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REVIEWS
OF
MODERN PHYSICS

THERMIONIC EMISSION

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INTRODUCTORY REMARKS

THERMIONIC devices have become such an essential factor in so many purely scientific and technical applications that it is difficult to realize at the present time that only sixteen years ago the very existence of a pure electron emission from incandescent solids was questioned by many physicists of good repute.[1] The apparently trivial observations made by Edison on the discharge of negative electricity from the carbon filament of an incandescent lamp to an auxiliary electrode in the bulb was the beginning of a series of scientific investigations carried out by O. W. Richardson, A. Wehnelt, I. Langmuir, W. Schottky and a large number of other investigators. Their observations have led to the development of a number of hot cathode devices, the application of which in the radio and electrical industry in general has been of far reaching importance.

The use of the hot cathode is becoming increasingly important not only in these high vacuum devices, but also in connection with various types of gas discharges and arcs. It has appeared, therefore, that it might be well to take stock, as it were, of the state of our knowledge of thermionic phenomena at the present time. There is a certain measure of reason for this as a considerable period has intervened since the publication of the classical work on the subject by O. W. Richardson,[2] while the most recent summaries are available only in German treatises, such as those of W. Schottky.[3] To these excellent discussions of the subject the writer wishes here to express his indebtedness in the preparation of the following paper.

I. TECHNIQUE OF ELECTRON EMISSION

A. Equations for emission. On the basis of certain theoretical considerations, which will be discussed in a subsequent section, O. W. Richardson derived an equation for electron emission as a function of the temperature of the form

$$I = aT^{1/2}\epsilon^{-b/T} \tag{1}$$

where I = emission per unit area,
T = absolute temperature,
and a and b are constants characteristic of the emitting surface.

Although Richardson[4] and M. v. Laue[5] had also pointed out that an equation of the form

$$I = AT^2\epsilon^{-b_0/T} \tag{2}$$

would be just as valid theoretically, and would be in satisfactory agreement with observed data, it was shown by S. Dushman[6] that on the basis of the third law of thermodynamics, A in this equation should be a universal constant having the value 60.2 amps/cm^2 per deg^2 while b_0 should vary with the nature of the emitter.

As will be discussed more fully in subsequent sections, b or b_0 is a measure

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[1] In this connection it is of historical interest to read the discussion on this point by I. Langmuir in Proc. Inst. Rad. Eng. **3**, 261 (1915), and G. E. Review **18**, 327 (1915).

[2] O. W. Richardson, The Emission of Electricity from Hot Bodies, Longmans, Green and Company (1921).

[3] W. Schottky, H. Rothe and H. Simon, Wien-Harms' Handbuch der Experimentalphysik **13**, Akadem. Verlagsgesellschaft, m.b.H. Leipzig (1928).

[4] O. W. Richardson, Phil. Mag. **28**, 633 (1914).

[5] M. v. Laue, Jahrb. d. Elektronik u Radioakt. **15**, 205, 257 (1918).

[6] S. Dushman, Phys. Rev. **21**, 623 (1923).

of the latent heat of evaporation of the electrons, i.e., the energy necessary to get the electrons through the surface. While these are expressed in degrees Kelvin in the above equations, it is also customary to express them in terms of volts by means of the relation

$$b_0 k = \Phi_0 e \tag{3a}$$

where k denotes Boltzmann's constant, e, the charge on the electron, and Φ_0 is known as the "work function." Substituting the well-known values for e and k, it is readily shown that

$$\Phi_0 = 8.62 \times 10^{-5} b_0 \text{ (volts)}. \tag{3b}$$

It has been the object of a large number of investigators to determine the values of these emission constants a and b(or A and b_0) as accurately as possible, and in the following sections the data thus obtained will be reviewed. Since it has been found actually that the observed value of A in equation (2) is not independent of the composition of the emitting surface, a great many theoretical investigations have been published with the object of explaining this apparent anomaly. While these views will be discussed in a subsequent section, it would seem at the present time that the reliable data available are insufficient to draw any definite conclusions on this point. Therefore more emphasis should be laid on experimental investigations to obtain accurate emission data on those substances for which data are at present unavailable, and furthermore it is necessary to obtain data, independent of emission measurements, on the values of the work functions themselves, since from such data combined with observations on emission more exact values of the constant A could be obtained.

B. General remarks on conditions requisite for accurate determinations of emission constants. From equation (2) it is seen that

$$\frac{dI/I}{dT/T} = \frac{b_0}{T} + 2.$$

For tungsten, $b_0 = 52{,}400$, and therefore for $T = 2400°K$, the temperature coefficient of emission is approximately 24. In general, the value of b_0 is lower the lower the range of temperatures at which emission data can be obtained under practical conditions, so that the ratio b_0/T does not vary within very wide limits.

Thus the observations on emission should be made under conditions which will make it possible to determine the temperature accurately. Furthermore, since the emitting source is either in the form of a filament, or an extended surface, care has to be taken to determine as accurately as possible the actual area at the maximum temperature, and to introduce proper corrections, where necessary, for temperature gradients along the emitting surface. The most important precautions, however, in connection with observations on emission are those regarding the removal of adsorbed and occluded gases from the emitter itself, and the necessity of maintaining as nearly perfect vacuum conditions as possible. Most of the observations on emission made up to 1914, and a considerable number of those made since then, are almost worthless because of the poor vacuum conditions under which they were made. As a result largely of the work of I. Langmuir and his associates it has become recognized that adsorbed gases may alter the emission profoundly, and, furthermore, that if there is sufficient residual gas in the hot cathode tube, positive ion bombardment tends to decrease the emission, especially from coated surfaces or those covered with monatomic films of "active" substances.

At the present time it is not necessary to describe in detail the methods available for obtaining ideal vacuum conditions and for removing adsorbed gases from the surface of the emitter. These are described in several treatises on this subject,[7] as well as in numerous papers. It is also hardly necessary to remark that all stop-cocks, greased joints, etc., should be avoided in connection with the exhaust and preparation of tubes containing cathodes for which it is desired to determine the electron emissivity.

While the evaporation of tungsten with the bulb immersed in liquid air was used by Langmuir in his first investigations in this field, other "getters" (clean-up agents for producing high vacuum) have come into use with the advent of vacuum devices for radio. For this purpose, magnesium, calcium, barium and alloys of rare-earth metals ("Mischmetal") have been utilized. According to investigations carried out in this laboratory by Mrs. M. R. Andrews, barium cleans up practically all residual gases at ordinary temperatures, while magnesium is ineffective in the case of hydrogen, and calcium does not take up nitrogen to any great extent.

Extremely low pressures may also be obtained by the use of a side tube containing charcoal (which has previously been well exhausted) immersed in liquid air. In this case, however, care has to be taken to see that the liquid air is maintained at constant level during the series of measurements.

C. Forms of hot cathode tubes for investigation of emission. One of the simplest forms of hot cathode devices is that used by I. Langmuir[8] in his first investigations on the emission from tungsten and thoriated tungsten. Two filaments, one of tungsten, and the other of the metal under investigation are sealed into a lamp bulb. Platinum flush seals are inserted in the walls of the bulb opposite to the filaments, and the tube is exhausted on a high vacuum system consisting of mercury condensation pump with liquid air trap between bulb and pump. During exhaust, the bulb is baked out

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[7] *References on High Vacuum Technique*

(1) L. Dunoyer, Vacuum Practice, G. Bell and Sons, London, 1926.
(2) F. H. Newman, The Production and Measurement of Low Pressures, D. Van Nostrand Company, New York, 1925.
(3) G. W. C. Kaye, High Vacua, Longmans, Green and Company, 1927.
(4) S. Dushman, High Vacuum, G. E. Review, 1922, also translated by R. G. Berthold and E. Reimann, Julius Springer, Berlin (1926).
(5) A. Goetz, Physik u. Technik des Hochvakuumes, Friedr. Vieweg and Sohn, Akt. Ges., Braunschweig (1926).

[8] I. Langmuir, Phys. Rev. **2,** 450 (1913); also Phys. Zeits. **15,** 516 (1914).

for about one hour to the maximum temperature to which the particular glass may be subjected without collapsing. Then the filaments are flashed for a few minutes at very high temperatures (just below the melting point), and for a longer time at lower temperatures (2400°K approximately for tungsten), to eliminate occluded gases and to dissociate or evaporate any oxide films on the surface. This high temperature treatment should be continued until, as indicated by a proper type of low pressure gauge, the evolution of gas has practically ceased, and the pressure in the tube is as low as possible. The bulb is sealed off, immersed in liquid air, and the tungsten filament heated at the same time to a temperature of about 2900–3000°K. At these temperatures the tungsten evaporates fairly rapidly, "cleans up" residual gases, and forms a deposit on the walls which is subsequently used as anode in the emission observations. The evaporation should be continued until the resistance of the deposit as measured between the flush seals is less than 100 ohms.

The tungsten filament and deposit are used as anode in the subsequent emission measurements on the second filament, and it is advisable to carry out these measurements with the bulb immersed in liquid air in order to clean up any further traces of gases which may be evolved from the heated cathode.

The filaments used should preferably have comparatively low voltage drop, but should be long enough to minimize the effect of errors in correcting for lead losses (see below.) To determine the temperature of the filament, accurate observations should be made on the voltage drop and filament current.

A more convenient modification of Langmuir's arrangement has been used by S. Dushman[9] and his associates in precision measurements on electron emission from various metals. Instead of volatilizing tungsten on the walls, a piece of calcium wire inserted in a tungsten spiral is used and the metal evaporated while the tube is on the pump. Care should be taken in using this method to see that the calcium wire used is not badly oxidized and the tube should be exhausted as soon as possible after the wire has been sealed in.

K. H. Kingdon[10a] and K. H. Kingdon and I. Langmuir[10b] have used a form of tube which, while more complicated in construction, has the advantage that no corrections have to be made for lead losses. The filament under investigation is suspended along the axis of three co-axial cylinders of similar diameter and arranged with minimum distance of separation between them. The emission is measured to the central cylinder, while the two end cylinders are connected to the filament and act as "guard rings" to prevent any electrons emitted from the ends of the filament from reaching the central anode.

When the material for which it is desired to obtain emission data cannot be drawn in wire form and is available only in the form of sheets, both the

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[9] S. Dushman *et al*, Phys. Rev. **25**, 338 (1925): **29**, 857 (1927).

[10a] K. H. Kingdon, Phys. Rev. **24**, 510 (1924).

[10b] K. H. Kingdon and I. Langmuir, Phys. Rev. **22**, 148 (1923).

problem of heating the surface to a uniform temperature and that of measuring the maximum temperature accurately becomes very difficult. In the case of molten metals, A. Goetz has overcome these difficulties by an ingenious method which will be described in connection with the discussion of his observations.

D. Temperature scale. For a number of substances data are now available by means of which very accurate determinations may be made of the temperature of the emitting surface. The results of the large number of investigations on this subject have been reviewed comprehensively by E. Lax and M. Pirani.[11] Data on the total radiation from a black body an various solids have also been summarized by W. W. Coblentz.[12] References to some of the more important materials are given in the following section.

Undoubtedly the most accurate method for determining the temperature consists in the measurement of the brilliancy (candles per cm^2). The temperature coefficient, that is, the ratio of dB/B to dT/T (where B denotes the brightness in international candles per cm^2) for tungsten varies from 22.75 at $T=1000°$K to 8.45 at $T=3000°$K.[13] Thus with the exception of the electron emission and the rate of evaporation, the candle power shows the greatest variation with temperature, and therefore any inaccuracy in the determination of this value involves less error in that of the temperature than is involved in the determination of any other property of the material, such as resistance or watts radiated.

While the values of B as a function of T have been determined for a number of substances, it is possible to obtain a fair approximation to the true temperature of a material for which the average luminous emissivity[14] is unknown by the following methods.

By means of a photometer it is possible to determine the temperature T_c, at which the material emits light of the *same color* as a black body. This gives a value for the temperature which is higher than the true temperature. For tungsten the color temperatures corresponding to different values of the true temperature as reported by Worthing and Forsythe are given in Table I.

TABLE I. *Relation between color temperature (T_c), brightness temperature (T_s) and true temperature (T) for tungsten.*

T_c for tungsten	T	$(T_c-T)/T$	T_s for tungsten
1006	1000	0.006	966
1517	1500	.011	1420
2033	2000	.0165	1857
2557	2500	.023	2274
3094	3000	.031	2673

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[11] Handbuch der Physik **19,** 1–45, **21,** 190–272, Julius Springer, Berlin, (1929).

[12] International Critical Tables **5,** 238–245 (1929).

[13] H. A. Jones and I. Langmuir, G. E. Review **30,** 310, 354, 408 (1927).

[14] By average luminous emissivity is meant the ratio of the total normal brightness to that of a black body at the same temperature. For tungsten this ratio varies from 0.464 at $T=1000°$K to 0.440 at $T=3000°$K (Forsythe and Worthing, Astrophys. J. **61,** 126 (1925)).

The *brightness* of the material may be compared with that of a standard lamp for a given wave-length. Usually the determination is made for red light ($\lambda = 0.665\mu$). The temperature thus determined is known as the brightness temperature, T_s, and it is *lower* than the true temperature by an amount which increases with decrease in e_λ, the spectral emissivity (for this wave-length) at any given temperature, and also increases with the temperature. Thus for tungsten, e_λ for $\lambda = 0.665\mu$ varies from 0.456 at $T = 1000°K$ to 0.415 at $T = 3000°K$ and the observed values of T_s are given in the last column of Table I.

Therefore from determinations of both T_c and T_s it is possible to deduce fairly approximate values to the true temperatures. On the other hand, it is of course possible to determine the actual value of e_λ by methods described by both Langmuir and Worthing and Forsythe, and thus to calculate T, the true temperature, from optical pyrometer measurements of T_s.

Further information on methods of determining temperatures by optical methods is given in these publications as well as in reviews by W. E. Forsythe.[15] Methods of measuring temperatures by optical methods have also been discussed by P. D. Foote and C. O. Fairchild.[16]

At temperatures below 1100–1200°K, optical methods become impracticable and it is then necessary to refer to some other property of the material such as the watts radiated per unit area or the resistance. The former method is more accurate whenever data are available on the total radiant emissivity. Naturally a correction has to be applied for the cooling effect of the leads (see below), which can be obtained by means of measurements on different lengths of the filaments. Data on the energy radiated as a function of the temperature have been summarized in the review by Lax and Pirani[17] which contains complete references to the literature. The metals mentioned in this summary are the following: W, Mo, Ta, Pt, Os, Au, Ni, Fe, C, Ag, Cu, Zr.

(1) *Tungsten*:—The temperature scale for tungsten has been determined accurately as a result of the work of I. Langmuir and H. A. Jones[13] in the Research Laboratory of the General Electric Company at Schenectady; W. E. Forsythe and A. G. Worthing[18] in the Research Laboratory of the National Lamp Works of the General Electric Company at Cleveland, and C. Zwikker[19] in the Research Laboratory of the Philips' Lamp Company in Eindhoven, Holland.

The best method for determining the temperature, as mentioned previously, is to make a vacuum lamp with a V-shaped filament from a sample of the same wire as used in the emission observations. This filament is treated during exhaust in the *same manner* as the filament in the emission tube. The

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[15] W. E. Forsythe, J. Opt. Soc. Am. and Rev. Scientific Inst. **16**, 307 (1928); J. Am. Ceramic Soc. **12**, 780 (1929).

[16] P. D. Foote and C. O. Fairchild, Symposium on Pyrometry, Am. Inst. Mining and Metallurgical Engineers, **338** (1920), p. 324. See also in the same publication the papers by W. E. Forsythe (p. 291) A. G. Worthing (p. 367), and E. P. Hyde (p. 285).

[17] Lax and Pirani, Handbuch der Physik **21**, 236–240.

[18] W. E. Forsythe and A. G. Worthing, Astrophys. J. **61**, 126 (1925).

[19] C. Zwikker, Physica **5**, 249 (1925), Archives Neerlandaises des Sciences **9**, 207 (1925).

lamp is then either pyrometered against a standard lamp, or else the candle power emitted from a definite area is measured as a function of filament current and volts. Knowing the brightness (candles/cm^2) it is then possible to determine from the tables published by the above investigators the temperature as a function of filament current.

However, a very convenient method, and one which yields results almost as accurate, is to determine the watts consumed by the actual cathode used, and after correcting this for lead losses to calculate the watts/cm^2. From the tables, the corresponding temperature may then be determined quite accurately. According to Worthing and Forsythe, the energy radiated from tungsten as a function of the absolute temperature is given in watts/cm^2 by the relation.

$$\log_{10} E = 3.680(\log_{10} T - 3.3) - 1040/T + 1.900.$$

For a filament of known length, but unknown diameter, the value of $VA^{1/3}/l$ is a function of the temperature (independent of diameter), where V = voltage drop corrected for lead loss, and A is the current. Values of this function have also been tabulated by the above mentioned investigators.

(2) *Molybdenum and tantalum*: The brightness (candles/cm^2) and intensity of radiation (watts/cm^2) for seasoned molybdenum and tantalum have been determined by A. G. Worthing.[20] Either function, therefore, may be used as a measure of the temperature.

(3) *Platinum*: The spectral emissivity of well aged platinum as a function of the temperature has been determined by Worthing[21] for the wave-length $\lambda = 0.665\mu$. The value varies linearly with temperature from 0.295 at $T = 1200°\text{K}$ to 0.310 at $T = 1850°\text{K}$. The procedure used by L. A. DuBridge[22] in measuring electron emission from this metal consisted in determining the brightness temperature by comparison with a calibrated optical pyrometer in which a standard tungsten lamp was used and then correcting for the difference in emissivities of tungsten and platinum by means of Worthing's values given above.

W. Geiss[23] has determined the total radiation intensity for the metal and finds that this may be expressed as a function of the temperature by the relation

$$W = aT^n \cdot \sigma T^4 \text{ watts/cm}^2$$

where $a = 6.22 \times 10^{-4}$
$n = 0.767$
σ = Stefan-Boltzmann constant
$= 5.75 \times 10^{-12}$ watts cm^{-2} deg.$^{-4}$

The total radiation emissivity from this metal as a function of temperature has also been investigated by C. Davisson and J. R. Weeks.[24]

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[20] A. G. Worthing, Phys. Rev. **28**, 190 (1926).

[21] A. G. Worthing, Phys. Rev. **28**, 174 (1926).

[22] L. A. DuBridge, Phys. Rev. **31**, 236 (1928); **32**, 961 (1928).

[23] W. Geiss, Physica **5**, 203 (1925).

[24] C. Davisson and J. R. Weeks, J. Opt. Soc. and Rev. Scient. Inst. **8**, 581 (1924).

(4) *Carbon*: The spectral emissive power of graphite at $\lambda = 0.660\mu$ has been determined by C. H. Prescott and W. B. Hincke[25] for the temperature range 1250°K to 2700°K. From their data the true temperature may be calculated from values of the brightness temperature as determined by an optical pyrometer.

Assuming that carbon has an average total emissivity of 0.85, the energy radiated as a function of the temperature may also be calculated by means of the Stefan-Boltzmann law.

(5) *Nickel:* The spectral emissivity of this metal at three different wavelengths has been measured by A. G. Worthing.[26] The emissivity does not change with temperature, and for $\lambda = 0.665\mu$ the mean value 0.375 was obtained over the range 1200°K to 1650°K.

The total radiation from nickel and cobalt has been measured by C. L. Utterback.[27] The following equations were derived as expressions for the relation between energy and temperature. For nickel,

$$E = C_1 T^{5.29} \text{ for } 650° < T < 1400°\text{K}$$

$$E = C_2 T^{4.75} \text{ for } 1450° < T < 1600°\text{K}$$

For cobalt

$$E = C_3 T^{5.20} \text{ for } 672° < T < 1320°\text{K}$$

$$E = C_4 T^{4.62} \text{ for } 1380° < T < 1590°\text{K}$$

The exact values of the constants are not given.

(6) *Oxide coated filaments.* The temperature scale for these filaments differs both with the treatment and composition of the surface layer and with the nature of the coated material. Therefore this point is more conveniently treated in connection with the discussion of the emission data.

E. Lead loss correction. Owing to cooling effect by the leads, the length of filament from which the emission is obtained is less than the actually measured length. The problem of correcting for this effect of leads was first discussed by I. Langmuir,[28] and then by A. G. Worthing.[29] The paper by W. E. Forsythe and A. G. Worthing[18] gives tables from which the effect of temperature distribution along a filament may be calculated. A mechanical method for solving the differential equation involved in such problems has been developed by V-Bush and K. E. Gould.[30] However, a most comprehensive discussion of the whole problem has been published in a recent paper by I. Langmuir, S. MacLane and K. B. Blodgett,[31] and the following remarks represent a summary of the relations derived in this paper.

We consider a filament fastened to two leads which are presumably at a low temperature as compared with the maximum temperature T_m, at the

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[25] C. H. Prescott and W. B. Hincke, Phys. Rev. **31**, 130 (1928).

[26] A. G. Worthing, Phys. Rev. **28**, 174 (1926).

[27] C. L. Utterback, Phys. Rev. **34**, 785 (1928).

[28] I. Langmuir, Trans. Faraday Soc. **17**, 21 (1921).

[29] A. G. Worthing, Jr. Frank. Inst. **194**, 597 (1922).

[30] V. Bush and K. E. Gould, Phys. Rev. **29**, 337 (1927).

[31] I. Langmuir, S. MacLane and K. B. Blodgett, Phys. Rev. **35**, 478 (1930).

center of the filaments. If the whole filament were at this temperature, the observed value of any property (e.g., watts radiated, electron emission), which we shall denote by H, would be H_m. The ratio $f = H_m/H$ therefore gives the correction factor by which the observed value has to be multiplied to correct for the effect of leads. Let ΔH denote the decrease in H due to one lead. Then

$$f = \frac{H_m \cdot}{H_m - 2\Delta H} \cdot \tag{4}$$

This decrease may be represented by a volt equivalent ΔV_H, and if ΔV denotes the actual decrease in voltage drop due to a single lead, it may readily be shown that

$$f = \frac{V + 2\Delta V}{V + 2\Delta V - 2\Delta V_H} \cdot \tag{5}$$

The magnitude of ΔV_H obviously depends upon the manner in which H varies with T, and also upon the ratio of the maximum temperatures T_m to that of the junction between filament and lead, T_0.

The accurate evaluation of these corrections is, therefore, a somewhat tedious matter. However, in many cases only approximate results are desired and for this purpose the following empirical type of equation may be used:

$$\Delta V_H = P(T_m/1000) - Q(T_0/1000) - R.$$

The values of the constants, P, Q and R for pure tungsten are given for different properties in Table II.

TABLE II. *Constants in formula for lead loss correction for tungsten filaments.*

H	P	Q	R	Range T_m	Range T_0
Voltage*	0.154*	0.081*	0.056*	1000–2500	any value
Candle Power	.338	.182	−.004	600–3500	300–1400
Electron Emission	.440	.158	.072	1000–3500	300– 900
Watts Radiated	.293	.160	.084	1100–3000	300– 900

* For voltage (watts input), a term, $-2.1 \times 10^{-8}\, T_0 \cdot T_m$, is to be added to the right-hand side of the above equation.

For electron emission from tungsten filaments covered with monatomic films of more electropositive elements, the values of ΔV_H will be different from those given in the table, but may be calculated by methods indicated in the original paper. For other materials than tungsten, which obey the Wiedemann-Franz law, the lead-loss correction may also be calculated approximately.

However, it would seem best in most cases either to use the guard ring principle and thus eliminate the necessity for lead-loss corrections completely, or else to measure emission on two different lengths of filaments over the same range of temperature values.[32]

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[32] As, for instance, in the paper by S. Dushman and J. Ewald, Phys. Rev. **29**, 857 (1927).

F. Corrections for effect of anode voltage (Schottky effect). Equations (1) and (2) for electron emission were derived on the assumption that the field strength at the cathode is zero. Actually it is observed that the emission increases with applied anode voltage and it is therefore necessary, in order to determine the emission constants accurately, to apply some correction factor which depends upon the voltage.

An explanation of the effect of field strength on emission was first suggested by W. Schottky in 1914,[33] and hence the phenomenon is generally known as the *Schottky Effect.* As this theory has been discussed very fully by K. T. Compton and I. Langmuir,[34] it is sufficient to state that on the basis of the "electric image" theory Schottky derived a relation of the form

$$i_v = i_0 \epsilon^{(4.39/T)(dV/dx)^{1/2}} \tag{6}$$

where i_v and i_0 represent the emission at anode voltages V and 0 respectively while dV/dx denotes the voltage gradient at the emitting surface.

While this gradient can be calculated in certain simple cases from the geometrical arrangement of anode and cathode, it is much more convenient in practice to plot log i_v against $V^{1/2}$. From this plot, which should be linear if relation (6) is valid, the value of i_0 can then be determined accurately. It will be observed also that from equation (6) it follows that

$$2.303T\frac{\Delta \log_{10} i}{\Delta V^{1/2}} = 4.39S^{1/2} \tag{7}$$

where S is a constant for a given geometrical arrangement of electrodes. Hence it is possible from the plot of log i versus $V^{1/2}$ to calculate S.

Combining Schottky's equation (6) with (2) it follows that

$$\left.\begin{aligned} I_V &= AT^2\epsilon^{-(b_0-\Delta b_0)/T} \\ \text{where} \quad \Delta b_0 &= 4.39(dV/dx)^{1/2} = 4.39(VS)^{1/2} \end{aligned}\right\} \tag{8}$$

and I_V = electron emission per cm² at anode voltage V.

The following table[35] gives values of Δb_0 for $V = 100$ for the case of a filament in the axis of a cylindrical anode. The values of filament and anode diameters are such as to give field strengths, at $V = 100$, which are of the same

TABLE III. *Values of Δb_0 for $V = 100$.*

Diameter of filament	Diameter of anode	dV/dx (volts/cm)	Δb_0
0.001 cm	1.00 cm	2.96×10^4	747
.005	0.50	8.69×10^3	409
.005	1.00	7.55×10^3	381
.01	1.00	4.34×10^3	289
.1	1.00	8.69×10^2	129

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[33] W. Schottky, Phys. Zeits. **15,** 872 (1914), also Zeits. f. Physik **14,** 63 (1923).

[34] K. T. Compton and I. Langmuir, Reviews of Modern Physics **2,** 124 (1930).

[35] S. Dushman and J. Ewald, G. E. Review **26,** 154 (1923).

order of magnitude as those which may be expected in ordinary thermionic devices or in experimental tubes.

While Schottky himself showed that equation (6) is valid over quite a range of temperatures, the relation was applied to derive emission data at zero field strength by S. Dushman and his associates[36] to filaments of tungsten, molybdenum and tantalum, by C. Zwikker[37] to tungsten, and by L. A. DuBridge[38] to platinum. In all these investigations a linear relation was observed between log i and $V^{1/2}$, with values of Δb_0 which could be expected from the geometrical arrangement of electrodes. W. S. Pforte[39] also confirmed the validity of Schottky's equation for a tungsten filament in the axis of a cylindrical anode (where dV/dX could be calculated directly) up to an anode potential of 2000 volts, while N. A. de Bruyne[40] has checked relation (7) quantitatively for field strengths as high as 2.5×10^6 volts/cm.

It would appear, however, as a result of the investigations of J. Becker and D. Mueller[41] that for thoriated tungsten filaments and coated filaments in general, Schottky's theory is not valid for low anode voltages, and that consequently it is not correct to use equations (6) and (7) to extrapolate to zero field strength from observations at anode potentials above 100 volts. N. B. Reynolds[42] has observed, for the case of thoriated tungsten filaments, that while log i varies linearly with $V^{1/2}$ for voltages above 100 (corresponding to field strengths greater than 10^4 volts/cm) the emission decreases much more rapidly as the field strength is decreased below this value.

A discussion of the possible explanations for these observations in the case of monatomic films as emitters has been given by Compton and Langmuir in their review.[34]

It should be observed here that for very high field strengths (in excess of 10^6 volts/cm) emission is observed from filaments even at room temperatures. This "auto-electronic" emission or cold cathode emission does not follow Schottky's relation and is virtually independent of temperature. The observations and their theoretical interpretation are discussed in a subsequent section.

In the following summary of emission data, the values of the emission constants for pure metals have been calculated, whenever possible, from data which have been corrected for the effect of field strength by means of Schottky's equation. On the other hand, in the *case of composite surfaces, the emission constants*, except where otherwise stated, *must be regarded merely as reference values* from which the emission may be calculated for anode potentials exceeding 100 volts by applying equation (6). Such emission constants cannot represent, therefore, the true values of the emission constants. It is to be hoped that in the near future further investigations will

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[36] S. Dushman, H. N. Rowe, J. Ewald and C. A. Kidner, Phys. Rev., **25**, 338 (1925).

[37] C. Zwikker, Arch. Neérland, **9**, 207 (1925).

[38] L. A. DuBridge, Phys. Rev. **32**, 961 (1928).

[39] W. S. Pforte, Zeits. f. Physik **49**, 46 (1928).

[40] N. A. de Bruyne, Proc. Roy. Soc. A., **120**, 423 (1928).

[41] J. Becker and D. Mueller, Phys. Rev. **31**, 431 (1928).

[42] N. B. Reynolds, Phys. Rev. **35**, 158 (1930).

help to clear up this question[55] and thus make it possible to derive values of the emission constants which will apply to zero field strength and will correspond, therefore, to the conditions assumed in the derivation of equation (2).

II. ELECTRON EMISSION DATA FOR ELEMENTARY SUBSTANCES IN SOLID STATE

Table IV gives emission constants for a number of elements. The values a and b refer to Richardson's equation (1), while A and b_0 refer to equation (2). The sixth column gives values of $\Phi_0 = 8.62 \times 10^{-5}\, b_0$, the work-function, in volts, while the next two columns give values of the emission in amps/cm^2 at the corresponding values of T. The last column gives the references in the footnotes. The letter (R) denotes that this reference is also given in

TABLE IV. *Electron emission constants for elementary substances*

Element	a	$b \times 10^{-4}$	A	$b_0 \times 10^{-4}$	Φ_0	I_T	T	Reference
C	2.37×10^6	4.87	5.93	4.57	3.93	2.84×10^{-3}	2000	R(8)
Ca	1.74×10^4	3.65	0.12	3.50	3.02			R(43)
			60.2	2.60	2.24	4×10^{-3}	1100	(44)
Cs			162	2.10	1.81	2.5×10^{-11}	500	(45)
Hf			14.5	4.10	3.53	2.8×10^{-4}	1600	(46b)
Mo		5.26	60.2	5.15	4.44	1.6×10^{-3}	2000	(47)
		5.35	60.2	5.09	4.38	2.34×10^{-3}	2000	(46a)
				3.96	3.48			(48)
	2.1×10^7	5.00	61	4.74	4.08	1.3×10^{-2}	2000	R(49)
	1.1×10^8	5.36	323	5.10	4.39	1.12×10^{-2}	2000	R(50)
Ni	4.61×10^6	3.40	26.8	3.21	2.77			R(51)
Pt			1.7×10^4	7.25	6.27	9.2×10^{-10}	1600	(52)
Ta		4.98	60.2	4.72	4.07	1.38×10^{-2}	2000	(47)
	8.32×10^6	5.08	29.5	4.85	4.18	3.2×10^{-3}	2000	(53)
	1.12×10^7	5.00	34.0	4.70	4.04	7.0×10^{-3}	2000	R(42)
Th			60.2	3.89	3.35	4.3×10^{-3}	1600	(46a)
W			60.2	5.240	4.52	1×10^{-3}	2000	(average)
		5.51	60.2	5.236	4.52	1×10^{-3}	2000	(54)
		5.53	60.2	5.250	4.53	9.1×10^{-4}	2000	(47)
		5.77	60.2	5.225	4.50	1.12×10^{-3}	2000	(46a)
	1.05×10^7	5.30	43.6	5.100	4.40	1.45×10^{-3}	2000	(48)
Zr			330	4.79	4.13	8.5×10^{-5}	1600	(46b)

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[43] F. Horton, Phil. Trans. **A207**, 149 (1907).

[44] S. Dushman, Phys. Rev. **21**, 623 (1923).

[45] K. H. Kingdon, Phys. Rev. **25**, 892 (1925).

[46a] C. Zwikker, Proc. Amst. Acad. Sciences **29**, 792 (1926). Used his emission data to calculate A and b_0.

[46b] Phys. Zeits. **30**, 578 (1929).

[47] S. Dushman, Rowe, Ewald and Kidner, Phys. Rev. **25**, 338 (1925).

[48] M. J. Martin, Phys. Rev. **33**, 991 (1929).

[49] I. Langmuir, Trans. Am. Electrochem. Soc. **29**, 125 (1916).

[50] I. Stoekle, Phys. Rev. **8**, 534 (1916).

[51] W. Schlichter, Ann. d. Physik **47**, 573 (1915).

[52] L.A.DuBridge, Phys. Rev. **32**, 961 (1928).

[53] H. J. Spanner, Ann. d. Physik **75**, 609 (1924).

[54] C. Davisson and L. H. Germer, Phys. Rev. **20**, 300 (1922).

[55] The recent investigations of W. B. Nottingham (Phys. Rev. **35**, 1126 (1930) promise to contribute considerable information on this topic.

Richardson's book, "Emission of Electricity from Hot Bodies." The data are the same, with slight changes or additions, as those originally published by the writer in International Critical Tables, 6, 53–57 (1930), and the following remarks on the relations between the emission constants and on conversion factors are taken from the introductory statement to the tables giving these emission data.

As pointed out by Richardson, it is impossible, within the range of temperatures (T_1 to T_2) over which emission data can be observed, to distinguish between equations (1) and (2). In this range

$$\frac{b_1 - b_0}{2.303} = \frac{3 \log_{10} (T_1/T_2)}{2(1/T_2 - 1/T_1)} \tag{9a}$$

or approximately

$$b_0 = b - 1.5\frac{(T_1 + T_2)}{2} = b - 1.5T_A \tag{9b}$$

and

$$\log_{10} (a/A) = 1.5 \log_{10} T_A + (b - b_0)/(2.303T_A). \tag{10}$$

In these equations T_1 and T_2 represent the upper and lower values of the range of temperatures over which the emission data are recorded, and T_A therefore represents the average value. Wherever only the values of a and b (or Φ) are available, equations (9b) and (10) have been used to calculate values of A and b_0 (or Φ_0), and both sets of values are given in the table.

The unit of $I_T = 1$ ampere/cm$^2 = 3 \times 10^9$ esu/(sec. cm^2) $= 0.1$ emu/(sec. cm^2) $= 6.28 \times 10^{18}$ electron/(sec. cm^2), while a and A are given in amps/cm^2 deg$^{1/2}$ and amps/cm^2 deg^2 respectively.

Notes on emission constants for solids. In general most data obtained before 1913–1914 are quite unreliable and have been omitted to a large extent from the table. References to these older data may be obtained in Richardson's book.

Tungsten. The most satisfactory data are those obtained by C. Davisson and L. H. Germer,[54] C. Zwikker[46] and S. Dushman and his associates.[47] The agreement between the three sets of results is as good as can be expected, and the average values given in the table may be regarded as probably the most accurate emission data obtained for any substance.

Molybdenum. The values of A and b published by the writer in 1925[47] have been corrected for the revised temperature scale published more recently by A. G. Worthing. They are in good accord with Zwikker's data,[46a] and while the latter gives as most probable value, $A = 65$, the results are in satisfactory agreement with the value $A = 60.2$.

The value $b = 39{,}600$ was obtained by M. J. Martin[48] on a thoroughly degassed sample of molybdenum from emission data for the range 1300°K to 1600°K. While this value is in good agreement with the work function determined for the same metal from the long wave limit for the photoelectric effect, it is abnormally low compared with any of the other published values.

A possible explanation would be the presence of traces of alkaline earth metals which would not be eliminated by treatment at 1600°K.

For comparison there are also given the less accurate values obtained by Langmuir[49] and Stoekle.[50]

Tantalum. The most reliable data are those observed by S. Dushman and his associates.[47] It will be observed that these results do not differ greatly from those obtained by Langmuir[8] in 1913, and the difference may be readily accounted for by differences in temperature scale. Spanner's[53] original emission data are not given in his paper, but merely plots of log (I/T^2) versus $1/T$. These were enlarged and used to derive the values of A and b_0 given in the table. For this reason, and also because, apparently, no correction was made for end losses or Schottky effect, these values are probably only approximate.

Platinum. A great many investigations have been carried out on the emission constants from this metal. The values of the constants obtained by these different investigators as tabulated by L. A. DuBridge[56] together with some additional values are given in Table V. The values given in Table IV obtained by DuBridge as the result of a prolonged de-gassing of the metal under extremely good vacuum conditions undoubtedly represent the most accurate data obtained for this metal.

TABLE V. *Concurrent values of emission constants for platinum.*

Author	Reference	A	$b_0 \times 10^{-4}$	Φ_0
Wilson	R(57)	10.7×10^{-4}	2.56	2.18
Lockrow	(58)	1.36×10^{-2}	4.40	3.87
Richardson	R	53.8	4.73	4.08
Richardson	R	39.8	4.75	4.10
Suhrmann	(59)	30.1	4.85	4.18
Schlichter	R(51)	51.6	4.91	4.23
Lockrow	(58)	4.46×10^{-2}	5.00	4.31
Du Bridge	(56)	11.5	5.45	4.69
Deininger	R(60)	16.2	5.85	5.02
Horton	R(43)	11.5	5.90	5.08
Spanner	(53)	28.8	6.06	5.22
Wilson	R(57)	366	6.30	5.45
Du Bridge	(56)	235	6.50	5.60
Richardson	R	265	6.55	5.65
Wilson	R(57)	620	7.00	6.00
Du Bridge	(56)	6450	7.20	6.20
"		8130	7.30	6.30
"		14000	7.42	6.40
Langmuir	(49)	1.45×10^7	7.80	6.71

It should be pointed out, however, that in spite of the thorough degassing of the metal, it may still be questioned whether the surface was thoroughly free of adsorbed oxygen. As shown by Langmuir,[61] oxygen condenses readily

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[56] L. A. DuBridge, Phys. Rev. **31**, 736 (1928).

[57] H. A. Wilson, Phil. Trans. **208A**, 251 (1908).

[58] L. Lockrow, Phys. Rev. **19**, 97 (1922).

[59] R. Suhrmann, Zeits. f. Physik **13**, 17 (1922).

[60] F. Deininger, Ann. d. Physik **25**, 285 (1908).

[61] I. Langmuir, J. Am. Chem. Soc. **38**, 2221 (1916), and other papers.

on *clean* platinum as a monomolecular film which is stable even at higher temperatures. Such a film would have the same effect as in the case of tungsten and oxygen, that is, a considerable decrease in emission, as shown by the increase in both A and b_0. This point is discussed further in the section dealing with effect of gases on emission.

Attention has been drawn by DuBridge[62] to the interesting fact that large values of A occur concurrently with large values of b. This is very evident from the data in Table V. The significance of this observation will be discussed in connection with that of the "constant" A in a subsequent section.

Other elements. The data for carbon are probably as reliable as can be expected in view of the lack of knowledge of an accurate temperature scale. On the other hand, the values given for calcium are probably only roughly approximate, while those for nickel correspond to emission currents which are certainly considerably greater than any actually observed by the writer on vacuum treated wires. In fact, it is quite likely that the emission from nickel, iron, and other metals of Group VIII, like that observed in the case of platinum, is extremely low, corresponding to work-functions of at least 5 volts.

Thorium, zirconium and hafnium. Earlier emission data for solid filaments of these three metals were published by C. Zwikker[46a] in 1926. In the case of thorium the observations were in quite satisfactory agreement with the value $A = 60.2$; but in the case of the other two metals very large values of A were obtained. It seemed possible to account for these results by the presence of oxide films which could not be volatilized readily from the emitting surfaces. This suggestion is in agreement with observations made K. H. Kingdon, S. Dushman and others in the case of oxide films on tungsten, molybdenum, and tantalum that such films yield large values of A and also abnormally high values of b_0. More recently Zwikker[46b] has published further data on the emission from zirconium and hafnium which apparently are in agreement with these views. Table VI gives Zwikker's values for the emission constants as observed during successive stages of ageing of filaments. The final values are those given in Table IV as probably the most accurate.

TABLE VI. *Concurrent emission constants for zirconium and hafnium (Zwikker).*

Metal	A	$b_0 \times 10^{-4}$	Φ_0
Zirconium	37,200	6.06	5.22
	9,500	5.80	5.00
	3,000	5.23	4.51
	330	4.79	4.13
Hafnium	55,000	5.95	5.13
	6,600	5.69	4.90
	1,000	5.03	4.34
	70	4.39	3.78
	145	4.10	3.53

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[62] L. A. DuBridge, Proc. Nat. Acad. **14,** 788 (1928).

III. ELECTRON EMISSION FROM MONATOMIC FILMS

A. Thorium on tungsten.

(1) *Thermal treatment of thoriated tungsten filaments.* During the course of development of ductile tungsten wire for use in the lamp industry it was discovered that a small addition of thorium oxide (about 0.5 to 0.75 percent by weight) prevents offsetting of the filaments when operated on alternating currents. In 1913 I. Langmuir and W. Rogers[63] discovered that by proper thermal treatment of such wire a very much higher electron emissivity could be obtained than that observed from filaments of pure tungsten. Subsequently Langmuir investigated more thoroughly the conditions under which this high electron emission may be obtained and developed a comprehensive theory of the phenomena involved in the activation and deactivation of thoria-doped tungsten filaments.[64] At the present time the amount of thoria added to tungsten for use as a hot cathode varies between one and two percent. It should be observed here that the magnitude of the saturation emission obtained by the thermal treatment described below is independent of the actual thoria content, but for practical purposes, such as increased rate of activation and longer life under operating conditions, it has been found advantageous to have the thoria content as large as practicable.

The procedure adopted in obtaining thorium emission consists of two operations:

(a) By flashing the filament for a short interval (usually one or two minutes) at temperatures above 2700°K, some of the thoria is reduced to thorium. The thorium atoms immediately begin to diffuse towards the surface, but evaporate rapidly at the surface at these high temperatures.

(b) If the temperature is now lowered to about 2100–2200°K, the diffusion is still quite rapid, but the evaporation is decreased and the thorium accumulates on the surface as an adsorbed layer one atom thick.

For any temperature there is thus obtained for the density of thorium atoms on the surface an equilibrium state which depends upon the relative importance of the three factors: reduction of ThO_2; diffusion and evaporation of Th atoms. The observed emission thus depends upon the fraction θ, of the surface which is covered with thorium atoms. As has been shown by Langmuir, the rate of activation at any temperature is given by the relation

$$N_0\frac{d\theta}{dt} = DG(1-\theta) - E \tag{11}$$

where N_0 = number of atoms of thorium per unit area for the surface completely covered, D = diffusion constant, G = concentration gradient, and E = rate of evaporation. If the thorium atoms could accumulate on the surface as a layer more than one atom thick, the rate of diffusion would be given by DG. But the actually observed form of relation for the rate of acti-

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[63] I. Langmuir and W. Rogers, Phys. Rev. **4**, 544 (1914).

[64] I. Langmuir, Phys. Rev. **22**, 357 (1923).

vation shows that the thorium atoms evaporate much more rapidly from underlying thorium atoms than when in direct contact with the tungsten atoms. Hence there is an "induced evaporation" whose rate is given by $DG\theta$. This type of evaporation is to be carefully distinguished from the normal temperature evaporation of thorium atoms when in contact with tungsten atoms, the rate of which is denoted by E, and which is much lower at any given temperature than that of the induced evaporation.

The ranges of temperatures at which the different types of reaction predominate in thoriated tungsten filaments are found to be as follows:

(i) $T \geqq 2600$°K. *Reduction range.*

Marked reduction of ThO_2 occurs, accompanied by extremely rapid rates of diffusion and evaporation. The equilibrium value of θ is approximately 0, i.e., the surface is in the completely inactive condition.

(ii) $T = 2300$–2600°K. *Deactivating range.*

The lower the temperature, the lower the rate of formation of fresh Th by reduction, and this becomes negligibly small at the lower limit of temperatures. In this range of temperatures, the rate of normal evaporation is greater than the rate of diffusion, so that an activated surface becomes deactivated, and tends to an extremely low equilibrium value.

(iii) $T = 2000$–2300°K. *Activating range.*

In this range of temperatures the rate of diffusion usually exceeds that of evaporation and θ tends to approach the value 1 as the temperature is decreased to the lower limit.

(iv) $T = 1800$°–2000°K. *Operating range.*

Rate of evaporation and that of diffusion are so low that the value of θ changes only very slowly or not at all over prolonged periods of time. Ordinarily thoriated tungsten filaments are operated commercially at about 1900°K.

(2) *Value of* N_0. From considerations based on the size of the unit crystal lattice for both tungsten and thorium, Langmuir concludes that

$$N_0 = 7.56 \times 10^{14} \text{ atoms per cm}^2$$

(3) *Rate of production of metallic thorium.* The heat of the reaction involved in the reduction of ThO_2 by W is $Q_r = -138{,}000$ cal. per gram-atom. For a filament of 0.00389 cm radius and containing 1 percent oxide (corresponding to 4.4×10^{20} ThO_2 molecules per cm^3) the average concentrations of metallic thorium in parts per million obtained at different temperatures are as follows:

1800°	1900°	2000°	2100°	2200°	2400°	2800°	3000°K
1.4	2.8	5.0	8.4	14	32	118	200

(4) *Rate of diffusion of thorium atoms.* The diffusion constant D (in cm^2 sec.$^{-1}$) as a function of temperature is given, according to Langmuir's observations, by

$$\log_{10} D = 0.044 - 20540/T \tag{12}$$

corresponding to a heat of diffusion, $Q_0 = 94{,}000$ cal. per gram-atom.

Subsequent investigations in the Research Laboratory at Schenectady have shown, however, that the rate of diffusion of thorium in thoriated tungsten filaments is governed to a great extent by the crystal structure of the metal. Consequently the value given above must be regarded as valid only for the type of thoriated wire used at that time (1915–1922). For thoriated wire as used at present the values of D, as calculated by the methods developed by Langmuir, apparently vary with the diameter of the wire and also with the mode of temperature treatment during manufacture. The more detailed discussion of these phenomena and their interpretation will be given in a separate paper by N. B. Reynolds and the writer.

(5) *Normal evaporation of thorium.* The rate of evaporation, E, in atoms per cm^2 per sec. is given by the relation

$$\log_{10} E = 31.434 - 44500/T. \tag{13}$$

The heat of evaporation of Th atoms from tungsten is therefore $Q_E = 204{,}000$ cal. per gram-atom. This is higher than the value of the heat of evaporation for tungsten from tungsten, which, according to Langmuir and Jones,[13] is 191,880 cal. per gram-atom.

This value of E applies only for the range $\theta = 0.1$ to $\theta = 0.85$ approximately. For values of $\theta < 0.1$, E decreases, while for values of $\theta > 0.85$, it increases.

(6) *Variation in emission constants with θ.* The fraction θ is defined according to Langmuir by the relation

$$\theta = \frac{b_\theta - b_{\mathrm{W}}}{b_{\mathrm{Th}} - b_{\mathrm{W}}} \tag{14a}$$

where b_θ, b_{Th} and b_{W} represent the values of b_0 in the emission equation for the partly covered surface, completely covered surface and pure tungsten respectively.

This may evidently be expressed in the form

$$b_\theta = b_{\mathrm{W}} + C\theta \tag{14b}$$

where $C = (b_{\mathrm{Th}} - b_{\mathrm{W}})$.

If $\log A_\theta$ is a linear function of b_θ, it also follows that

$$\theta = \frac{\log I_\theta - \log I_{\mathrm{W}}}{\log I_{\mathrm{Th}} - \log I_{\mathrm{W}}} \tag{15}$$

where I_θ, I_{Th} and I_{W} are the values of the electron emission per unit area at the same temperature for the three surfaces. This relation is obviously more convenient to use in practice, and although the values of $\log A_\theta$ for thoriated tungsten, as will be shown below, do not vary linearly with θ over the whole range, equation (15) leads to values of θ which are not very different from those obtained by the use of the more rigorous equation (14a).

Table VII gives values of A_θ and b_θ for different states of activation as observed by Dushman and Ewald.[65] The values of θ were calculated by

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[65] Dushman and Ewald, Phys. Rev. **29**, 857 (1927).

means of equation (14a) using the values $b_{\mathrm{Th}} = 30{,}500$ and $b_{\mathrm{W}} = 52{,}400$. The last two columns give values of I_θ for $T = 1900°\mathrm{K}$, and of Φ_0.

In this table (as in nearly every other table of emission data) the values of the emission constants have been derived from measurements carried out at anode voltages of 100 to 500 by applying Schottky's equation (6). Consequently, in view of the remarks made in a previous section, these constants do not represent the correct values for zero field strength.

The values of A_θ and b_θ for $\theta = 0.18$ are to be regarded as doubtful. On the whole, the observed values point to the conclusion that from $\theta = 0.95$ to $\theta = 0$, log A_θ varies linearly with b_θ and therefore with θ, while a minimum value occurs for A_θ at $\theta = 0.05$.

TABLE VII.

θ	A_θ	b_θ	I_θ	Φ_0
1	3.0	30,500	1.166	2.63
0.95	1.50	31,460	0.349	2.71
.83	2.08	34,150	.118	2.94
.72	3.74	36,570	.0594	3.15
.56	7.76	40,070	.0195	3.45
.43	10.86	42,840	.0064	3.69
.25	15.81	47,050	.0010	4.06
.18	(8.2)	48,360		4.17

K. H. Kingdon[66] has also published values of emission constants for thoriated tungsten filaments. For the relation between A and θ he has suggested an empirical equation of the form

$$A_\theta = a_1^{\theta} + a_2^{1-\theta} - 1 \text{ amps/(cm}^2\text{ deg.}^2) \tag{16}$$

where a_1 gives the value of A for $\theta = 1$; and a_2 for $\theta = 0$. For the case of thorium on tungsten he finds $A = 7$ and $b_0 = 31{,}200$, while for tungsten he uses the values $A = 60$ and $b_0 = 52{,}200$. As pointed out by Kingdon, "The artificial nature of expression (16) makes it seem likely that this is not the true expression for A_θ, but merely one which approximates to the true expression in the cases studied."

TABLE VIII. *Values of I as a function of θ for thoriated tungsten for $T = 1900°K$.*
$\log_{10} I_\theta = 0.0667 - 3.7088(1 - \theta)$

θ	I (amps/cm^2)	θ	I	θ	I
1.0	1.166	0.7	8.99×10^{-2}	0.4	5.51×10^{-3}
0.9	4.964×10^{-1}	0.6	3.83×10^{-2}	0.2	1.00×10^{-3}
0.8	2.113×10^{-1}	0.5	1.63×10^{-2}	0	2.28×10^{-4}

Richardson has, however, shown that for various adsorbed surfaces there exists a linear relation between log A and b, and, as a matter of fact, if in equation (16), a_1 is very much greater than a_2, then for all values of θ except those near $\theta = 0$, log A_θ becomes a linear function of θ that is, of b_θ.

It is of interest to point out in this connection that since θ is approxi-

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[66] K. H. Kingdon, Phys. Rev. **24**, 510 (1924).

mately a linear function of log I_θ, the value of the emission decreases exponentially with θ. Table VIII shows the variation in I_θ with θ, calculated by means of equation (15) for $T = 1900°\mathrm{K}$, which is the approximate temperature for commercially operated thoriated tungsten cathodes

The effect of accelerating fields on the work-function from thoriated tungsten has been investigated by W. B. Nottingham.[67] From his measurements he has deduced the conclusion that for *zero field*

$$A = 59, \quad b_0 = 36{,}500 \quad \Phi_0 = 3.15 \text{ volts}$$

when maximum emission was obtained, and

$$A = 56, \quad b_0 = 36{,}000 \quad \Phi_0 = 3.10 \text{ volts}$$

for a thorium layer *thicker* than that required to give maximum emission. This result, he points out, is in agreement with Langmuir and Kingdon's observation that the contact potential between Th—W and W is 1.46 volts, since subtracting this value from the work function for W (4.53 volts) gives 3.07 volts.

TABLE IX. *Emission, emission efficiency and other constants for thoriated tungsten* ($\theta = 1$)

T	$I\left(\frac{\text{amps}}{\text{cm}^2}\right)$	$\frac{I}{W}\left(\frac{\text{amps}}{\text{watt}}\right)$	D (cm^2 sec.$^{-1}$)	$E\left(\frac{\text{atoms}}{\text{cm}^2\text{ sec.}}\right)$	I
1000	1.73×10^{-7}	2.87×10^{-7}			8.01×10^{-9}
1100	3.31×10^{-6}	3.22×10^{-6}			2.69×10^{-7}
1200	3.95×10^{-5}	2.38×10^{-5}			5.33×10^{-6}
1300	3.27×10^{-4}	1.27×10^{-4}			6.21×10^{-5}
1400	2.03×10^{-3}	5.30×10^{-4}	2.36×10^{-15}	0.445	5.36×10^{-4}
1500	1.00×10^{-2}	1.81×10^{-3}	2.24×10^{-14}	58.5	3.51×10^{-3}
1600	4.06×10^{-2}	5.24×10^{-3}	1.61×10^{-13}	4.18×10^{3}	1.83×10^{-2}
1700	1.40×10^{-1}	1.32×10^{-2}	9.15×10^{-13}	1.81×10^{5}	7.91×10^{-2}
1800	4.28×10^{-1}	3.09×10^{-2}	4.29×10^{-12}	5.15×10^{6}	2.93×10^{-1}
1900	1.164	6.24×10^{-2}	1.71×10^{-11}	1.03×10^{8}	9.50×10^{-1}
2000	2.864	1.19×10^{-1}	5.94×10^{-11}	1.53×10^{9}	2.75
2100			1.83×10^{-10}	1.75×10^{10}	
2200			5.10×10^{-10}	1.61×10^{11}	
2400			3.06×10^{-9}	7.80×10^{12}	
2600			1.39×10^{-8}	2.08×10^{14}	
2800			5.11×10^{-8}	3.48×10^{15}	

Table IX gives values of the emission and emission efficiency for completely activated surfaces and also values of D and E according to Langmuir, as functions of the temperature. Since at temperatures exceeding 2000° K evaporation becomes so rapid that the maximum value of θ can no longer be obtained, values of I and I/W for such temperatures are not given in the table.

These values have been calculated from the values of $A = 3.0$ and $b_0 = 31{,}500$. The last column gives values of I calculated for zero field by means of Nottingham's constants, $A = 59$, $b_0 = 36{,}500$.

Finally reference should be made to Table VIII in Langmuir's original paper for data on the values of G_r, the concentration gradient, θ_r, the equilibrium value of θ, the electron emission, and life and time of activation as

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[67] W. B. Nottingham, Phys. Rev. **36**, 386 (1930).

functions of T for a filament 0.00389 cm in diameter and containing 1 percent ThO_2.

Attention may also be drawn to the differences between the values for A and b_0 for thoriated tungsten and those given in Table IV for metallic thorium, as observed by Zwikker. Thus it is observed that *the electron emission for solid thorium is less than that for a monatomic film on tungsten.*

B. Monatomic films of other rare earth and alkaline earth metals adsorbed on tungsten and molybdenum.

If other rare earth oxides are used instead of ThO_2 in "doping" the tungsten, and the filaments thus obtained are treated thermally, emission phenomena are obtained which resemble those observed for thoriated tungsten. The behavior of such filaments has been investigated by S. Dushman, D. Dennison and N. B. Reynolds,[68] and their observations may be summarized briefly as follows:

The monatomic films produced by reduction of the oxide at high temperature and subsequent activation at lower temperatures are not as stable as those obtained with thoria, owing both to more rapid diffusion and evaporation. This makes it difficult to obtain accurate emission data for completely covered surfaces. The values of A and b_0 obtained for different films with filaments 0.01 cm diameter are given in Table X along with values of D, the diffusion constant in $cm^2\ sec.^{-1}$ at $T=2000$, Q_D, the heat of diffusion (gram-calories per gram-atom), and E, the rate of evaporation in atoms/cm^2 sec. at 2000°K.

TABLE X. *Emission constants, rates of diffusion and evaporation for films of rare earth metals on W and Mo.*

Emitter	A	b_0	$D\times10^{11}$	Q_D	$E\times10^9$
Ce-W	8.0	31,500	95	83,000	1450
La-W	8.0	31,500	—	—	—
U-W	3.2	33,000	1.3	100,000	>Th
Yt-W	7.0	31,300	324	78,000	68
Zr-W	5.0	36,500	1820	62,000	—
Th-W	3.0	30,500	5.9	94,000	1.53
Th-Mo	1.5	30,000	102,000	52,000	5400

The emission phenomena for films of *thorium on molybdenum* have been investigated by N. B. Reynolds and S. Dushman.* In the table are given values of the emission constants and also values of D and E at $T=2000$. While the values of A and b_0 are lower than those obtained for films of tungsten, the actual emission per watt is approximately the same owing to the lower radiant emissivity of molybdenum. On the other hand, owing to the extremely large values of both D and E, θ decreases rapidly below unity for values of $T>1700$°K. For the heat of evaporation of thorium from molybdenum the value obtained was $Q_E=170{,}000$ cal./gm-atom (approximately).

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[68] S. Dushman, D. Dennison and N. B. Reynolds, Phys. Rev. **29**, 903 (1927).

* Unpublished data.

Comparing the emission constants given above for monatomic films of zirconium with those given in Table IV for pure zirconium filaments, it is observed that as in the case of thorium, *the emission from monatomic films is considerably greater than that observed from the solid metal.*

In connection with investigations on the emission from oxide-coated cathodes there have also been made certain observations on the emission from monatomic films of barium on tungsten and oxidized tungsten. While the phenomena observed with these films are discussed in detail in a subsequent section, it is of interest to mention briefly the results obtained by J. A. Becker.[69] The variation in emission with θ for a film of barium on tungsten as observed by him is shown in Fig. 1.[70] For such films he finds that under the conditions $0 < \theta < 0.85$,

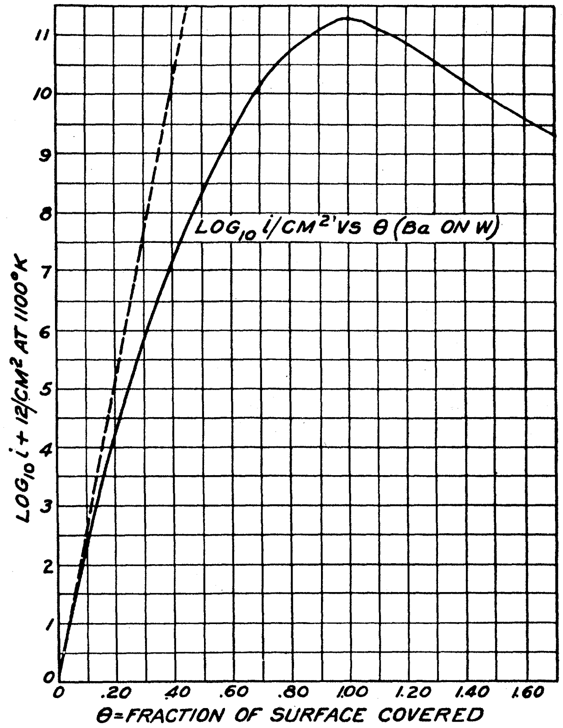

Fig. 1. Variation of electron emission with fraction of tungsten surface covered with barium (J. A. Becker[70]).

$$\log (i/i_0) = 1.1(\log i_1/i_0)(1 - \epsilon^{2\theta})$$

where i_1 and i_0 denote the values of emission for $\theta = 1$ and $\theta = 0$ respectively. Furthermore, the *decrease* in work function, $\Delta\Phi$, is given by

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[69] J. A. Becker, Phys. Rev. **33**, 1082 (1929).

[70] J. A. Becker, Phys. Rev. **34**, 1323 (1929).

$$\Delta\Phi = 1200\pi N(4.77 \times 10^{-10}\, l) \text{ volts}$$

where N = number of barium ions per cm^2, and l = diameter of ion.

C. Caesium on tungsten and oxidized tungsten.

(1) *General remarks.* The emission phenomena for monatomic films of caesium adsorbed on tungsten and oxidized tungsten were first investigated by I. Langmuir and K. H. Kingdon [71,72,73]. The phenomena observed are different in many respects from those observed in the case of thorium on tungsten, mainly because the caesium is adsorbed from the vapor and hence the equilibrium value of θ depends not only on the rate of evaporation of caesium atoms from the surface (that is, on the temperature of the latter), but also on the rate at which caesium atoms strike the surface, and therefore on the pressure of the vapor, that is, the bulb temperature.

In a bulb containing caesium at 30°C the adsorbed layer on pure tungsten gives a maximum emission of about 10^{-4} amp./cm^2 at a filament temperature of 700°K. At higher filament temperatures the rate of evaporation increases and θ decreases with consequent decrease in emission. On the other hand, if the filament is first heated in oxygen, the presence of O atoms on the W atoms retards the evaporation of adsorbed Cs atoms and a much greater value of the maximum emission is obtained. The process of oxidation has been described by Kingdon [71] as follows:

"After flashing the filament to 2700°K in vacuum for a short time, it is heated at about 1900°K in oxygen at a pressure of about 0.02 mm for a few seconds. (Somewhat similar results are obtained if the oxygen is merely allowed to come in contact with the clean, cold filament). The excess oxygen is then pumped out, and caesium distilled in. Some caesium is presumably adsorbed on the filament, but the electron emission which may be obtained at temperatures of from 700°K to 1000°K is very small. If, however, the filament is heated for a few seconds at from 1200° to 1600°K, on returning to the lower temperatures it will be found that the emission has increased many fold and is of the order 0.35 amp./cm^2 at 1000°K, with the bulb at 30°C. The heating at from 1200° to 1600°K probably frees the surface of excess oxygen and of adsorbed deleterious gases such as CO. The remaining oxygen is probably held on as negative oxygen ions, and these ions adsorb the caesium more strongly than a tungsten surface does. With the bulb at 30°C the emission is at a maximum at a filament temperature of about 1000°K. At higher filament temperatures the caesium evaporates from the filament faster than it can be renewed by condensation from the vapor in the bulb, and the emission decreases."

(2) *Electron emission as a function of the pressure of caesium vapor and temperature of filaments.* Fig. 2, taken from the paper by Langmuir and Kingdon,[73] shows $\log_{10} I$ as a function of the reciprocal of the absolute tem-

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[71] I. Langmuir and K. H. Kingdon, Phys. Rev. **24**, 510 (1924).

[72] Phys. Rev. **25**, 892 (1925).

[73] Proc. Roy. Soc. **A107**, 61 (1925).

perature of the tungsten filament (plotted as abscissa) for various bulb temperatures, the values of which are indicated on each curve. It is observed that each curve consists of three parts:

"(I) A low temperature region in which the emission apparently follows Richardson's equation, giving a straight line descending to the right in Fig. 2.

"(II) An intermediate region where the plot in Fig. 2 is curved, the current reaching a maximum as the temperature is raised and then falling. This region may be regarded as a transition curve between the straight portions I and III.

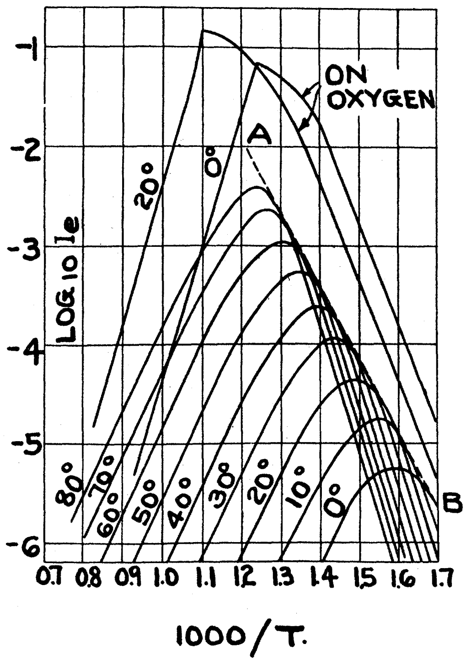

Fig. 2. Thermionic emission from tungsten in caesium vapor as a function of filament temperature for various bulb temperatures. (I. Langmuir and K. H. Kingdon[73]).

"(III) A high temperature region, where the plot in Fig. 2 becomes straight again, but the current decreases with rising temperature. An equation of the Richardson type may be used to represent these lines, but the quantity b would then have a negative value.

"Fig. 2 shows that both in Regions I and II the straight lines at the various pressures are approximately parallel to one another. The envelope of the family of curves is a straight line, shown as the dashed line AB. All the curves of the family are, in fact, very nearly alike, and differ principally in being displaced in a direction parallel to AB. These displacements are found to be proportional to the logarithms of the pressures of caesium.

"These conclusions may be summarized by saying that these electron emission data are given by the equation

$$\log I_e + M \log p = f(1/T + N \log p) \tag{17}$$

where M and N are constants and f denotes a function characteristic of the shape of the curves in Fig. 2. From the data we find that the actual values of M and N are

$$M = -0.83;\ N = 4.4 \times 10^{-5}\,\text{deg.}^{-1}$$

"The pressures of caesium vapor used in these calculations were found by measurements of the positive ion currents obtained with filament temperatures of about 1500°K, where all the atoms that strike the filament are converted to ions. The vapor pressures obtained in this way are accurately given by the equation (p in dynes/cm^2)

$$\log_{10} p = 10.65 - 3992/T. \tag{18}$$

"From these considerations it may readily be seen that in Regions I and III the electron emission of a tungsten filament of temperature T in caesium vapor at a pressure p is expressible approximately by the equation

$$I_e = \alpha p^{\gamma} \epsilon^{-\beta/T} \tag{19}$$

where α, β and γ are constants.

"The data illustrated in Fig. 2 give the following values of the constants, when I_e is in amperes per cm^2 and p in baryes, (Table XI)."

TABLE XI. *Emission constants for Cs-W and Cs-O-W as function of vapor pressure of Cs.*

Conditions	α	β	γ
Caesium on Tungsten			
Region I	6.65×10^{14}	+31300	−0.70
Region III	8.6×10^{-12}	−19100	+1.66
Caesium on Adsorbed Oxygen			
Region I	1.04×10^{10}	+23400	−0.62
Region III	2.95×10^{-11}	−32200	+1.96

Similar observations to those shown in Fig. 2 have been made by T. J. Killian[74] for the emission from tungsten and oxidized tungsten filaments in rubidium and potassium vapors, the results being adequately represented by equation (19) with different values of the constants.

(3) *Electron emission constants for Cs-O-W filaments.* Fig. 3[71] shows the variation in emission from a Cs-O-W filament, with both bulb temperature and filament temperature, in region I where the surface is largely covered with caesium. It will be observed that a change in bulb temperature from −185° to + 60° C decreases the emission at 625°K ($10^3/T = 1.60$) eighty fold. As Kingdon points out: "The only curves from which any reliable estimates of the electron emission constants for a caesium-oxygen-tungsten filament can be made are those taken with the tube immersed in liquid air. Here there is no continual condensation of caesium on the filament, and the rate of evaporation of the absorbed layer is so small at 600 to 700°K that a temperature characteristic may be taken without changing the condition of

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[74] T. J. Killian, Phys. Rev. **27**, 578 (1926).

the surface appreciably. Such runs give the values of the constants in Eq. (2) as $A = 0.003$ *amp./cm² deg.²*; $b_0 = 8300°$. As a little oxygen or tungsten was undoubtedly exposed, b_0 is a little higher and A is almost certainly much larger than the value which would characterize a complete film of caesium on oxygen on tungsten. However, as an approximation, we may take the values *for a complete caesium film to be* $A = 0.001$ *amp./cm² deg.²*, $b_0 = 8300°$" (*corresponding to* $\Phi_0 = 0.695$ *volts.*)

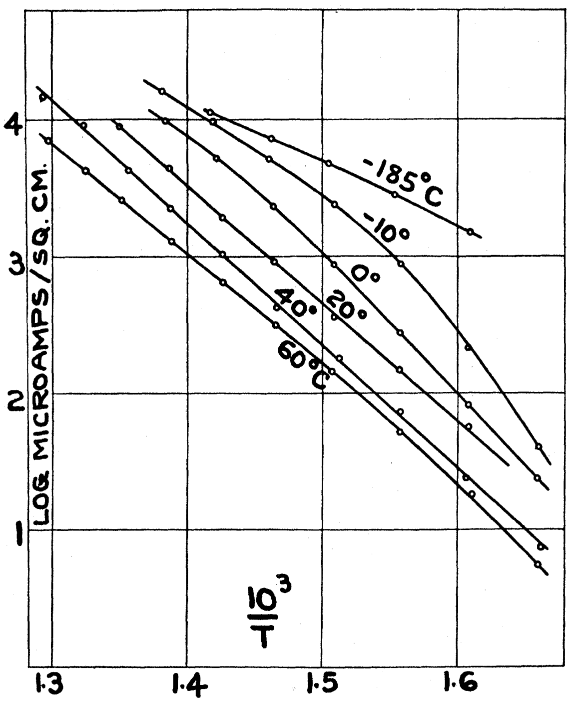

Fig. 3. Variation in electron emission from a Cs-O-W filament with both bulb temperature and filament temperature. (K. H. Kingdon[71]).

(4) *Relation between* A_θ *and* b_θ *for Cs-O-W and Cs-W filaments.* In order to account for the course of the curves shown in Fig. 3, Kingdon has used an equation of the form

$$I_\theta = [a_1{}^\theta + a_2{}^{1-\theta} - 1]A_0T^2\epsilon^{[-b_1\theta+b_2(1-\theta)]/T} \tag{20}$$

which is the result of combining his empirical relation for A_θ (equation (16) above) with equation (14) for b_θ.

For a complete film of oxygen on tungsten he has derived the values $A = 5 \times 10^{11}$ *amp/cm² deg.²*, $b_0 = 107{,}000°$($\Phi_0 = 9.22$ volts). These are to be compared with the values given above of A and b_0 for complete caesium films. The values of A and b_0 for O-W filaments incompletely covered with Cs will vary between these extremes according to equation (20), and thus lead to an explanation of the curves in Fig. 3. "At the high bulb temperatures and low filament temperatures the surface is practically completely covered with caesium, and the emission is small on account of the small A term. As the bulb temperature is lowered, a very small fraction of the filament surface is bared of caesium and the increase in the A term increases the emission in spite of the decrease due to the increase in b. The same argument shows that at a constant bulb temperature, the slight decrease in the amount of caesium on the surface at the higher filament temperatures gives the curves too steep a slope, and this slope is not even an approximate measure of b_0 on account of the large variation in A."

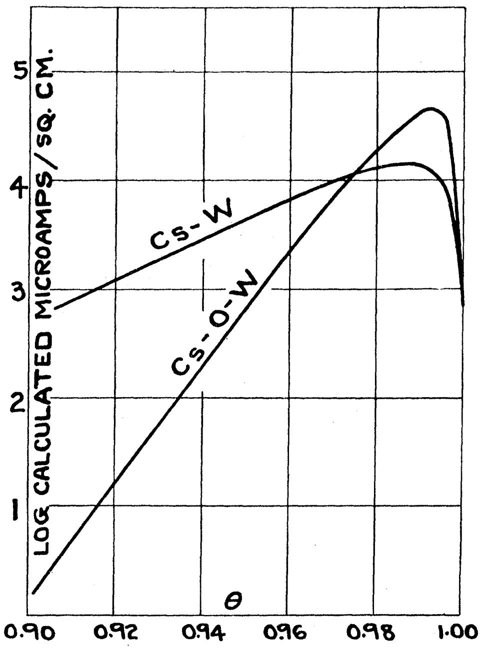

Fig. 4. Calculated variation of electron emission from Cs-O-W surface as function of fraction of surface covered. (K. H. Kingdon[71]).

With the values given above of A and b for Cs-O-W and O-W, Kingdon has calculated the electron emission for Cs-O-W filaments at 625°K as a function of θ. These values which are to be regarded as only approximate are shown in the curve in Fig. 4. Similarly for Cs-W the emission has been calculated from the values

$$A = 0.001, \ b = 8300°; \ A_w = 60.2, \ b_w = 52{,}200°.$$

It will be observed from the curves that for Cs-O-W the emission is a maximum at $\theta = 0.99$, while for Cs-W the maximum emission is obtained at about $\theta = 0.985$.

As shown by Kingdon, log A_θ for Cs-O-W is approximately a linear function of b_θ (and therefore of θ) for values of $b_\theta > 10{,}000$, while for lower values of b_θ, log A decreases much more rapidly than b_θ.

Mention should also be made here of the emission constants obtained by L. R. Koller[75] for films of Cs on oxygen on silver (such as are used in caesium photoelectric cells). Using cathodes of 10 cm^2 area he was able to measure thermionic emission at temperatures below 473°K. The constants determined from these measurements were $A = 9.8 \times 10^{-2}$ *amps/cm*^{2} *deg.*^{2} and $b_0 = 8700$ ($\Phi_0 = 0.65$ *volts*).

(5) *Emission of positive ions from tungsten filaments in caesium vapor.* In connection with the further discussion of the phenomena of electron emission from caesiated tungsten, it is necessary to refer briefly to the important observations on the positive ion emission from tungsten filaments in caesium vapor.

In 1923 it was shown by Langmuir and Kingdon[76] that "A tungsten filament heated to 1200°K or more in saturated caesium vapor converts all caesium atoms which strike it into caesium ions. Thus when the filament is surrounded by a negatively charged cylinder, a positive ion current flows from the filament, which is independent of the filament temperature (above 1200°K) and independent of the applied potential, if this is sufficient to overcome the space charge effect of the positive ions. At lower voltages the currents follow the 3/2 power law, and are smaller than the corresponding electron currents obtainable from the same filament in the ratio of the square roots of the masses of the electrons and caesium ions.

"The reason that the caesium atoms lose their valency electrons so readily upon contact with the filament, is merely that the electron affinity of tungsten (Richardson work function) is 4.53 volts, while the electron affinity of a caesium atom (ionizing potential) is only 3.88 volts. Experiments showed, in fact, that if the work function for the filament is lowered to 2.69, by allowing a monatomic layer of thorium atoms to accumulate on the surface (by diffusion from the interior of a thoriated tungsten filament), the positive ion emission becomes negligible.

"The positive ions must be attracted to a tungsten surface because of the electron image force. Thus it is that below about 1200°K the caesium ions evaporate so slowly from a tungsten surface that this becomes partly covered by adsorbed caesium ions. The presence of these ions, however, lowers the electron affinity of the surface so that when about 20 per cent of the surface is covered, the work function falls below the ionizing potential of the caesium. With more caesium on the surface the caesium atoms which strike the filament no longer escape in the form of ions but remain in the atomic state. Thus the positive ion currents disappear below about 1100°K. But the lowering of the electron affinity raises the electron emission, and when the surface becomes more completely covered by caesium as the temperature is lowered, the electron emission rises to a maximum (of about 10^{-5} amps per cm^2 at 700°) and then decreases rapidly at still lower temperatures, in accordance with Richardson's equation."

Thus it is possible to determine the vapor pressure of caesium at any given

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[75] L. R. Koller, Phys. Rev. **33**, 1082 (1929).

[76] I. Langmuir and K. H. Kingdon, Science **57**, 58 (1923); Proc. Roy. Soc., **A107**, 61 (1925).

bulb temperature from measurements of the positive ion current from a positively charged tungsten filament in presence of the vapor and maintained at a temperature above 1200°K. It was, in fact, by this method that the vapor pressure relation for caesium was determined which was used in a previous section. In the same manner T. J. Killian[74] has also measured the vapor pressure curve for rubidium and potassium.

The emission phenomena from different monatomic films on tungsten are well illustrated by Fig. 5 taken from a paper by I. Langmuir[77] in which log I is plotted against $1/T$. Thus it will be observed that at $T = 1600$°K, the emissions from Th-W, pure W and O-W are in the ratio: $10^5 : 1 : 10^{-5}$. "The

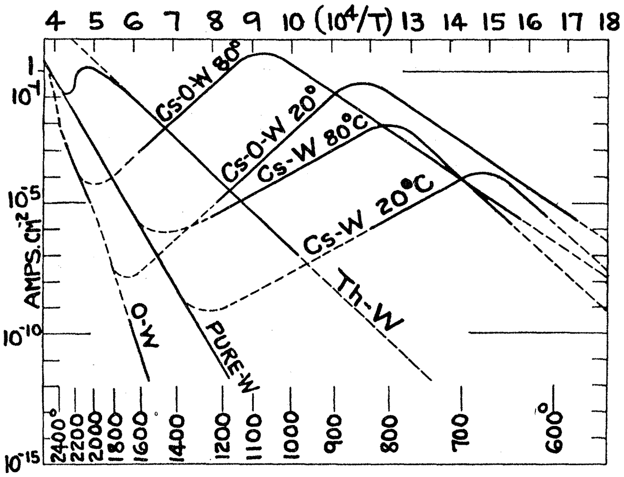

Fig. 5. Emission characteristics from various monatomic films on tungsten.

upper end of the line 'Th-W' shows a deviation from a straight line corresponding to the loss of adsorbed thorium by evaporation; at temperatures-approaching 2400°K the emission becomes that of pure tungsten. . . . . The two curves marked 'Cs-W' give the electron emission of pure tungsten filaments in presence of caesium vapor saturated at 20° and 80°C. The falling off of emisson as the temperature is raised above 700° or 800°K is due to evaporation of caesium so that θ progressively decreases."

The curve marked O-W gives the emission from monatomic films of oxygen. "If heated to 1800°K or more, this film gradually evaporates off the filament as atomic oxygen (un-ionized), no tungsten oxide being found. When caesium vapor is brought into contact with a filament covered with an oxygen film, the filament gives an electron emission represented by the curves marked "Cs-O-W," which is almost 10^5 times greater than from "Cs-W" in the neighborhood of 1000°–1100°K."

(6) *Rate of activation of caesiated filaments.* Further observations on the rate at which tungsten and oxidized tungsten filaments become covered with adsorbed caesium atoms and on the values of θ for optimum electron emission

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[77] I. Langmuir, Industrial and Eng. Chem. **22**, 390 (1930).

have been reported by J. A. Becker.[78] Fig. 6 taken from his paper shows typical curves for the rate of increase in emission after a Cs-O-W filament has been heated to 1040° and then changed suddenly to the value indicated on the curve. While at the higher temperature the positive ion current is measured, and from this result the rate is determined at which caesium atoms strike the surface. After reversing the voltage, to draw electrons from the filament, the temperature is changed suddenly to the lower value and the value of log I_e (the electron current) determined as a function of the time.

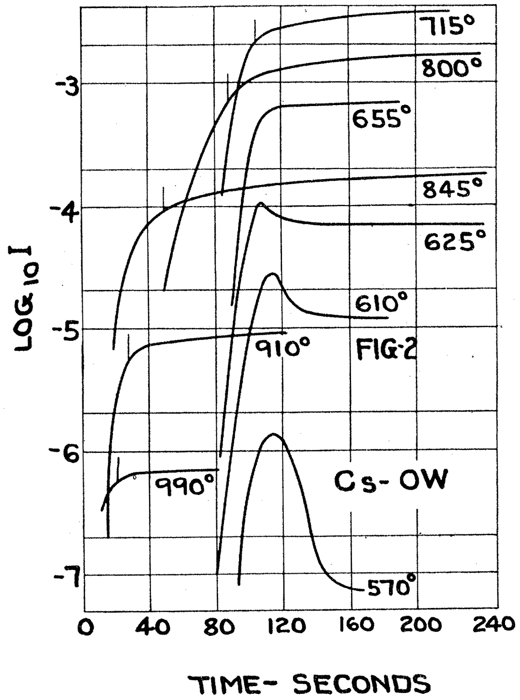

Fig. 6. Rate of increase in thermionic emission after a Cs-O-W filament has been heated to 1040°K and then changed suddenly to the value indicated on curve.

It will be observed that at temperatures below 650°K the emission passes through a maximum. "If the lower temperature is above 650°K the emission no longer passes through a maximum, but approaches its steady value rather more suddenly than one might expect. The arrows in Fig. 6 indicate the time necessary for sufficient caesium to have struck the surface to form an amount that is actually on the surface when equilibrium prevails. . . . . For Cs on W similar observations were made. The important point to note in these curves is that t_m, the time required to reach the maximum, is independent of T so long as $T < 650°$K. This suggests that below 650°K every atom that strikes the filament sticks to it until enough are adsorbed to give the optimum activity. . . . . This must mean that the fraction of the atoms

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[78] J. A. Becker, Phys. Rev. **28**, 341 (1926).

that stick is the same at all these temperatures. It would be odd, indeed, if this fraction were anything but unity."

This conclusion was checked by the further observation that t_m varies inversely as i_p, the positive ion current per cm^2, that is, as the rate at which caesium strikes the surface.

From these observations, Becker concludes that the value of N_0, the number of Cs atoms per cm^2 for $\theta = 1$, is 3.7×10^{14} for Cs-W surfaces, and 4.1×10^{14} for Cs-O-W surfaces.

(7) *Equilibrium values of θ as a function of T and evaporation characteristics.* "For T between 1040° and 650° K the fraction of the surface covered, i.e., θ, should have values between zero and one. Hence the time required to reach the optimum activity should be less than t_m. This is actually found to be the case if we draw electrons, and from the times we can determine the values of θ for various filament temperatures." In this manner Becker has determined θ as a function of T for Cs-W and Cs-O-W.

Since at equilibrium the rate of arrival of caesium atoms is equal to the rate of evaporation, such data can be used to determine the evaporaton characteristics. If the filament is negative, only atoms evaporate, whereas if the filament is positive both atoms and positive ions evaporate. Becker finds that "the work necessary to remove an atom decreases as θ increases, while the work necessary to remove an ion increases with θ."

(8) *Work function for emission of electrons and positive ions.* From the above discussion it is evident that while in general the observations made by Becker are in agreement with those made by Langmuir and Kingdon, there are certain differences, While the latter assume that adsorbed surfaces cannot be more than one atom deep, and they conclude that maximum emission is obtained for $\theta < 1$, Becker concludes from his observations that at sufficiently low temperatures θ can exceed 1. From thermodynamical considerations, for which the reader is referred to the original paper, Langmuir and Kingdon derive for Φ_e the work function for electron emission, the value 1.24 volts for $\theta = 0.90$ and conclude that Φ_e decreases linearly as θ increases, whereas Becker concludes that Φ_e has a minimum value of 1.36 volts for $\theta = 1$ and shows a non-linear increase for $\theta < 1$, until it reaches the value 4.52 for pure tungsten. For the heat of evaporation of positive ions of caesium from pure tungsten, Langmuir and Kingdon derive the value 4.0 volts for $\theta = 0$, which increases to 4.3 volts for $\theta = 0.9$. In the case of caesium films on adsorbed oxygen, the heat of evaporation of ions is deduced as 5.13 volts for $\theta = 0.95$.

(9) *Adsorption phenomena.* It is evident from the preceding discussion that the emission phenomena observed for films of caesium (and presumably other alkali metals) on tungsten or tungsten covered with a monatomic film of oxygen, are extremely complex. The photoelectric behavior of caesium on oxidized copper and silver shows similar characteristics and undoubtedly in both the thermionic and photoelectric emission, the work function varies considerably with variations in the nature of the layer on which the alkali metal is deposited. As shown by Langmuir and Kingdon, these phenomena are to be interpreted as due to variations in Φ and are consequently intimate-

ly related to the adsorption characteristics of caesium on various surfaces. More recently J. A. Becker has investigated these phenomena in greater detail[79] than in his first paper and has determined the rate of evaporation of caesium from Cs-O-W surfaces as a function of θ and T. The results obtained are shown graphically in Fig. 7. From these observations it is possible to calculate the mean life, τ, of a caesium atom as a function of θ and T. Thus at $T=700°K$, τ decreases from 665 seconds for $\theta=0.8$ to 28 seconds for $\theta=1.00$, and with increase in temperature for constant value of θ, τ decreases.

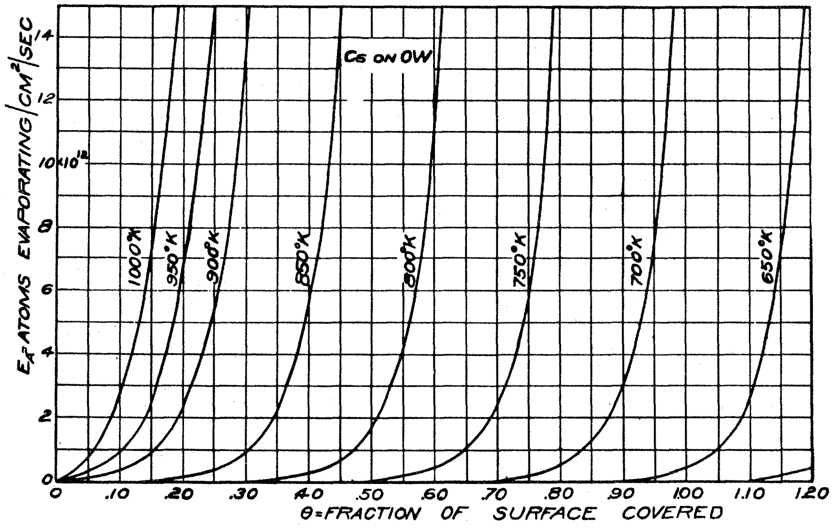

Fig. 7. Rate of evaporation of caesium from Cs-O-W surfaces as a function of temperature and of fraction of surface covered, θ.

IV. CALORIMETRIC DETERMINATION OF WORK FUNCTION FOR METALS

As shown by Richardson the emission of electrons involves a cooling effect which may be regarded as the latent heat of evaporation of electrons (either at constant volume or constant pressure). From measurements on this cooling effect, it is therefore possible to calculate a value of the work function corresponding to the constant b (or b_0) in the emission-temperature equations (1) and (2).

The theory underlying such measurement as well as a description of the experimental arrangement, are given in the treatises of Richardson and of Schottky and Rothe. Also the publications of C. Davisson and L. H. Germer[80] give very complete details.

The cooling effect as determined experimentally may be designated by the volt equivalent value Φ_c. From this value the constants b and b_0, or Φ and Φ_0 respectively, are determined by the relations

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[79] J. A. Becker, Trans. Am. Electrochem. Soc. May, 1929.

[80] C. Davisson and L. H. Germer, Phys. Rev. **20**, 300 (1922); **24**, 666 (1924).

$$\begin{aligned} \frac{b_0 k}{e} &= \Phi_0 = \Phi_c - \frac{2kT}{e} \\ \frac{bk}{e} &= \Phi = \Phi_0 + \frac{3}{2}\,\frac{kT}{e} = \Phi_c - \frac{kT}{2e} \end{aligned} \tag{21}$$

where T is the temperature of the cathode in the calorimetric determination.

"The first experiments to detect and measure this effect were made by Wehnelt and Jentzsch[81] using the emission from lime-coated wires." While their results were in qualitative agreement with values from emission measurements, the first definite proof of the phenomenon was obtained by H. L. Cooke and Richardson from experiments with osmium filaments. Subsequently similar measurements were carried out with other metals by the same investigators and others. Table XII[82] gives the results of these investigations under Φ_0(cal), and for comparison are given the values of Φ_0 from emission data on similar filaments. Davisson and Germer and also Lester made determinations by both methods on the same filaments.

TABLE XII. *Calorimetric determinations of work function for homogeneous cathodes.*

Author	Material	T	Φ (cal.)	Φ_0 (therm.)
Cooke and Richardson[83]	Os		4.7	—
	W	1922	4.24	4.48
H. Lester[84]	W		4.48	4.48
Davisson and Germer[80]	W	2270	4.52	4.48
Michel and Spanner[85]	W	2420	4.57	5.0
Wehnelt and Liebreich[86]	Pt		5.9	5.0
H. Lester[84]	Mo		4.59	4.33
	Ta		4.51	4.2
	C		4.55	—

The converse phenomenon, that is, the absorption of heat by metals when electrons impinge on them, has also been observed by Richardson and Cooke[87] and these investigators have determined, in this manner, work functions for a number of metals. However, the results obtained cannot be regarded as very accurate.

More recently Van Voorhis[88] has measured the heat of condensation of electrons by a method involving the use of Langmuir collecting electrodes[89] in a gas discharge. The values of Φ_0 found by this method for molybdenum

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[81] Wehnelt and Jentzsch, Verh. d. Deutsch. physik. Ges. **10**, 610 (1908); Ann. d. Physik **28**, 537 (1909).

[82] From treatise by Schottky, Rothe and Simon, p. 136 with slight additions. See also Richardson's book p. 188.

[83] Cooke and Richardson, Phil. Mag. **25**, 624 (1913); **26**, 472 (1913).

[84] H. Lester, Phil. Mag. **31**, 197 (1916).

[85] Michel and Spanner, Zeits. f. Phys. **35**, 395 (1925).

[86] Wehnelt and Liebreich, Physikal. Zeits. **15**, 548 (1914).

[87] Richardson's book, pp. 189–195.

[88] Van Voorhis, Phys. Rev. **30**, 318 (1928); Compton and Van Voorhis, Proc. Nat. Acad. Sci. **13**, 336 (1927).

[89] Langmuir, G. E. Review **26**, 731 (1923); Langmuir and Mott Smith, G. E. Review **27**, 449, 538, 616, 762, 810 (1924).

were as follows: 4.76 volts in argon, 4.04 or 4.35 volts in hydrogen, and 4.77 or 5.01 volts in nitrogen. The double values were due to differences in treatments of the surface. It will be observed that these values are higher than those obtained thermionically or by calorimetric methods in vacuum. Likewise, Schottky and von Issendorff[90] have deduced, from energy measurements on probe electrodes in a mercury discharge, that the work function in case of iron and nickel is between 4 and 5 volts. Whether this method can be developed to yield accurate data on Φ_0 seems questionable in view of the many corrections which have to be introduced in order to determine the desired result.

V. ELECTRON EMISSION FROM METALS AT THE MELTING POINT

Wehnelt and Seeliger[91] measured the emission (of both electrons and positive ions) from copper and silver at the melting point. Their results for a and Φ (corresponding to b in equation (1)) were as follows:

Metal	a (amps/cm^2 deg.$^{1/2}$)	Φ
Cu—solid	9.22×10^5	3.85 volt
fluid	4.93×10^5	3.71
Ag—solid	3.41×10^3	3.09
fluid	1.77×10^3	2.9

The most careful and extensive investigations on this subject have been carried out by A. Goetz[92] since 1923. A specially designed vacuum furnace was used and the thermionic emission was observed for a series of temperatures below and above the melting points of the metals.

In the first publication, plots of log I/T vs. $1/T$ are given for copper, iron, and manganese. In the case of iron it was observed that at the transition temperatures for the different crystal modifications, the value of a in Richardson's equation changed, but not that of b. At the melting points of all three metals the value of b was observed to increase considerably.

Fig. 8 shows a typical plot of log (i/T^2) vs. $1/T$ as obtained for copper (melting point 1358°K) in the more recent investigation.From these observations, it is found that A and Φ_0 vary with T as shown in Table XIII.

TABLF XIII. *Emission constants for copper* (Goetz).

T	$b_0\times10^{-4}$	Φ_0	A
1316	5.02	4.33	65
1380	1.98	1.79	6.0×10^{-10}
1400	3.19	2.75	4.0×10^{-5}
1430	4.55	3.92	6.2×10^{-1}
1480	6.37	5.50	1.5×10^5
1530	7.75	6.69	1.2×10^9

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[90] Schottky and von Issendorff, Zeits. f. Physik **26**, 85 (1925).

[91] Wehnelt and Seeliger, Zeits. f. Physik **38**, 443 (1926).

[92] A. Goetz, Phys. Zeits. **24**, 377 (1923), **26**, 206 (1925); Zeits. f. Physik **42**, 329 (1927); **43**, 531 (1927). Schottky and Rothe also give a very complete summary of these investigations in their treatise.

Fig. 9 shows a plot of Φ_0 vs. T. At the melting point the value decreases abruptly and then increases gradually. Similar results were observed for silver and gold. The values of the emission constants for these metals near the melting point are shown in Table XIV.

TABLE XIV. *Emission constants for silver and gold* (Goetz).

Metal	State	T	$b_0 \times 10^{-4}$	Φ_0	A
Ag	solid	1233	4.64	4.0	
	fused	1240	1.98	1.71	3.0×10^{-8}
	fused	1450	3.78	3.26	2.9×10^{-2}
Au	solid	1315	5.00	4.32	40
	fused	1385	2.91	2.51	5.8×10^{-6}
	fused	1530	4.98	4.30	13

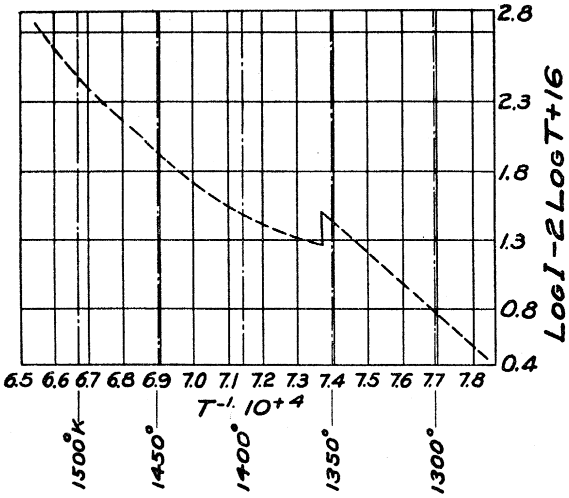

Fig. 8. Variation of thermionic emission through the melting point of copper.

As Schottky has pointed out, it is difficult to attach any interpretation to these results. They indicate, however, that the work function varies considerably with the temperature.

The emission from solid and fused potassium and sodium has been investigated by A. F. A. Young[93] and Young and Richardson.[94] Earlier investigations on these metals were undoubtedly inaccurate because of the presence of gas. Young's observation in the case of potassium did not yield any constant values of the emission constants, since they varied with both anode voltage and temperature. Thus the value of $b \times 10^{-4}$ varied from 1.58 to 1.32 at 200°C, and from 0.576 to 0.505 at 30°C, with corresponding variations in a. However, no abrupt change in work function was observed at the melting point.

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[93] A. F. A. Young, Proc. Roy. Soc. **104A,** 611 (1923).

[94] Young and Richardson, Proc. Roy. Soc. **107A,** 377 (1925).

The measurements made by Young and Richardson gave values of $b \times 10^{-4}$ varying from 1.90 to 0.693. It is of interest to note that a plot of values of $\log A$ vs. b_0 shows an approximately linear relation. In order to interpret the observations it was suggested that two modifications of potassium are present, the more active one concentrating at the surface in the form of "patches."

VI. Oxide Coated Cathodes

The emission from oxides of the alkaline earth metals was first observed by. A. Wehnelt[95] and has since then been the subject of many investigations not only on account of its technical importance, but also because of the complex nature of the phenomena which characterize the behavior of these materials when used as coatings on metallic filaments. A bibliography of the earlier work (to 1920) in the physics and chemistry of oxide coated cathodes has been given by H. D. Arnold[96] and a discussion of this work and of the various theories theories held before that time on the nature of the emission phenomena will be found in that paper as well as in the treatises by Richardson and Schottky, Rothe and Simon.[97]

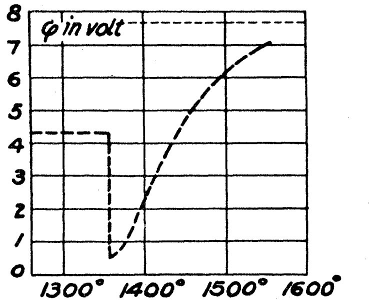

Fig. 9. Variation of work function of copper through the melting point.

In reviewing the numerous publications which have appeared on this subject, it has been considered best to discuss this work under the following headings:

(A) Preparation of cathodes.
(B) Determination of temperature.
(C) Emission constants.
(D) Determination of work function calorimetrically.
(E) Activation and de-activation phenomena and theory of emission.

A. Preparation of oxide coated cathodes

The various methods for producing filaments coated with alkaline earth oxides are described in the treatise by Schottky, Rothe and Simon[98] and

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[95] A. Wehnelt, Ann. d. Physik **14,** 425 (1904).

[96] H. D. Arnold, Phys. Rev. **16,** 70 (1920).

[97] Schottky, Rothe and Simon, vol. 13, of Wien Harms "Handbuch der Experimentalphysik."

[98] See C. Davisson, I. C. T. **6,** 53 (1929).

also by H. D. Arnold,[96] L. R. Koller,[99] E. F. Lowry[100] and E. R. Wagner[101]. As core material, platinum (alloyed with six to ten percent iridium, or with ten percent rhodium) or with 5 percent nickel, or an alloy of nickel, cobalt, iron and titanium designated as "Konel" metal[100] may be used. The oxides have also been used successfully on a tungsten filament which has been nickel plated and then oxidized to form a film of oxide on the surface. In many cases the metals are used in the form of narrow ribbons or twisted wires.

The oxides (usually a mixture of equal parts by weight of BaO and SrO) are put on the core metal either in the form of carbonates or nitrates. According to Arnold, "Barium in the form of carbonate, and strontium in the form of hydroxide or carbonate, was mixed with some carrier such as resin or paraffin, which would burn away when heated in the air. In the coating process four applications of the strontium mixture were followed by four of the barium mixture, and this process was then repeated, making a total of sixteen separate applications. After each application the wire was raised momentarily to a temperature of about a thousand degrees, which burned away most of the organic carrier. When the coating was complete the wire was heated to about 1200° for two hours. At the end of this time there remains a fairly heavy coat of BaO and SrO (from 2 to 3 milligrams per sq. cm surface), while next to the core is a firmly adhering layer which is built up due to chemical reactions between the coating and the core. Analysis shows this coating to consist of barium and strontium combined with platinum, rhodium and iridium, the compound present in largest amount being barium platinate ($BaPtO_3$). The compound with rhodium seems to be more readily formed, but due to the small percentage of rhodium present this compound makes up only a small fraction of the total.

"The filament thus formed can be handled without undue precaution as long as it is not exposed to moisture or carbon dioxide."

In the case of the nitrates, according to Koller, "The method of applying the coating was to dip the wire into a solution containing respectively three percent of barium nitrate and two percent of strontium nitrate and then burn it for a few seconds at a high temperature in an atmosphere of carbon dioxide. This process was then repeated until the coating reached the desired thickness. About 40 cycles were usually sufficient.

"Such a coating consists largely of the carbonates, as can readily be demonstrated by dipping a filament in hydrochloric acid, which results in a rapid evolution of gas. This evolution of gas takes place even after a filament has been burned for several hundred hours."

The coating can also be applied in the form of a water paste consisting of equal parts of the carbonates of barium and strontium. This is then baked on the filaments in an atmosphere of CO_2 (Lowry). Or the oxides may be used in the form of a suspension either in alcoholic solution of colophonium or pure paraffin oil. The mixture is then applied to the wire in thin layers

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[99] L. R. Koller, Phys. Rev. **22** 671 (1925).

[100] E. F. Lowry, Phys. Rev. **35**, 1367 (1930).

[101] E. R. Wagner, Electronics, July (1930), p. 178.

followed by heating in air first for a short period to 500°C and then to 1000°C. (W. Espe[102].)

In general it is not advisable to heat the filaments to too high a temperature before they are inserted in the tube and de-gassed on the pump. Such cathodes are apt to be very difficult to activate.

The subsequent treatment of the cathodes, during exhaust, is necessary in order to form or activate them. The first stage consists in glowing the filaments to a moderately high temperature to decompose the carbonates or nitrates, and eliminate occluded gases. The anodes and other metal parts should be treated after this operation with high frequency, to de-gas them. The second stage consists in the activation or formation process. J. A. Becker[103] designates this also as the "breakdown process," and describes it as follows :"This process consists in glowing the oxide coated platinum filament at about 1500°K for several minutes. A rather high positive potential gradient is then applied to the filament for something like two to thirty minutes. During this time the emission from the filament increases greatly. When it attains rather large values such as 0.1 to 1.0 amps. per cm^2, the applied field and the filament temperature are so adjusted that the current is just limited by space charge." In the case of nickel or Konel filaments the maximum temperature should not be over about 1000°C. Approximately a similar procedure has been used by W. Espe[102] in his investigations on oxide coated filaments.

The activation may also be accomplished by thermal treatment alone without the application of anode voltage. This seems to apply specially to filaments of nickel or Konel. In the case of the latter Lowry has shown that a treatment at 8.5 watts per cm^2 (corresponding to about 1075°C) for several minutes, followed by a more prolonged treatment at about 950°C is sufficient to activate the cathodes. Lowry also states in the same connection that, "Similar results have been obtained with oxide coated platinum filaments." The experience in the Research Laboratory at Schenectady has shown that application of anode voltage is not essential, although in some cases especially in those in which platinum or tungsten filaments are used as core material, the operation of drawing electrons from the cathode often increases the rate of activation. Other investigators have also observed activation of oxide coated platinum filaments by thermal treatment exclusively (M. S. Glass,[104] Reimann and Murgoci[105] and Koller[99]).

Mention should also be made in this connection of a type of oxide coated cathode developed in Europe and used to a considerable extent in vacuum devices made on the continent.[97] A solution of barium azide (BaN_6) is brushed on the inside of the metal (usually nickel) anode and the cathode is made of tungsten which has been electroplated with an extremely thin film of copper or nickel and then oxidized by heating in air. During exhaust, the

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[102] W. Espe, Wiss. Veroeff. d. Siem. Konz. **5**, 29, 46 (1927).

[103] J. A. Becker, Phys. Rev. **34**, 1323 (1929).

[104] M. S. Glass, Phys. Rev. **28**, 521 (1926).

[105] A. L. Reimann and R. Murgoci, Phil. Mag. **8**, 440 (1930).

anode is heated by the high frequency method, the azide dissociates and metallic barium is deposited on the oxide layer on the cathode. The latter is then glowed for a considerable time to activate the deposit and the tube is then sealed off. This method apparently offers two advantages: firstly, much smaller filament diameters of wire may be used, which therefore require smaller heating currents, and secondly, the barium volatilized all over the bulb walls acts as a "getter" and therefore maintains an even better vacuum in the tube than can be obtained with the more commonly used magnesium getter. However, in this country, this type of cathode has not been commercially utilized to any extent, as far as the writer is aware.

The various methods used in the manufacture of oxide coated cathodes have also been described by Hodgson, Harley and Pratt,[106], and a comparison given in their paper of the emission from the different filaments during life.

B. Temperature scale for oxide coated cathodes.

As might be inferred from the description of the process of preparing and activating this type of cathode, the thermal emissivity varies considerably with variations in materials and in method of forming.

For the filaments used by the Western Electric Co. in their vacuum tubes, Dr. C. Davisson kindly furnished the writer the following information:[98]

Material of filament core: Platinum 95 percent, nickel 5 percent.

Electrical resistivity:

$$\rho = 2.2 \times 10^{-5}(1 + 0.00208t - 4.6 \times 10^{-7}t^2) \qquad (22)$$

ohms cm, where t = Centigrade temperature.

The coating is a mixture of the oxides of barium and strontium plus a small admixture of nickel (and platinum) which is transferred from core to coating during the preparation and activation of the filament.

Emissive Power:

$$\epsilon = 0.4 + 2.5 \times 10^{-4}T \text{ for the range } 800^\circ - 1200^\circ\text{K.}''$$

From the last relation it follows that the total energy radiated is given by the relation,

$$W = 5.735 \times 10^{-12}(0.4 + 2.5 \times 10^{-4}T)T^4 \text{ watts/cm}^2 \qquad (23)$$

$$= 3.727 \text{ watts/cm}^2 \text{ at } T = 1000^\circ \text{ K.}$$

For *pure platinum* C. Davisson and L. H. Germer[107] give the following relation for the resistivity:

$$\rho_t = 0.4217(1 + 0.003946t - 5.85 \times 10^{-7}t^2) \qquad (24)$$

where t is the temperature in degrees Centigrade.

F. Detels[108] obtained from a series of measurements with blank and oxide-coated platinum wires (ten percent iridium) a linear relation for the resistivity of the form

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[106] B. Hodgson, L. S. Harley and O. S. Pratt, Journal I. E. E. **67**, 762 (1929).

[107] C. Davisson and L. H. Germer, Phys. Rev. **24**, 666 (1924).

$$\rho_t = \rho_0(1 + 2.65 \times 10^{-4}t) \tag{25}$$

where t = Centigrade temperature.

For coated tungsten wires the ratio of resistance at the high temperature to that at room temperature also furnishes a convenient method of determining the temperature, provided of course, that a proper correction is made for cooling effect of leads.

E. F. Lowry[100] has given brightness temperature measurements for ribbon filaments of coated platinum and Konel. The latter is a much better radiator. By enlarging the curve shown in the original paper, the values given in Table XV were obtained for the energy radiated as a function of T. The second column gives the values derived from Davisson's relation, equation (23), and the third column, Lowry's values for Konel metal. The last two columns give the hot to cold ratio of resistance for Western Electric and platinum-iridium (10 percent) alloy, according to equations (22) and (25) respectively.

TABLE XV. *Resistivity and energy radiated for coated filaments* ($BaO+SrO$)

T	Energy radiated (watts/cm^2)		ρ_t/ρ_0	
	W.E. Pt-Ni	Konel	W.F. Pt-Ni	Pt-Ir
300°K	0.022		1.00	1.00
700	0.79	1.66	1.80	1.11
800	1.41	3.01	1.96	1.13
900	2.35	4.72	2.12	1.16
1000	3.73	6.57	2.26	1.19
1100	5.67	8.91	2.40	1.21
1200	10.70		2.53	1.24
1300	15.15		2.65	1.27
1400	20.93		2.75	1.29
1500	28.31		2.85	1.32

While the temperature-coefficient of resistance is much smaller than that of the energy radiated, it has the considerable advantage that the value is the same for both coated and blank wires. Therefore, if it can be measured accurately for the latter, the temperature determined for the coated wire is independent of any knowledge of the thermal emissivity, which in the case of coated wires may vary even for filaments apparently identical in composition and treatment. On the other hand, as mentioned previously, the error due to cooling effect of leads may be considerable on account of both the short lengths ordinarily used and the relatively low temperatures at which the filaments are operated

Because of these difficulties in the accurate determination of temperature, it has been found more convenient often to compare the electron emission from various coated filaments at the same watts imput. (Such a series of plots is shown by Arnold[96] and also by R. W. King[109]. This topic, however, will be discussed further in the following section.)

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[108] F. Detels, Jahrb. d. drathlos. Telegr. **30,** 10, 52 (1927).

[109] R. W. King, Bell System Tech. J. **2,** No. 4 (1923).

C. Thermionic emission constants for coated filaments.

As pointed out by H. Rothe[110] and W. Espe,[102] the electron emission from coated filaments does not exhibit the same distinct saturation values as those observed for homogeneous metal filaments. The space current increases with voltage very rapidly, especially at higher temperatures, even when it is considerably below the limit put by space charge relations. Furthermore the emission is apt to change with time and there are pronounced fatigue effects, which may lead to erroneous values of the emission constants. In fact, as will be pointed out more fully in the following section, the behavior of oxide

TABLE XVI. *Thermionic emission constants for oxide-coated filaments.*

Year	Oxide	a	$b\times10^{-4}$	ϕ (volts)	A	$b_0\times10^{-4}$	Φ_0	Remarks	Ref
1904	BaO	1.11×10^{8}	4.5	3.9			3.65	Pt. core	(95)R
	CaO	7.2×10^{7}	4.3	3.75			3.48	“ “	(95)R
1907	CaO	6.36×10^{11}	4.8	4.15			3.9	“ “	(111)R
1908	CaO	1.75×10^{7}	4.3	3.75	4.2×10^{-8}	4.05	3.48	“ “	(112)R
1908	Al_2O_3	6.40	3.73	3.21	2.1×10^{-5}	3.48	3.00	“ “	(113)R
	BaO	4.70×10^{7}	4.16	3.58	2.7×10^{2}	3.99	3.44		
	BeO	1.03	2.39	2.06	4.56×10^{-6}	2.19	1.88		
	CaO	4.30×10^{7}	4.03	3.48	2.49×10^{2}	3.86	3.33		
	CdO	0.37	3.02	2.60	1.65×10^{-6}	2.82	2.43		
	CeO_2	1.95×10^{3}	3.71	3.20	8.62×10^{-2}	3.51	3.02		
	Co_2O_3	6.67×10^{3}	4.97	4.28	2.17×10^{-2}	4.72	4.06		
	CuO	3.5×10^{-3}	2.25	1.94	1.55×10^{-8}	2.05	1.76		
	Fe_2O_3	3.57×10^{3}	4.69	4.04	1.16×10^{-2}	4.44	3.82		
	La_2O_3	6.9×10^{2}	3.79	3.26	3.03×10^{-3}	3.59	3.10		
	MgO	3.37	3.95	3.40	1.10×10^{-5}	3.70	3.19		
	NiO	2.79×10^{4}	5.12	4.41	9.1×10^{-2}	4.87	4.19		
	SrO	5.07×10^{7}	4.49	3.87	2.58×10^{2}	4.30	3.71		
	ThO_2	35.	3.56	3.06	1.54×10^{-4}	3.36	2.89		
	Yt_2O_3	1.86×10^{4}	3.63	3.13	8.22×10^{-2}	3.43	2.95		
	ZnO	0.31	3.51	3.02	1.0×10^{-6}	3.26	2.81		
	ZrO_2	6.57×10^{3}	3.66	3.15	2.9×10^{-2}	3.46	2.98		
1914	Nernst Fil.	1.11×10^{5}	4.6	4.0					R
1916	CaO			2.54					(114)
1920	BaO+SrO	8×10^{4} to 2.4×10^{5}	1.94 to 2.38	1.55 to 1.90	.418 to 1.23	1.76 to 2.20	1.51 to 1.89	Pt. alloy core	(96)
1924	Al_2O_3	3.3×10^{5}	4.58	3.95	1.4	4.37	3.77	Pt.-alloy core	(115)
	B_2O_3	1.2×10^{5}	4.81	4.15	0.49	4.59	3.95		
	BaO	$8.\times10^{5}$	2.15	1.85	4.0	1.97	1.70		
	BeO	9.8×10^{5}	4.01	3.45	4.9	3.83	3.30		
	CaO	4.8×10^{6}	2.78	2.4	25.7	2.60	2.24		
	MgO	8.5×10^{6}	3.49	3.01	45.7	3.31	2.85		
	SrO	1.3×10^{6}	2.49	2.15	6.9	2.31	1.99		
	Sc_2O_3	2.5×10^{6}	4.18	3.6	10.7	3.97	3.42		
	SiO_2	1.6×10^{6}	5.57	4.8	5.0	5.31	4.58		
	ThO_2	4.6×10^{3}	3.65	3.15	0.016	3.41	2.94		
	TiO_2	4×10^{4}	4.64	4.0	0.13	4.39	3.78		
	Yt_2O_3	1.26×10^{6}	3.60	3.1	5.4	3.39	2.92		
	ZrO_2	$1.\times10^{5}$	4.18	3.6	0.35	3.94	3.40		
1925	BaO+SrO				1.07×10^{-3}	1.21	1.05	Pt-Ir core	(99)
1926	BaO+SrO	100	1.073	0.92	9.6×10^{-4}	0.953	0.82	German tube	(110)
		60	.969	.83	5.7×10^{-4}	.849	.73	“ “	
		10	.747	0.64	9.8×10^{-5}	.627	.54	“ “	
		1.66×10^{3}	1.309	1.13	1.6×10^{-2}	1.189	1.02	“ “	
		2.5×10^{4}	1.444	1.24	0.24	1.324	1.14	Dutch “	
1927	SrO	0.75×10^{3}	1.64	1.41				200 V	(102)
		2.4×10^{3}		1.44				300V	
	CaO+BaO+SrO				8.3×10^{-3}	1.44	1.24	See table XVII	(102)
1927	BaO+SrO				2.97×10^{-2}	1.58	1.36		(108)
					9.3×10^{-4}	1.58	1.36		
1928	BaO				2.5		1.66	W core	(116)
1928	BaO+SrO				1.0×10^{-2}	1.16	1.00	West. Electric (Zero Field) See table XVIII.	(97)

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[110] H. Rothe, Zeits. f. Physik **36,** 737 (1926).

[111] F. Horton, Phil. Trans. **A207,** 149 (1907).

[112] F. Deininger, Ann. d. Physik **25,** 258 (1908).

[113] F. Jentzsch, Ann. d. Physik **27,** 129 (1908).

[114] W. Germershausen, Phys. Zeits. **16,** 104 (1915); Ann. d. Physik **51,** 705 (1916).

[115] H. J. Spanner, Ann. d. Physik **75,** 609 (1924).

[116] J. M. Eglin, Phys. Rev. **31,** 1127 (1928).

coated cathodes is so different from that of filaments of pure metals that it is extremely difficult to obtain precision data on emission constants comparable with those given in Table IV. This is especially true of the values of A.

Table XVI gives emission constants obtained by the various investigators. The relative accuracy varies with the conditions under which the observations were made, and an attempt will be made in the following paragraphs to point out those data which are to be regarded as more reliable.

In the case of most of the data, expecially those obtained by earlier investigators, no corrections were made apparently for either temperature distribution along the cathode or the effect of field strength. Since oxide coated filaments are operated at comparatively low temperatures (below 1200°K), the lead loss correction is extremely important. Moreover, since the resistivity of platinum or nickel is less than that of tungsten, the voltage drop along an oxide coated filament is also quite low. (This is specially true of the filaments used in commercial vacuum tubes.) Hence the errors due to neglecting these considerations are apt to be large.

With regard to the effect of field strength it is certain from the work of J. A. Becker and others that for the type of filament under consideration, Schottky's relation is not valid. Consequently, either the extrapolation to zero field strength must be made on the basis of other considerations, or emission data must be investigated to as low field strengths as possible.

For these two reasons, but mainly on account of ignorance of the proper method of correcting for effect of field strength, the values of the thermionic constants given in Table XVI cannot be regarded, in the large majority of cases, as more than a first approximation to the true values of A and b_0 (or Φ_0). Undoubtedly further investigations in this field are necessary before such precise data will be available.

Of the earlier data, those published by Jentzsch[113] are of interest because of the number of oxides investigated. A comparison of these data with those obtained by Spanner[115] in 1924 shows marked differences in a number of cases. The paper by the latter gives the values of Φ (not Φ_0) and plots of log. $(I/T^{1/2})$ vs. $1/T$. These plots were enlarged and used to determine values of a. From these, the values of A and b_0 were calculated in the manner described in connection with Table IV. Spanner used short filaments and therefore his data probably involve large lead loss corrections. However, since the values calculated from his plots for W, Ta, and Pt are not radically different from those obtained by other investigators, it seems reasonable to conclude that, on the whole, his data are probably fairly accurate.

From his measurements Spanner concluded that Φ, the work function corresponding to b in equation (1), is a simple function of the atomic number N, and of the number of valence electrons, Z, for the metal, of the form:

$$\Phi = \frac{7Z^{3/2}}{4N^{1/2}} + 1 \text{ volt}.$$

It is, however, questionable whether this relation has any significance.

The emission constants reported by Arnold[96] in 1920 are the first satisfactory data, but are not as accurate as those reported on similar filaments by Davisson[98] in 1928. Because it is of great technical importance to obtain electrons as "cheaply" as possible, the investigators from the Bell Laboratories have reported their observations on thermionic emission in the form of plots such as those shown in Fig. 10, taken from a paper by R. W. King.[109] The emission in milliamps/cm² is plotted against the power input (watts/cm²)

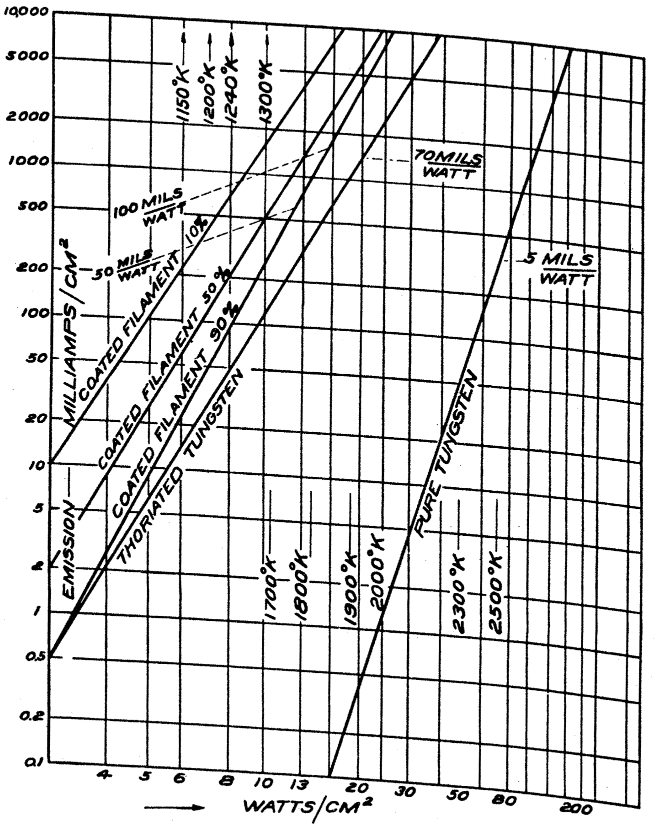

Fig. 10. Emission from coated filaments as a function of power input.

on specially designed cross-section paper, as explained by Arnold.[96] The figure shows the variation in emissions for commercially manufactured filaments. Plots for thoriated tungsten and pure tungsten are shown for comparison.

The remarkably low value for Φ_0 obtained by Koller[99] after careful evacuation and prolonged activation has also been observed by other investigators subsequently.

The data reported by Rothe[110] were taken on commercial tubes, four of German manufacture and one of Dutch. No correction was made for cooling effect of leads or field strength. Rothe himself considers the values of A as not very reliable. A noteworthy feature of these observations is the relatively low temperature range over which it was found necessary to operate the filaments. Thus, on the tube from Holland, the emission varied from 1.2×10^{-5} amp./cm_2 at $T=595$°K to 76.5×10^{-3} at $T=905$°K. In calculating values of A and b_0 from values of a and b given in the original paper, the average temperature was therefore taken as $T=800$°K. At $T=1000$°K the emission calculated from Rothe's values of a and b varies from 69 to 800 milliamps/cm^2 (see Table XIX). These values are higher than those observed by most of the other investigators, except under special conditions. This may be accounted for either by assuming that Rothe's values for T are too low or else that he was using filaments made by the barium azide process. While nothing is stated by him regarding the manner of preparation of the cathodes, it is quite probable that these were of the azide type, since at that time a considerable number of tubes were made by this process in Europe and especially in Holland. It should, however, be stated that in the paper by Becker[103] emission data are mentioned which are of the same magnitude as those observed by Rothe.

TABLE XVII. *Work function for oxide coated filaments* (*W. Espe*[102]).

Coating	$b\times10^{-4}$	Φ	$b_0\times10^{-4}$	Φ_0	Anode volts
CaO—1	1.98	1.71	—	—	100
—2	1.97	1.70	—	—	200
—3	2.22	1.90	2.02	1.74	200
—4	2.27	1.96	2.04	1.76	200
—5	2.23	1.92	2.08	1.79	300
SrO—1	1.67	1.44	1.44	1.24	300
—2	1.635	1.41	1.46	1.26	200
—3	1.67	1.44	1.51	1.29	300
—4	1.68	1.45	1.50	1.29	200
BaO—1	1.27	1.095	1.13	0.97	300
—2	1.265	1.09	1.13	0.97	300
—3	1.29	1.11	1.16	1.00	300
—4	1.31	1.13	1.19	1.03	300
CaO	2.24	1.93	2.05	1.77	
SrO	1.66	1.43	1.475	1.27	
BaO	1.29	1.11	1.15	0.99	

Results of comprehensive investigations in this field have been published by W. Espe[102] and F. Detels.[108] The former has emphasized the effect of the anode voltage at which the emission is observed. Representative results for SrO on Pt-Ir are given in Table XVI. For coatings of CaO to which 5 percent of BaO and SrO were added he observed values of A ranging from 0.2×10^{-3} to 20×10^{-3} amps./cm^2 deg^2, according to degree of activation. The values of the work functions obtained by him for each of the oxides are given in Table XVII, taken from his paper. The values for CaO-1 were calculated from preliminary tests, those for CaO-2 were obtained with a "heavy" layer, While all the other values were obtained with "thin" layers. The final values deduced by Espe as most reliable are given in the last three lines in the table. The maximum error in b (or b_0) is stated to be about 300.

Detels[108] observed that during activation both A and b_0 decrease simultaneously. These observations will be discussed in a subsequent section. The values of emission constants given in Table XVI are typical of minimum values obtained after a prolonged period of activation. Corrections were introduced for temperature distribution along the filament. In fact, the original paper gives quite a comprehensive treatment of this topic. Since the emission-voltage curves apparently flattened out at 100–200 volts anode potential, the saturation values were used to calculate A and b_0. Therefore no correction was introduced for effect of field strength.

TABLE XVIII. *Most probable characteristics of Western Electric filaments (C. Davisson*[97]*).*

Temp:—	900°K	950°K	1000°K	1050°K	1100°K
I_0 (milliamps/cm^2)	20	45	90	170	310
P_r (power radiated, watts/cm^2)	2.3	3.0	3.7	4.6	5.6
P_e (power absorbed by emission. watts/cm^2)	0.02	.045	.09	.17	.31
Efficiency (milliamps/watt) $I_0/(P_r+P_e)$	8.6	15	24	31	53
Life (in thousands of hours)	(730)*	(170)*	20	20	7.4

* These figures are computed.

Eglin's observations[116] are of interest because they represent results obtained for films of metallic barium deposited on tungsten in vacuo, by evaporation from regular coated filaments.

The values forWestern Electric filaments were furnished by Dr. Davisson[97] and represent the average of a very large number of observations. It will be observed that the value of Φ_0 is stated to be that obtained for zero field strength. Table XVIII, also from the same source, gives the most probable characteristics of this type of cathode at anode potentials comparable with 150 volts. With regard to life, (see last line of Table XVIII), Dr. Davisson states that, "For filaments operated with anode potentials comparable with 150 volts, and required to supply a space-charge limited current of approximately 10 milliampes per cm^2, the average life is given by,

$$L = 1.5 \times 10^{-5}\epsilon^{22000/T} \text{ hours.''}$$

TABLE XIX. *Comparison of emission from* $BaO+SrO$ *at* $T=1000°K$.

Author	Year	b_0	I(milliamps/cm^2)
Arnold	1920	1.76	9.5
		2.20	.35
Spanner	1924	1.97	11.25 (BaO)
Koller	1925	1.21	6.6
Rothe	1926	.95	69.
		.85	117.5
		.63	182.
		1.19	110
		1.32	800
Espe	1927	1.44	4.6
Detels	1927	1.58	44.1 1.4
Davisson	1928	1.00	91.8

Table XIX shows the values of the emission at $T=1000°K$ for coatings of

BaO and SrO, as calculated from the values of A and b_0 obtained by different investigators and given in TableXVI. With the exception of results by Rothe which have been discussed already, it will be observed that the emission at this temperature, varies between 10 and 100 milliamps per cm^2, approx mately.

In commercial practice the different types of oxide coated cathodes are usually operated at an energy input of approximately 4 watts/cm^2 with an emission efficiency of about 50 milliamps/watt, corresponding to 200 milliamps/cm^2.

A survey of the data in Table XVI shows that the values of the work function for the oxides of Ba, Sr, and Ca obtained by earlier investigators are considerably higher than those observed more recently. This point has been emphasized by Espe in a special table giving the values of Φ obtained both from thermionic and calorimetric observations by various investigators since 1904. [See also Reimann and Murgoci[105] and Lowry[100]]. Espe ascribes this observed decrease in values of Φ to improved vacuum technique, since "even very slight amounts of residual gases can cause an increase in the work function." (This will be discussed in the section on "The Effect of Gases on Thermionic Emission.") Furthermore, there has naturally been a considerable improvement in the technique of preparation and activation of the cathode materials. In view of these considerations we must regard as most reliable the values deduced by Koller, Espe, Detels and Davisson. The values given by the last named investigator, since they represent carefully weighted averages of an extremely large number of emission curves, are to be regarded as probably the most accurate emission constants available at present on oxide-coated cathodes.

A determination of the work function for pure platinum, coated with oxides of barium and strontium, from emission data has been reported by C. Davisson and L. H. Germer.[107] The values obtained for Φ varied from 1.79 initially to 1.38 volts in the steady state, whereas the direct determination on the same filament by the calorimetric method (see following section) gave 1.79 volts. These observations as well as those made by all the other investigators show not only the effect of ageing on the emission constants but also that, in contrast to the results obtained with pure metal filaments, it is virtually impossible to obtain data of the same reproduceable nature. It may be, as J. A. Becker,[103] Schottky[98] and others have suggested, that the work function of a composite surface is not independent of temperature, and that therefore, "no great significance is to be put on any work functions determined in this manner," that is, from plots of log $I/T^{1/2}$ or of log I/T^2 vs. $1/T$. Nevertheless the fact that the slopes of these lines show a wide range of values is characteristic of this type of cathode.

The tacit assumption made so far in the discussion, that the base or core metal has no effect on the emission constants, is founded to some extent on the results of the early investigations of F. Deininger.[112] He observed that the work functions for the various oxides were independent of the nature of the core material. Schottky and Rothe[97] have expressed the same opinion in their treatise (1929). This conclusion has, however, been questioned in a very recent paper by E. F. Lowry[100] as a result of an investigation on the behavior of Konel metal filaments coated with BaO and SrO. The composition of this metal has been given in a previous section and it was also pointed out in that connection that the material is a much better radiator than platinum. While no values of the thermionic emission constants are given, it is stated by Lowry that, "the same anode current may be obtained from oxide coated Konel at 775° C as can be obtained from platinum coated with the same oxides at 950° C." The theory suggested in explanation of this result will be given in connection with the discussion of activation phenomena in general.

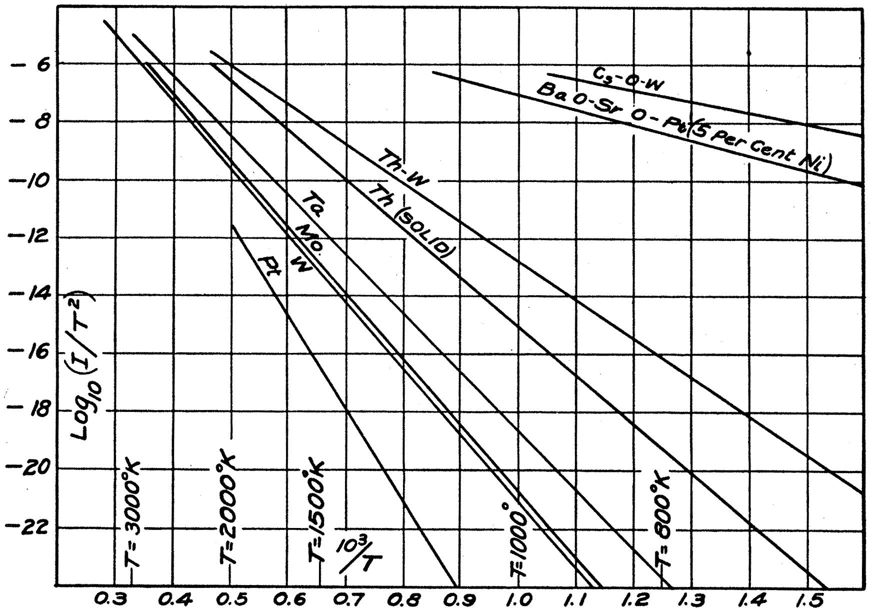

Fig. 11. Comparison of emission from coated filaments with that from pure metals.

The thermionic properties of the rare earth elements have been investigated by E. E. Schumacker and J. E. Harris.[117] Cerium, lanthanum, praesodymium, neodymium, and samarium were tested as chemically pure metals, while alloys with aluminum were tried in the case of the following metals: yttrium, europium, gadolinum, terbium, dysprosium, holmium erbium, thulium, ytterbium and lutecium. "Due to inherent difficulties in the methods that had to be used in making the measurements," the authors express the opinion that "no great accuracy can be claimed for the data" actually obtained. From the plots of log i versus $1/T$ given in the paper, it appears that the values of b_0 vary from about 40,000 to 30,000 for nearly all these elements. However, in view of the fact that the fraction of the

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[117] E. E. Schumacher and J. E. Harris, J. Am. Chem. Soc. 48, 3108 (1926).

surface active for emission probably changes in an indeterminate manner with temperature, these values may be quite inaccurate. The temperature at which an emission comparable to that of tungsten at $T=2000°$ K (1.0 milliamp/cm^2) is obtained is as low as 1200° K for thulium and is higher for the other elements. Thus the observed emission is lower in all these cases than that observed for coatings of barium and strontium oxides.

Finally, it is of interest to compare the emission from the latter with that obtained from pure metals and monatomic films on metals. Fig. 11 shows, plots of log (I/T^2) vs. $1/T$ for a few of the more important emitters ranging from Cs-O-W which has the lowest values of b (or b_0) to platinum, which apparently has the highest value of b observed up till now for a pure metal. The upper limit of each plot (lowest value of $1/T$) as shown corresponds to the melting point in the case of pure metals or to the temperature at which the surface atoms evaporate very rapidly in the case of emitting films. For example, in the case of thoriated tungsten this temperature (for maintaining $\theta=1$) is 2000° K–2100° K, and for oxide coated cathodes about 1200° K.

(D) Calorimetric determination of work function for oxide coated cathodes.

As in the case of metallic filaments, a number of investigators have attempted to determine the work function from observations on the cooling effects. The earlier investigations have been discussed by Richardson. Table XX gives a summary of the most reliable results. The third column gives the value of the absolute temperature at which Φ (cal.) was determined calorimetrically. The values under Φ (therm.) were obtained in all cases, except those of Spanner and Michel's results, from thermionic emission

TABLE XX. *Calorimetric determinations of work function for oxide coatings.*

Author	Oxides	T	Φ (cal.)	Φ (therm.)	Ref.
Schneider	CaO		3.45	3.45	(118)
W. Wilson	BaO—50% SrO—50%		1.97 2.28	2.02 2.16	(119) (120) (96)
	BaO—50% SrO—25% CaO—25%		2.39 2.54	2.34 2.59	
	CaO		3.22 3.25	3.28 3.49	
Davisson and Germer	BaO—50% SrO—50%	1064	1.79 (1.61)	1.79 (1.65)	(107)
Michel and Spanner	CaO	1493	2.40	2.45	(121)
	SrO	1458	2.15	2.27	
	BaO	950	1.85	1.69	
	BaO+SrO	1064	1.61	1.79	

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[118] H. Schneider, Ann. d. Physik **37**, 569 (1912).

[119] W. Wilson, Proc. Nat. Acad. Sci. **3**, 426 (1917).

[120] W. Wilson, Phys. Rev. **10**, 79 (1917).

[121] G. Michel and H. J. Spanner, Zeits. f. Physik **35**, 395 (1925).

measurements on the same filaments. Spanner and Michel's determination of Φ (cal.) are compared with Spanner's results for Φ (therm.) as given in Table XVI. Davisson and Germer calculated Φ_0 from their determinations of Φ and these are given in brackets. In view of the experimental difficulties involved in such measurements, the agreement between the values obtained for Φ by the two methods must be regarded as very satisfactory.

Michel and Spanner have suggested that the measurements on oxide coatings really yield the work function for the core metal. Schottky however, disagrees with this conclusion.

(E) Activation and emission phenomena in oxide coated filaments.

As has been mentioned previously, the phenomena in this type of filament are quite different from those observed with metallic filaments such as tungsten. The activation phenomena are similar in certain respects to those observed with thoriated and caesiated tungsten cathodes. It is therefore to be surmised that the increase in emission is due to some material diffusing to the surface during activation. The additional feature, however, of the necessity of applying plate voltage in order to obtain activation requires a further assumption. Furthermore, the large variation in emission constants obtained by different investigators and even by the same observer on filaments of the same composition and similar treatment—these observations lead to the inference that the number of factors controlling the emission must be greater than in the case of monatomic films on metals. To these characteristics of coated filaments must also be added the following characteristics:

(1) Lack of definite saturation emission.

(2) "Changes in activity with time following upon or accompanying (a) changes in temperature, (b) changes in plate potential, and (c) current sent into or drawn from the filament." (Becker).[103]

(1) *Evidence for metallic barium as "active" material.* That the active material produced by thermal treatment alone must be metallic barium has been shown by Koller[99] as follows: On deactivating a coated filament by heating at 1600° K for a short interval, the activity could be restored by glowing at 900° K. It was found that the rate of activation at the latter temperature increases with time of flashing at 1600° K, passes through a maximum and then decreases. "The explanation is that active material is formed at the high temperature but the rate of evaporation is too high to permit it to remain on the surface. At lower temperatures the surface becomes partially covered by some of the material which diffuses from inside the oxide coating. The rate at which the surface becomes covered depends on the concentration within the coating. This increases with the length of time of flashing up to the point where further flashing results in more active material being lost by evaporation than is formed." Similar observations have been made by M. S. Glass.[104]

Koller also observed that the activity is decreased by a pressure as low as 5×10^{-3} mm oxygen, and that water vapor has the same effect in "poisoning" the emission. Reimann and Murgoci[105] have shown that "poisoning" also occurs in presence of an electrical discharge in carbon monoxide, and Lowry finds that the activity is destroyed by overheating.

These observations are in accord, as mentioned above, with the theory that the barium forms an adsorbed layer one atom thick either on the surface of the oxide, as assumed by most investigators, or on the surface of the core material as assumed by Lowry and also by Reimann and Murgoci. It follows that the emission observed under varying conditions of treatment must be ascribed to the effect of these conditions on θ, the fraction of the surface covered with barium atoms. That the rate of evaporation of barium atoms from such a film must be considerably less than that of barium as metal follows, as pointed out by Koller, Schottky and Rothe[97] and others, from the analogy with the behavior of monatomic films of thorium and caesium on tungsten. Further evidence for this lower rate of evaporation of adsorbed barium is presented in a later section.

To these arguments in favor of barium as active material must be added the fact that in the barium azide process for the manufacture of cathodes the barium is deposited on the filament in the atomic state and that the emission observed is often actually greater than that observed at the same temperature for filaments coated with the oxides in the more usual manner. (See the comments in a previous section on the emission data obtained by Rothe).[110]

Furthermore, there are a number of observations on the emission of tungsten filaments on which metallic barium has been deposited by evaporation at relatively low temperatures of activated coated filaments. Thus from data given in Becker's paper[103] it follows that for a monatomic film of barium on tungsten the emission at $T=1000°$ K is about 0.4 amp/cm^2, which is higher than the average emission of 0.09 amp/cm^2 at the same temperature for a regular coated filament according to Davisson's data in Table XVIII.

Reimann and Murgoci state that the emission obtained in their laboratories by Ryde and Harris from monatomic layers of barium on tungsten and of barium on tungsten covered with oxygen is of the same order of magnitude as that given by ordinary oxide coated filaments at the same temperature.

It should also be added that chemical tests on activated filaments, immediately after removal from the tube, have shown the presence of the alkaline earth elements in the metallic conditions.[101]

(2) *Thermal formation of barium.* Regarding the mechanism of production of barium there exist two divergent opinions. One view is that the metal is produced by thermal reaction between the oxide and core-material; the other view is that the barium is produced by electrolysis of the oxide. The first theory is apparently held by Koller and is supported by Lowry and other investigators. The second theory is favored by Rothe, Espe, Detels, Becker and Reimann and Murgoci.

Lowry's experiments on the activation of coated Konel metal filaments by purely thermal treatment certainly favors the chemical reaction theory, at least for this type of filament. There is some evidence, however, that even in the case of platinum or tungsten filaments coated with oxides activation may be produced, although rather slowly, by thermal treatment alone.

In experiments in this laboratory with "unipotential" cathodes of nickel covered with oxides of barium and strontium, such as used for arc discharges in the rare gases and mercury[122] the cathodes are activated completely by high-frequency heating without application of voltage.

The theory of the formation of barium by thermal reaction has also received strong support from L. J. Davies[123] and A. Gehrts.[124] The former mentions that regular activated filaments have been produced by thermal treatment alone, while the latter advances considerable experimental evidence in favor of the same point of view, as for instance, the evaporation of barium during the process of activation by purely thermal treatment. Gehrts assumes that firstly the oxide is dissociated under these conditions, that secondly both barium and oxygen diffuse to the surface and that while the latter evaporates, the former remains on the surface as an adsorbed layer. Reaction of the oxide with core material is also considered as a possible source of barium, and in this respect the theory is similar to that advanced by Lowry. Gehrts also discusses in his paper the electrolytic formation theory of barium and advances reasons for disagreeing with this theory.

The theory suggested by V. C. Macnabb[125] may be regarded as an electrochemical variant of these views, inasmuch as he assumes that electrical bombardment of the cathode by ions, preferably those produced by discharge in CO_2, is necessary in order to produce the oxides "in an emissive state." According to this investigation, "The best source of the necessary gas to be used in processing is in the filament itself and can best be obtained by leaving on the filament a large percentage of uncombined oxides as the gas liberated from the filament is probably CO_2 or of some nature that is not poisonous to the filament." It is concluded furthermore, "That the combined layer of the oxides with the core comprise little or no part of the active part of the filament and only serve as a mechanical bond, and that the core material, if it has no chemical reaction with the coating, is not critical in aiding or preventing electron emission."

That the dissociation of the BaO by heat alone, in accordance with the equation

$$BaO \rightarrow Ba + \tfrac{1}{2}O_2$$

occurs at temperatures below the melting point of nickel would appear highly improbable. Calculations on this point by Dr. D. S. Villars and the writer lead to the conclusion that with the most favorable 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

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[122] See publications by A. W. Hull, Trans. A. I. E. E. **47**, 753 (1928) and C. G. Found and J. Forney, ibid **47**, 747 (1928) on hot cathode neon lamps.

[123] This theory is given in the discussion of the paper by Hodgson, Harley and Pratt, reference 106.

[124] A. Gehrts, Zs. f. Techn. Physik **11**, 246 (1930).

[125] V. C. Macnabb, J. Opt. Soc. Am. and Rev. Sci. Inst. **19**, 33 (1929).

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.

E. R. Wagner[101] agrees with Macnabb in assuming that activation occurs by bombardment with ions produced in CO_2. From consideration of the magnitudes of the free energies involved in the different reactions he concludes that at 1000° C the dissociation of the carbonates to oxides is practically complete, but that the reduction of BaO by Ni would not occcur to a sufficient extent to account for the observed emission.

According to the views sponsored by Macnabb and Wagner, the activation by plate voltage (regarded as proof of the electrolytic formation theory) is therefore to be regarded as essentially a removal of adsorbed oxygen by sputtering with the positive ions of the gas. Dr. A. W. Hull has also suggested to the writer similar views on this subject. However, as mentioned in the following section, it is probable that at least in certain cases formation of barium by electrolysis also occurs to a considerable extent, and that while this process does not necessarily continue during the life of the filament, it furnishes the mechanism by which the barium is formed during the activation stage.

(3) *Formation of barium by electrolysis.* As shown by Reimann and Murgoci[105] the electrical conductivity of the oxide coating increases during activation at the same rate as the thermionic emissivity. Furthermore, "both the thermionic emission and the conductivity are 'poisoned' similarly by exposure of the oxide to (a) oxygen, (b) a discharge in carbon monoxide, and (c) a discharge in hydrogen. Complete recovery of the formed condition by re-forming is possibly only a few times in succession after poisonings by (a) and (b), but any number of times after poisoning by (c)."

Horton[126] and Spanner[115] observed that the electrical conductivity (c) of the oxides of the alkaline earth metals increase with the temperature according to an exponential law of the form

$$c = \alpha\epsilon^{-\beta/T} \tag{26}$$

where α and β are constant. Reimann and Murgoci found that for activated filaments the ratio $\beta/b = 1$ approximately, where b is the emission constant. It is evident that β corresponds to a heat of dissociation into ions and Span-

TABLE XXI. *Ionizing potentials (V_i); energy of dissociation (V_d) and work functions for oxides (Spanner).*

Oxide	V_i	Φ	V_d
BeO		3.45 volts	1.54 volts
MgO	7.61 volts	3.01	1.6
CaO	6.09	2.4	1.45
SrO	5.67	2.15	1.32
BaO	5.19	1.85	1.11

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[126] F. Horton, Phil. Mag. **11**, 505 (1906).

ner finds for this energy the values (expressed in electron volts) shown in Table XXI under V_d. The second column gives for comparison the ionizing potentials (V_i) of the metallic atoms, and the third column gives Spanner's values of Φ observed on the same cathodes that were used for determining V_d.

During electrolysis the barium ions (Ba^{++}) migrate to the core and after neutralization diffuse back towards the surface. Reimann and Murgoci assume that the oxygen ions (O^{--}) do not migrate although it is difficult to understand how the relatively heavier Ba^{++} ions can diffuse through the BaO lattice. Becker[103] concludes that in the initial stages an appreciable part of the current is carried by ions, but after the filament has been activated and barium is dispersed through the oxide (by diffusion) only a relatively small part (about 0.5 percent) of the current is carried by ions, and the rest is presumably carried by electrons through the coating.

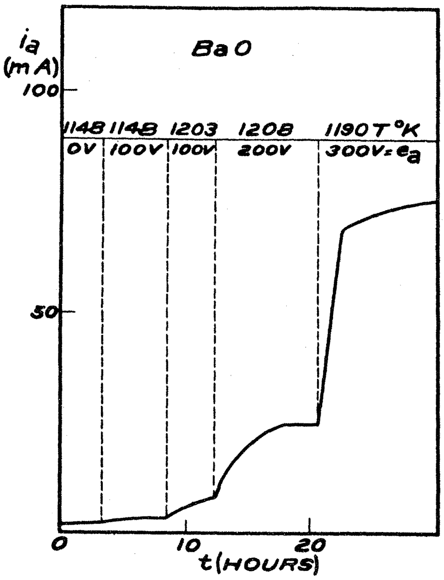

Fig. 12. Progress of activation of a BaO coating on platinum-iridium.

By sending electrons into a barium oxide coated filament, Becker has shown that "the amount of barium brought to the surface by electrolysis is directly proportional to the quantity of electricity sent into the filament."

(4) *Evolution of oxygen from oxide coated cathodes.* The evolution of oxygen during activation by application of plate current was observed by Horton[126] who actually found that in the initial stages the rate of evolution of gas is within eight percent of that required by Faraday's law. Rothe[110] also observed that gas is evolved during activation by application of plate current, and the same phenomenon has been remarked by Espe[102] and Detels[108]. The latter identified the gas as oxygen by collecting it and examining the

spectrum in a discharge tube. H. A. Barton[127] has demonstrated by positive ray analysis that doubly charged oxygen molecules (O_2^{--}) are evolved during activation.

It is therefore well established that in the process of activation by application of plate voltage and drawing electrons the oxide is decomposed like an electrolyte, with liberation of oxygen at the outer surface (towards the anode) and deposition of barium presumably on the core metal. The activity of the surface is thus increased until an equilibrium state is established between evaporation of barium, diffusion of the metal from the core, and recombination of barium and oxygen on the surface.

The effect of both increased cathode temperature and increased plate voltage during activation is illustrated by Fig. 12 taken from Espe's paper which shows the activation of a BaO coating on platinum-iridium. Fig. 13 shows the manner in which the emission increased with time when a plate voltage of 220 V was applied to a filament coated with a mixture of the oxides. The final emission current thus depends upon the temperature and plate voltage. A change in either of these variables is therefore followed by time changes in the emission until a new equilibrium state has been re-established (fatigue effects).

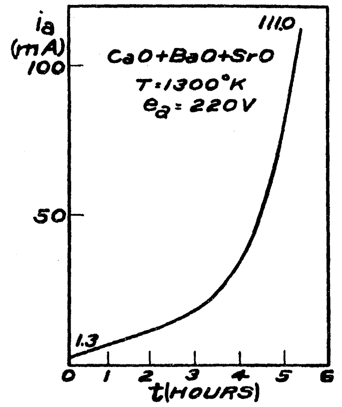

Fig. 13. Increase in emission of coated filament with 220 volts on plate.

(5) *Changes in emission constants during activation.* Before discussing in greater detail these fatigue effects observed with activated filaments, it is of interest to mention the observations on the variation in the constants A and b_0 during activation.

Espe observed that while b_0 remained fairly constant, A increased considerably. Fig. 14 shows plots of log $(i/T^{1/2})$ vs. $1/T$ taken on a SrO coating at an anode potential of 200 volts. "In curve I," he states, "the cathode was but slightly electrolyzed in advance, so that comparatively few pure metal particles could be present. Consequently, the quantity A is very low to

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[127] H. A. Barton, Phys. Rev. **26**, 360 (1925).

begin with, but grows very rapidly during the measurements at higher temperatures as is brought out in the next measurement (curve II). The increase continues in the subsequent measurement (curve III) until we reach stable conditions and the curve becomes capable of reproduction. If the anode potential is raised to 300 volts, the intermediate period of adjustment is followed by a final state which gives curve IV. The latter curve can be reproduced and is parallel to curve III. While the curves I and II would give entirely wrong results, the curves III and IV give fully reliable data."

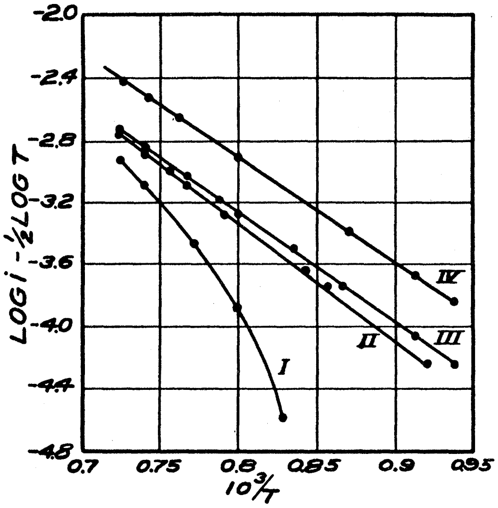

Fig. 14. Emission characteristics of a filament coated with SrO.

On the other hand, Detels has observed that both A and b_0 decrease during activation. Fig. 15 shows plots of log (I/T^2) vs. $1/T$ taken at intervals of two hours during formation with a plate current of 70 to 100 milliamperes and voltage of approximately 100. The numbers on the plots indicate the order. Thus curve V was taken after four and a half hours' run, and the other curves at subsequent periods (up to 3 days). A plot of Φ_0 vs. log A, such as shown in Fig. 16 indicates that the decrease in log A was approximately proportional to that in Φ_0. Thus A varied from 10^{15} to 10^{16} at the beginning to 9.3×10^{-4} at the end, while Φ_0 decreased from 7 to 1.36 volts.

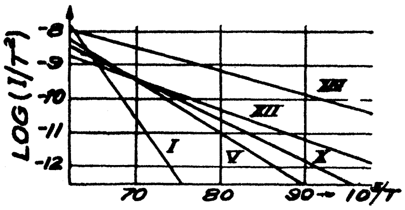

Fig. 15. Showing that both A and b_0 decrease during activation.

Similar observations were made with oxidized nickel wires covered with alkaline earth oxides. The values of A and Φ_0 during formation are given in Table XXII.

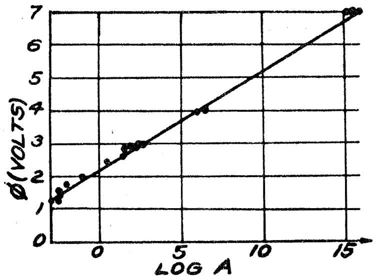

Fig. 16. Showing that during activation the decrease in log A is practically proportional to that in ϕ_0.

We shall now proceed to discuss the different processes which apparently occur in activated filaments and govern the observed electronic emissivity.

TABLE XXII. *Variation in emission constants during activation of oxide coated nickel (Detels).*

Time (hours)	Φ_0 (volts)	A(amps/cm^2. deg.^{2})
$\frac{1}{6}$	2.37	27.5
$1\frac{1}{2}$	1.83	1.24
2	1.36	0.0373
$2\frac{1}{4}$	1.36	0.0297

(6) *Evaporation of barium.* Becker[103] has shown that a pure tungsten filament adjacent to an activated coated filament maintained at a temperature above 1250° K increases enormously in activity owing to evaporation of barium from the oxide coating. Fig. 1, to which reference has been made in a previous section, from Becker's paper, shows the increase in emission from the tungsten filament with increase in θ. The temperature of evaporation was 1260° K. On glowing the tungsten filament to 1700° K, the barium was removed completely.

J. M. Eglin[116] finds that the rate of evaporation of barium from a coated filament produced by the azide process is of the order of 10^{-9} of that of barium in bulk. That is, the adsorbed barium, like thorium or calcium on tungsten, has an extremely low rate of evaporation as compared with the metal itself.

At higher temperatures *BaO molecules evaporate* along with barium atoms. C. Davisson (quoted by Arnold[96]) found that the rate of evaporation of the oxide is given by the relation

$$m = 4.6 \times 10^8 T^{1/2} \epsilon^{-46000/T}$$

where m = rate in gr/cm^2 sec.

C. Zwikker[127a] has also reported data obtained by Reernik which give a

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[127a] C. Zwikker, Physica 8, 241 (1928).

considerably higher rate of evaporation at the same temperature. (A plot of the two sets of data is given by Becker.)

C. Davisson and H. A. Pidgeon[128] found by evaporating barium oxide from a coated filament at 1373° K to an adjacent tungsten filament that the emission from the latter was increased by a factor 10^9 and "that the maximum emission occurs when there are approximately 2.4×10^{14}molecules BaO per cm^2 of secondary. This is reckoned to be not more than 30 percent of the number required to form a layer one molecule deep."

(7) *Evaporation and diffusion of oxygen.* According to Becker, "When current is drawn from a coated filament at a sufficiently high temperature and if this current is not limited by space charge, oxygen evaporates." The evolution of this gas was measured by the decrease in activity of an adjacent tungsten filament. In this manner it was found possible to determine the factors upon which the rate of evaporation of oxygen depends. "Such experiments," Becker states, "have shown that the rate of oxygen evaporation increases with (1) the temperature of the filament, (2) the amount of current drawn from it, (3) the plate potential, and (4) the composition or state of the oxide."

It should be mentioned in this connection that Espe and others have observed that in well-exhausted tubes with oxide coated cathodes Langmuir's space charge relation, viz., that the space current varies as $V^{3/2}$, is applicable, thus proving not only the absence of positively charged ions, but also that absence of sharp saturation for the emission is not due to the presence of residual gas. Therefore any oxygen liberated during the operation of the tube must be either negatively charged or else "cleaned up" by the barium on the surface of the cathode and on the walls of the tube (by evaporation from the cathode).

Becker has also given evidence for assuming that oxygen diffuses from the surface into the oxide and presumably recombines to some extent with the barium diffusing from the surface of the core.

(8) *Diffusion of barium in the oxide.* The barium deposited on the oxide core interface must reach the outer surface by diffusion. As Becker points out a semi-quantitative proof of diffusion is based on the life of oxide coated filaments. From the total amount of electricity carried through the core during a life of 15,000 hours he finds, on the theory that only 0.001 of the current is carried by ions, that over 9×10^6 layers of barium should be deposited at the core surface. Since there are actually only about 2×10^4 layers of oxide on a filament and only a portion of these disappear during the life, it is concluded that "by far the largest part, about 0.998, of the barium which is produced by electrolysis must diffuse into the oxide, and must recombine with oxygen to form barium oxide."

Reimann and Murgoci have suggested that the barium deposited on the core diffuses back to the surface along the surfaces of the oxide crystals, in analogy with the diffusion of thorium along grain boundaries in the case of

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[128] C. Davisson and H. A. Pidgeon, Phys. Rev. **15**, 553 (1920).

thoriated tungsten filaments. This *theory of barium circulation*, that is, that the barium migrates to the core as ions and returns to the surface along the surfaces of the oxide crystals, leads to the conclusion, based on the observed life of oxide coated filaments, that the average life of an adsorbed atom of barium on the surface is of the order of 10^{-3} seconds. "This result," they point out, "is in excellent agreement with the value (also 10^{-3} seconds) calculated by W. Schottky[129] from J. B. Johnson's[130] measurements of the 'flicker' of oxide cathodes. Incidentally it is plain that Schottky's result when considered in conjunction with the great length of life of oxide cathodes, constitutes independent evidence in support of an essential part of our theory, viz., the repeated appearance of the same particles of barium at the emitting crystal surface."

On this basis, "the concentration of the film is determined, in any given case, by the requirement of statistical equilibrium between the rate of removal of the barium atoms from the emitting surface (as ions) and the rate of their replenishment by diffusion." Also this theory offers an explanation of the forming and poisoning of the conductivity under conditions in which the emission is also formed or poisoned. "Conductivity and emission are formed and poisoned together, simply because they both depend on the same thing, viz., the presence of uncombined barium at the surface of the crystals."

(9) *Effect of oxygen on the activity*. As Becker remarks, "It is a well known fact that when current is drawn from a coated filament the activity of this filament changes rapidly at first and then more and more slowly. The magnitude and even the direction of the change in activity depend greatly upon the composition of the oxide, the plate potential, the degree of break-down (activation) and the temperature of the filament. For a well broken down (activated) filament we have invariably found that the activity decreases rapidly and then more and more slowly. . . . . It was shown above that if the temperature and the plate potential are high, oxygen is formed by electrolysis and evaporates. Presumably, therefore, the decay in activity is caused by oxygen which has come to the surface and some of which stays there because the temperature does not remove it rapidly. Because of its electron affinity, some of the oxygen should be negatively charged and if the oxygen stays on top of the surface layer of barium, it should produce electrical fields which hinder the escape of electrons. Consequently the activity should decrease. If more and more oxygen is brought to the surface, the rate at which it disappears from the surface either by evaporation or diffusion should increase rapidly until the rate of disappearance is equal to the rate of production. We thus have a satisfactory picture of the cause of the decay in activity when current is drawn."

Becker does not believe that oxygen on the surface combines with the barium, since a deactivated filament (due to oxygen on the surface) can be

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[129] W. Schottky, Phys. Rev. **28**, 74 (1926).

[130] J. B. Johnson, Phys. Rev. **26**, 71 (1925).

restored by glowing at a high temperature, such as 1200° K, at which temperature the oxygen leaves the surface by evaporation.

It is difficult to believe, however, in view of the fact that adsorbed oxygen on thorium, cerium and other rare earth metals forms layers which are stable even at extremely high temperatures, that films of oxygen on barium can be removed by heating at such a relatively low temperature. Is it not possible that in Becker's experiments the restored activity is due to increased rate of diffusion of barium from inside the coating?

Other observations on filaments which have not been activated lead Becker to conclude that, "From analogy with caesium on tungsten it is to be expected that a little oxygen increases the activity, while more oxygen decreases it. Whether the activity is increased or decreased depends upon just where the oxygen is located with reference to the surface barium atoms. If the oxygen is beneath the barium layer, the activity is raised because the negative oxygen induces more positive barium ions and the moment of the additional barium ions and their images more than counterbalances the moment of the oxygen ions and images. If, on the other hand, the oxygen is on top of the surface layer of barium, the activity is decreased because now the moment due to the oxygen is greater than the moment due to the barium.

"By combining the hypothesis with the experimental facts we may draw the following conclusions: oxygen is deposited by electrolysis just beneath the partial surface layer of metallic barium or strontium. If the temperature is high enough some or all of this oxygen rather rapidly arrives at the top of the barium layer where it forms an outer oxygen layer which is a more stable layer than the inner oxygen layer. If the temperature is low enough the first oxygen that is deposited stays in the inner layer. As the oxygen concentration increases, the field tending to pull electrons and negative oxygen ions toward the plane of the barium ions increases and some of the oxygen reaches the top of the barium layer. At the peak the factors tending to increase the activity are balanced by those tending to decrease it. Beyond the peak the net result of electrolysis is the increase in concentration of the outer layer of oxygen. We believe that some of the oxygen also diffuses inward into the oxide. If the filament is glowed either before or after the peak, oxygen leaves the inner layer; it reaches the outer layer or diffuses into the oxide."

(10) *Theories of transfer of electrons in coating and effect on work function.* Reimann and Murgoci conclude from their experiments that, "The coating is probably in very imperfect contact with the core metal, so that the space current passes from core metal to coating mainly in the form of thermionically emitted electrons." Thus the electrons are emitted from the barium *adsorbed on the core.* On the basis of this theory, "it is seen that it is *á priori* by no means certain whether the Richardson straight line represents the thermionic properties of the contaminated core-metal or those of the coating. Either the core metal emits electrons at a greater rate than the coating can re-emit them, in which case a fraction of the electrons emitted by the core-metal returns to it, or else the coating emits more electrons than it receives

from the core metal, so that it re-absorbs a fraction of them. In other words, the thermionic emission of the cathode as a whole is limited either by the coating or by the core metal, whichever of the two systems in series has the lesser thermionic emissivity.

"It appears that, at least in certain cases, it is the contaminated core-metal, and not the coating, by which the emission is limited. Since, according to our assumption, the coating receives as many electrons from the space that separates it from the core-metal as it permanently loses, by re-emission, from its outer surface, there can be no net heat loss from the coating, and the only cooling that the cathode will suffer by its electron emission will be that due to the evaporation of electrons from the contaminated core metal. The work-function of the cathode, calculated from the latent heat of evaporation of electrons, will therefore in any case be that of the contaminated core-metal. Occasional comparisons have been made, e.g., by Davisson and Germer,[107] between the work-function measured in this way and that determined from the slope of the Richardson straight line, and the two determinations have been found to be in good agreement. But we have already seen that the slope of the Richardson straight line corresponds to the work-function of whichever of the two systems (core metal or coating) has the lesser emissivity. Thus in those cases where there is agreement between the work-functions determined by the two methods, we may conclude that, if the coating is indeed in poor contact with the core metal, it is the core metal which limits the emission. This conclusion accords well with the fact of experience that the nature of the core metal has a considerable influence on the thermionic properties of coated cathodes."

On the other hand, if the unit of barium circulation in the coating is made large enough, the emission becomes limited by the coating. The gradual increase in size of the crystals of oxide during life would thus lead to a decrease in emission because of reduction in the number of grain boundaries along which diffusion of barium may occur. Under these conditions, "the temperature variation of the emission may not be a measure of the true work function at all, the surface concentration of barium being different at each temperature. The relative importance of this falsification of the work function measurements will depend upon the size of the units of barium circulation."

Lowry's views on the mechanism of electron transfer also involve the hypothesis that the *barium forms an adsorbed layer on the core.* Therefore, the electrons emitted from the latter must diffuse through the interstices in the oxide coating, "which, however, does offer some impedance to their progress." As Lowry remarks, "These coatings are very porous. When viewed through a microscope they have the appearance of a light fluffy fall of snow. . . . . Suppose now that this coating should become more compact so that its pores are partially closed. The natural consequence would be that the apparent activity of the filament would be measurably impaired. This is precisely the type of phenomenon that does occur. It is well known that *glowing the filament for a comparatively short interval of time at a con-*

siderable overvoltage will practically ruin its emission. It has been the author's experience, at least, that a filament which has been so mistreated cannot, in general, be reactivated to anything like its original characteristics. It is also true that such filaments will, after such reactivation as is possible, *yield large emissions if very high anode voltages are applied.* The net result of such an overheating of a filament is essentially to increase the impedance of the tube by an appreciable amount. This we believe to be caused by a partial closing of the pores of the coating. Preliminary microscopic examination of some such filaments actually showed a sintering or glazing of the coating until it had the appearance of a crackled enamel.

"Exactly similar behavior is shown by filaments whose activity has gradually decreased during a long period of use. Such worn out filaments always retain an appreciable amount of coating. In fact, a fairly close inspection shows that they still possess nearly as thick a layer of oxide as they had initially. In this case also large emissions may be drawn if sufficiently high anode voltages are applied.

"If the loss of activity in these cases were due solely to a loss of metallic barium due to vaporization, it should be possible to cause these filaments to regain all their initial activity by electrolysis or by positive ion bombardment. As stated above, it is rarely, if ever, that it is possible to do this.

"*The process of electron diffusion through a porous,* poorly conductive coating may also explain the *phenomenon of non saturation* which is commonly met with in this type of cathode. It follows logically that large numbers of electrons will become enmeshed in the pores of the coating or occluded on the surface of the particles of poorly conducting material composing it. It is quite possible also that the numbers of electrons so entrapped will vary somewhat with the anode voltage applied. This process will give rise to an effect similar to a negative space charge within the confines of the coating itself. The space currents obtainable then at any given anode voltage and filament temperature represent the number of electrons per second it is possible to drag out of or through this negative charge built up within the coating layer. The result will be that much higher anode voltages will be required to approach a saturation than if this pseudo space charge did not exist. At temperatures in the neighborhood of 1000° C the electron emission from these filaments is so enormous that it is next to impossible to obtain anything approaching saturation owing to the very considerable heating effects of the emission itself. At these temperatures also the conductivity of the coatings will be increased appreciably, affording a better opportunity for the electron charge to leak off."*

Thus Lowry's arguments for assuming that barium is adsorbed on the core rather than on the oxide are two fold: (1) the fact that the nature of the core affects the emission, since at the same temperature the emission from coated Konel filaments is considerably greater than that obtained from coated platinum filaments, (2) the observed decay in emission during life

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* The italicized portions are due to the writer.

can be interpreted only as due to a gradual sintering of the coating which results in increased "impedance" to the passage of electrons from the barium film on the core.

Concluding remarks on oxide coated cathodes

It is evident from the foregoing remarks that there are a great many contradictory opinions regarding the interpretation of activation and emission phenomena observed with this type of cathode. That the active source of electrons is a monatomic film of barium is apparently certain, but one school holds the opinion that the barium is adsorbed on the surface of the oxide, while the other school advances equally cogent reasons for believing that the adsorbed layer is formed on the core underneath the oxide.

Regarding the process of activation, there are three different suggestions (1) electrolysis of the oxide, (2) thermal reaction of the oxide with core material, and (3) bombardment by positive ions. It would seem most probable that the exact mechanism of activation actually varies with the composition of the core material and the manner in which the oxide is deposited on this core, so that while certain types of filaments require anode voltage for activation, with or without the presence of positive ions, other types can certainly be activated by purely thermal methods.

The similarity, at least in certain respects, between the phenomena observed with oxide coated filaments and those observed with oxidized tungsten filaments on which caesium has been deposited, on the one hand, and with thoriated tungsten on the other, is certainly significant. An analogy to oxide-coated cathodes may also be found in the phenomena observed with certain types of photoelectric surfaces, such as caesium on oxidized silver, or copper oxide on copper. In a very interesting paper, Wo. Ostwald[131] has pointed out that combinations of metal+oxide, or metal+alkali or alkaline earth oxide act not only as sources of electrons photoelectrically, but also as rectifiers and as contact catalysts. He regards all these as "disperse systems possessing low work functions for electron emission" which is presumably due to the strong field of force exerted by the oxygen atoms. These ideas are certainly extremely suggestive, and should promise an incentive for further investigation in this field.

VII Effect of Gases and Positive Ion Bombardment on Electron Emission

The earlier investigations (1903–1913)[132] dealt mainly with the effect of a hydrogen atmosphere on the emission from platinum. Since decrease in pressure and degassing of the metal led to a decrease in emission, it was concluded that the emission phenomenon itself is due to chemical reactions in presence of residual gases. Langmuir's investigations (1913 and subsequently) showed that in case of tungsten, improvement in vacuum actually increased the emission to a perfectly definite value, if care was taken to

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[131] Wo. Ostwald, Kolloid Zeits. **51**, 370 (1930).

[132] These are discussed very fully by Richardson, loc. cit., Chap. 4.

eliminate at the same time effects due to space charge. Langmuir also studied the effect of low pressures of various gases on the emission from tungsten, and subsequent investigators have reported results observed with other emittors.[133] While a number of these observations have been mentioned incidentally in previous sections in connection with the discussion of emission constants, they are discussed more fully in the present section.

The effects of gases on the emission are of a two-fold nature. Firstly, they may form *adsorbed monomolecular* or *monatomic* films on the surface of the cathode. Secondly, and especially with anode voltages in excess of a certain critical value, (which varies with the nature of the gas) positive ions are formed which sputter atoms off the surface of the emitter and may thus affect the emission considerably.

The theory of the formation of monomolecular films was proposed by Langmuir in 1914[134] and was elaborated more completely in a subsequent paper, published in 1918,[135] from which the following remarks are of interest: "When gas molecules impinge against any solid or liquid surface, they do not, in general, rebound elastically, but condense on the surface, being held by the field of force of the surface atoms. These molecules may subsequently evaporate from the surface.[136] The length of time that elapses between the condensation of a molecule and its subsequent evaporation depends on the intensity of the surface forces. Adsorption is the direct result of this time lag. If the surface forces are relatively intense, evaporation will take place at only a negligible rate, so that the surface of the solid becomes completely covered with a layer of molecules. In cases of true adsorption this layer will usually be not more than one molecule deep, for as soon as the surface becomes covered by a single layer, the surface forces are chemically saturated. Where, on the other hand, the surface forces are weak, the evaporation may occur so soon after condensation that only a small fraction of the surface becomes covered by a single layer of adsorbed molecules."

The fraction of the surface covered, denoted by θ, is therefore a function of the rates of formation and of destruction of the film. It varies with the temperature, nature of both gas and solid surface, and with the rate of positive ion bombardment. Hence the amount by which the electron emission is affected depends upon the value of θ for the particular adsorbed layer. The phenomena thus resemble those described already in connection with the discussion of monatomic films of thorium, caesium and barium.

The effect of gases on the emission from *tungsten* has been discussed very fully by Langmuir.[137] Table XXIII illustrates the results obtained for different gases. As has been mentioned previously, oxygen decreases the

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[133] These have been summarized by Schottky and Rothe in their treatise, pp. 204–210.

[134] I. Langmuir, Phys. Zeits. **15**, 520 (1914).

[135] I. Langmuir, J. Am. Chem. Soc. **40**, 1361 (1918).

[136] This condensation-evaporation theory is more fully discussed in Phys. Rev. **8**, 149 (1916).

[137] To the references given above should be added the review in J. Am. Chem. Soc. **38**, 2221 (1916).

TABLE XXIII. *Effect of gases on emission from tungsten.*

Gas	Pressure in mm Hg	a	$b\times10^{-4}$	References
Vacuum	0.00007	1.62×10^{-2}	5.55	(8)
H_2	.012	2.58×10^{2}	8.25	(8)
	.007	3.63×10^{9}	11.5	
	.0017	3.67×10^{7}	10.5	
	.0005	2.05×10^{3}	8.5	
N_2	.002	10.5	7.32	(8)
		7.95×10^{-1}	6.82	
O_2		3.25×10^{4}	9.43	(8)
		A	$b_0\times10^{-4}$	
O_2		5×10^{11}	10.7	(10a)

emission from tungsten enormously ($1:10^{-5}$). It forms adsorbed layers which are quite stable up to temperatures of 1800° K.

In the case of hydrogen, the observed effects are probably due to the indirect formation of oxygen. Thus the hydrogen reduces traces of oxides on the leads and this is dissociated in presence of the heated filament to form oxygen which is adsorbed on the surface. This reaction has long been familiar in lamp manufacture as a cause of early blackening.

"Nitrogen has no effect on the electron emission from tungsten if low voltages are used in making the measurements of the thermionic current. But if voltages high enough to cause ionization of the nitrogen are employed, then the tungsten is attacked by rapidly moving positive nitrogen ions, and simultaneously, the electron emission is greatly decreased, indicating that a film of adsorbed nitrogen is formed. If the filament is now allowed to cool to room temperature and the remaining nitrogen is pumped out, and the filament is then heated again to the same temperature as before, it is found that the electron emission is at first the same as it was in the presence of nitrogen, showing that the electron emission is determined not by the gas around the filament, but by the film adsorbed on it. Gradually the adsorbed film distills off, and the electron emission returns to its normal value."[138]

Carbon monoxide and carbon dioxide have the same effect as oxygen. Hydrocarbon vapors give up carbon to heated tungsten filaments with formation of carbides.[139] As a result the emission is decreased to approximately one third. As mentioned by Langmuir, "A filament which has taken up carbon is no longer sensitive to the effect of bombardment by positive nitrogen ions. In other words, nitrogen has no effect on the electron emission from such a filament even if high anode voltages are used. Still more remarkable is the fact that oxygen instead of lowering the electron emission of a carbon-containing filament gradually raises it. The carbon is then gradually oxidized and the electron emission returns to the value corresponding to

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[138] However, some very recent experiments (which will be described in a forthcoming publication) have led Dr. Langmuir to the conclusion that the adsorbed film is formed, not by nitrogen, but by oxygen liberated from oxides on the filament leads by active nitrogen.

[139] M. R. Andrews, Jr. Phys. Chem. **27**, 270 (1923); M. R. Andrews and S. Dushman, Jr. Phys. Chem. **29**, 462 (1925).

pure tungsten. Then when the carbon has all been removed, the oxygen begins to attack the tungsten and the electron emission suddenly decreases to one percent or less of its former value. After the excess oxygen has been consumed it is found that the electron emission is again sensitive to the effect of bombardment by positive nitrogen ions, the thermionic current decreasing as the voltage is raised."

The effect of oxygen on activated *thoriated tungsten* is even more permanent than in the case of pure tungsten. Only by flashing to 2900° K can the thorium oxide be volatilized. It is then necessary to treat the filament at 2300° K in order to reactivate it. The effect of oxygen on a monatomic film of thorium occurs at such low pressures that it was only in presence of the extremely high vacuum produced by volatilizing tungsten with the bulb immersed in liquid air that Langmuir was able to obtain thorium emission in his first experiments. Subsequently it was found that the residual oxygen could be eliminated by other "getters" such as potassium, magnesium, calcium, etc., volatilized on the bulb walls, and this method made it possible to produce commercial radio tubes using this type of cathode.

It is instructive to realize that even at the lowest pressures ordinarily attained under best exhaust conditions the rate at which oxygen can condense on any surface is extremely high. According to the kinetic theory of gases, the number of molecules striking 1 square centimeter per second is given by

$$n = \frac{1}{4} n_0 \left(\frac{8RT}{\pi M} \right)^{1/2}$$

where n_0 = number per cm^3 at temperature T,
M = molecular weight of gas.

In the case of oxygen at 25°C and 1 mm pressure, $n = 3.623 \times 10^{20}$ molecules/cm^2 sec. Assuming, as deduced by Langmuir, that for thorium films on tungsten, the number of atoms per cm^2, $N_0 = 7.56 \times 10^{14}$, and that 1 molecule of oxygen is adsorbed for every atom of thorium, it is evident that even at 2×10^{-6} mm pressure, *it would require only one second* to cover a thorium film completely with oxygen. Hence in order to obtain a life of several thousand hours, as is actually obtained with such filaments, the residual oxygen pressure must be less than 10^{-9} dyne/cm^2 or 10^{-15} atmospheres.

It is this type of phenomenon that makes it so difficult to obtain emission data from absolutely clean surfaces of metals. Even if the pressure is reduced to an extremely low value, and the surface has been cleaned by heating at a high temperature, there is no assurance that on cooling to lower temperatures no adsorbed layers will be formed by condensation of the residual gases.[140]

In the case of *thoriated tungsten*, Kingdon[10] has shown that nitrogen at a pressure of 0.0001 to 0.005 mm causes an approximately five-fold increase is emission.

The effects of oxygen and other gases on *molybdenum* are very similar

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[140] S. Dushman, "High Vacuum."

to those observed with tungsten. Since MoO_3 is less volatile than WO_3, it is much more difficult to obtain clean molybdenum surfaces than in the case of tungsten. In this connection it should be observed that according to the calorimetric determinations made by Van Voorhis[141] the work function for molybdenum is apparently between 0.75 and 1.00 volt higher in presence of nitrogen and argon.

Tantalum oxide also is extremely non-volatile and therefore the emission from tantalum wire which has not been heated to a high temperature is very low. R. Suhrmann[142] observed that continued heating of a tantalum filament led to a decrease in emission. The emission constants obtained for filaments in different states of degassing are shown in Table XXIV.

TABLE XXIV. *Effect of gas on emission from tantalum.*

	a	$b \times 10^{-4}$	Φ (volt)
Partly degassed	1.19×10^5	3.64	3.14
More completely degassed	3.61×10^4	3.64	3.14

According to H. Simon[143] hydrogen increases the emission from tantalum, which would account for Suhrmann's observations. Schottky[144] points out that tantalum becomes brittle in hydrogen, and that its resistance changes. Apparently a hydride is formed on the surface and Φ is thereby decreased, as in the case of platinum.

The increase in emission from *platinum* in presence of hydrogen has been mentioned above. The earliest observations were made by H. A. Wilson and O. W. Richardson, while more recent investigations have been carried out by L. Lockrow,[145] R. Suhrmann,[146] and L. A. DuBridge.[147] The last two have also determined the effect of gas on the photoelectric threshold frequency (ν_0). The concurrent values of emission constants given in Table V, especially the observations of DuBridge, show that the emission for degassed platinum is extremely small as compared with that for platinum in hydrogen. Table XXV gives additional values observed by Suhrmann and Lockrow for filaments which were only partly outgassed.

TABLE XXV. *Effect of gas on emission from platinum.*

Author	a	$b \times 10^{-4}$	A	$b_0 \times 10^{-4}$	Φ_0
Suhrmann	7.59×10^8	5.79	(less degassed)		4.99
	1.21×10^7	5.31	(more degassed)		4.57
Lockrow	3.02×10^3	4.60	1.36×10^{-2}	4.40	3.87
	9.90×10^3	5.20	4.46×10^{-2}	5.00	4.31
	9.7×10^8	5.84	(in hydrocarbon vapor)		

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[141] Van Voorhis, Phys. Rev. **30,** 318 (1927).

[142] R. Suhrmann, Zeits. f. Physik **13,** 17 (1923).

[143] H. Simon, Zeits. f. techn. Phys. **8,** 434 (1927).

[144] Schottky, Handbuch, p. 209.

[145] L. Lockrow, Phys. Rev. **19,** 97 (1922).

[146] R. Suhrmann, Zeits. f. Physik **13,** 17 (1923).

[147] L. A. DuBridge, Phys. Rev. **29,** 451 (1927); **31,** 236 (1928).

Suhrmann[148] observed that with increase in period of heat treatment, ν_0 increased from a minimum value corresponding to $\Phi_0=4.14$ to a constant maximum value which corresponded to $\Phi_0=4.62$. In the case of silver, a similar decrease was noted from $\Phi_0=4.72$ to $\Phi_0=4.28$, while in that of gold the threshold frequency showed only slight variation from $\Phi_0=4.72$. The observations made by DuBridge on the effect of gases on the photoelectric threshold frequency for platinum are much more complete and are discussed in a subsequent section.

The progressive decrease with ageing in the constants A and b_0 for *zirconium* and *hafnium* observed by C. Zwikker[149] have been mentioned previously. Traces of oxides cause an increase in both constants as compared with those for pure metals. The same conclusion holds valid for the alkali and alkaline earth metals.

The effect of oxygen, carbon monoxide and dioxide in "poisoning" the emission from fully activated *oxide coated cathodes* has been discussed already. It is evident that any gas which tends to form an adsorbed layer on top of the barium atoms must tend to decrease the emission. On the other hand, if this gas forms a film *under* the barium, it may increase the emission. This probably accounts for so many discrepant observations recorded by different investigators on the effect of oxygen on the emission from this type of cathode. No systematic investigations have been published on the effect of gases on the emission constants from coated filaments, but probably the variation in emission actually observed is to be ascribed, partly at least, to effect of residual oxygen in the bulbs. Koller[99] has shown that in presence of even 0.005 mm oxygen, A is increased from 1.07×10^{-3} to 4.27×10^{3}, and b_0 from 12,100 to 35,900.

TABLE XXVI. *Sputtering data for thorium on tungsten in various gases.*

Ion	V_0	n at 150 volts
H	>600	0.000
He	(about) 35	.00015
Ne	45	.023
Ar	47	.080
Cs	52	.084
Hg	55	.044

The effect of bombardment by *positive ions* of nitrogen on the emission from pure tungsten has been mentioned already. On the other hand, mercury, argon and other rare gases have no effect whatever on the emission. In fact, positive ions of these gases sputter off any films due to adsorbed films of oxygen or other gases, so that in presence of traces of mercury, oxygen has no appreciable effect on the emission.

The removal of thorium from monatomic films on tungsten, by positive ion bombardment, has been investigated by K. H. Kingdon and I. Lang-

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[148] R. Suhrmann, Zeits. f. Physik **33**, 63 (1925).

[149] C. Zwikker, Phys. Zeits. **30**, 578 (1929).

muir.[105] While hydrogen ions produce no sputtering even up to 600 volts energy, ions of A, Cs, Hg and Ne all start to sputter the thorium ions at about 50 volts energy. Table XXVI shows the results obtained with ions of 150 volts energy. V_0 denotes the threshold voltage for sputtering, and n denotes the ratio of the number of thorium atoms removed to number of ions. In these experiments the thoriated tungsten filament was maintained cold.

A. W. Hull[150] has observed that with hot filaments and large positive ion currents, the threshold voltages are somewhat lower, viz: 27 volts for Ne, 25 for A and 22 for Hg. "These values are independent of temperature over the range 1900–2300°K." Fig. 17, taken from Hull's paper, shows the characteristics of a thoriated tungsten filament in mercury vapor at about 0.005 mm. At low voltages the electron current is limited by space charge. As the voltage is increased above the ionizing potential of the gas, the emission increases rapidly at first, but decreases as soon as the voltage rises above the threshold value for sputtering.

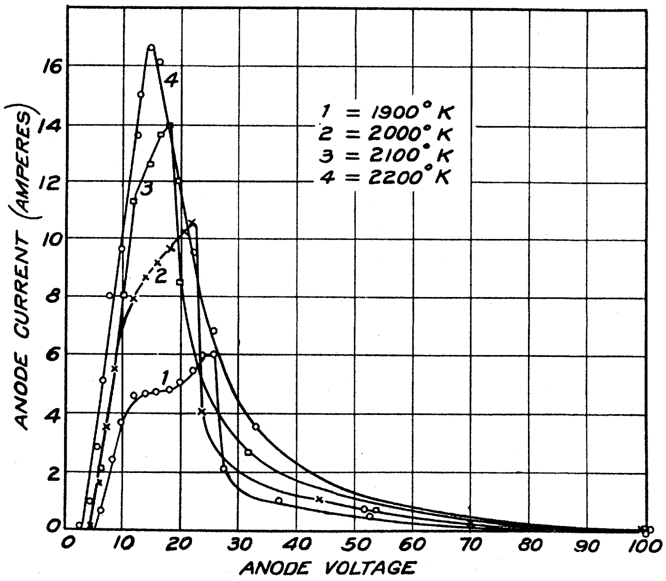

Fig. 17. Characteristics of a thoriated filament in mercury vapor at 0.005 mm pressure.

Similar observations have been made by Dr. Hull and other investigators in this laboratory, with oxide coated cathodes of the "unipotential" type. In all cases "disintegration (of the emitting film) does not occur when the voltage is below a critical value," and it is because of the existence of this phenomenon that it has been found possible to construct gaseous discharge tubes using hot cathodes, with a consequent extremely low cathode drop.[151]

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[150] A. W. Hull, Trans. A. I. E. E. **47**, 753 (1928).

[151] Hull, Reference 150, C. G. Found and J. Forney, Trans. A. I. E. E., **47**, 747 (1928).

VIII. PHOTOELECTRIC THRESHOLD AND THERMIONIC WORK FUNCTION[152]

The maximum kinetic energy, ($\frac{1}{2}mv^2$), of electrons emitted from a surface by monochromatic radiation of frequency ν, is given by Einstein's relation

$$\tfrac{1}{2}mv^2 = h\nu - P = h(\nu - \nu_0) \tag{27a}$$

where $P = h\nu_0$ is the work which must be done by the electrons in overcoming surface forces. The frequency, $\nu_0 = P/h$, is known as the *threshold frequency*, and is related to the work-function, Φ_0, by the equation

$$\Phi_0 \epsilon = h\nu_0$$

that is

$$\Phi_0 = \frac{\nu_0}{8106 \times 3 \times 10^{10}} = \frac{12336}{\lambda_0} \tag{28}$$

where Φ_0 is expressed in volts, and λ_0 is the wave-length in Angstroms.

The energy of the emitted electrons is determined by measurements on the potential, V, required to retard them to zero, and by plotting V against corresponding values of ν, the value of ν_0 is determined from the intercept on the axis of ν, in accordance with the relations

$$\begin{aligned} V\epsilon &= \tfrac{1}{2}mv^2 \\ &= h(\nu - \nu_0) \end{aligned} \tag{27b}$$

While there have been published a large number of results for threshold frequencies for different metals, most of these results were obtained on sur-

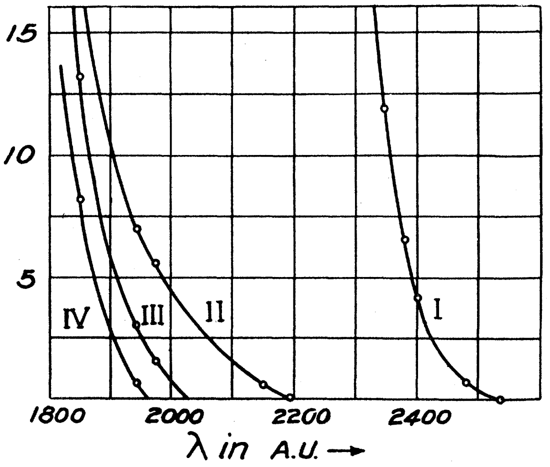

Fig. 18. Photoelectric emission of platinum as function of wave-length for various stages in outgassing.

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[152] The writer wishes to acknowledge his indebtedness in this connection to Dr. A. L. Hughes and Dr. L. A. DuBridge for permission to use the material in the chapter on this subject in their forthcoming volume on "Photo-electricity."

faces which were not cleaned and only in a relatively few cases have attempts been make to measure the photoelectric frequency, ν_0, and the thermionic work function, Φ_0, on the *same* surface.

By far the most careful investigation of this nature has been carried out by L. A. DuBridge[153] on platinum. Figs. 18 and 19 show the photoelectric and thermionic curves respectively for the metal during successive stages of outgassing by heating. Curve I, taken with a fresh specimen shows a threshold at 2540A (corresponding to 4.86 volts). The value of Φ_0 under similar conditions was 4.7 volts. Continued degassing caused a decrease in λ_0 and increase in Φ_0, and the final values as shown in curves *V* and 5 are 1962A (corresponding to 6.30 volts) and $\Phi_0 = 6.35$ volts. This result thus established the conclusion that for a *thoroughly degassed metal the photoelectric and thermionic work-function are identical.*

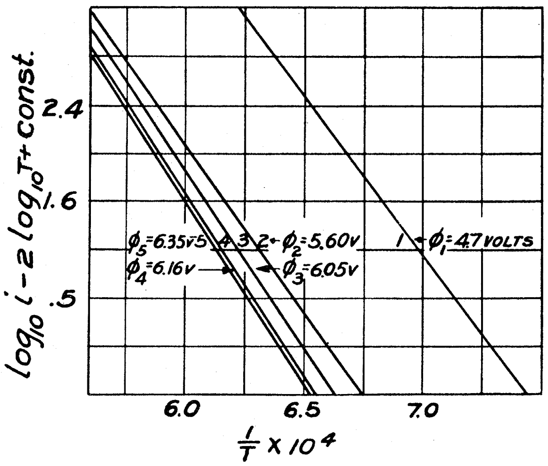

Fig. 19. Thermionic emission of platinum during various stages in outgassing.

These measurements, together with those obtained by other investigators are given in Table XXVII. The numbers in brackets give the corresponding references. In the following paragraphs these results are discussed at further length. The values observed by M. J. Martin[154] on molybdenum are low. The only explanation that can be suggested is that some impurity having a lower value of Φ_0 was present in the metal and was not eliminated at the highest temperatures to which the metal was heated in these experiments (approximately 1800°K, whereas in Dushman's experiments the metal was heated to about 2500°K). Martin also observed that "the photoelectric sensitivity showed a decrease with rise in temperature in the range from 0°C to 1000°C."

A. H. Warner[155] investigated the photoelectric behavior of degassed tung-

[153] L. A. DuBridge, Phys. Rev. **31**, 236 (1928); **29**, 451 (1927).

[154] M. J. Martin, Phys. Rev. **33**, 991 (1929).

[155] A. H. Warner, Phys. Rev. **33**, 815 (1929); Proc. Nat. Acad. **13**, 56 (1927).

sten. The long wave limit was found to be 2570 ± 50A, (4.80 volts), and was independent of temperature. This is to be compared with the thermionic value, 4.52 volts.

TABLE XXVII. *Photoelectric determination of* Φ_0.

Metal	Φ_0 (in volts) Photoelectric	Thermionic
Pt	6.30 (153) 4.62 (160) 4.40 (161)	6.27 (153) T*
Mo	3.22 (154) 4.33 (161)	3.48 (154) 4.44 (T)
W	4.80 (155) 4.52 (161)	4.52 (T)
Ta	3.93 (161)	4.07 (T)
Fe	4.72 (156) 4.2 (161)	
Ni	4.12 (161)	
C	4.82 (161)	
Ag	4.30 (160) 3.85 (161)	4.08
Au	4.72 (160) 4.71 (161)	4.42
Al	3.57 (161)	
Zn	3.68 (161)	
Hg	4.53 (157) (158)	
Sn—β	4.50 (159)	
—γ	4.38 (159)	
—l	4.21 (159)	

* *T* refers to values of ϕ_0 in Table IV.

A. B. Cardwell[156] observed the long wave limit for thoroughly outgassed iron as between 2580Å and 2652Å. This corresponds to a work function of 4.72 ± 0.07 volts. The variation in photoelectric sensitivity was found to be quite complex and is probable related to the change in crystal structure of the metal.

C. B. Kazda's[157] determination of the value of λ_0 for mercury has been checked by H. K. Dunn,[158] while A. Goetz's[159] determinations on the β-(Tetragonal), γ-(hexagonal) and liquid (l) tin were carried out under very carefully controlled conditions.

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[156] A. B. Cardwell, Proc. Nat. Acad. **14,** 439 (1928).

[157] C. B. Kazda, Phys. Rev. **22,** 523 (1923).

[158] H. K. Dunn, Phys. Rev. **29,** 693 (1927).

[159] A. Goetz, Phys. Rev. **33,** 373 (1929).

R. Suhrmann[160] and S. C. Roy[161] have used a somewhat indirect method for determining ν_0. The theory of this method was first developed by Richardson,[162] and has also been discussed by W. Wilson[163] and A. Becker.[164] The photo current (I_p) is determined as a function of the temperature of the source of illumination and log (I_p/T^2) is plotted as a function of $1/T$. The slope of the straight line gives the value of Φ_0 corresponding to ν_0.

R. Suhrmann determined Φ_0 for platinum, silver and gold. His value for the first metal (4.62 volts) is much lower than that of DuBridge. The values for the other two metals are given in the table and also the values obtained by Goetz from thermionic data (see section V) S. C. Roy s values for Ta, W, Ag, and Au do not depart greatly from those obtained by the thermionic method.

While numerous attempts have been made to measure the threshold frequency for the alkali and alkaline earth metals, none of the results obtained can be considered as very satisfactory. A. F. A. Young's[165] determinations of Φ_0 by photoelectric method, made simultaneously with emission observations, showed that the photoelectric values were consistently higher than those obtained from thermionic data. Undoubtedly even slight traces of residual gases affect the results considerably.

The same remarks apply to a large number of other determinations of threshold frequency for various elements. For this reason discussion of these observations has been omitted. Summarizing the conclusions to be derived from the data in Table XXVII it has been shown by DuBridge that the determination of the work function for emission from the threshold frequency gives reliable results, if care is taken to work with thoroughly degassed surfaces. On the other hand, since it is extremely difficult to maintain a surface in this condition at ordinary temperatures, the photoelectric method is apt to lead to erroneous or at least only approximately correct results.

IX. CONTACT DIFFERENCE OF POTENTIAL

The contact difference of potential (ΔV) between two surfaces 1 and 2 is connected with the work functions for the two surfaces by the relation,[166]

$$\Delta V = \Phi_1 - \Phi_2 + \frac{T}{11600} ln \frac{A_2}{A_1} \tag{29}$$

where A_1 and A_2 are the values of the constants in the T^2 equations. Usually it has been assumed that $A_1 = A_2$, and that, therefore, the observed contact difference should correspond to the difference in the work functions as measured thermionically. The earlier work has been discussed by Richardson,[166]

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[160] R. Suhrmann, Zeits. f. Physik **33,** 63 (1925).

[161] S. C. Roy, Proc. Roy. Soc. **A112,** 599 (1926).

[162] O. W. Richardson, Phil. Mag. **23,** 615 (1912); **24,** 570 (1912).

[163] W. Wilson, Proc. Roy. Soc. **A93,** 359 (1912).

[164] A. Becker, Ann. d. Physik **78,** 83 (1919).

[165] A. F. A. Young, Proc. Roy. Soc. **104,** 611 (1923).

[166] Richardson, Emission of Electricity from Hot Bodies (1921), p. 41.

and further remarks on this topic will also be found in the comprehensive review by K. T. Compton and I. Langmuir,[167] as well as in the treatise by Schottky, Rothe and Simon.

An attempt to check the validity of the above equation by measurements with adsorbed films has been made by I. Langmuir and K. H. Kingdon.[168] The electron current was measured from a standard filament (*b*), that is, one maintained at a definite temperature and state of activation, to an adjacent filament (*a*) as a function of the potential difference, V_{ab}. On changing the surface of *a*, another characteristic was determined and "the voltage displacement of these two characteristics from one another then measured the contact potential difference between the two states of the surface *a*."

The observed values of ΔV compared with those calculated from values of Φ_0 and A in Table IV are shown in Table XXVIII.

TABLE XXVIII. *Calculated and observed values of the contact potential for various surfaces (Langmuir and Kingdon).*

Surfaces	ΔV (calc.)	ΔV (obs.)
ThW-W	1.81	1.46
CsOW-W*	3.55	3.1
W-OW	4.12	0.8

* The value $A = 0.003$ amp/cm²deg² was used for the film.

The comments of the authors on these results are as follows:

"The agreement is not good. In no case was there any indication of a contact potential difference of 4 volts between tungsten and oxidized tungsten. It is believed that the differences between the observed and calculated values are well outside the experimental error in the contact potential measurements for the ThW-W and W-OW combinations. However, it may not be justifiable to use electron emission constants determined at elevated temperatures to calculate contact potential differences between surfaces at room temperature. An attempt was made to measure contact potentials between hot surfaces, but the work was not completed."

It is evident that while the relation between Φ_1, Φ_2 and ΔV has received experimental confirmation in the case of atomically homogeneous surfaces (e.g., pure metals), the same result is not true for composite surfaces. Since, however, the investigations on this problem by J. A. Becker, N. B. Reynolds and W. B. Nottingham, have been fully discussed in the review by Compton and Langmuir, further discussion in the present paper is unnecessary.

X. THE THERMIONIC CONSTANT A

The data on emission constants given in the previous sections show that while the constant A in the T^2 equation should have the theoretical value

$$A_0 \equiv \frac{2\pi m e k^2}{h^3} = 60.2 \text{ amps/cm}^2 \text{ deg}^2 \tag{30}$$

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[167] K. T. Compton and I. Langmuir, Review of Modern Physics, **2**, 124 (1930).

[168] I. Langmuir and K. H. Kingdon, Phys. Rev. **34**, 129 (1929).

actual observations lead to values of A which are both greater and less than A_0. The theoretical value is observed for only a few pure metals; for monatomic films of more electropositive elements, $A < A_0$, while for films of more electronegative elements and for platinum, $A > A_0$.

There have been published a number of papers dealing with the problem of the explanation for this discrepancy, and while it cannot be stated that a completely satisfactory explanation of all the observations has been obtained nevertheless it is of interest to review these investigations. In the following discussion the subject has been dealt with under the following four headings:

(A) Observations on the relation between A and b_0.

(B) Derivation of A from thermodynamical considerations.

(C) Application of new electron theory to the problem of thermionic emission.

(D) Application of wave mechanics to the same problem.

(A) Observations on the relation between A and b_0.

In 1915, Richardson[169] showed that if the various values of log A for platinum, in vacuum and in presence of gas, are plotted against the corresponding values of b, a *linear relation* is obtained. Similar results were obtained from plots of the emission constants for tungsten as observed by Langmuir in vacuum and in presence of various gases,[170] and also by plotting the emission constants for potassium.[171]

L. A. DuBridge[172] has pointed out more recently that a relation of the form

$$\log_{10} A = c + s \cdot b_0 \qquad (31a)$$

apparently holds valid for the emission data from a number of surfaces. In this relation c and s are empirically determined constants.

The same type of relation has also been found to hold valid for emission constants for zirconium and hafnium during ageing, and for oxide coated cathodes during activation.

From the linear plots given by DuBridge, and from data published by other investigators, the values of the constants in equation (31a) may be calculated. Adopting the method used by DuBridge, this relation may be expressed in the form

$$\log A = \log A_0 + \beta(b - b_0),^* \qquad (31b)$$

where $\beta = 2.303\ s$ in equation (31a). This may again be expressed, as suggested by Schottky in the form,

$$A = A_0 \epsilon^{\alpha} \qquad (32)$$

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[169] O. W. Richardson, Proc. Roy. Soc. **A91,** 524 (1915).

[170] Richardson, Emission of Electricity, p. 135 (1921).

[171] Richardson and Young, Proc. Roy. Soc. **A107,** 393 (1925).

[172] L. A. DuBridge, Proc. Nat. Acad. **14,** 788 (1928).

* Unless otherwise specified, natural logs are to be understood in this and subsequent equations.

where $\alpha=\beta(b-b_0)$, and substituting this in the T^2 equation for emission, we have.

$$\begin{aligned} I &= A_0 T^2 \epsilon^{-(b-\alpha T/T} \\ &= A_0 T^2 \epsilon^{-b'/T} \end{aligned} \tag{33}$$

where
$$b' = b - \alpha T \tag{34}$$

In Table XXIX the values of β and b_0 have been calculated by means of equation (31b). The last column gives the value of α corresponding to the values b and Φ in the preceding columns. It will be observed, that in the case Th-W, Cu (liquid), and oxide coated cathodes, where $b < b_0$, *α is negative.*

TABLE XXIX. *Constants in the relation between A and b_0 for various emitters.*

Emitter	Authority	$\beta\times10^4$	$b_0\times10^{-4}$	$b\times10^{-4}$	Φ	ϵ^α
W	Du Bridge	4.56	5.24	6.40	5.53	1.98×10
Th-W	Du Bridge	1.76	5.24	3.05	2.63	2.11×10^{-2}
Pt	Du Bridge	3.41	5.88	7.27	6.27	1.14×10^2
K	Du Bridge	24.70	0.748	1.908	2.21	2.75×10^{12}
Cu (liquid)	Du Bridge	6.91	5.27	4.11	3.54	3.31×10^{-4}
Zr, Hf	Zwikker	4.08	4.46	5.62	4.84	1.13×10^2
BaO	Detels	6.79	2.87	1.71	1.47	3.78×10^{-4}

Further reference to this table will be made in a subsequent section, where the significance of both equation (34) and the coefficient ϵ^α will be discussed more fully.

(B) Thermodynamical derivation of A.

Richardson's derivation of an equation for emission was based on the classical electron theory of metallic conduction. Assuming that the free electrons within the metal are held within the metal by an electric force at the surface and that only those electrons can escape which possess energy in excess of a certain critical value, he showed that the electron emission as a function of the temperature must be expressed by an equation of the form[173]

$$I = aT^{1/2}\epsilon^{-b/T} \tag{35}$$

where $a = N(kT/2\pi m)^{1/2}$
and N = number of electrons per cm^3 of the metal
k = Boltzmann constant,
m = mass of electron.

Subsequently Richardson pointed out[174] that an equation of the form

$$I = AT^2\epsilon^{-b_0/T} \tag{2}$$

where A is a universal constant, could be derived on the basis of the quantum theory. In the derivation of this constant, he applied certain hypotheses

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[173] O. W. Richardson's Treatise, also given by I. Langmuir, reference (49).

[174] O. W. Richardson, Phil. Mag. **28**, 633 (1914).

which had been utilized by Debye and Keesom in calculating specific heats at low temperatures, and obtained a relation of the form

$$A = (k^2me/h^3)f,$$

where e denotes the electronic charge and f corresponds to a numerical coefficient different from 2π, so that the actual value calculated from his relation corresponds to about 5 amp. cm^{-2} deg.$^{-2}$ instead of 60.2 as calculated subsequently by Dushman.

M. v. Laue[175] and W. Schottky[176] showed that the electrons emitted from an incandescent solid could be regarded as an electron gas having the properties of an ideal monatomic gas, and R. C. Tolman[177] applied the third law of thermodynamics to calculate the entropy of this electron gas.

It was these considerations that led Dushman[178] to the deduction that the constant A in equation (2) should be a universal constant of which the value is determined, in accordance with the theory derived by Sackur and Tetrode, by the third law of thermodynamics, with the value A_0 given by (30).

The considerations on which this result was based may be presented briefly as follows:

The emission of electrons from a metal may be regarded as thermodynamically equivalent to the evaporation of a monatomic gas of molecular weight Nm, where N is Avogadro's number ($=6.06\times 10^{23}$) and m is the mass of the electron. That is, at any temperature, T, there exists an equilibrium pressure, P, of the electron gas, and in accordance with the second law of thermodynamics the latent heat of evaporation at this temperature is given by Clapeyron's equation

$$L = RT^2\frac{d\log P}{dT} \tag{36}$$

where $L=$heat of vaporaization per gram molecular weight
and $R=$gas constant per gram molecular weight
$=Nk=1.987$ cal./deg.

Hence

$$\log P = \frac{1}{R}\int^T \frac{LdT}{T^2} + i \tag{37}$$

where i is an integration constant.

If C_p denotes the specific heat of the electron gas at constant pressure, and c_p that of the electrons in the metal, L can be expressed as a function of T by the relation

$$L = L_0 + \int_0^T C_p dT - \int_0^T c_p dT \tag{38a}$$

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[175] M. v. Laue, Jahrb. d. Rad. **15,** 205, 257 (1918); Ann. d. Physik **58,** 695 (1919) Phys. Zeits. **20,** 202 (1919).

[176] W. Schottky, Phys. Zeits. **15,** 872 (1914); **20,** 49, 220 (1919).

[177] R. C. Tolman, J. Am. Chem. Soc. **42,** 1185 (1920); **43,** 866 (1921).

[178] S. Dushman, Phys. Rev. **21,** 623 (1923).

where L_0 = heat of vaporization at $T=0$.

For a monatomic gas, $C_p=(5/2)R$; while for electrons in a solid the experimental evidence shows that as a first approximation we may assume $c_p=0$. Hence (38a) becomes

$$L = L_0 + 5RT/2 \tag{38b}$$

O. Sackur[179] and H. Tetrode[180] showed that in the case of a monatomic gas

$$i = \log\left[\frac{(2\pi)^{3/2}k^{5/2}\cdot m^{3/2}}{h^3}\right]. \tag{39}$$

Introducing these relations into (37) it follows that

$$P = \frac{(2\pi)^{3/2}k^{5/2}m^{3/2}}{h^3}T^{5/2}\epsilon^{-L_0/RT}. \tag{40}$$

But according to the kinetic theory of gases, the number of electrons, n, striking the cathode per unit area in unit time, is given by the relation

$$n = P/(2\pi mkT)^{1/2} \tag{41}$$

Therefore, if we assume no reflection of electrons, the current per unit area is given by

$$\begin{aligned} I &= ne = Pe/(2\pi mkT)^{1/2} \\ &= A_0T^2\epsilon^{-b_0/T} \end{aligned} \tag{2}$$

where $b_0=L_0/R$.

A more rigorous investigation has been made by P. W. Bridgman[181] of the conditions under which the coefficient in equation (2), which we shall denote by A, is equal to A_0. The conclusion is reached that "A necessary and sufficient condition is that the difference between the specific heat of neutral metal and of a charge on its surface vanish," that is,

$$C_{pm} - C_{pp} = 0 \tag{42}$$

where the subscripts m and p refer to metal and surface charge respectively.

Theoretically it is necessary, of course, to take into account the fact that the electrons in evaporating leave a positive charge on the surface. This was first pointed out by Bridgman[182] and in the second paper, referred to above, he shows that while condition (42) is probably valid for uncoated metals, it may not hold for coated surfaces, or the entropy of the surface charge may not vanish at $T=0$.

The problem has also been investigated by L. Tonks and I. Langmuir,[183] and the following discussion summarizes their arguments.

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[179] O. Sackur, Ann. d. Physik **36**, 598 (1911); **40**, 67 (1913).

[180] H. Tetrode, Ann. d. Physik **38**, 434 (1912).

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

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

[183] L. Tonks and I. Langmuir, Phys. Rev. **29**, 524 (1927); L. Tonks, **32**, 284 (1928).

The term, L, in equation (36) is actually made up of two terms, that is,

$$L = L_p + L_s \tag{43}$$

where L_p = cooling effects due to evaporation of electrons under reversible conditions,

and L_s = latent heat of surface charge.

If L_c denote the cooling effect measured calorimetrically, then

$$L_p = L_c + kT/2. \tag{44}$$

Furthermore, from emission data there is obtained the derivative

$$-k\frac{d \log (I/T^2)}{d(1/T)} = -kb' \tag{45}$$

where b' corresponds to the quantity previously designated by b_0.

From these relations it follows, as shown by Tonks and Langmuir, that

$$L_s = kb' - L_c + 2kT. \tag{46}$$

Now according to the measurements of Davisson and Germer on tungsten,[184] $kb'/e = -4.48$ volts, $L_c/e = 4.91$ volts, and for $T = 2270$, $2kT/e = -0.391$ volts. Hence $L_s/e = 0.04$ volt, which is less than the probable error of the measurements. It therefore appears "that the surface heat of charging for all pure metals is probably but a small fraction of the work function."

This conclusion is also in agreement with Millikan's observations on stopping potentials for clean surfaces of the alkali metals in vacuum. From equations (27) and (29) it follows that the contact potential between surfaces 1 and 2 is given by

$$\begin{aligned} eV_{12} &= h(\nu_{01} - \nu_{02}) \\ &= kT \log (A_2/A_1) + k(b_1 - b_2) \end{aligned} \tag{47}$$

Since $h\nu_0 = kb$, it follows that A must be the same for all metals.

For the difference in L_s for two surfaces, the relation derived is of the form

$$L_{s1} - L_{s2} = kT \log (A_1/A_2) + eP_{12} \tag{48}$$

where P_{12} is the Peltier heat. As this is negligible, it is possible to calculate the following values of L_s/e from the values of A given previously, assuming $L_s = 0$ for tungsten:

Th-W	-0.39 V at $T = 1500$°K
Cs-O-W	-0.62 V at $T = 650$°K
O-W	$+2.92$ V at $T = 1600$°K

The signs show that charging the surface positive is attended by the evolution of heat in the first two cases, and by absorption in the last case. The values of L_s calculated by means of equation (48) are evidently considerable, but since no direct measurements of L_c are available, it is not possible to check these conclusions.

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[184] Davisson and Germer, Phys. Rev. **20**, 300 (1922), see Table 12.

It should be noted that according to Bridgman's critical examination of the problem, "It is not necessary that the surface heat vanish in order that the emission formula (2) shall be valid; provided only that it be proportional to the temperature."

In a still more recent paper on the photoelectric effect,[185] Bridgman has deduced the conclusion that the value of A must depend not only on that of L_s but also on the variation in ν_0 with temperature.

The difference between observed values of A and the theoretical value A_0 has been ascribed by K. F. Herzfeld[186] as due, at least in part, to the energy of expansion of the emitting substance. As a consequence Φ_0 must depend on the specific volume, and the observed value of A must be greater than A_0, whenever the temperature coefficient of expansion is positive. Furthermore, this increase in A must be accompanied by a shift to the red in the threshold frequency, ν_0, with increase in temperature. DuBridge actually observed a shift of about 50A between 800° and 1200°C. This corresponds to a value for α in equations (32) and (34) of 4.5, and would, therefore, give a value of $\epsilon^\alpha = A/A_0 = 90$, whereas the observed ratio is approximately 250. On the other hand, in case of tungsten, the value of ν_0 shows no change with temperature, and therefore we should have $\alpha = 0$ and $A = A_0$. Herzfeld's theory thus gives the right order of magnitude for the ratio A/A_0 in at least two cases. Whether it is capable of accounting for negative values of α is, however, questionable. It would be of interest in this connection to investigate more thoroughly the thermionic emission from the alkali metals and also the effect of temperature on the values of the photoelectric threshold frequencies.

(C) Thermionic emission on basis of new electron theory.

So far the derivation of the constant A has been considered from the point of view of classical thermodynamics. In the present section we shall discuss a treatment of the problem of thermionic emission, on the basis of the statistical mechanics of Fermi and Dirac, which we owe to A. Sommerfeld[187] and other investigators associated with him.

The starting point for Sommerfeld's theory is the formula derived by Fermi[188] for the distribution-in-energy of an assemblage of N particles in volume V at temperature T. This may be written in the form

$$F(E) = \frac{2\pi G V (2m)^{3/2}}{h^3} \cdot \frac{E^{1/2}}{B^{-1}\epsilon^{E/kT} + 1} \tag{49}$$

where G = the statistical weight
m = mass of particle.

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[185] P. Bridgman, Phys. Rev. **31**, 90 (1928).

[186] K. F. Herzfeld, Phys. Rev. **35**, 248 (1930).

[187] A. Sommerfeld, Zeits. f. Physik **47**, 1 (1928).

[188] The remarks on this theory in the present section are based largely on the comprehensive discussion of the subject by K. K. Darrow, Phys. Rev. Supplement **1**, 90 (1929). See also the recent treatise by L. Brillouin, "Les Statistiques Quantiques," Paris (1930).

$$N = \int_0^\infty F(E)dE \tag{50}$$

while B is a function defined as follows:

(1) For a gas at high temperatures or low pressures, the Maxwell-Boltzmann distribution law is known to apply very satisfactorily. Hence B must be so small that the second term in the denominator of (49) is negligible by comparison with the first. Since in the classical statistical mechanics the formula derived is of the form

$$F(E) = \frac{2N\pi}{(\pi kT)^{3/2}} E^{1/2}\epsilon^{-E/kT} \tag{51}$$

it follows that for this case

$$B = \frac{Nh^3}{GV(2\pi mkT)^{3/2}} \cdot \tag{52}$$

Let us consider the case of 1 gm molecular weight of hydrogen ($m = 3.33 \times 10^{-24}$) at $T = 10$ and V(molecular volume) $= 2{,}240$ cm.^{3} Assuming $G = 1$, $B = 1.56 \times 10^{-3}$. Since B decreases with increase in m, V and T, it is evident that in case of gases, even at high pressures, B is extremely small compared to 1, and that consequently $B^{-1}\epsilon^{E/kT}$ will be very large compared to unity.

(2) The conditions are, however, quite different for the electrons in a metal. Assuming that the concentration of electrons is the same as that of the atoms it is found that B is very large, even at 1000–2000°K. Thus for tungsten at ordinary temperatures, $N/V = 6.36 \times 10^{22}$. Substituting $m = 9 \times 10^{-28}$ and $T = 2000$ in equation (51), and assuming $G = 2$, we obtain the result $B = 146$ approximately. This indicates that equation (52) cannot be used to substitute for B in equation (49). The gas is said to be in a "degenerate" state.

Carrying out the integration indicated by (50), Fermi has obtained, as a first approximation, the result

$$2mkT \log B = h^2 \left(\frac{3n}{4\pi G}\right)^{2/3} \tag{53}$$

where $n = N/V$ = number of corpuscles per cm.^{3}

Equation (53) can be written in the form.

$$B^{-1} = \epsilon^{-W_i/(kT)} \tag{54}$$

where

$$W_i = \frac{h^2}{2m}\left(\frac{3n\nu}{4\pi G}\right)^{2/3}$$

n = number of atoms per cm.^{3} $= N/V$
V = atomic volume
$N = 6.062 \times 10^{23}$
ν = number of free electrons per atom (assumed to be the same as the number of valence electrons)
$G = 2$ for electron.

The magnitude W_i which has been introduced here is evidently a quantity of energy and may be expressed in terms of atomic constants in the following forms:

$$\left.\begin{aligned} W_i &= 5.78 \times 10^{-27}(n\nu)^{2/3}\text{ ergs} \\ &= 3.634 \times 10^{-15}(n\nu)^{2/3}\text{ electron-volts} \\ &= 26.07\nu^{2/3}V^{-2/3}\text{ electron-volts} \end{aligned}\right\} \tag{55}$$

For tungsten and potassium, *assuming* $\nu = 1$, the values thus calculated for W_i are 5.77 and 2.1 volts respectively. Sommerfeld designates W_i as the "inner work function." It represents the zero point energy due to the kinetic energy of agitation of the electrons in the metal. It thus corresponds to the thermodynamical function, ψ, defined by Gibbs as the *free energy at constant pressure* (per electron). The electron pressure may be derived from this quantity in accordance with the relation

$$p_0 = 2W_i n\nu/5 \tag{56}$$

which gives values for p_0 of the order of 2×10^5 atmospheres approximately.

Substituting in equation (49) from (54) it is seen that the exponential term in the denominator becomes

$$B^{-1}\epsilon^{E/(kT)} = \epsilon^{(E-W_i)/(kT)} \tag{57}$$

which leads to the following conclusions regarding the form of $F(E)$ for $T = 0$.

For $E < W_i$ the exponential in (57) becomes equal to zero. Hence $F(E) = CE^{1/2}$ where C denotes the coefficient in equation (47).

For $E > W_i$, the exponential becomes infinitely great. Hence $F(E) = 0$.

Thus the form of $F(E)$ at $T = 0$ is that of the full curve shown in Fig. 20. As the temperature is increased from $T = 0$ the plot for $F(E)$ assumes the form shown in the dotted curve.

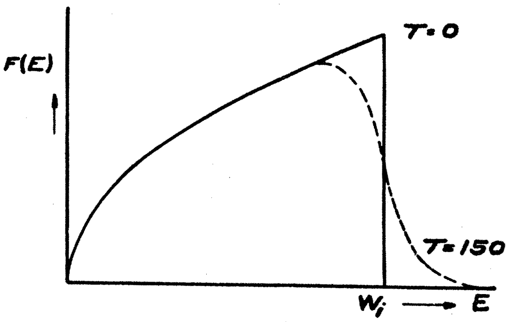

Fig. 20. Distribution of energy among electrons in a metal by the Fermi statistics.

The corresponding plots for the distribution in velocities $u = (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)^{1/2}$ (the velocities in random directions) are shown in Fig. 21. The velocity u_0 is given by the relation

$$\tfrac{1}{2}mu_0^2 = W_i. \tag{58}$$

The dotted curve gives the plot for $T = 1500$°K. It shows that for velocities in excess of u_0 a practically Maxwellian distribution is obtained.

From these distribution functions it is possible, as shown by Sommerfeld, to deduce the equation for emission by the following procedure. It is assumed that the thermionic current is produced by all those electrons which strike the boundary surface of the metal with velocities such that the *components normal to the surface*, $\dot{x}$, are greater than those corresponding to the relations

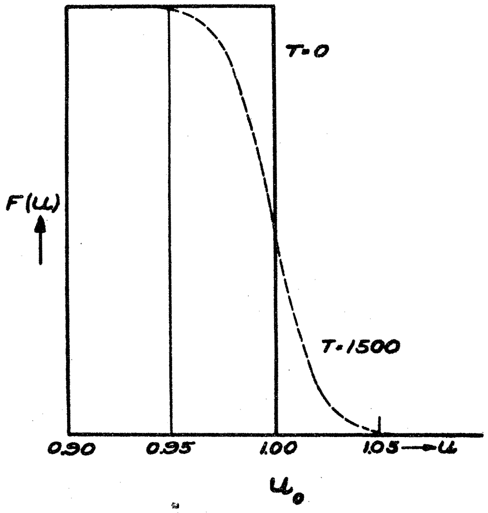

Fig. 21. Distribution of velocities among the electrons in a metal by the Fermi statistics.

$$\tfrac{1}{2}mx_0^2 = W_a \tag{59}$$

where W_a is the "external work function."

Denoting by $N(W)\,dW$ the number of electrons having *normal energies* between W and $W+dW$ which strike unit area per unit time, the relation deduced is of the form[189]

$$N(W) = \frac{4\pi m}{h^3} kT \log\left(1 + \epsilon^{-(W-W_i)/(kT)}\right) \tag{60}$$

Hence

$$\left.\begin{aligned} N(W) &= \frac{4\pi m}{h^3}(W_i - W)\ \mathit{for}\ \frac{W - W_i}{kT} \ll 0 \\ &= \frac{4\pi m}{h^3} kT\ (\text{approx.})\ \text{for}\ W \cong W_i \\ &= \frac{4\pi m}{h^3} \cdot kT\epsilon^{-(W-W_i)/kT}\ \text{for}\ \frac{W - W_i}{kT} \gg 0 \end{aligned}\right\} \tag{61}$$

Consequently the distribution curve is linear for $T=0$, as shown in Fig. 22, and takes the form of the dotted curve for $T \gg 0$. For values of $W > W_i$,

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[189] The derivation here given is taken from the paper by L. Nordheim, Phys. Zeits. **30,** 177 (1929).

this part of the curve follows a Maxwellian distribution law, which is in agreement with observations on the velocity distribution for the electrons emitted from a hot cathode.

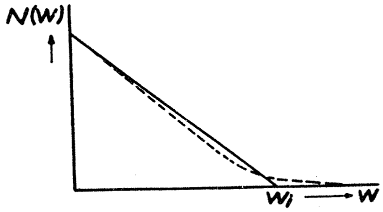

Fig. 22. Distribution function for electrons for energy normal to surface.

By forming the integral of $N(W)dW$ for the limits $\dot{x}=\dot{x}_0$ to $\dot{x}=\infty$, and for the limits of $\dot{y}$ and $\dot{z}$ the values 0 and ∞, the electron current per unit area is obtained in the form

$$I = A_0 G T^2 \epsilon^{-(W_a - W_i)/kT} \tag{68}$$

It should be observed that if the "classical" value of B, given by equation (52), is used, the resulting equation for emission is that derived originally by Richardson (equation (35)) in which W_a/k corresponds to his value b.

Equation (62) differs from that derived on the basis of classical thermodynamics in two respects:

(1) The presence of the factor G, to which has been assigned the value 2 by R. H. Fowler, on the basis of the Goudsmit-Uhlenbeck hypothesis of electron spin,

(2) The substitution in the exponential factor of the classical b_0 by $(W_a - W_i)/k$.

However, the fact that both classical thermodynamics and the Fermi statistics lead to the same value A_0 for the coefficient of T^2, is extremely significant. Apparently the statistical method does not indicate any reason for deviations in the observed values of A from a theoretical value $2A_0$. Before proceeding to discuss the views which Nordheim and Fowler have advanced to account for such deviations, it is, however, necessary to make a few remarks about the energy quantity, W_a, introduced in the above equations.

This energy is the work required to overcome the attraction of the positive charges in the metal for the electrons. It corresponds, therefore, to the energy required to remove an electron (initially at rest) from the crystal lattice, and may be identified, according to H. Bethe[190] and L. Rosenfeld and E. E. Witmer,[191] with the potential energy of the electrons in the lattice as calculated from the refractive index, μ, of the crystal for electron beams. If V denote the volt-velocity of the electrons in the incident beam, the "wave-length" of the electrons in vacuum is given by the de Broglie relation,

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[190] H. Bethe, Naturwiss. **16**, 333 (1928).

[191] L. Rosenfeld and E. E. Witmer, Zeits. f. Physik **49**, 534 (1928).

$$\lambda = h/(2meV)^{1/2} \tag{62}$$

and the refractive index, by

$$\mu = (1 + W_a/V)^{1/2} \tag{63}$$

where W_a is naturally expressed in electron-volts.

Values of W_a calculated by the investigators mentioned above range between 10 and 20 volts, while W_i, as calculated by equation (54), on the assumption that $\nu = 2$ or 3, is about 2 to 6 volts less than W_a. This is in agreement with the values of

$$b_0 = \frac{W_a - W_i}{k} \tag{64}$$

determined from emission data.

(D) Theory of penetration of electrons through potential barrier.

According to Sommerfeld's derivation of the equation for emission, it is assumed that *all* the electrons in the metal reaching the inner wall with normal energy greater than W_a are transmitted. However, L. Nordheim[192] has shown, from considerations based on the application of wave mechanics, that in general some of the electrons will be reflected at the boundary. The transmission coefficient, D, is a function of the normal kinetic energy W, denoted by $D(W)$, and hence the actual emission is given in any particular case by the relation

$$I = A_0 G\bar{D}T^2\epsilon^{-(W_a - W_i)/(kT)} \tag{65}$$

where $\bar{D}$ is a mean transmission coefficient.

The value of $\bar{D}$ depends upon the nature of the potential distribution on both sides of the boundary. It may be calculated for any given distribution by considering the transmission of electrons across the boundary as "the passage of plane wave-trains of electrons over (or through) a hill of potential energy."[193]

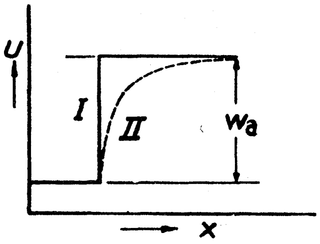

Fig. 23. Potential energy as function of distance from homogeneous cathode.

Let us consider, for instance, a potential distribution such as that shown in Fig. 23 by the straight line plot (I). For $0 < x_0$, the potential energy $U = 0$,

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[192] L. Nordheim, Zeits. f. Physk. **46**, 833 (1927); Physikal. Zs. **30**, 177 (1929); Proc. Roy. Soc. **A121**, 626 (1928).

while for $x > 0$, $U = W_a$. Owing to the effect of the image force, the potential energy for $x > 0$ will have the value $W_a - e^2/4x$ and will therefore be represented by the dotted curve II. Solving the Schroedinger differential equation in ψ for these conditions, Nordheim finds that for case I, Fig. 23,

$$\left.\begin{aligned} D(W) &= 0 \text{ for } W < W_a. \\ D(W) &= \frac{4[(W - W_a)W]^{1/2}}{[W^{1/2} + (W - W_a)^{1/2}]^{1/2}} \text{ for } W > W_a \end{aligned}\right\} \qquad (66)$$

The *mean* value in the latter case is given by

$$\bar{D} = 2(\pi kT/W_a)^{1/2}. \qquad (67)$$

This means, according to Fowler,[193] that, "The resulting current at the ordinary temperatures of thermionic emission is very much the same as if 20 percent of all those electrons are transmitted which are incident on the boundary with energy greater than W_a for more gradual slopes the fraction is higher and rapidly approaches unity as the slope is eased off. For the image force hill of case II, Fig. 23, the fraction is about 95 percent." Hence, wave mechanics makes no serious modifications to classical calculations, and D is approximately unity.

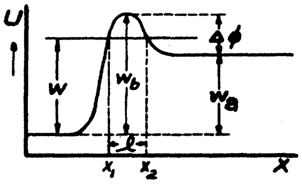

Fig. 34. Potential energy as function of distance for electropositive surface layer on cathode.

It may, however, happen that the potential energy as a function of x is represented by a "hill" such as shown in Fig. 24, in which the potential energy which the electrons have to exceed in order to cross the boundary is *diminished* from its normal value, W_b, to a *lower value*, W_a, by a surface layer (as, for instance, in the case of films of thorium on tungsten).

According to classical mechanics, an electron having the kinetic energy W, where, $W_b > W > W_a$, could not penetrate the barrier; that is, $D(W) = 0$ for $W < W_b$. But *in the new mechanics there exists a certain definite probability that the electron wave-train can pass through the hill.* The probability increases with decrease in the width, l, of the hill, and is significant for values of l which correspond to only a few de Broglie wave-lengths. The analogy with a similar phenomenon in optics has been pointed out by various writers, while the principle here stated has also been used by R. W. Gurney and E. U. Condon[194] and by G. Gamow[195] to develop a theory of radioactive disintegration.

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[193] R. H. Fowler, Robert Boyle lecture, Oxford, May 1929. This will be referred to as "R. B. Lect."

[194] R. W. Gurney and E. U. Condon, Phys. Rev. 33, 127 (1929).

The probability of transmission of the electrons varies exponentially with the values of l and of $\Delta\Phi = W_b - W_a$. Nordheim[196] has calculated $D(W)$ for the idealized case shown in Fig. 25, with the results shown in the plot in Fig. 26.

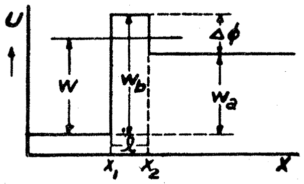

Fig. 25. Simplified potential energy curve for same case as in Fig. 24.

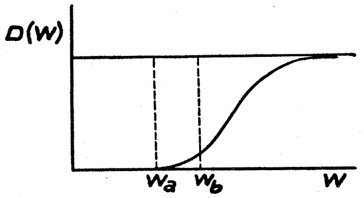

Fig. 26. Transmission coefficient for electrons for case shown in Fig. 25.

For $W > W_b$, $D(W)$ is approximately unity. For $W_b > W > W_a$ and the condition

$$\epsilon^{-(W_b-W_a)/(kT)} \ll \epsilon^{-2\sigma l(W_b-W_a)^{1/2}} \tag{68}$$

$$\bar{D} \sim \frac{8(\pi kTW_a)^{1/2}}{W_b}\epsilon^{-2\sigma l(W_b-W_a)^{1/2}} \tag{69}$$

where $\sigma = 8\pi^2 m/h^2 = 4.069 \times 10^{13}$ cgs units
and $l =$ width of potential barrier.

Substituting for $\bar{D}$ in equation (65) it is evident that

$$\begin{aligned} A &= A_0 G\bar{D} \\ &= A_0 G\frac{8(\pi kTW_a)^{1/2}}{W_b}\epsilon^{-2\sigma l(W_b-W_a)^{1/2}} \end{aligned} \tag{70}$$

Hence

$$\log A = \log CT^{1/2} - 2\sigma l(k\cdot\Delta b_0)^{1/2} \tag{71}$$

where C is a constant, and $k\cdot\Delta b_0$ *is the decrease in work function due to the surface layer of thickness* l.

It will be recognized that this relation is similar in form to the empirical relation, equation (31a) or (31b), deduced by DuBridge and thus *accounts for the decrease in both* A *and* b_0 *observed for electropositive films.*

For instance, let us consider the case of Th-W for which $A = 3.0$, $b_0 = 30{,}500 = 2.63$ volt/k, while for tungsten $A = 60.2$, $b_0 = 52{,}400 = 4.53$ volt/k. Assuming the theoretical value $A_0G = 120$, it follows that for Th-W, $\bar{D} = 0.025$.

$$W_a = 5.77 + 2.63 \text{ volts} = 8.40 \times 1.59 \times 10^{-12} \text{ erg.}$$

$$W_b = 5.77 + 4.53 \text{ volts} = 10.30 \times 1.59 \times 10^{-12} \text{ ergs.}$$

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[195] G. Gamow, Zeits. f. Phys. **51,** 204 (1928).

[196] See also R. H. Fowler, Proc. Roy. Soc. **A122,** 36 (1929) for a correction of certain formulae derived by Nordheim, reference 192.

For $T = 1500°\text{K}$

$$\bar{D} = 0.025 = 1.4\epsilon^{-2\sigma l \cdot 10^6 (1.9 \times 1.59)^{1/2}}$$

Therefore $l = 2.85 \times 10^{-8}$ cm. This appears to be a perfectly reasonable value for the thickness of a monatomic film. It can also be shown that this satisfies the condition expressed by relation (68).

From equations (71) and (31b) it follows that we should find

$$2\sigma l(k \cdot \Delta b_0)^{1/2} = \beta \Delta b_0$$

or

$$l = \frac{\beta \times 10^{-5}}{9.53}(\Delta b_0)^{1/2}.$$

For $\Delta b_0 = 10{,}000$, and the values of β given in Table XXIX, this relation leads to values of l varying from 10^{-7} to 10^{-8} cm, which again seems a reasonable, result.

While this theory apparently accounts for values of A less than $2A_0$, it is inadequate to explain the results obtained by DuBridge for clean platinum and by Kingdon for oxygen on tungsten. With regard to the latter, Fowler remarks as follows:[197] "It is impossible to believe here that $\Phi_0(=9.2$ volts) is a true work function and $A(=5 \times 10^{11})$ an emission coefficient. It is much more likely that a great part of the whole new factor $10^{10}\ \epsilon^{-4.7/kT}$ introduced by the oxygen is really a temperature dependent emission coefficient, representable in this form over a short temperature range."

Schottky has suggested, as mentioned previously, that

$$A = A_0\epsilon^{\alpha} \tag{32}$$

where

$$b = b_0 - \alpha T. \tag{34}$$

Hence, if these relations are to account for DuBridge's relation (31a) it is necessary, as in (31b) to assume that α varies linearly with changes in b_0. Fowler has discussed this assumption, which amounts essentially to the hypothesis of a *negative* specific heat of electricity for platinum and oxygen, and concludes that this theory is not admissible.

Perhaps it is best, under the circumstances, to await further experimental data before attempting to develop any theoretical explanations. Furthermore, if Nottingham's conclusion is valid that by correcting for the effect of field strength, the value of A for Th-W is increased to practically the theoretical value A_0, then it may prove that the theory discussed in the previous paragraphs is not required. It may be that further investigations on other emitters for which apparently $A < A_0$ will show that this is due to incorrect extrapolation to zero field strength, while the explanation offered byHerzfeld for platinum and by Fowler for oxygen may be found adequate for these cases.

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[197] Fowler, Proc. Roy. Soc. **A122,** 36 (1929).

XI. Electron Emission in Intense Electric Fields

The investigations on the emission of electrons in presence of very intense fields have been discussed in the review by Compton and Langmuir. It has been shown by the investigations of Millikan and Eyring;[198] Millikan and Lauritsen;[199] de Bruyne;[200] and the research staff of the General Electric Company, London,[201] that with extremely high anode voltages, emission occurs even at room temperature, and that the observations on this so-called "cold cathode effect" or "auto-electronic" emission are in agreement with the empirical relation,

$$I = A(T + cF)^2 \epsilon^{-b/(T+cF)} \tag{72}$$

where F is the field strength and A and c are constants which vary with the condition of the surface.

An explanation of this phenomenon has been deduced on the basis of Schroedinger's theory by J. R. Oppenheimer[202] and by R. H. Fowler and L. Nordheim.[203] In the following discussion, we shall summarize the derivation given by the last named investigators, which follows the same line of reasoning as was involved in the consideration of the value of the emission constant A in the previous section.[204]

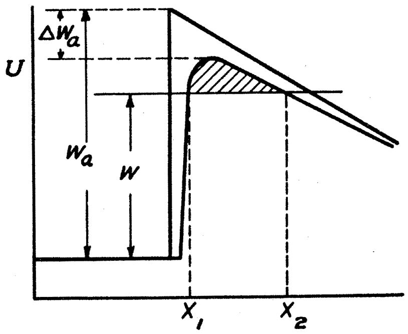

Fig. 27. Variation in potential energy with distance for case of intense electric fields.

For relatively weak fields, the effect of field strength, as mentioned previously, is given by Schottky's theory. The decrease in work-function varies with field strength in accordance with equation (8) which may be stated in the form

$$\Delta W_a = eF^{1/2}. \tag{73}$$

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[198] Millikan and Eyring, Phys. Rev. **27**, 51 (1926); **31**, 900 (1928).

[199] Millikan and Lauritsen, Proc. Nat. Acad. Sci., **14**, 15 (1928); Phys. Rev. **33**, 598 (1929).

[200] de Bruyne, Proc. Camb. Phil. Soc. **120**, 423 (1928).

[201] Phil. Mag. **1**, 609 (1926).

[202] J. R. Oppenheimer, Phys. Rev. **31**, 66 (1928); Proc. Nat. Acad. Sci., **14**, 789 (1928).

[203] R. H. Fowler and L. Nordheim, Proc. Roy. Soc. **A119**, 173 (1928); L. Nordheim, Physikal Zs. **30**, 177 (1929); Fowler, R. B. Lecture.

[204] A solution of the problem has also been given by C. Eckart, Phys. Rev. **35**, 1303 (1930).

The value of F is determined by the *geometrical* arrangement and dimensions of the cathode. In presence, however, of very strong fields the emission occurs from points or extremely small areas and is due to the fact that according to the new mechanics there exists a definite probability that electrons can traverse a potential barrier.

Under these conditions the potential distribution at an emitting spot is of the form shown in Fig. 27. Owing to the Schottky effect, the sharp corner indicated in the upper plot becomes rounded off as indicated in the lower curve, the decrease ΔW_a being given by equations (73). Because the temperature is low, there are no incident electrons with sufficient energy to go over the top of the hill, and therefore *all must go through the barrier.*

The potential energy, U, is of the form

$$\left.\begin{aligned} U &= W_a - \frac{e^2}{4x^2} - xF \quad \text{for } x > x_0 \\ &= 0 \qquad\qquad\qquad\quad \text{for } x < x_0 \end{aligned}\right\} \tag{74}$$

with

$$U_{\max} = W_a - \Delta W_a. \tag{75}$$

The solution of Schroedinger's equation for these conditions yields for the electron emission at $T = 0$ the relation

$$I = \frac{e}{2\pi h W_a}\left(\frac{W_i}{b_0 k}\right)^{1/2} F^2 \epsilon^{-\alpha/F} \tag{76}$$

where

$$\alpha = \frac{4}{3}(b_0 k)^{3/2}\left(\frac{8\pi^2 m}{h^2}\right)^{1/2}$$

and W_i, W_a and $b_0 k$ express the inner work function, external work function and ordinary thermionic work function respectively in the same cgs units.

For these energies in *volts*, I in *amps/cm*^{2} and F in volts/cm,[205]

$$I = \frac{6.2 \times 10^{-6}}{W_a}\left(\frac{W_i}{\Phi_0}\right)^{1/2} \epsilon^{-6.8 \times 10^7 \Phi_0^{3/2}/F} \tag{77}$$

Hence at low temperatures the electron current should be given by a relation of the form

$$I = BF^2 \epsilon^{-\alpha/F} \tag{78}$$

where α and B are constants, or $\log(I/F^2)$ plotted against $1/F$ should yield a straight line. As in the case of temperature emission, the effect of the term F^2 is so small compared to the exponential term that experimentally this also amounts to a linear relation between $\log I$ and $1/F$, a result which is in agreement with the empirical relation expressed in equation (72).

Equation (77) has been subjected to a more rigorous experimental test in an extensive investigation by Stern, Gossling and Fowler.[205] As they

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[205] The numerical factor in the exponent is the corrected value given in a subsequent paper by T. E. Stern, B. S. Gossling and R. H. Fowler, Proc. Roy. Soc. **A124**, 699 (1929).

point out, both the emitting area, S, and the effective field-strength, $F=\beta F_m$ (where β is a constant and F_m the measured field strength) may be derived by means of relations deduced from equation (76) or (77) From data obtained by previous investigators, especially by Gossling,[206] and Millikan and Eyring,[198] the value of β is found to vary from 1.5 to 115, with values of S ranging from 1.2×10^{-10} cm² to 8×10^{-8} cm² in different runs. The test of the validity of equation (77) is the fact that the calculated value of S comes out a constant for a series of values of F in any one set of observations under the same conditions.

Of special interest is the discussion by the above mentioned investigators of the effect of a surface-layer in reducing simultaneously both B and α in equation (78), the reduction in α corresponding to a decrease in Φ_0 for the emitting surface because of the presence of a surface film.

A solution of the Schroedinger equation for this case leads to the deduction that the film-thickness (denoted by a) increases as Φ_0 decreases. If the emitting area is calculated on the assumption of a film-free surface (as in equation (76)) a value of S is derived which is considerably less than the true emitting area S_0 derived for the case of a film of definite thickness. Table XXX shows values of these different quantities calculated from three different experimental sets of observations. The first horizontal line for each set of observations refers to the film-free surface. These observations were used to determine values of β, assuming $\Phi_0=4.5$ (corresponding to the work-function for pure tungsten) and from these the values of Φ_0, a, and S_0 were calculated for the cases in which a film was present. The fact that S_0 remained constant, while S, the apparent emitting area, varies with a and Φ_0, shows the validity of the theoretical relations deduced on the basis of wave mechanics.[207]

TABLE XXX. *Film thickness and emitting area of cathodes in intense electric fields.*

Number of experiment	β	Φ_0	S(cm²)	S_0(cm²)	a(cm)
1	19.4	4.5	5.1×10^{-9}	5.1×10^{-9}	
	19.4	2.81	4.6×10^{-10}	5.1×10^{-9}	1.5×10^{-8}
	19.4	1.58	1.8×10^{-10}	5.1×10^{-9}	2.5×10^{-8}
2	6.72	4.5	1.2×10^{-10}	1.2×10^{-10}	
	6.72	1.41	4.8×10^{-13}	1.2×10^{-10}	3.9×10^{-8}
	6.72	1.50	1.5×10^{-10}	1.2×10^{-10}	0.5×10^{-8}
	6.72	1.52	8.7×10^{-12}	1.2×10^{-10}	2.2×10^{-8}
3	2.9	4.5	8×10^{-8}	8×10^{-8}	
	2.9	3.95	3.9×10^{-8}	8×10^{-8}	0.4×10^{-8}
	2.9	2.85	4.1×10^{-9}	8×10^{-8}	1.8×10^{-8}
	2.9	2.33	8×10^{-10}	8×10^{-8}	2.8×10^{-8}

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[206] Gosling, Phil. Mag. **1**, 609 (1926).

[207] In this connection attention may be drawn to the paper by P. W. Bridgman (Phys. Rev. **34**, 1411 (1929) in which is discussed the bearing of classical thermodynamics on emission in strong fields.

With regard to the effect of temperature on the auto-electronic emission, equation (72) gives the empirical relation suggested by Millikan and Eyring. However, W. V. Houston[208] has shown that on the basis of the same considerations as those used by Fowler and Nordheim, the emission as a function of both T and F differs from equation (76) only in the substitution for F^2 of the expression

$$\left\{F^2 + \frac{32\pi^4 mk^2}{3h^2} b_0 k T^2\right\}.$$

The temperature variation is thus quite small and decreases as F increases, so that for very large values of the latter, the emission is practically independent of T.[209]

XII. Thermal Emission of Positive Ions[210]

The earlier observations on positive ion emission from heated salts and metals have been discussed by O. W. Richardson in his book. The emission observed in these cases occurs, in general, at temperatures below those observed for electron emission; it decreases with time according to an exponential law and varies with the conditions of treatment of the emitter.

(A) Emission due to vapor of alkali metals.

As has been mentioned in connection with caesiated filaments, atoms of an alkali vapor striking an incandescent filament for which the work function, Φ_0, is greater than the ionizing potential, V_i, of the incident atoms are thereby ionized and if the filament is positively charged, a positive ion current is observed the magnitude of which (I_p) is practically independent of the filament temperature, above a certain value, and varies linearly with the pressure of the vapor in accordance with the equation[211]

$$I_p = pe/(2\pi mkT)^{1/2} \qquad (79)$$

where m = mass of positive ion.

T = temperature of vapor corresponding to pressure p.

For caesium on tungsten, the lower limit of temperature is about 1100° K. As the temperature of the filament is decreased below this value, the alkali atoms are adsorbed more and more, thus decreasing Φ_0, until finally when $\Phi_0 \leqq V_i$ the positive ion emission is reduced to zero. The degree of ionization of caesium vapor at any temperature may be calculated by means of a modification of Saha's equation [212] which Langmuir and Kingdon have derived[213]

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[208] W. V. Houston, Phys. Rev. **33**, 361 (1929).

[209] N. A. de Bruyne, Phys. Rev. **35**, 172 (1930) notes that he has failed to observe the effect of temperature stated by Millikan and Lauritsen.

[210] Although this topic has also been treated by Compton and Langmuir in their review, it has been considered advisable to summarize the observations in this field in the present paper.

[211] K. H. Kingdon, Phys. Rev. **23**, 774 (1924).

[212] Saha, Phil. Mag. **40**, 472 (1920); **46**, 534 (1923).

[213] Langmuir and Kingdon, Proc. Roy. Soc. **A107**, 61 (1925).

on the basis of the work of Fowler and Milne.[214] This equation has the form

$$\log_{10}\frac{n_e n_p}{n_a} = \frac{11,600V_i}{2.303T} + \frac{3}{2}\log_{10} T + 15.385 \tag{80}$$

where n_e, n_p and n_a denote the numbers of electrons, positive ions and atoms respectively, per cm,^{3} V_i is the ionizing potential of the vapor in volts, and T is the absolute temperature.

The values of V_i for the different alkali and alkaline earth metals are as follows:

Li	5.37	Ca	6.09
Na	5.12	Sr	5.67
K	4.32	Ba	5.19
Rb	4.16	Cs	3.88

Hence, in presence of a tungsten filament ($\Phi_0 = 4.53$), only K, Rb and Cs may be expected to give positive ion currents. Equation (80) has been applied by Langmuir and Kingdon to calculate the degree of ionization of caesium atoms incident upon a heated tungsten filament. Under these conditions, the value of n_e is obtained from the electron emission, I_e, for pure tungsten by means of the relation

$$n_e = \frac{I_e}{e}\left(\frac{2\pi m_0}{kT}\right)^{1/2} = 4.034 \times 10^{13}\frac{I_e}{T^{1/2}} \tag{81}$$

and this is then substituted in the value of $K = n_e n_p / n_a$ derived from (80) to obtain the ratio n_p/n_a. Thus for tungsten at 1200°, the calculated value of this ratio is 577, which means "that out of 578 caesium atoms incident on the filament, an average of only one will leave the surface as a neutral atom, while 577 leave as ions. This conclusion is in accord with the experiments."

On the other hand, if the caesium atoms strike a thoriated tungsten filament ($\Phi_0 = 2.69$) at $T = 1200°\text{K}$, $n_p/n_a = 8.9\text{x}10^{-5}$ which indicates negligible ionization. In their paper, Langmuir and Kingdon give values of n_e and n_p/n_a for a series of temperatures for caesium vapor in contact with tungsten and thoriated tungsten, and have also confirmed the validity of equation (80) by direct measurements of I_e and I_p.

Following up this work, T. J. Killian[215] has shown that the same theory is quantitatively applicable to potassium and rubidium in contact with tungsten and oxidized tungsten, and from the observations he has been able to derive vapor pressure curves for the metals, which are in agreement with those obtained by the more usual methods. It is also of interest to mention that a beautiful confirmation was obtained of the space charge equation for positive ions.

More recently E. Meyer[216] has reported on positive ion emission in potas-

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[214] Fowler and Milne, Monthly Notices, Roy. Astr. Soc. **83**, 403 (1923). See discussion in review by Compton and Langmuir, p. 135.

[215] T. J. Killan, Phys. Rev. **27**, 578 (1926).

[216] E. Meyer, Inaug. Diss. Berlin (1930).

sium vapor as affected by variation in filament material. The results obtained for tungsten, molybdenum and tantalum were found to be in qualitative agreement with equation (80).

(B) Emission from catalysts.

The phenomenon of positive ion emission from certain catalysts is apparently best explained on the basis of the same theory as that used for the emission from tungsten and similar metals in caesium or rubidium vapor. C. H. Kunsman[217] observed that certain iron oxide crystals containing about 1 percent of some alkali metal or alkaline earth used in the Fixed Nitrogen Research Laboratory as a catalyst also provide a copious source of positive ions. Also it was found that the emission varies with the temperature in accordance with Richardson's equation.

H. A. Barton, G. P. Harnwell and C. H. Kunsman[218] have analyzed the ions emitted by means of the mass spectrograph and find that these ions are singly charged and have the same mass as that of the alkali or alkaline earth metal added to the iron oxide crystals. In the case of the alkaline earth metals a preliminary reduction of the mixture in hydrogen at a red heat was found to increase the emission. Platinum gave emission due to Na^+ and K^+ which diminished with time.

While the catalyst may be painted on platinum ribbon in the same manner as oxide coatings, a more convenient method devised in the Fixed Nitrogen Research Laboratory consists in the use of a thin-walled platinum tube with small perforations, in which the material is contained.

A potassium ion emitter prepared by a totally new method has been described by F. G. Cottrell, C. H. Kunsman and R. A. Nelson,[219] while A. K. Brewer[220] has discussed the photo-electric and thermionic properties of this source. The emitter consists of a platinum wire over which a thin layer of special potassium glass is fused. By electrolysis in molten potassium nitrate, a deposit of potassium is formed on this filament. The outer surface of the glass tube is then covered with platinum by cathodic sputtering, short distances being left uncoated at each end of the glass tube in order to provide insulation between the platinum deposit and the filament. By applying a potential between these, potassium can be electrolyzed to or from the external coating. The combination is used as an emitter for either electrons or positive ions. The emission of positive ions becomes detectable at 270° C. while that of electrons is detectable above 425° C. Also the electrode exhibits photo-electric sensitivity in the near ultraviolet with a threshold wavelength, of which the exact value depends upon the direction of current between the platinum coating and filament and on the temperature.

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[217] C. H. Kunsman, Science **62,** 269 (1925); Proc. Nat. Acad. Sci. **12,** 659 (1926). Phys Rev. **27,** 249 (1926); Jr. Physical Chem. **30,** 189 (1926).

[218] H. A. Barton, G. P. Harnwell and C. H. Kunsman, Phys. Rev. **27,** 739 (1926).

[219] F. G. Cottrell, C. H. Kunsman and R. A. Nelson, J. Opt. Soc. Am. **20,** 152 (1930).

[220] A. K. Brewer. Phys. Rev. **35,** 1360 (1930).

(C) Emission of positive ions of metals.

Another type of positive ion emission observed by H. B. Wahlin[221] and L. P. Smith,[222] is that in which the ions are charged atoms of the electrode material itself. This has been demonstrated by Wahlin by measurements with the mass spectrograph in the case of chromium, molybdenum, tungsten, rhodium, ruthenium, tantalum and columbium. All these metals give alkali metal ions when first heated, but this disappears after a few minutes. In the case of iron, nickel, copper, zirconium, platinum and palladium the emission of alkali ions persists for a much longer time. The emission of positive ions of the metals becomes measurable when the temperature is raised to a point at which appreciable evaporation occurs, and L. P. Smith has investigated more extensively this ion emission from tungsten and molybdenum.

The variation in emission with temperature is observed to follow the equation for electron emission. From the plot of log (I/T^2) vs. $1/T$ the work function for positive ion emission is found to be 6.55 volts for tungsten and 6.09 volts for molybdenum, whereas the values calculated from a thermodynamical energy cycle are 11.08 and 10.51 volts respectively. Again the integration constant A is actually found to be about 10^6 times smaller than that calculated by a method similar to that used by Dushman and Bridgman in calculating the theoretical value of A_0 for electron emission. Regarding the cause of these differences, no satisfactory explanation is apparent at present. Consequently it must be concluded "that the mechanism of emission of electricity from hot metals is not clearly understood, especially as regards the emission of positive ions, for, unlike the evaporation of electrons and neutral atoms, the evaporation of ions is not strictly represented by an equation based upon thermodynamical arguments under equilibrium conditions."

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[221] H. B. Wahlin, Phys. Rev. **34**, 164 (1929); Langmuir and Compton, loc. cit.

[222] L. P. Smith, Phys. Rev. **34**, 1496 (1929); **35**, 381 (1930). This gives references to previous literature on this subject.