrm{U}-\mathrm{W})^{1/2}dx}}{(\mathrm{W}-\mathrm{U})^{1/4}} + \frac{a'\epsilon^{\varkappa\int_{x_0}^{x}(\mathrm{U}-\mathrm{W})^{1/2}dx}}{(\mathrm{W}-\mathrm{U})^{1/4}}. \qquad (101)$$

Finally, for $x > x_d$, U is again less than W, and we have therefore

$$\psi = \frac{a\epsilon^{-\varkappa\int_{x_0}^{x_d}(\mathrm{U}-\mathrm{W})^{1/2}dx}}{(\mathrm{W}-\mathrm{U})^{1/4}}\epsilon^{\iota\varkappa\int_{x_d}^{x}(\mathrm{W}-\mathrm{U})^{1/2}dx} + \frac{a'\epsilon^{\varkappa\int_{x_0}^{x_d}(\mathrm{U}-\mathrm{W})^{1/2}dx}}{(\mathrm{W}-\mathrm{U})^{1/4}}\epsilon^{\iota\varkappa\int_{x_d}^{x}(\mathrm{W}-\mathrm{U})^{1/2}dx}. \qquad (102)$$

From this it is evident that the electron current travelling in the positive direction has been weakened by the factor

$$\mathrm{D}(\mathrm{W}) = \frac{\left(|a|\epsilon^{-\varkappa\int_{x_0}^{x_d}(\mathrm{U}-\mathrm{W})^{1/2}dx}\right)^2}{|a|^2} = \epsilon^{-2\varkappa\int_{x_0}^{x_d}(\mathrm{U}-\mathrm{W})^{1/2}dx}. \qquad (103)$$

The mean transmission coefficient $\overline{\mathrm{D}}$ is, as we saw on page 257, given by

$$\overline{\mathrm{D}} = \frac{\int_{\mathrm{C}}^{\infty}\mathrm{D}(\mathrm{W})\epsilon^{-\frac{\mathrm{W}}{k\mathrm{T}}}d\mathrm{W}}{\int_{\mathrm{C}}^{\infty}\epsilon^{-\frac{\mathrm{W}}{k\mathrm{T}}}d\mathrm{W}} \qquad (91)$$

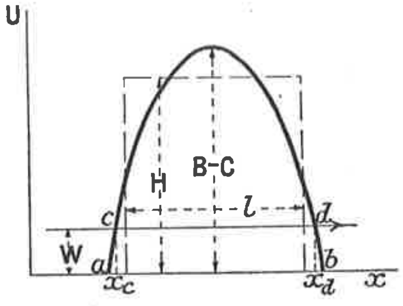

FIG. 54.

It is evident that this is the same as the transmission through the hill of Fig. 54, on which electrons impinge with a Maxwellian velocity distribution. Thus (91) becomes

$$\bar{\mathrm{D}} = \frac{1}{k\mathrm{T}}\int_0^\infty \mathrm{D}(\mathrm{W})\epsilon^{-\frac{\mathrm{W}}{k\mathrm{T}}}d\mathrm{W}, \qquad (104)$$

and, if B — C is of the order of an electron-volt, as it generally is, this may, on account of the exponential factor, be replaced by the approximate expression

$$\bar{\mathrm{D}} = \frac{1}{k\mathrm{T}}\int_0^{\mathrm{B}-\mathrm{C}} \mathrm{D}(\mathrm{W})\epsilon^{-\frac{\mathrm{W}}{k\mathrm{T}}}d\mathrm{W}. \qquad (105)$$

Except in the case of geometrically very simple forms of hill, the evaluation of $\bar{\mathrm{D}}$ is a matter of considerable difficulty. However, if we perform the calculation for an idealized, square-shouldered hill, such as is shown dashed in Fig. 54, we may still expect to be able to arrive at a rough estimate of the kinds of heights and thicknesses that would be necessary to produce any given reflexion. We may, of course, ignore the steepness of the sides and the sharpness of the corners of this idealized hill, since we are not at present interested in the reflexion this actual hill would produce, but only in that produced by the curved hill it roughly replaces.

Let the imagined rectangular-shaped hill have a thickness l and a height whose energy-equivalent is H. Then eqn. (103) becomes

$$\mathrm{D}(\mathrm{W}) = \epsilon^{-2\varkappa l(\mathrm{H}-\mathrm{W})^{1/2}}, \qquad (106)$$

and substituting this in (105) we obtain

$$\bar{\mathrm{D}} = \frac{1}{k\mathrm{T}}\int_0^{\mathrm{H}} \epsilon^{-2\varkappa l(\mathrm{H}-\mathrm{W})^{1/2}-\frac{\mathrm{W}}{k\mathrm{T}}}d\mathrm{W}. \qquad (107)$$

For $\mathrm{W} \ll \mathrm{H}$, we may write $\mathrm{H}^{1/2}\left(1 - \frac{1}{2}\frac{\mathrm{W}}{\mathrm{H}}\right)$ for $(\mathrm{H} - \mathrm{W})^{1/2}$. On account of the factor $\epsilon^{-\frac{\mathrm{W}}{k\mathrm{T}}}$ we may still make this substitution even for those W for which it is no longer valid, without incurring serious error, provided only that H is large enough, and so obtain

$$\bar{\mathrm{D}} = \frac{1}{k\mathrm{T}}\int_0^{\mathrm{H}} \epsilon^{-2\varkappa l\mathrm{H}^{1/2}+\varkappa l\frac{\mathrm{W}}{\mathrm{H}^{1/2}}-\frac{\mathrm{W}}{k\mathrm{T}}}d\mathrm{W} = \frac{\epsilon^{-\varkappa l\mathrm{H}^{1/2}-\frac{\mathrm{H}}{k\mathrm{T}}} - \epsilon^{-2\varkappa l\mathrm{H}^{1/2}}}{\frac{\varkappa lk\mathrm{T}}{\mathrm{H}^{1/2}} - 1}. \qquad (108)$$

If, for example, we take H to be 1 electron-volt, $l = 3$Å. and $T = 1000$°K., then $\varkappa l H^{1/2} = 1{\cdot}53$, $H/kT = 11{\cdot}6$ and $\frac{\varkappa l k T}{H^{1/2}} = 0{\cdot}13$. Thus, where H is of this order, we may, neglecting small quantities, replace (108) by

$$\bar{D} = \frac{\epsilon^{-2\varkappa l H^{1/2}}}{1 - 0{\cdot}00013T}. \qquad (109)$$

The temperature dependence is seen to be quite trivial. That it is less than in (96), even as it is less for an image-force hill [27] than it is for the rectangular step-up of Fig. 49, is to be ascribed to the absence of the effects of sharp corners.

As an example of the application of this result to the interpretation of experimental data, let us consider the case of fully activated thoriated tungsten. Nottingham's [28] velocity-distribution data for the electrons emitted from this system suggest that B — C for this case is about 1·5 e.v.* Let us, then, take, say, 1·25 volts to be the height of the nearly equivalent rectangular hill. According to the measurements of Dushman and Ewald,[14] the value of $\bar{D}(= A/A_0)$ is about 1/40. If we substitute this and the assumed value of H in (109), and take T to be 1500°K., we find for l the value 3·4Å. This is of the correct order of magnitude for the thickness of a hump such as we should expect an adsorbed monatomic contamination to produce.

The question now arises : Is it possible to have a $\bar{D}$ which varies strongly with the temperature, so that the empirical A and χ obtained from the Richardson line do not truly represent the emission constant and the work function respectively ? As Fowler [19] has pointed out, this will be the case when the potential hump is wide and correspondingly powerful, letting through only an inappreciable fraction of the electrons with energies between C and B. It is easily seen from (104), by taking D(W) to be 0 or 1 according as the electrons have not or have sufficient energy to go over the top of the hump, and substituting B — C for 0 as the lower limit of integration,

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* Nottingham's own interpretation of his results differs slightly from that given in Chapter I and leads to a value of 1·3 e.v. for B — C.

that $\bar{D}$ will then behave somewhat like $A'\epsilon^{-\frac{B-C}{kT}}$ and that the metal will "really emit electrons very much as if it had an apparent work function $\chi + B - C$ instead of the true χ. Thermionic analysis would present it with a large χ and a normal $\bar{D}$ instead of with the true χ and a very small temperature-dependent $\bar{D}$." We should, however, hardly expect such a condition in the case of clean metals or of metals having a surface contamination of a merely monatomic order of thickness.

Reverting to the case of a relatively narrow hump, whose mean transmission coefficient is given roughly by (109), we see that, very nearly, log A must vary linearly with $lH^{\frac{1}{2}}$. Now, as we saw in Chapter III, there is a remarkable empirical relationship between log A and χ for metals whose surfaces hold various kinds and quantities of contamination, viz.:

$$\log A = \xi + \eta\chi, \quad \eta > 0, \qquad . \qquad . \quad (110)$$

where ξ and η are constants. It is at once evident that if it could be shown that $lH^{\frac{1}{2}}$, or the equivalent quantity for such humps as actually occur in nature, is proportional to the depression $C' - C$ of the work function due to the contamination, or to some power of the latter not much different from unity, then the empirical relationship (110) would be satisfactorily accounted for. Such a possibility has been discussed by Fowler,[19] who showed that the values of η found by DuBridge[11] with contaminated platinum and by Richardson and Young[31] with contaminated potassium are such as, with the assumption that $B - C$ is equal to $C' - C$, and apart from the difficulty of the high A-values in the case of platinum, would indicate a thickness of the hump of the order of 10^{-7} cm. and 7×10^{-7} cm. respectively.

While, however, the assumption that the height of the hump corresponds to the reduction in the work function appears to be fairly reasonable in the case of relatively thick humps, we shall not expect this to be true where the contamination is of only atomic thickness. In this case we shall probably not be far wrong if we assign to the electrical double layer, and with it the hump, a thickness of something like 3Å.

The image contribution to the work function beyond a hump of this thickness must be of the order of 1 e.v., and, as will be evident on reference to Fig. 9, the energy-equivalent of the height of the hump above the final image level must be less than C′ − C by at least this amount. In the case of monatomic contaminations, therefore, we should not expect such a relationship as (110) to apply.

Anomalous Values of A.—We have seen that values of A less than A_0 can be accounted for, at least qualitatively, by means of reflexions at the surface of the emitting body. On the other hand, values of A greater than A_0 cannot be so accounted for, and in so far as such values have been well established experimentally, it becomes necessary to seek some other explanation. Thus, as we saw in Chapter II, platinum has been found by DuBridge [12] in experiments which must inspire considerable confidence, to have the relatively enormous empirical A of 17,000 amp./cm.²deg.².

We have seen that for a hypothetical metal the specific heat of whose internal electrons is zero the emission formula is

$$i = (1 - \bar{r})A_0T^2\epsilon^{-\chi/kT}, \qquad . \qquad . \quad (111)$$

where χ is a constant with respect to the temperature and A_0 has the value $4\pi mek^2/h^3$. Where the specific heat of the internal electrons is not zero, however, while the emission formula is still (111), in which A_0 has the value just given, χ is no longer strictly constant, but varies slightly with the temperature. This temperature dependence of χ naturally affects the slope of the Richardson line and so the *empirical* value found for $(1 - \bar{r})A_0$.

In order to arrive at an estimate of the importance of this effect, it will be convenient once again to consider Sommerfeld's picture of a metal. On the basis of this picture, one readily finds as a second approximation to the exact emission formula

$$i = (1 - \bar{r})A_0T^2\epsilon^{-\frac{1}{kT}\left\{C - \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} + \frac{\pi^2}{12}\frac{2m}{h^2}\left(\frac{8\pi}{3n}\right)^{2/3}k^2T^2\right\}}. \qquad (112)$$

This differs from the first approximation hitherto considered by the third, temperature-dependent term in χ. The inclusion of this term is, as Fowler [20] has pointed out, equivalent to taking account of the specific heat of the internal electrons. Eqn. (112) may be rewritten

$$i = (1 - \bar{r})\mathrm{A}_0{}'\mathrm{T}^2\epsilon^{-\frac{1}{k\mathrm{T}}\left\{\mathrm{C} - \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3}\right\}}, \qquad (113)$$

where

$$\mathrm{A}_0{}' = \mathrm{A}_0\epsilon^{-\frac{\pi^2}{12}\frac{2m}{h^2}\left(\frac{8\pi}{3n}\right)^{2/3}k\mathrm{T}}, \qquad (114)$$

the symbol A_0 being retained for $4\pi mek^2/h^3$.

We see at once that the exponent in the factor by which $\mathrm{A}_0{}'$ differs from A_0 is of the wrong sign to account for values of the empirical A in *excess* of 120 amp./cm.^{2}deg.^{2}. As Fowler[19] has pointed out, however, observed specific heats of electrons in metals are sometimes negative, instead of positive as they should be according to Sommerfeld's theory. Incidentally they may also be anything up to ten times as large as this theory would lead us to expect.

For most metals, n is of the order of 10^{23}. We shall not expect it ever to be much less than 10^{22}. If we assume the latter value and take T to be 2000°K., we obtain for $\mathrm{A}_0{}'/\mathrm{A}_0$ the value $\epsilon^{-0\cdot084}$ or 0·92, whose difference from 1 is quite unimportant.[19] Even the tenth power of this, 0·43, corresponding to a specific heat of the internal electrons ten times as great as it should be according to Sommerfeld's theory, is still not different in order of magnitude from 1, and this, or its reciprocal 2·3, is about the greatest factor by which $\mathrm{A}_0{}'$ should ever differ from 120 amp./cm.^{2}deg.^{2}. This conclusion confirms that to which we were led by a different reasoning in Chapter I (p. 36), viz. that "we shall not expect the values of A_0 for different metals to differ by factors of more than a few units." *

In addition to the slight temperature variation of χ just considered, Fowler[19] has discussed two other conceivable ways in which χ might be dependent upon the temperature, so giving rise to an apparent A greater than A_0. These are an increase with rising temperature of n or a diminution of the inner potential C/e. If n increases with rising temperature (incidentally, it could hardly decrease), it would have a direct effect on the specific heat of the internal electrons. Thus to account for the case of platinum there would have to be

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* The A_0 of Chapter I is, of course, the same as the $\mathrm{A}_0{}'$ of the present discussion.

between room temperature and 1700°K. a change of about 10 per cent. in n or of 5 per cent. in C. There might, of course, also be a combination of the two. It must be remembered, however, that while the necessary temperature variation of χ which might be due to either or both these causes is not, theoretically, impossible, it does not appear from such photoelectric evidence as we have (cf. Chapter II), that it does, in fact, occur.

In recent years there has been some discussion as to whether the simple thermodynamical-statistical theory considered at the beginning of the present chapter, which, so long as c_p' is small, does not admit of any important departure of A_0' from 120 amp./cm.^{2}deg.^{2}, really correctly takes account of all the factors involved. Let us, therefore, examine this theory a little more closely than we have done hitherto.

The reason why, when c_p' is negligible, the theory we have considered does not allow of any important departure of A_0' from A_0 is that according to it, χ must be practically equal to $\frac{k}{R}l_0$, where l_0 is the molecular latent heat of evaporation of electrons at absolute zero, and that consequently χ must be practically independent of the temperature.

Whence comes this quantity l_0? It comes from the integration of eqn. (23) of Chapter I, viz.,

$$\frac{dl}{dT} = c_p - c_p'. \quad . \quad . \quad . \quad (115)$$

This, in turn, is obtained by equating the heat that is absorbed when the temperature of the emitting body is raised from T to T + dT and one gram-molecule of electrons then allowed to evaporate isothermally at T + dT to the heat absorbed when the evaporation occurs at the temperature T and the system is subsequently heated, without further transition of electrons from one phase to the other, to T + dT. Obviously, no exception could be taken to such a derivation in the case of non-electrical systems. Have we, however, in the present case, which involves the transference of an electric charge, left something out of account?

The actual course of events in the above thermodynamical processes is not quite so simple as we have imagined. Although the evaporating electrons almost certainly originate from the interior of the conductor, the loss of electrons sustained by the latter does not remain uncompensated, since charges can reside permanently only on the *surfaces* of conductors. Thus, after the evaporation, it is the *surface* of the conductor, not its whole volume, which has lost electrons. It might appear, therefore, that just as in the simple theory the practical temperature independence of χ depends upon c_p' being sufficiently small, so in any modified theory which takes account of the surface charging it would depend upon one's being able to neglect surface charging heat effects.

As a result of a detailed thermodynamical investigation, P. W. Bridgman[3] has been led to the conclusion that a necessary and sufficient condition for the equality of A_0' and A_0 "is that the difference between the specific heat of neutral metal and of a charge on its surface vanish." The problem has also been studied in two other papers by Bridgman,[4] and in addition by Tonks[37, 38] and Langmuir[38] and by Herzfeld.[22] In all these papers the theory is developed that abnormal values of A may be explained in terms of surface charging heat effects.

Davisson and Germer,[9] on the other hand, have come to a different conclusion. After enumerating the complications due to the electrical nature of the system, they stated that "it has been shown[7] . . . for a system of simple geometry that when these features of the system are properly allowed for, one arrives at exactly the same relations as when he proceeds on the erroneous assumption that the vapour is uncharged."

The discussion of the heat of surface charging in its relation to thermionic theory was begun at a time when little was known about the mechanism of the emission, and for all that was known to the contrary the emitted electrons might have had their origin in the actual surface of the emitter. In such a case, the possible importance of an associated heat effect at the surface in determining the equilibrium between the electron vapour and the metal would be obvious. Now, however, that we know that the internal electrons have free paths of hundreds of atomic diameters and, judging by the success of the Nordheim-Sommerfeld theory, that the emitted electrons come, in the main, from well below the surface, the question of the heat of surface charging no longer appears to have the same importance. According to the modern theory, the surface charging is merely a secondary phenomenon, a readjustment that takes place after the actual emission, and it is difficult to see how an investigation of the energy changes accompanying such a readjustment can tell us anything about the primary phenomenon of the electron emission itself.

To sum up, it must be admitted that, in examining every possible alternative at present known, we have been unable to find any really plausible and satisfactory explanation of the discrepancy, in the case of platinum, between theory and experimental data. We can only hope that future developments, either experimental or theoretical, may bridge the gap. In the meantime it is satisfactory to note that the case of platinum is quite exceptional in this respect. The great bulk of other experimental data appear to support, in a most reassuring manner, the conclusions both of the simple, straightforward thermodynamical-statistical theory and of the more recent theory of Nordheim and Sommerfeld.

LITERATURE.

1. H. Bethe, *Naturwiss.*, **15**, p. 786, 1927 ; **16**, p. 333, 1928 ; *Ann. d. Phys.*, **87**, p. 55, 1928.
2. Bose, *ZS. f. Phys.*, **26**, p. 178, 1924.
3. P. W. Bridgman, *Phys. Rev.*, **27**, p. 173, 1926.
4. P. W. Bridgman, *Phys. Rev.*, **14**, p. 306, 1919 ; **31**, p. 90, 1928.
5. E. Brody, *ZS. f. Phys.*, **6**, p. 79, 1921.
6. A. H. Compton, *J. Franklin Inst.*, **192**, p. 145, 1921.
7. C. Davisson, *Phil. Mag.*, **47**, p. 544, 1924.
8. C. Davisson and L. H. Germer, *Phys. Rev.*, **30**, p. 705, 1927 ; *Proc. Nat. Acad. Sci.*, **14**, p. 619, 1928.
9. C. Davisson and L. H. Germer, *Phys. Rev.*, **30**, p. 634, 1927.
10. P. A. M. Dirac, *Proc. Roy. Soc.* (*A*), **112**, p. 661, 1926.
11. L. A. DuBridge, *Phys. Rev.*, **31**, pp. 236 and 912, 1928.
12. L. A. DuBridge, *Phys. Rev.*, **32**, p. 961, 1928.
13. S. Dushman, *Phys. Rev.*, **21**, p. 623, 1923.
14. S. Dushman and J. W. Ewald, *Phys. Rev.*, **29**, p. 857, 1927.
15. C. Eckart, *Proc. Nat. Acad. Sci.*, **13**, p. 460, 1927.
16. A. Einstein, *Berl. Sitzungsberichte*, 1924, p. 261 ; 1925, p. 3.
17. H. Faxén and J. Holtsmark, *ZS. f. Phys.*, **45**, p. 307, 1927.
18. E. Fermi, *ZS. f. Phys.*, **36**, p. 902, 1926.
19. R. H. Fowler, *Proc. Roy. Soc.* (*A*), **122**, p. 36, 1929.
20. R. H. Fowler, *Proc. Roy. Soc.* (*A*), **117**, p. 549, 1928.
21. R. H. Fowler and L. W. Nordheim, *Proc. Roy. Soc.* (*A*), **119**, p. 173, 1928.

22. K. F. Herzfeld, *Phys. Rev.*, **35,** p. 248, 1930.
23. H. Jeffreys, *Proc. Lond. Math. Soc.*, **23,** p. 428, 1924.
24. M. v. Laue, *Jahrb. d. Rad. u. Elektronik,* **15,** pp. 205, 257 and 301, 1918.
25. L. W. Nordheim, *Phys. ZS.*, **30,** p. 177, 1929.
26. L. W. Nordheim, *ZS. f. Phys.*, **46,** p. 833, 1928.
27. L. W. Nordheim, *Proc. Roy. Soc. (A)*, **121,** p. 626, 1928.
28. W. B. Nottingham, *Phys. Rev.*, **41,** p. 793, 1932.
29. W. Pauli, jr., *ZS. f. Phys.*, **41,** p. 81, 1927.
30. O. W. Richardson, *Phil. Mag.*, **28,** p. 633, 1914.
31. O. W. Richardson and A. F. A. Young, *Proc. Roy. Soc. (A)*, **107,** p. 377, 1925.
32. L. Rosenfeld and E. E. Witmer, *ZS. f. Phys.*, **49,** p. 534, 1928.
33. E. Rupp, *Ann. d. Phys.*, **1,** p. 801, 1929 ; **5,** p. 453, 1930.
34. O. Sackur, *Ann. d. Phys.*, **36,** p. 958, 1911 ; **40,** p. 67, 1913.
35. A. Sommerfeld, *ZS. f. Phys.*, **47,** p. 1, 1928.
36. H. Tetrode, *Ann. d. Phys.*, **38,** p. 434, 1912.
37. L. Tonks, *Phys. Rev.*, **32,** p. 284, 1928.
38. L. Tonks and I. Langmuir, *Phys. Rev.*, **29,** p. 524, 1927.
39. G. E. Uhlenbeck and S. Goudsmit, *Naturwiss.*, **13,** p. 953, 1925 ; *Nature,* **117,** p. 264, 1926.

CHAPTER VI.

THE EMISSION OF IONS.

While the particles thermally emitted from metals and from electronic semi-conductors are, in the main, electrons, those emitted from electrolytes are ions. These may be either positive or negative (rarely both together), but the electrolytes that emit positive ions are much more numerous than those that emit negative. In addition, as we saw in Chapter III, positive ions are emitted from certain metals when heated to suitable temperatures in alkali metal vapours. They are also emitted from metals containing alkaline and certain other impurities. Finally, a slight positive emission has been observed to occur from pure metals when heated to very high temperatures. We shall, in the present chapter, briefly examine these various cases.

Section I.

THE EMISSION OF IONS FROM ELECTROLYTES.

The great bulk of the experimental work on the thermionic properties of electrolytes has been done with heated salts, and relatively little with glasses, and so it is with the former that we shall mainly have to deal in what follows. There appears to be no essential difference in thermionic behaviour between the two.

Results of Earlier Experiments.—The conditions under which most of the quite early experiments on the thermionic properties of heated salts were performed were far from simple. The space between the electrodes was generally not exhausted to a pressure sufficiently low to be regarded as any approach to a good vacuum; indeed, a considerable number of the experiments were conducted simply in air at atmospheric pressure. In such cases it was well-nigh impossible to be sure whether the currents observed were true thermionic emission currents or were due to some other cause, such as a volume ionization of salt vapour in the inter-electrode space ionization by collision, or ionization resulting from chemical action in which the gas took a part. Only in later years were the experiments so simplified that it was possible to draw definite conclusions from them. Such of these more simple experiments as were carried out up to 1921 and the conclusions to which they led have been discussed at length by O. W. Richardson.*

It was found that at sufficiently strong fields the ion currents obtained from heated salts generally saturate, as do the electron currents obtained from metals and from oxide cathodes. These saturated currents depend upon the temperature, but in a manner that is often rather complex and is, moreover, not always easy to determine, since in general they also exhibit complex time changes, associated with the presence of impurities. "There is," writes Richardson, however (p. 268 of his book), "a very considerable amount of experimental evidence which goes to show that when a salt is heated under conditions such that the emission of ions is always caused by the same substance the currents increase rapidly and continuously with rising temperature, and the relation between the saturation current and the temperature is that expressed by the formula . . . which has been found to govern the temperature relations of other thermionic currents."

As already stated, either positive or negative ions may be emitted, the former being the more common. Concerning the nature of these, Richardson, discussing certain experiments by himself and others in which the ratio of charge to mass of the ions was measured, writes (p. 280): "These experiments and innumerable others . . . establish quite definitely the conclusion that the positive ions emitted by heated salts are charged atoms of some metal. This metal is not necessarily a constituent part of the salt which appears to be under investigation, but may arise from the presence of some impurity

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* O. W. Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co., 2nd edition (1921), Chapter VIII.

which has a greater power of emitting positive ions." He further draws attention (p. 283) to the ascertained fact that, with only two exceptions then known (the ions from zinc and cadmium halides), these ions are always but *singly* charged, even in such cases where the charge usually carried by the ion of the corresponding metal in electrolysis is more than single.

Finally, Richardson points out (p. 298) that "so far as the relative efficiency of different salts in emitting ions when they are heated is concerned, it is clear that the electropositiveness of the metallic constituent is a most important factor," and goes on to say that in his experience "the salts of the alkali metals are the leaders in this kind of activity, the comparative efficiency of the metals within this group increasing with increasing atomic weight."

These are the main general conclusions it was possible to draw from the experimental evidence available in 1921. Since that date a considerable amount of further work has been done, chiefly by G. C. Schmidt and his students, as a result of which much new light has been shed on the phenomena. This work we shall now discuss.

Nature of the Ions.—In an investigation of the thermionic emission from a large number of salts at temperatures of the order of 600°–700°K., Schmidt[24] has found that positive ions are the only ones emitted from CdI_2, $CdBr_2$, $CdCl_2$, ZnI_2, $ZnBr_2$, $ZnCl_2$, $FeCl_2$, AlF_3, $AlCl_3$, $MgCl_2$, CaF_2, NH_4I, NH_4Br, NH_4NO_3, TlI, TlBr, TlCl, $PbCrO_4$ and CuI_2. The first fourteen of these were later reinvestigated by Gossmann,[11] and in addition $Cd(NO_3)_2$, $NaNO_3$ and KNO_3, and only positive ions found up to a temperature of 720°K. In the case of $NaNO_3$ and KNO_3, Schmidt[25] found only positive ions up to 1270°K. In addition, Kahra,[14] Bölling[6] and Murawkin[21] have been unable to find any but positive emission from various glasses up to the highest temperatures—in some cases as high as 1600°K.

On the other hand, negative as well as positive ions have been found by Schmidt[25] to be given off from alkali and silver halides when sufficiently strongly heated, although in the majority of cases the positive emission is considerably stronger than the negative. Indeed, except at relatively high temperatures the silver halides[24] and all the alkali halides examined except lithium and potassium chlorides were found to emit in measurable quantities only positive ions. The lowest temperatures (K.) at which emissions of the two signs could be detected in the case of the alkali halides are given in Table XVIII. Ions of both signs were also obtained,[24] but with the negative preponderating, from (possibly impure) $BaCl_2$.

TABLE XVIII.

LOWEST TEMPERATURES AT WHICH POSITIVE AND NEGATIVE EMISSIONS FROM ALKALI HALIDES ARE DETECTABLE.

Salt . .	NaCl	KCl	LiCl	CsCl	KBr	LiBr	NaI	KI	KF
Pos. Emission	850	770	900	790	830	800	790	720	710
Neg. Emission	1160	850	900	1070	1040	1090	1040	940	1030

Finally, only negative ions have been found by Schmidt [26] to be emitted from pure $PbCl_2$ and by Kahra [14] from pure PbF_2, $PbBr_2$, and PbI_2.

When these results are considered in conjunction with what is known concerning the mechanism of electrolysis in these salts, it becomes evident, as Schmidt has pointed out, that there is a far-reaching correspondence between the thermionic and the electrolytic phenomena exhibited by them. Thus, according to Tubandt,[33] only the positive ions take any active part in the electrolysis (at relatively low temperatures) of solid AgI, AgBr and AgCl, while in $PbCl_2$ and PbF_2 only the negative ions are mobile. We have seen that at relatively low temperatures the silver halides thermally emit only positive ions, while the lead halides emit only negative. Again, according to several investigators, only positive ions carry the current in the electrolysis of various glasses, and the emission obtained from glasses by Kahra, Bölling and Murawkin was also only positive. Finally, while v. Seelen,[27] Phipps and Leslie,[23] and Tasulachov [32] have shown that at relatively low temperatures only the Na^+ ions carry the current in NaCl, an appreciable current of Cl^- ions has also been found in this salt by Phipps and Leslie between 830°K. and 930°K., and by Tasulachov above 870°K. These results are analogous to those of Schmidt, who observed only positive emission from NaCl at relatively low temperatures but both positive and negative at high.

From such comparisons as these, Schmidt [24] has been led to make the following generalization :—

> " Salts in which only the positive or only the negative ions are mobile emit at the corresponding temperatures only positive or only negative ions respectively. If in electrolysis the mobility of one kind of ion preponderates, then the more mobile ions are at the corresponding temperature emitted in the greater quantity."

In the light of more recent experimental work, however, it would appear that while this rule is undoubtedly a good qualitative guide to the thermionic phenomena to be expected in a large number of cases, the correspondence between the electrolytic and the thermionic phenomena is less detailed than Schmidt believed it to be. Thus, for example, according to Tasulachov, the proportion of negative to positive-ion current in the electrolysis of NaCl increases from about 8 per cent. at 870°K. to about 60 per cent. at 970°K. Yet while Schmidt was able to observe positive emission from this salt at all temperatures above 850°K., he first began to detect negative only at 1160°K. Were the ratio of negative to positive emissions anything like that of negative to positive ion currents in electrolysis, he surely must have detected a negative emission at a much lower temperature than this.

With regard to the chemical identity of the emitted ions, Volmer,[34] employing a magnetic deflexion method, has found that the ratios of charge to mass of the positive ions emitted from CdI_2, $CdCl_2$, $ZnCl_2$, CuI_2, $PbBr_2$ and CaF_2 are of the same order as those of the doubly charged atoms of the corresponding metals, i.e. the ions which we should expect to function in electrolysis.

For the last three salts this result is not in agreement with the earlier one discussed by Richardson to which reference has already been made, viz. that thermally emitted positive ions are in general but singly charged even when the charges carried by the ions in the electrolysis of the same salt are more than single.

Also the case of $PbBr_2$ is remarkable, in that this salt is one of those in which, according to the researches of Tubandt,[3] only the negative ion is mobile and from which Kahra [1] obtained only negative thermions. Apparently, however, it is only in the case of the very pure lead halides that no positive ions are emitted, for Schmidt,[24] working with salts which were less pure than those of Kahra, obtained only positive thermions from $PbBr_2$ and PbI_2, and some positive, as well as negative, from $PbCl_2$. Volmer's result with $PbBr_2$ is very interesting, indicating that the effect of an impurity is not necessarily the emission of ions derived from itself, but that its presence may bring about the emission of such ions of the bulk salt as would not in its absence be emitted at all. It may be that this occurs only in consequence of some chemical action, e.g. an " exchange of partners " between the metal atoms of the bulk salt and those of the impurity. If in the new salt so formed whose metallic ions are those of the original bulk salt, these ions are mobile, Schmidt's rule would not be violated. That chemical actions frequently play an important part in the emission from impure heated salts has long been suspected from the nature of the time changes characteristic of the emission from them.*

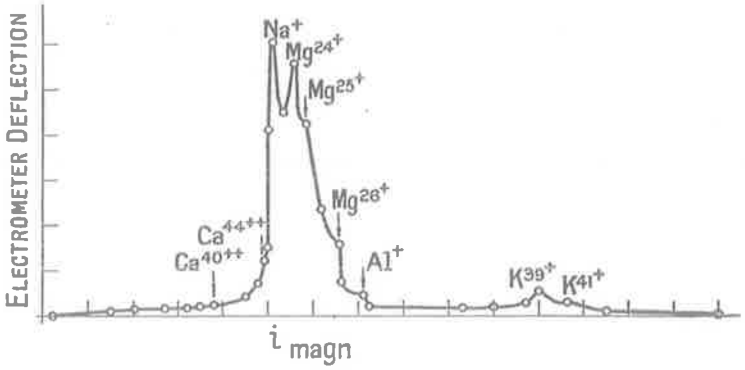

FIG. 55.—Mass spectrogram of the positive emission from an impure specimen of aluminium phosphate.

The important rôle played by impurities is well illustrated by Fig. 55, which is a mass spectrogram obtained by Murawkin

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* See O. W. Richardson, " The Emission of Electricity from Hot Bodies," Longmans, Green & Co., 2nd edition (1921), p. 262.

of the positive emission from a specimen of aluminium phosphate at 1220°K. It will be seen that all the principal maxima are those of impurity ions, and that the maximum for Al^+, the only ion derived from the bulk salt, is comparatively weak.

The positive emissions obtained at high temperatures (900°–1600°K.) from a large number and variety of glasses have also been analysed by Murawkin. A few typical examples will serve to show the kind of results obtained :—

(1) *Lindemann glass*, made from Li_2O, BeO and B_2O_3 (proportions not stated). The ions from this glass were analysed between 1330° and 1470°K., and those from a more refractory modification, containing Al_2O_3 in addition to the ingredients stated, between 1070° and 1510°K. At the lowest temperatures the ions emitted in largest quantity were O_2^+. In addition, oxygen appeared as O^+ between 1070° and 1440°K. and it was just detectable as O^{++} at 1510°K. Li^+ appeared at all temperatures. Be^+ appeared less strongly than Li^+ at low temperatures but more strongly at high. B_3^+ was also found at all temperatures.

(2) *A special glass*, made from 67 per cent. SiO_2, 18 per cent. K_2O, 10 per cent. MgO and 5 per cent. BaO. The temperature range covered was from 1070° to 1280°K. The strongest emission at all temperatures was that of K^+. In addition O_2^+ was found at all temperatures, and at the higher temperatures also O^+. Mg^+ appeared at 1070° and again between 1240° and 1280°K. Si^+ was found at 1210°K. and at higher temperatures.

(3) *Thuringian glass*, made from 69·9 per cent. SiO_2, 6·6 per cent. K_2O, 16·5 per cent. Na_2O, 3·75 per cent. CaO and 3·25 per cent. not specified. At all temperatures in the range covered (1010°–1370°K.) the strongest emission was that of K^+. Also Na^+ appeared at all temperatures, and either equally strongly or more so Na_2^+. Calcium was found as Ca^{++} between 1070° and 1190°K., and oxygen as O_2^+ at 1070°, 1230° and 1370°K. Finally, there was a weak Si^+ emission at the higher temperatures.

From these results it again appears that Schmidt's rule does not apply in detail, there being no *complete* correspondence between the thermionic and electrolytic phenomena, for, as Murawkin has pointed out, if there were, there could hardly be such a considerable emission of positive ions of strongly electronegative elements like oxygen and silicon. Indeed, we have no *à priori* reason for expecting a complete correspondence between emission and electrolysis, since, after all, the former is a surface phenomenon, while the latter is governed by conditions in the interior of the electrolyte.

Time Changes.—The time changes exhibited by the emission from heated electrolytes may be of various types, depending on the purity of the specimen used, the method by which it has been applied to its metallic support and the conditions under which it is worked. Other things being equal, they are less important at high than at low temperatures, and frequently vanish altogether at temperatures in the neighbourhood of the melting-point of the electrolyte.[26]

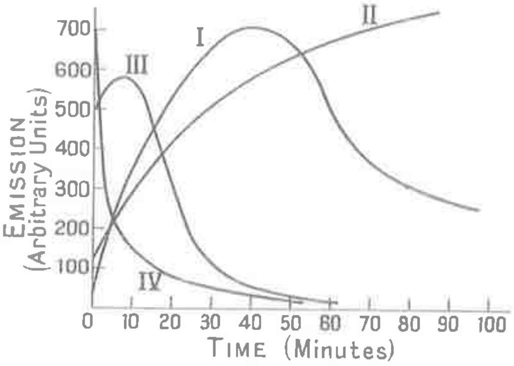

FIG. 56.—Time changes in the positive emission from specimens of CdI_2 variously prepared.

Some typical emission-time curves obtained by Schmidt[26] using CdI_2 coated on a platinum wire, in each case at about 600°K., are shown in Fig. 56. Curve I represents a very common type of time change, and was obtained with a coating applied to the wire from an aqueous solution. Curve II refers to a deposit formed on the wire by sublimation. In the case of curve III the salt was twice recrystallized before being applied to the wire. This curve is somewhat similar to curve I, but has a much less marked rising portion. Finally, in the case of curve IV, very elaborate pains were taken to purify the salt before its application to the wire, by first subliming it in a vacuum and then recrystallizing it several times. From this curve the initial rise with time is entirely absent.

Similar results were obtained with other salts. The positive-ion emitters ZnI_2, AgCl, TlCl, TlBr and TlI in addition to CdI_2, and the negative-ion emitter $PbCl_2$, all gave only falling curves after they had been very carefully purified. On the other hand, a sample of AgI which Schmidt had no reason to think was other than pure gave a rising curve at certain temperatures. Since, however, purity is only a matter of degree, and purification was found to convert initially rising into falling curves in all the other cases, it would appear probable that rising emissions are always due to the presence of some impurity.

Not all impurities will bring about an initial increase in the emission, however. Thus Schmidt [26] has found that while CdI_2 containing iodine as an impurity gives a higher emission than pure CdI_2, the emission falls with time in much the same way in both cases. He has never found that the addition of an impurity which precludes chemical action gives a rising emission.

An interesting case reported by Schmidt [26] of an impurity which does cause the emission to rise initially is that of ZnI_2 in CdI_2. The emission of each of these salts, when pure, falls with time; yet if a trace of ZnI_2 is added to CdI_2 an initial rise in the emission is observed. Schmidt has suggested that this effect might in some way be due to the iodine derived from the ZnI_2 by its chemical dissociation. His picture is of the degree of dissociation, and so the amount of free iodine (which, as we have seen, enhances the emission), increasing with time. In that case, however, the time-increase of the degree of dissociation would have to be accounted for. Perhaps a simpler picture is the following: Schmidt [24] has found that not only does iodine enhance the emission from CdI_2, but Cd depresses it, and similarly, Zn depresses the emission from $ZnCl_2$. Probably Zn impurity in CdI_2 would also depress the emission. In that case the Zn and I derived from the ZnI_2 impurity in the CdI_2 would to some extent neutralize one another's effects. If now the zinc diffuses to the surface, whence it evaporates, more rapidly than the iodine, the excess of the latter becomes greater and greater, Birkenberg [5] has found that while after prolonged heating the emission from CdI_2 can be enhanced only by exposure to moisture if the salt has been applied to its carrier wire in aqueous solution, in the molten form, or by sublimation in a vacuum, the emission given by the same salt when it has been applied by sublimation *in air* regenerates itself spontaneously after merely standing cold for some time, not exposed to water vapour. It is probable that the gradual diffusion to the surface of moisture which has been included in the salt during its sublimation is responsible for this. A similar spontaneous regeneration of the emission was observed in the case of TlCl applied to its wire by sublimation in air.

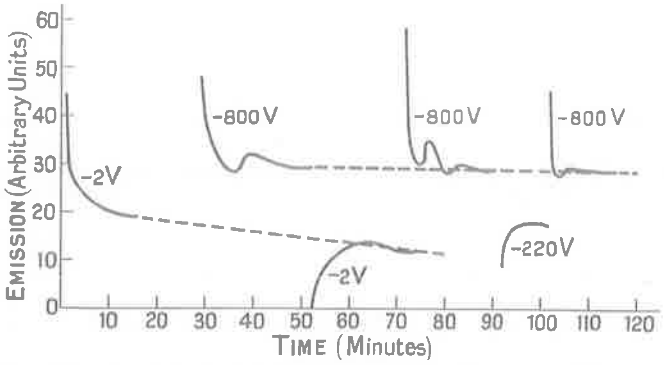

FIG. 58.—Time changes in the positive emission from a specimen of AgCl brought about by changes in the potential of the collector.

An exception to the rule that surface moisture enhances the emission was found by Birkenberg in the case of AgCl, a salt which is, incidentally, insoluble in water. Nevertheless a freshly prepared specimen was observed to show the initial fall of emission with time. The cause of the fall in this particular case remains obscure.

A time effect associated with changes in the accelerating field has recently been observed by Zentgraf.[41] This is illustrated in Fig. 58. The full curves show the time variations of positive-ion current obtained from AgCl kept at a constant temperature of 638°K. when different negative potentials were applied to the collecting electrode. Similar effects were observed with AgBr, TlCl, TlBr, TlI, CdI_2, and with tho negative emitter $PbCl_2$. There can be little doubt that these current variations are associated in some way with variations in the electrolytic polarization of the salts.

We may summarize the results of the various investigations concerned with time changes as follows :—

(1) Most pure salts whose surfaces are not contaminated by moisture give an emission which is at all temperatures constant with time.

(2) Time changes, if existent, are relatively more important at low than at high temperatures. In the neighbourhood of the melting-point of a salt they usually vanish altogether.

(3) A rising emission is due to the presence of impurities. Not all impurities bring about this effect, however. The effect, when it occurs, is probably associated with some chemical change.

(4) A falling emission is in general due to contamination of the surface of the salt by moisture. The latter enhances the emission, and the fall occurs in consequence of the progressive disappearance of the moisture by evaporation.

(5) Complex time changes due to polarization effects may be observed when the potential of the collecting electrode is suddenly changed.

Section II.

THE EMISSION OF POSITIVE IONS FROM METALS.

Earlier Investigations dealing with Impure Metals.— Ordinary impure metals generally give an appreciable emission of positive ions, derived from the impurities, at much lower temperatures (order of magnitude 1000°K.) than they do of electrons. Of the large number of experiments devoted to the study of this emission, those carried out up to 1921 have been fully discussed by Richardson.* We shall here confine ourselves to a brief summary of the most important results arrived at in this earlier work.

The positive emissions from impure metals generally fall with time of heating, the rate of fall increasing with the

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* O. W. Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co., 2nd edition (1921), Chapter VI.

temperature. In the simplest cases, the fall is of the exponential type, the emission approaching zero asymptotically. This is just what one would naturally expect on the assumption that the ions are charged " impurity " atoms or molecules, for in that case, as the emission proceeds the amount of the relevant impurity remaining must become less and less.

There are also less simple cases in which the emission, while ultimately approaching zero asymptotically, does not fall exponentially from the beginning. Sometimes it even passes through a maximum before the final fall toward zero. When it is considered how complex a phenomenon positive-ion emission must be, however, this can hardly occasion surprise. In general the impurity from which the ions are derived first has to reach the emitting surface by diffusion, and its rate of arrival there must depend on the volume distribution of the impurity in the metal. Then, the rate of evaporation of any particular kind of ion from the surface may depend not only on the rate of arrival at the surface of the corresponding material, but also on the " electron affinity " of the surface, which in turn must vary with the nature and degree of its contamination. And finally, as we shall see later, several different kinds of positive ion may be emitted at the same time, and in such a case it is not to be expected that the emission-time relationship for all of them together will be of any very simple form.

If a wire has been subjected to such a severe heat treatment that its positive emission has fallen to a small fraction of its original value, and another, " fresh " wire is heated near it, the emission from the first wire is generally thereby temporarily regenerated. This must obviously be due to the distillation from the fresh wire to the old of some of the impurity from which the positive emission is derived. Regeneration of the emission from a heat-treated wire may also be brought about by heating the glass vessel containing it, making the wire the cathode in a luminous discharge, or heating it in air. Undoubtedly the explanation is that all these things lead to fresh contamination of the wire of a kind favourable to positive emission. Finally, the emission may be regenerated by subjecting the wire to mechanical strain. This probably encourages the diffusion of residual impurity to the surface by providing fresh paths for it, just as the mechanical straining of a monocrystalline thoriated tungsten wire enables reduced thorium to diffuse easily to its surface.

The emission (i_p) of positive ions from a metal having a given distribution of impurity near its surface has been found to vary with the temperature according to a law of the type

$$i_p \propto f(\mathrm{T})\epsilon^{-\omega/k\mathrm{T}}, \quad . \quad . \quad . \quad (1)$$

where ω is a constant and f is a function, such as a small power, of T, whose variation with T is sufficiently moderate. This is similar to the formula for electron emission. The ω for the positive emission has, however, generally only something like a quarter the value of that for the corresponding electron emission. But this does not mean that the work of extraction of a positive ion from the metal is necessarily correspondingly less than that of an electron. The condition of affairs in the case of a positively emitting metal is not simply related to a state of equilibrium, as it is in the case of a metal emitting electrons, and so the usual thermodynamical reasoning does not apply. The temperature variation of the positive emission depends as much on the diffusion and evaporation characteristics of the material from which the ions are derived, and the associated changes with temperature in the condition of the surface, as it does on the work of extraction of the ions for any one surface condition.

The velocity distribution of thermally emitted positive ions has been found to be of the same type as that of electrons, viz. Maxwellian.

Measurements of the ratio of charge to mass of the ions emitted from different impure metals have, on the assumption that each particle carries a single charge, given values for the atomic weight of the ions between about 13 and 160. However, by far the most common value found has been in the neighbourhood of 39, indicating that the ions were charged atoms of potassium. The value 23, indicating Na^+, has also been found, but only in relatively few cases. That K^+ ions should be emitted so much more than Na^+, despite the fact that sodium is more abundantly present as an impurity in most ordinary metals than potassium, is probably due to the greater ease with which potassium is ionized, its ionization potential being only 4·32 volts, as against 5·11 volts in the case of sodium.

More Recent Work on the Emission of Ions from Impure Metals.—The results of the earlier experiments on the positive emission from ordinary impure metals have on the whole been well confirmed by later work. Thus Barton, Harnwell and Kunsman [4] have found maxima corresponding to both sodium and potassium ions in the mass spectrum of the positive emission from heated platinum. They did not, however, find the emission of sodium ions to be much less intense than that of potassium, as had generally been observed by earlier investigators ; on the contrary, their Na^+ maximum was slightly higher than that corresponding to K^+. The emission was found to decrease with time of heating. Recently Barnes [1] has observed, in addition to the usual Na^+ and K^+ emissions, also a weak emission of Rb^+ and Cs^+ ions from platinum when first heated at a dull red.

It has been found by Wahlin [35] that in addition to platinum, also iron, nickel, copper, zirconium and palladium emit ions of the alkali metals for a considerable time when heated. The emission is particularly persistent in the case of iron. Thus a specimen of electrolytic iron showed measurable K^+ emission after having been heated for 200 hours in a vacuum of 10^{-8} mm. at 1120°K. Specimens of tungsten, molybednum, tantalum and rhodium were also found to emit alkali ions initially, but these disappeared after a few minutes' heating. As a result of subsequent work,[36] Wahlin was able to add chromium, ruthenium, columbium, silver, gold, zinc, manganese, vanadium, cobalt, osmium, iridium, uranium, thorium and antimony to the list of metals that emit alkali ions when first heated.

L. P. Smith [28, 29] has found in the positive emission from tungsten and molybdenum heated at fairly high temperatures not only Na^+ and K^+ ions, but also a certain amount of Al^+. This is shown, for example, in Fig. 59, which is a mass spectrum of the emission from a specimen of tungsten at 2000°K. The resolving power of the spectrograph was sufficient to separate the two isotopes of potassium. Impurity ions other than those of the alkali metals have also been found by Wahlin,[37, 38] Barnes,[1] and Wolfke and Rolinski.[40] Maxima which could plausibly be attributed to Th^+ and to ThO^+ were observed by Wahlin [37] in the mass spectra obtained with specimens of thoriated tungsten, and also [38] maxima corresponding to U^+ and UO^+ in the case of tungsten containing uranium dioxide additive. Barnes found CbO^+ ions to be emitted from heated columbium and Ba^+ from a specimen of rhodium containing a trace of barium impurity when it was heated to about 2070°K. Finally, according to Wolfke and Rolinski, heated palladium, after having served as the cathode in the electrolysis of a dilute solution of sulphuric acid, will emit very light positive ions, which are probably protons. They found this emission to be of an " explosive " character, falling rapidly with time. They failed, however, to detect any continuous positive emission from a heated palladium tube through whose walls hydrogen was caused to diffuse. Undoubtedly, in order that hydrogen shall escape from heated palladium in the form of ions it is necessary for the surface to be in a suitable condition.

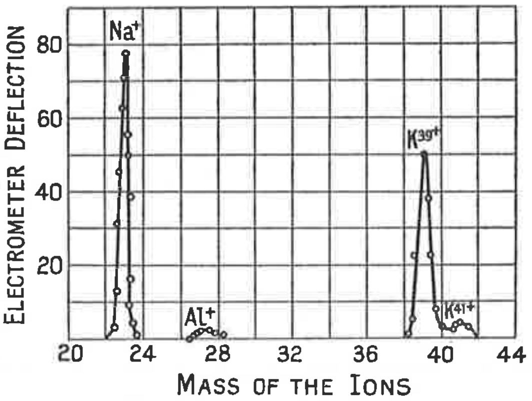

FIG. 59.—Mass spectrogram of the positive emission from a specimen of impure tungsten.

Two interesting types of " impurity emitter " have been developed in recent years in which the impurity is deliberately added to the bulk metal and which give copious emissions of positive ions for very long periods of time. One of these consists of iron containing about 1 per cent. of an alkali or alkaline earth oxide, and when heated to dull redness this emits positive ions which are mainly, or at least largely, singly charged atoms of the metal of the additive. The other consists of platinum in contact with potash or soda glass through which potassium or sodium is electrolytically supplied to it at a controlled rate. The ions in this case are singly charged atoms of potassium or sodium.

The iron type of emitter was first described by Kunsman.[15, 16] It is prepared by coating a metal carrier, such as a twisted platinum ribbon, with magnetic oxide of iron finely ground with about 1 per cent. of the oxide of an alkali or alkaline earth metal and suspended in a suitable medium, such as paraffin. About 1 per cent. of aluminium oxide may also be added—the emission from mixtures containing aluminium oxide are rather more stable than from those not containing it. The mixture is then fused on to the carrier by heating it to about 1200°K., either in air, or preferably, in an atmosphere of nitrogen. The coating may be brought to any desired thickness by repeating the coating and fusing process. Finally, the coated ribbon is mounted in a vacuum tube and the coating reduced in an atmosphere of hydrogen. On now being heated to dull redness in a vacuum, the system gives a considerable emission of positive ions—Kunsman has in some cases obtained currents as high as 10^{-4} amp./cm.^{2}. At first the emission falls with time, but after about two hours the rate of fall becomes inappreciable. The lives of these emitters are very great, positive ions continuing to be emitted in appreciable quantities after weeks of heating. At any given temperature, the emission is strongest for mixtures containing cæsium oxide and weakest for those containing alkaline earth oxides.

The initial time changes observed[16] in the emission at 1000°K. from reduced mixtures containing potassium and barium oxides, from an unreduced mixture containing barium oxide, and from an uncoated platinum ribbon, are shown in Fig. 60. It is seen that even the unreduced barium oxide mixture gave *some* emission, although this was only about one-fifth as great as that from a corresponding reduced mixture. Other unreduced mixtures were also found to give a little emission. In the case of a potassium oxide mixture the emission before reduction was less than one-hundredth of that obtained at the same temperature after reduction.

The positive-ion emission from these emitters has been found by Kunsman to vary with the temperature in the same kind of way as does the electron emission, the slopes of the Richardson lines for ions being, however, much less steep than those for electrons. At the same time, for reasons already given (p. 287), the slope of a Richardson line for ions, unlike that for electrons, can hardly be simply related to the work of extraction of the corresponding kind of particle.

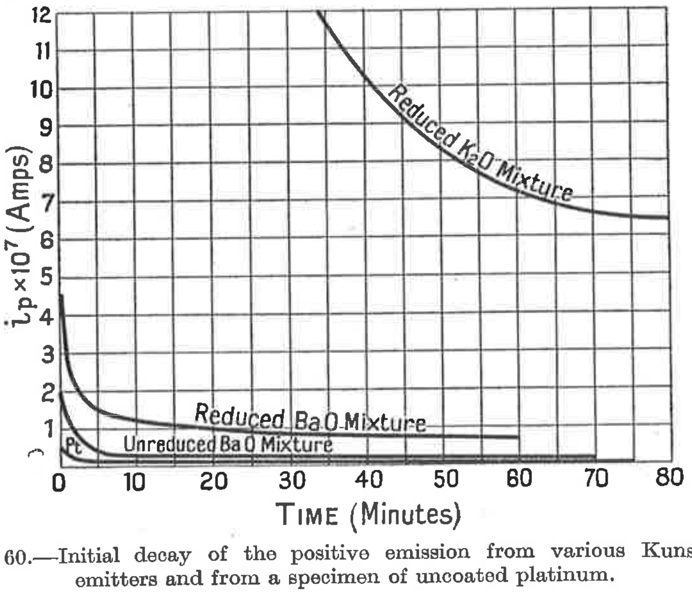

FIG. 60.—Initial decay of the positive emission from various Kunsman emitters and from a specimen of uncoated platinum.

An analysis by Barton, Harnwell and Kunsman [4] of the ions emitted from various mixtures has shown that after a few hours' ageing they consist either wholly or in large part of singly charged atoms of the alkali or alkaline earth metal whose oxide is present in the mixture. The emission of these ions is in general purer from the mixtures in which the oxides are of the alkali metals, particularly the more electropositive and easily ionizable ones, than from those containing the alkaline earths. An idea of the purity of the emissions in the various cases is given by the mass spectra of the ions obtained from mixtures containing the oxides of the alkali and alkaline earth metals shown in Figs. 61 and 62 respectively. In Fig. 62, two curves are shown for each sample. Those marked I were taken early, and at a low temperature. It is noteworthy how persistently potassium appears in these, and to a lesser extent sodium, these being, indeed, the most important emissions present. After the curves I had been taken, the temperatures were increased, and after a prolonged ageing, the curves II were taken at the highest temperatures possible without burning out the filaments. The alkali ions do not appear nearly so strongly in these, the principal emissions now being those of the alkaline earth metal with whose oxide the mixture was prepared.

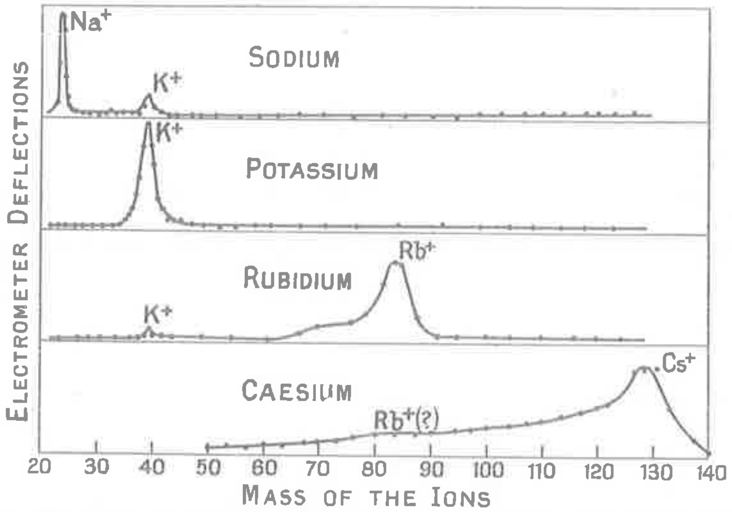

FIG. 61.—Mass spectrograms of the positive emission from Kunsman emitters containing oxides of the alkali metals.

As Kunsman has pointed out, the manner in which uncombined alkali or alkaline earth metal appears at the surface of these emitters, whence it evaporates as ions, is probably similar to that in which thorium appears at the surface of thoriated tungsten. It is most unlikely that the hydrogen, which reduces the iron oxide, can also reduce the oxides of such electropositive metals as those of the alkali and alkaline earth groups. The system after reduction therefore almost certainly consists of metallic iron containing the alkali or alkaline earth oxide as an impurity. At the operating temperature this oxide is probably slowly reduced by the iron, after which it diffuses to the surface.

It has been found that much more stable, though initially somewhat smaller, emissions are given by mixtures containing, in addition to the alkali or alkaline earth oxide, a roughly equal quantity of aluminium oxide, than by those in which no aluminium oxide is present. Kunsman[16] has suggested that possibly in the former case a double oxide is formed. If this is so, the double oxide would perhaps be less easily reduced by the iron than the simple alkali or alkaline earth oxide.

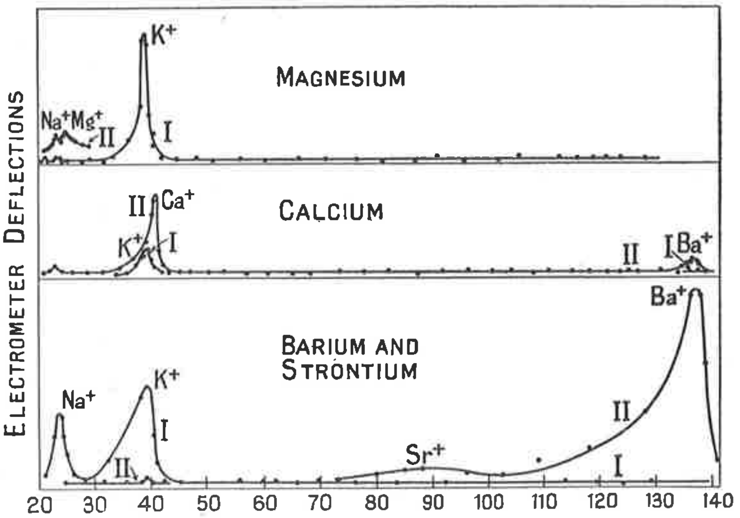

FIG. 62.—Mass spectrograms of the positive emission from Kunsman emitters containing alkaline earth oxides.

The platinum type of emitter has been described in one form by Cottrell, Kunsman and Nelson,[8] and by Brewer.[7] A platinum wire or ribbon, which can be heated by a current, is coated with a soda-free potash glass and the whole then dipped into molten potassium nitrate, and a quantity of potassium electrolysed, through the glass, on to the surface of the platinum core. A film of platinum is then sputtered on to the outer surface of the glass and contact made with it by wrapping a fine wire tightly round it. If the system is now heated and the outer film of platinum simultaneously held at a potential inferior to that of the platinum core, potassium is electrolysed from the inner to the outer surface of the glass and passes into the sputtered film, from whose outer surface it is then emitted in the form of ions. Both the rate of supply of potassium by electrolysis to the emitting film of platinum and the temperature can, of course, be controlled separately.

It has been found that the emission does not increase in proportion to the electrolytic current, but passes through a maximum when the current has a certain value corresponding to a potential difference between the two platinum electrodes of the order of only 1 volt. At any given temperature, the equilibrium quantity of adsorbed potassium on the surface of the sputtered platinum must increase with the electrolytic current, and when this quantity is too great the "electron affinity" (work function) of the system will be insufficient for the potassium to become ionized as it evaporates. It is undoubtedly to this that the existence of the maximum is due.

A modification of this type of emitter, due to Nelson,[22] consists of a potash or soda glass tube, closed at one end and provided with an internal coating of sputtered platinum. The tube is evacuated and immersed in a bath of molten alkali nitrate—KNO_3 if the tube is of potash glass, $NaNO_3$ if it is of soda glass—and alkali metal electrolysed on to the sputtered platinum coating by maintaining a suitable potential difference between it and the bath. The ions emitted from the platinum surface are collected by a nickel wire lying along the axis of the tube.

The Generation of Ions by Metals Heated in Alkali Vapours.—We have already dealt with certain aspects of the generation of positive ions by hot tungsten and other metals in the vapour of an alkali metal, such as cæsium. Let us now consider a thermodynamical-statistical theory of this phenomenon advanced by Langmuir and Kingdon.[17]

Let us suppose that within an enclosure of fixed volume, having walls of tungsten, there is present a mixture of cæsium atoms, ions and electrons. If the enclosure is small enough, space-charge effects will be sufficiently unimportant to be ignored. If, at the same time, the linear dimensions of the enclosure are large in comparison with the distance from the surface within which the image force is appreciable, the concentration of electrons within the enclosure will be determined uniquely by its temperature and by the work function of its walls, whether contaminated by adsorbed cæsium or not. Taking this fixed concentration of electrons into consideration, one may then, by a modification of Saha's theory, calculate the degree of ionization of the cæsium vapour for any given quantity of it contained within the enclosure.

The condition of equilibrium of a reacting mixture of gases contained in an enclosure of fixed volume at constant temperature is

$$\delta F = 0, \quad . \quad . \quad . \quad . \quad (2)$$

where F, the "free energy," is given by

$$F = U - TS, \quad . \quad . \quad . \quad . \quad (3)$$

U being the internal energy, T the temperature and S the entropy of the system.

Let us first consider the general case where there are N_1 gram-molecules of the first gas, N_2 of the second, and so on, present in the enclosure, whose volume is V. Then the internal energy of the gas mixture is given by

$$U = \Sigma N_1(c_{v_1}T + b_1), \quad . \quad . \quad . \quad (4)$$

where $c_{v_1}, c_{v_2}, \ldots$ are the molecular heats at constant volume of the gases and $b_1, b_2, \ldots$ are arbitrary constants. The entropy s_1 of a gram-molecule of the first gas is

$$s_1 = c_{v_1} \log T + R \log v_1 + k_1, \quad . \quad . \quad (5)$$

where v_1 is the molecular volume and k_1 is a constant, and analogous expressions will, of course, hold for the other gases. Thus, since

$$v_1 = \frac{V}{N_1}, \; v_2 = \frac{V}{N_2}, \text{ etc.}, \quad . \quad . \quad (6)$$

and the entropy of a mixture of gases is the sum of the entropies the constituent gases would have if each alone occupied the volume of the mixture, we have

$$S = \Sigma N_1(c_{v_1} \log T + R \log V - R \log N_1 + k_1). \quad . \quad (7)$$

Hence, substituting (4) and (7) in (3), we obtain

$$F = \Sigma N_1\{c_{v_1}T + b_1 - T(c_{v_1} \log T + R \log V - R \log N_1 + k_1)\}, \quad (8)$$

and we easily see that if, in the virtual change at the constant temperature and volume, N_1 increases by ν_1, N_2 by ν_2, etc., then (2) is expressed by

$$\Sigma\nu_1\{c_{v_1}T + b_1 - T(c_{v_1} \log T + R \log V - R \log N_1 + k_1 - R)\} = 0. \quad (9)$$

Now the heat effect L associated with the change is obviously given by

$$L = \Sigma\nu_1(c_{v_1}T + b_1), \quad . \quad . \quad . \quad (10)$$

and it is easily seen that the two parts, $\Sigma\nu_1 c_{v_1}T$ and $\Sigma\nu_1 b_1$, of this must be the change in thermal energy and the energy required for the chemical change respectively. If we write L' for the latter quantity, i.e. for that part of the heat effect which has nothing to do with change in thermal energy, we have, from (9),

$$\frac{L'}{RT} = \Sigma\nu_1\left(\frac{c_{v_1}}{R} \log T + \log V - \log N_1 + \frac{k_1}{R} - \frac{c_{v_1} + R}{R}\right). \quad (11)$$

Now let us consider the case represented by

$$\overset{(1)}{\mathrm{Cs}} \rightleftharpoons \overset{(2)}{\mathrm{Cs}^+} + \overset{(3)}{e}, \quad . \quad . \quad . \quad (12)$$

in which $\nu_1 = -1$, $\nu_2 = +1$, $\nu_3 = +1$, and let us write l' for the energy required to ionize one gram-atom of cæsium vapour. Then since $c_{v_1} = c_{v_2} = c_{v_3} = \frac{3}{2}R$, our equilibrium condition (11) becomes

$$\log \frac{(N_2/V)(N_3/V)}{(N_1/V)} = -\frac{l'}{RT} + \frac{3}{2} \log T + \frac{k_2 + k_3 - k_1}{R} - \frac{5}{2},$$

or, if n_1 is written for NN_1/V, n_2 for NN_2/V, etc., where N is Loschmidt's number,

$$\log \frac{n_2 n_3}{n_1} = -\frac{l'}{RT} + \frac{3}{2} \log T + \left(\frac{k_2 + k_3 - k_1}{R} + \log N - \frac{5}{2}\right). \quad (13)$$

This, with the correct numerical value substituted for the constant quantity in brackets, is Saha's equation in the form best suited to our purpose.

The value of the constant of eqn. (13) may be found by calculating, both thermodynamically and statistically, the gain in entropy of a gram-atom of cæsium associated with its complete ionization and equating the two expressions found. The validity of the result arrived at by this procedure is independent of whether or not either of the two states considered is of equilibrium, and therefore actually realizable. We are here concerned merely with mathematical convenience, not with physical realizability.

Let the gram-atom of cæsium vapour considered, both in the un-ionized and in the ionized state, be at the temperature 1°K., and let it in each case be subjected to such a pressure that it occupies a volume of 1 c.c. Then log T, log v_1, log v_2 and log v_3 all vanish, and we have, on account of (5),

$$s_2 + s_3 - s_1 = k_2 + k_3 - k_1. \qquad . \qquad . \quad (14)$$

That is the purely thermodynamical part of the procedure.

Let W_1 denote the thermodynamic probability of the cæsium in the un-ionized state and W_{23} that in the ionized state. Then by Boltzmann's hypothesis

$$s_2 + s_3 - s_1 = k \log (W_{23}/W_1), \qquad . \qquad . \quad (15)$$

where k is Boltzmann's constant. Now it is easily seen that W_{23}/W_1 is independent of the mass of the ion, so long as this is substantially the same as that of the un-ionized atom. The quotient in question is therefore the same as it would be in an imaginary (but of course actually impossible) case where the ion, the neutral atom and the electron all had the same mass. We shall therefore suppose, for simplicity, that we are dealing with such a case.

For the evaluation of W_{23} we have to consider the case of 2N " molecules," N of which are all of one kind (and have no individuality assignable to them) and the remaining N all of another, possessing between them the total energy 2E, where $E = \frac{3}{2}R$, and for the evaluation of W_1 we merely have to consider N molecules all of one kind, having the total energy E. Each thermodynamic probability may be determined in a manner similar to that employed in Chapter V, and when the electron spin is taken into account we easily find that

$$\mathrm{W}_{23} = \sigma_p{}^{\mathrm{N}} \,.\, 2^{\mathrm{N}}\left(\frac{8\pi m\mathrm{E}}{3h^3}\right)^{3\mathrm{N}}\left(\frac{\epsilon}{2\mathrm{N}}\right)^{3\mathrm{N}}\left(\frac{\epsilon}{\mathrm{N}}\right)^{2\mathrm{N}}$$

$$= (2\sigma_p)^{\mathrm{N}}\left(\frac{4\pi m\mathrm{E}}{3h^2}\right)^{3\mathrm{N}}\left(\frac{\epsilon}{\mathrm{N}}\right)^{5\mathrm{N}}, \quad . \quad . \quad . \quad (16)$$

and

$$\mathrm{W}_1 = \sigma_a{}^{\mathrm{N}}\left(\frac{4\pi m\mathrm{E}}{3h^2}\right)^{\frac{3\mathrm{N}}{2}}\left(\frac{\epsilon}{\mathrm{N}}\right)^{\frac{5\mathrm{N}}{2}}, \quad . \quad . \quad . \quad (17)$$

where m, h, σ_a and σ_p are the mass of the electron, Planck's quantum of action, and the numbers of relevant possible states (the $2j + 1$ of atomic theory) of a neutral atom and a positive ion respectively, so that

$$\frac{\mathrm{W}_{23}}{\mathrm{W}_1} = \left(\frac{2\sigma_p}{\sigma_a}\right)^{\mathrm{N}}\left(\frac{4\pi m\mathrm{E}}{3h^2}\right)^{\frac{3\mathrm{N}}{2}}\left(\frac{\epsilon}{\mathrm{N}}\right)^{\frac{5\mathrm{N}}{2}}, \quad . \quad . \quad (18)$$

or, since $\mathrm{E} = \frac{3}{2}\mathrm{R}$ and $\mathrm{N} = \mathrm{R}/k$,

$$\frac{\mathrm{W}_{23}}{\mathrm{W}_1} = \left\{\frac{2\sigma_p}{\sigma_a}\,\frac{(2\pi mk)^{3/2}}{h^3\mathrm{N}}\right\}^{\mathrm{R}/k}\epsilon^{5\mathrm{R}/2k}. \quad . \quad . \quad (19)$$

Hence, taking logarithms, we have

$$k \log\left(\frac{\mathrm{W}_{23}}{\mathrm{W}_1}\right) = \mathrm{R}\log\left\{\frac{2\sigma_p}{\sigma_a}\,\frac{(2\pi mk)^{3/2}}{h^3\mathrm{N}}\right\} + \frac{5}{2}\mathrm{R}. \quad . \quad (20)$$

Thus, finally, it is evident, from (13), (14), (15) and (20), that the equilibrium condition is given by

$$\log\frac{n_2 n_3}{n_1} = -\frac{l'}{\mathrm{RT}} + \frac{3}{2}\log\mathrm{T} + \log\left\{\frac{2\sigma_p}{\sigma_a}\,\frac{(2\pi mk)^{3/2}}{h^3}\right\}. \quad . \quad (21)$$

This may be simplified by substituting for $\log n_3$ its value, for which, by

$$n_3 = \frac{p}{k\mathrm{T}}, \quad . \quad . \quad . \quad . \quad (22)$$

where p is the partial pressure of the electrons, and eqns. (17) and (40) of Chapter V, we obtain

$$\log n_3 = \log\left\{\frac{2(2\pi mk)^{3/2}}{h^3}\right\} + \frac{3}{2}\log\mathrm{T} - \frac{l_0}{\mathrm{RT}}, \quad . \quad (23)$$

where l_0 has the same meaning as in Chapters I and V. In this way we find that

$$\log\frac{n_2}{n_1} = \frac{l_0 - l'}{\mathrm{RT}} + \log\frac{\sigma_p}{\sigma_a}. \quad . \quad . \quad (24)$$

Since in the case of the alkali metals σ_a is equal to $2\sigma_p$, this may be written

$$\frac{n_2}{n_1} = \tfrac{1}{2}\epsilon^{(\chi - \mathrm{U}_i)/k\mathrm{T}}, \qquad . \quad . \quad . \qquad (25)$$

where χ and U_i are the work function of the metal surface and the energy required to ionize an atom of the vapour respectively.

The above theory, while essentially the same as that of Langmuir and Kingdon, leads to a result which is somewhat simpler than theirs, as it takes no account of departures of the emission constant from the theoretical A_0. It was not then appreciated, as it is now, that such departures are probably due mainly to the existence of an appreciable reflexion of electrons impinging on the surface from without. This reflexion does not, however, enter into the theory of the density of the electron gas in equilibrium with the emitter, and when positive ions are drawn, i.e. when an electron-retarding field is applied, such equilibrium must actually exist near the surface.

But while under experimental, electron-retarding conditions, the electrons are, as assumed in the theory, in thermodynamical equilibrium with the emitter, this is not true of the neutral atoms and positive ions, and it becomes necessary to inquire whether, and to what extent, the applicability of the theory to experimental cases may be affected by this. Since the free paths are always much greater than the linear dimensions of the experimental tube, all the vapour particles that impinge on the filament do so with kinetic energies corresponding to the temperature of the relatively cold walls of the vessel, not to that of the hot filament. Furthermore, none of these particles are ions, since the field draws all ions permanently away from the filament; they are all neutral atoms. Nevertheless, neither of these circumstances will affect the proportion of ions to atoms that leave the filament if direct reflexion of either kind of particle from the filament is unimportant, i.e. if all or practically all impinging particles have an appreciable adsorption life on the filament before they leave it again. In that case the condition in which a particle evaporates can hardly be affected by either the velocity or the charge with which it reached the filament. We do not know for certain how much direct reflexion there is under all conditions, but at least we have a strong indication that the reflexion of *atoms* is not very important, in the observed fact that with a given cæsium vapour pressure, the rate at which a tungsten filament exposed to the vapour generates ions is constant when its temperature much exceeds a certain critical value. If an appreciable proportion of incident atoms were directly reflected, we should expect the ion current at high temperatures to show at least *some* temperature dependence.

Experimental data have been obtained by Langmuir and Kingdon[17] which provide a very satisfactory test of their theory. A tungsten filament held at 1300°K. or more in cæsium vapour at a certain pressure was found to give a constant ion current of $2{\cdot}43 \times 10^{-3}$ amp./cm.^{2}. This, then, may be taken as a measure of the rate of arrival of cæsium atoms at the filament surface. When the filament temperature was 1177°K., the ion current was only $2{\cdot}06 \times 10^{-6}$ amp./cm.^{2}, i.e. 1/1180 of the maximum. That is to say, at this temperature only one atom out of 1180 that struck the filament was converted into an ion.

The electron emission at 1177°K. was found to be $2{\cdot}22 \times 10^{-6}$ amp./cm.^{2}. A clean tungsten filament at the same temperature would have given only $3{\cdot}25 \times 10^{-12}$ amp./cm.^{2}. From these data we may arrive at an estimate of the work function of the contaminated surface. We do not know the value of the emission constant of the contaminated surface, but since at 1177°K. the contamination must have fallen very far short of a complete monatomic layer of cæsium, we shall probably not be seriously in error if we assume that the emission constant was the same as that of clean tungsten. On this assumption the lowering of the work function corresponding to the increase of emission produced by the contamination is readily found to be 1·363 e.v., making the work function of the contaminated surface $4{\cdot}54 - 1{\cdot}363$, i.e. $3{\cdot}17_7$ e.v. Of course, in order to obtain the data from which this result is calculated, an electron-accelerating, i.e. ion-retarding field had to be applied to the filament, and this must have made the equilibrium surface-concentration of contamination somewhat greater than it was when ions were drawn at the same temperature. In the case under consideration, however, where the two conditions differ only in regard to the return or non-return of one out of 1180 evaporating cæsium particles, this effect can hardly have been very important.

These data, together with the ionization potential of cæsium, which is 3·874 volts, are all we require in order to compare the theoretical n_2/n_1 with the experimental result. We have, by (25),

$$\begin{aligned}\frac{n_2}{n_1} &= \tfrac{1}{2}\epsilon^{-11600(3{\cdot}874-3{\cdot}177)/1177} \\ &= \frac{1}{1940}.\end{aligned}$$

In view of the uncertainty regarding the quantities involved in the calculation, this result must be considered in very satisfactory accord with the experimental 1/1180.

Since the state in which a particle evaporates from the surface of a metal can hardly be dependent in any way on whether it first arrived at the surface by condensation from without or by diffusion from within, it is probable that the theory of Langmuir and Kingdon also applies to the emission of "impurity" ions from metals. We have seen that the commonest impurity ions emitted are those of the relatively easily ionizable alkali metals, such as potassium. According to eqn. (25), this is what we should expect.

A rough determination of the work that must be performed in order to remove a positive ion of potassium from a nearly clean tungsten surface, leaving all parts of the emitter in equilibrium with one another after as before the loss of the ion, has been made by Moon and Oliphant.[20] It will be convenient to call this reversible work of extraction the positive-ion work function for the particular surface and kind of ion. It is evident that it is analogous to the electron work function.

A beam of K^+ ions, formed at the surface of a hot tungsten ribbon exposed to potassium vapour, was directed on to a heated tungsten target at whose surface either an ion-accelerating or an ion-retarding field could be established. When slow ions were directed on to the target and ions were also drawn from it, there was no net current to or from the target, and from this it must be inferred that every potassium particle evaporating from it did so as a positive ion. The current to the collector was then a measure of the rate of supply of particles to the target. The equilibrium quantity of potassium adsorbed on the surface of the target under these conditions could be determined from the galvanometer "throw" obtained when the target was suddenly flashed at a temperature high enough to make the whole of the adsorbed potassium evaporate as ions.

When an ion-retarding field was applied to the target, every ion leaving it was forced to return, and in consequence the amount of adsorbed potassium increased, until eventually, while the great majority of the particles still evaporated as ions, enough did so as atoms to balance the arrival rate. On now suddenly reversing the field, a much larger ion current was at first found to flow to the ion collector than in the steady state with the collector negative, and from the ion current-time relationship now observed the amount of potassium present on the target at any moment could readily be deduced. It was found, incidentally, that even at the beginning this amount was less than 1 per cent. of a complete monatomic layer.

The ion evaporation rate, as given by the current to the collector, was found, as might be expected for these small concentrations, to vary linearly with the amount of potassium on the surface. The rate of evaporation of ions per unit surface concentration of potassium was determined at four different temperatures and found to vary as $\epsilon^{-\omega_p/kT}$, where ω_p was about 4·4 electron-volts. The plausible assumption was made that ω_p represents the positive-ion work function, or at least something very near it. No great accuracy was claimed for the value found for this quantity, however, as the possible experimental errors were large and the temperature range covered rather small.

Experiments of a similar nature have recently been carried out by Evans,[9] using an improved apparatus in which the most important sources of error to which the experiments of Moon and Oliphant were subject were eliminated. In most of Evans' experiments the beam of particles directed on to the target was atomic, instead of, as in those of Moon and Oliphant, ionic. Beams of potassium, rubidium and cæsium were used. After alkali metal had been allowed to accumulate on the target for some time with an ion-retarding field applied to it, the field was suddenly reversed and the decay of the ion current asymptotically to a finite limit observed. Fig. 63 shows such a decay.

The decay was in every case found to be closely exponential, so that it could be represented by the equation

$$i_p = a(1 - \beta\epsilon^{-bt}), \qquad . \quad . \quad . \tag{26}$$

where a and β are constants, b is a function of the temperature and t is the time. When log b was plotted against 1/T, a straight line with negative slope was obtained, and it is easily seen that this slope is related in the usual way to the quantity

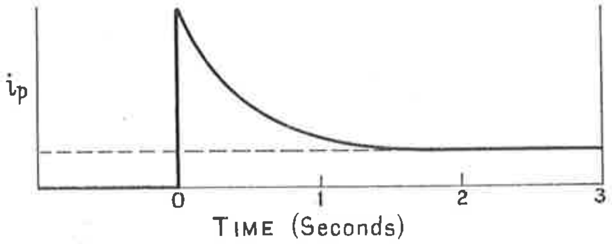

FIG. 63.

ω_p in the empirical positive-ion emission formula for a given quantity of alkali metal on the surface,

$$i_p \propto \epsilon^{-\omega_p/kT}. \qquad . \quad . \quad . \tag{27}$$

The values of ω_p, which we should expect to be equal to, or to differ but little from, those of the positive-ion work functions for the alkali metals on nearly clean tungsten were found to be $2{\cdot}4_3$, $2{\cdot}1_4$ and $1{\cdot}8_1$ electron-volts for potassium, rubidium and cæsium respectively. These figures must be regarded as much more accurate than that for potassium given by Moon and Oliphant.

Evans has made an interesting comparison between his measured values of ω_p and the amounts of work that would be required to remove the ions from the tungsten surface against their image attractions. For the calculation of the image works for the three kinds of ion he used values for the ionic radii (which were taken to determine the points of departure) obtained by Goldschmidt[10] from X-ray analyses of polar salts. The image works thus calculated are compared with the corresponding experimental values of ω_p in Table XIX. It is seen that in each case the calculated image work agrees with ω_p to within about 10 per cent.

TABLE XIX.

Comparison between Calculated Image Works of Extraction and Experimental ω_p for K^+, Rb^+ and Cs^+ Evaporating from Tungsten.

Ion.	Radius (Å.).	Obsd. ω_p (e.v.).	Calcd. Image Work (e.v.).
K^+ . .	1·33	$2{\cdot}4_3$	2·69
Rb^+ . .	1·49	$2{\cdot}1_4$	2·40
Cs^+ . .	1·75	$1{\cdot}8_1$	2·03

It is not known for certain whether the work required to remove an adsorbed positive ion from the surface is strictly comparable with the positive-ion work function which we have taken to be given sufficiently closely by ω_p. The positive-ion work function is the *reversible* work of extraction of a positive ion. The process of removing an adsorbed positive ion from the surface will not be reversible, however, unless practically all the adsorbed particles are ions. If they are not, the removal of an adsorbed ion will not leave the emitter in a state of equilibrium, and equilibrium can only be restored by a transference of negative charge from the surface to the interior of the metal. It will be clear from the discussion in Section IV of Chapter III (p. 183), however, that there is probably less difference (energetically) between an adsorbed ion and an adsorbed atom than between an ionized and an un-ionized atom in free space. Thus even if most of the adsorbed particles are atoms the quantities in the last two columns of Table XIX may still be nearly comparable. In any case, probably no theoretical significance is to be attached to the slight discrepancy between these quantities. As we saw in Chapter III, an ion is almost certainly a different thing when adsorbed on a metal surface from what it is when isolated in free space. Also, as Evans has pointed out, very close to the surface forces other than the theoretical image force are undoubtedly operative.

The Emission of Ions of the Bulk Metal.—The first indications of the emission from a metal of charged atoms of its own material were obtained in 1924 by Jenkins,[12] in observations of the positive emission from the tungsten filament of a Coolidge X-ray tube. Above about 2800°K. he observed a positive emission which increased rapidly with temperature, and which differed from that due to easily ionizable impurities previously observed in that, after certain initial changes, it was fairly constant with time. This was true except at temperatures approaching the melting-point of the filament, where a rapid decrease with time was noted. From the difficulty he experienced in deflecting the ions by a magnetic field, Jenkins concluded that they must have been relatively heavy ions, probably charged atoms of tungsten.

These observations, in so far as they concerned temperature and time changes, were later confirmed by Mitra,[18] working with commercial radio valves. The decay curves obtained seemed to be asymptotic, not to zero, but to some finite current value. L. P. Smith [30, 31] also observed a constant emission of positive ions above 2500°K. from tungsten filaments which had previously been severely heat-treated, and finding these ions to have a greater mass than those of potassium, the heaviest easily ionizable impurity likely to be present, conjectured that they might be W^+.

A mass-spectrographic analysis of these ions, and also of those emitted at very high temperatures from molybdenum, tantalum and rhodium, carried out by Wahlin,[35] definitely showed them to consist of the singly charged atoms of the respective metals. These results were confirmed by Smith [28] in the case of tungsten and molybdenum. Subsequent experiments by Wahlin [36, 39] and by Barnes,[2, 3] showed singly positively charged atoms of their own metal to be emitted also from chromium, ruthenium and columbium at temperatures where the rate of evaporation of these metals is appreciable, and from iron, nickel, copper and silver when heated to near their melting-points. Some of these emissions were very small indeed. For example, in the case of copper and silver they could be detected only by using as measuring instrument an electrometer having a sensitivity of the order of 10^{-15} amp./mm.

The temperature variation of this positive emission has been studied in the case of molybdenum by Smith [28, 29] and Barnes,[3] and in that of tungsten by Smith [31, 28, 29] and Moon.[19] In each case the data obtained may be represented by the empirical formula

$$i_p \propto \epsilon^{-\omega_p/kT}, \quad . \quad . \quad . \quad . \qquad (27)$$

where ω_p is a constant.

An elaborate thermodynamical theory of the emission has been developed by Smith,[28, 29] in which account is taken of all the thermal effects involved. According to this theory, which we shall not go into here, the value of the positive-ion work function χ_p is somewhat greater than ω_p, but in practice the difference is small, amounting to only 1 or 2 per cent. The differences between separate determinations of ω_p made with the same metal have generally been greater than this.

According to Smith,[28, 29] the value of χ_p for tungsten at absolute zero is 6·55 e.v., and that for molybdenum is 6·09 e.v.

Now we may reversibly extract an ion and an electron from a metal, either separately, or combined, as an atom, and then ionize the atom afterwards. Since the initial and final states are the same in both cases, so must be the amounts of work required to bring about the change, and we have, therefore,

$$\chi_p = U_i + \chi_a - \chi, \quad . \quad . \quad . \qquad (28)$$

where χ_a, the atom work function, is defined as the amount of work that must be performed in order reversibly to transfer a neutral atom from the condensed to the vapour phase.

Let us now apply this equation to the case of tungsten. The value of U_i, the work of ionization, though not definitely known, is believed to be about 7·1 e.v. The atom work function χ_a has been determined from evaporation data [13] and is equal to 8·3 e.v. And the electron work function χ is 4·5 e.v. Substituting these values in (36) we obtain 10·9 e.v. for χ_p. This does not agree at all well with Smith's experimental value, the discrepancy amounting to 4·3 e.v.

The agreement in the case of molybdenum is hardly better. For this metal, $U_i = 7{\cdot}35$ e.v., $\chi_a = 6{\cdot}33$ e.v. and $\chi = 4{\cdot}15$ e.v. Thus, according to (36), χ_p should be 9·53 e.v., or 3·5 e.v. greater than Smith's experimental value.

In both cases, however, much better agreement with the theoretical χ_p-values has been obtained in more recent experimental work. A careful redetermination of χ_p for molybdenum by Barnes[3] has yielded a value for this constant of 8·2 e.v., or only 1·3 e.v. short of the theoretical value. In the case of tungsten even better agreement has been obtained. Determinations by Moon[19] of the temperature dependence of the positive-ion current from four different tungsten filaments between 3000° and 3200°K. have all yielded values of χ_p between 10 and 11 e.v. The agreement with the theoretical value of 10·9 e.v. must be regarded as very satisfactory.

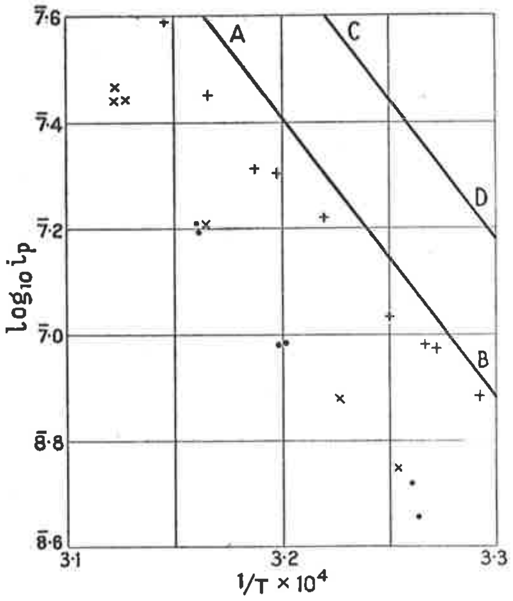

FIG. 64.

Moon's data have also been found to agree in order of magnitude with the requirements of the Saha-Langmuir-Kingdon theory. According to this theory we should have

$$\frac{i_p}{i_a} = \frac{\sigma_p}{\sigma_a} \epsilon^{-11600(7\cdot1 - 4\cdot54)/T},$$

where σ_a and σ_p have the same meanings as on page 298. It is known from spectroscopic data that σ_a for tungsten is equal to 1, but the value of σ_p is somewhat uncertain. There appear to be two possibilities regarding the structure of the tungsten ion, viz. either that there are four *d* electrons and one *s* electron outside the "hafnium core," or else that there are three *d* electrons and two *s* electrons.* In the former case σ_p would be equal to 2, and in the latter it would be 4. As regards i_a, complete data for the rate of evaporation of tungsten at various temperatures are given in a table by Jones and Langmuir.[13] Moon also made several determinations of this quantity, both by direct weighing and by calculation from the rate of change in resistance of his filaments, and found the results to check very well with Jones and Langmuir's data. Using the latter, it is then a simple matter to calculate from the above formula the theoretical relationship between log i_p and 1/T. The lines AB and CD in Fig. 64 represent this relationship for assumed values for σ_p/σ_a of 2 and 4 respectively. The points, on the other hand, are plots of experimental values of log i_p against 1/T obtained with three different filaments which had not developed serious "hot spots." Their proximity to either of the two theoretical lines is perhaps as close as could reasonably be expected, in view of the experimental uncertainty indicated by the "spread" of the points.

LITERATURE.

1. Le R. L. Barnes, *Phys. Rev.*, **42,** p. 487, 1932.
2. Le R. L. Barnes, *Phys. Rev.*, **40,** p. 1044, 1932.
3. Le R. L. Barnes, *Phys. Rev.*, **42,** p. 492, 1932.
4. H. A. Barton, G. F. Harnwell and C. H. Kunsman, *Phys. Rev.*, **27,** p. 739, 1926.
5. O. Birkenberg, *Ann. d. Phys.*, **1,** p. 157, 1929.
6. H. Bölling, *Phys. ZS.*, **33,** p. 625, 1932.
7. A. K. Brewer, *Phys. Rev.*, **35,** p. 1360, 1930.
8. F. G. Cottrell, C. H. Kunsman and R. A. Nelson, *Rev. Sci. Instr.*, **1,** p. 654, 1930; *J. Opt. Soc. Amer.*, **20,** p. 153, 1930.

* The author is indebted to Mr. J. W. Ryde for obtaining this information for him.

9. R. C. Evans, *Proc. Cambr. Phil. Soc.*, **29**, p. 161, 1933 ; *Proc. Roy. Soc.* (*A*), **139**, p. 604, 1933.
10. V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**, p. 253, 1929.
11. O. Gossmann, *ZS. f. Phys.*, **22**, p. 273, 1924.
12. W. A. Jenkins, *Phil. Mag.*, **47**, p. 1025, 1924.
13. H. A. Jones and I. Langmuir, *Gen. El. Rev.*, **30**, pp. 310, 354 and 408, 1927.
14. J. Kahra, *Ann. d. Phys.*, **1**, p. 135, 1929.
15. C. H. Kunsman, *Science*, **62**, p. 269, 1925.
16. C. H. Kunsman, *J. Franklin Inst.*, **203**, p. 635, 1927.
17. I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc.* (*A*), **107**, p. 61, 1925.
18. P. K. Mitra, *Phil. Mag.*, **5**, p. 67, 1928.
19. P. B. Moon, *Proc. Cambr. Phil. Soc.*, **28**, p. 490, 1932.
20. P. B. Moon and M. L. Oliphant, *Proc. Roy. Soc.* (*A*), **137**, p. 463, 1932.
21. H. Murawkin, *Ann. d. Phys.*, **8**, p. 385, 1931.
22. R. A. Nelson, *Rev. Sci. Instr.*, **2**, p. 173, 1931.
23. T. E. Phipps and R. T. Leslie, *J. Am. Chem. Soc.*, **50**, p. 2414, 1928.
24. G. C. Schmidt, *Ann. d. Phys.*, **75**, p. 337, 1924.
25. G. C. Schmidt, *Ann. d. Phys.*, **80**, p. 588, 1926.
26. G. C. Schmidt, *Ann. d. Phys.*, **82**, p. 664, 1927.
27. D. v. Seelen, *ZS. f. Phys.*, **29**, p. 125, 1924.
28. L. P. Smith, *Phys. Rev.*, **34**, p. 1496, 1929.
29. L. P. Smith, *Phys. Rev.*, **35**, p. 381, 1930.
30. L. P. Smith, *Phys. Rev.*, **33**, p. 279, 1929.
31. L. P. Smith, *Phys. Rev.*, **33**, p. 1082, 1929.
32. B. Tasulachov, reported by A. Joffé, *ZS. f. Phys.*, **62**, p. 730, 1930.
33. C. Tubandt, *ZS. f. Elektrochem.*, **26**, p. 358, 1920 ; *ZS. f. anorg. u. allgem. Chem.*, **115**, p. 105, 1921.
34. T. Volmer, *ZS. f. Phys.*, **26**, p. 285, 1924.
35. H. B. Wahlin, *Phys. Rev.*, **34**, p. 164, 1929 ; *Nature*, **123**, p. 912, 1929.
36. H. B. Wahlin, *Phys. Rev.*, **37**, p. 467, 1931.
37. H. B. Wahlin, *Phys. Rev.*, **35**, p. 653, 1930 ; **37**, p. 473, 1931.
38. H. B. Wahlin, *Phys. Rev.*, **39**, p. 183, 1932.
39. H. B. Wahlin, *Phys. Rev.*, **38**, p. 1074, 1931.
40. M. Wolfke and J. Rolinski, *Phys. ZS.*, **30**, p. 817, 1929.
41. M. Zentgraf, *Ann. d. Phys.*, **2**, p. 313, 1929.

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