ELECTRON EMISSION FROM METALS AS A FUNCTION OF TEMPERATURE

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Abstract

Electron emission from metals as a function of temperature.—(1) *General equation.* The emission of electrons from a metal may be considered as thermodynamically equivalent to the evaporation of a monatomic gas, for which an equation is derived on the basis of the Nernst heat theorem. If it is assumed that the specific heat of free electrons in the metal is negligible while the specific heat of the evaporated electrons is the same as that of a monatomic gas, the equation assumes the simple form $I = AT^2\epsilon^{-b_0/T}$, where $b_0 = \varphi_0 e/k$ (e is electronic charge, k is the Boltzmann constant, and $\varphi_0 = \varphi - \frac{3}{2}kT/e$, where φ is the Richardson work function). An equation of this form has been suggested before but not on the same theoretical grounds and a different value of A has been obtained. Its chief advantage over the usual Richardson equation, $I = A_1 T^{1/2}\epsilon^{-b/T}$, where $b = \varphi e/k$, is that A is theoretically a universal constant. (2) *The value of the universal emission constant A* is computed in two ways. Using the Sackur-Tetrode equation for the chemical constant i_0, A comes out 60.2 amp./cm^2 deg.^{2}, while the theory of rational units of Lewis, Gibson and Latimer gives 50.2 amp./cm^2 deg.^{2}. Recent experimental results of Davisson and Germer, and of Schlichter as well as data obtained by the writer agree with the new equation as well or better than with the old, but the temperature scale is not sufficiently accurately known to distinguish experimentally between the two values of A. (3) *The relation between A and the chemical constant* i_0 (or C_0) is derived.

Values of the work function in equivalent volts have been computed from the experimentally determined values of b_0, for *tungsten* (4.53), *thorium* (2.94), *molybdenum* (4.31), *tantalum* (4.40), and *calcium* (2.24) within $\frac{1}{2}$ to 1 per cent. The values for *uranium* (3.28), *zirconium* (3.28), *yttrium* (3.19) and *cerium* (3.07) are upper limits. In general, the values are lower the larger the atomic volumes. Experimental details will be given later.

Part I. Derivation of General Equation

Application of Nernst heat theorem to monatomic vapors.—On the basis of the second law of thermo-dynamics it has been shown that the heat of vaporization may be calculated by means of the well-known relation

$$L = RT^2 \frac{d \log P}{dT}, \tag{1}$$

where L = heat of vaporization per gram-molecular weight at the absolute temperature T;

R = gas constant per gram-molecular weight = 1.987 cal./deg.;

p = vapor pressure at temperature T.

If C_p denotes the specific heat of the vapor at constant pressure, and c_p that of the solid (or liquid), L can be expressed as a function of T by the following relation:

$$L = L_0 + \int_0^T C_p dT - \int_0^T c_p dT. \tag{2}$$

From Eqs. (1) and (2) it follows that

$$\log p = -\frac{L_0}{RT} + \frac{1}{R}\int^T \frac{\int_0^T C_p dT}{T^2} dT - \frac{1}{R}\int^T \frac{\int_0^T c_p dT}{T^2} dT + i, \tag{3}$$

where i is an integration constant, which varies only with the composition of the substance.

The quantum theory of specific heats, as developed by Debye and others, makes it possible to calculate the actual values of these integrals with a very satisfactory degree of accuracy for a large number of substances in the solid or gaseous states as the case may be.

O. Sackur[1] first showed that in the case of monatomic vapors the integration constant i could be expressed in terms of a *universal constant* i_0 and the molecular weight, by means of the relation

$$i = i_0 + 3/2 \log M, \tag{4}$$

where M is the molecular weight.

This conclusion has been subsequently confirmed by other investigators on the basis of dimensional considerations.[2]

At very low temperatures, it has been shown that the integral involving c_p becomes negligibly small. On the other hand, the specific heat of a monatomic gas at constant pressure is constant down to the lowest temperatures and is equal to $5/2\ R$. Consequently, under these conditions, Eq. (3) assumes the very simple form

$$\log p = - L_0/RT + 5/2 \log T + i_0 + 3/2 \log M. \tag{5}$$

Application to electron emission.—Now let us consider a metal in equilibrium with an electron atmosphere; also let us assume that the electron density in the space is so small that mutual repulsions may be neglected. We may then consider the evaporation of electrons from a metal as thermodynamically equivalent to the evaporation of a monatomic gas, for the electrons in the space necessarily have the same specific heat as the molecules of a monatomic gas. Now, experimental evidence shows that as a first approximation we may consider that the

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[1] Ann. der Phys. **36**, 598 (1911); **40**, 67 (1913).

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

electrons do not contribute to the specific heat of the metal. That is, with the possible exception of metals at extremely high temperatures, the specific heat of free electrons in the metal is zero. Hence, c_p is zero and Eq. (5) must also apply to the case of emission of electrons.

We may write this equation in the form

$$p = N^{3/2}m^{3/2}\epsilon^{i_0}T^{5/2}\epsilon^{-L_0/RT}, \qquad (6)$$

where N = Avogadro's constant = 6.06×10^{23} and m = mass of an electron = 8.995×10^{-28} gm.

Now, 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 $n = p/\sqrt{2\pi mkT}$, where k = Boltzmann's constant = 1.372×10^{-16} ergs/deg.

Since the electron atmosphere is in equilibrium with the hot metal, it follows that the number of electrons emitted must be equal to the number impinging if we assume that there is no reflection of electrons at the surface. Hence, the current per unit area per unit time is given by $I = ne = pe/\sqrt{2\pi mkT}$, where e = charge on electron.

Combining this with Eq. (6),

$$I = \left(\frac{N^{3/2}me\epsilon^{i_0}}{\sqrt{2\pi k}}\right)T^2\epsilon^{-b_0/T}, \qquad (7)$$

where $b_0 = L_0/R$, corresponding to b in Richardson's equation for electron emission.

It is evident that the expression in the brackets is a *universal constant.* Denoting this by A, it follows that the electron emission for any substance can be expressed as a function of the temperature by an equation of the form

$$I = AT^2\epsilon^{-b_0/T}, \qquad (8)$$

where b_0 is the only quantity that varies for different substances.

The value of the universal constant A.—(1) According to Sackur [1] and Tetrode, [2] the value of the chemical constant i_0 is given by the relation

$$i_0 = \log\left[\frac{(2\pi)^{3/2}k^{5/2}}{N^{3/2}h^3}\right]. \qquad (9)$$

Substituting in Eq. (7), we therefore obtain the following equation for the electron emission as a function of the temperature:

$$I = ne = \left(\frac{2\pi k^2me}{h^3}\right)T^2\epsilon^{-b_0/T}, \qquad (10a)$$

where the expression in the brackets corresponds to A in Eq. (8).

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[1] Ann. der Phys. **36**, 598 (1911); **40**, 67 (1913).

[2] Ann. der Phys. **38**, 434 (1912).

Using the values $k = 1.372 \times 10^{-16}$ ergs/deg., $m = 8.995 \times 10^{-28}$ gm, $h = 6.55 \times 10^{-27}$ erg/sec,

$$A = 1.80 \times 10^{11} \text{ e.s.u./cm}^2 \text{ deg.}^2 = 60.2 \text{ amp./cm}^2 \text{ deg.}^2. \qquad (10b)$$

(2) In 1914, G. N. Lewis and E. Q. Adams [1] developed a theory of ultimate rational units according to which the quantum constant is connected with the elementary unit charge by a simple numerical relation. More recently G. N. Lewis, G. E. Gibson and W. M. Latimer [2] have applied the same considerations in order to calculate the entropies of the elements. It can be shown that on the basis of their theory

$$\begin{aligned} A &= \frac{k^2 c^3 m \epsilon^{5/2}}{(4\pi)^6 e^5 \sqrt{2\pi}} = \frac{2^{5/2}\pi^{9/2}\epsilon^{-5/2}}{15} \cdot \frac{kme}{h^3} \qquad (11) \\ &= 1.53 \times 10^{11} \text{ e.s.u./cm}^2 \text{ deg.}^2 \\ &= 51.2 \text{ amp./cm}^2 \text{ deg.}^2. \end{aligned}$$

At the present stage, it is not possible on the basis of available vapor pressure data to decide definitely in favor of either of these values of A. On the one hand, it has been shown by A. C. Egerton [3] that the observations on the vapor pressures of zinc, cadmium, mercury and argon are in very good accord with the Sackur-Tetrode value of i_0, and similar results have been obtained by W. Nernst.[4] On the other hand, Lewis and his associates have made very careful calculations, based on experimental data, of the entropies of the four elements, helium, argon, cadmium and mercury, and find that in no case does the difference between the value of i_0 observed and that calculated on the basis of their theory exceed the probable experimental error.

PART II. HISTORICAL AND CRITICAL REMARKS ON THE GENERAL EQUATION FOR ELECTRON EMISSION

The generally accepted equation for electron emission is that first enunciated by O. W. Richardson, according to which

$$I = A_1 \sqrt{T} \epsilon^{-b/T}. \qquad (12)$$

In this equation A_1 and b are constants for any one substance. As pointed out by Richardson, b corresponds to L/R, where L is the latent heat of evaporation of the electrons. While the theoretical considerations on which the equation is based have not been considered quite satisfactory, the experimentally observed data on electron emission have actually been found to be in good agreement with the equation.

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[1] Lewis and Adams, Phys. Rev. **3**, 92 (1914).

[2] Lewis, Gibson and Latimer, J. Am. Chem. Soc. **44**, 1008 (1922).

[3] Egerton, Phil. Mag. **39**, 1 (1920).

[4] Nernst, Grundlagen des neuen Wärme-Satzes, Chap. 13 (1918).

That Richardson himself has not been altogether satisfied with the validity of this equation is evident from the fact that he has also suggested an equation similar in form to Eq. (8) above. In his book on "The Emission of Electricity from Hot Bodies,"[1] he pointed out that an equation of this form could be derived on the basis of the quantum theory. In the derivation of the value of A, he applied certain hypotheses which had been utilized by Debye and Keesom in calculating specific heats at low temperatures, and obtained a value which corresponds to 5 amp. cm^{-2} deg.^{-2} instead of 60.2 (or 51.2) as calculated in Part I. of this paper.

J. Eggert[2] pointed out that the Nernst Heat Theorem could be applied to calculate the degree of ionization of various metals at the extremely high temperatures which exist in fixed stars, and utilized for this calculation Eq. (6), p referring, obviously, to the pressure of the ions (or electrons) produced by dissociation of the metal atoms, and L_0 to the energy necessary for dissociation into positive ion and electron.

The same relations were also applied by Megh Nad Saha[3] to calculate the ionization in the solar chromosphere.

The bearing of Eq. (3) on the problem of electron emission from metals has been discussed very recently by both Tolman[4] and Laue.[5] Tolman's argument is briefly as follows. For the evaporation of a monatomic gas from a solid, the following entropy relation has been shown to be valid:

$$S = 5/2\, R \log T - R \log P + S_1 + 3/2\, R \log M. \tag{13}$$

In this equation S denotes the entropy at temperature T, P is the vapor pressure, S_1 is a constant for all monatomic gases and M denotes the molecular (or atomic) weight.

Tolman points out that while S_1 may be calculated on the basis of the equation derived by Sackur and Tetrode for i_0, there is still some doubt as to the validity of their arguments, and therefore he prefers to use the value calculated by Lewis and Gibson[6] from experimental data for helium.

According to this calculation, the value of the entropy for He at 298° K and 1 atmosphere pressure is 29.2. Hence,

$$S_1 = 29.2 - 3/2 \log 3.99 + 4.97 \log T - 1.987 \log (1.013 \times 10^6) = 24.21.$$

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[1] Second Edition, pp. 37–41; also Phil. Mag. **28**, 633 (1914).

[2] Phys. Zeits. **20**, 570 (1919).

[3] Phil. Mag. **40**, 472 (1920).

[4] R. C. Tolman, J. Am. Chem. Soc. **43**, 1592 (1921).

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

[6] J. Am. Chem. Soc. **39**, 2554 (1917), also R. C. Tolman, ib. **42**, 1185 (1920).

Tolman assumes now that electron emission is a phenomenon perfectly analogous to that of the evaporation of a monatomic substance, and that therefore Eq. (13) must also apply to this case. He calculates the pressure p of the electrons in equilibrium with the metal from the emission I. Substituting this value in Eq. (13) leads immediately to a value for S, the entropy at the temperature corresponding to the observed emission. From Langmuir's experimental data on the electron emission from tungsten, tantalum, and molybdenum at $T = 2000$, the values of S given in the fourth column of Table I. are obtained.

But $S = (F\phi + RT)/T$, where ϕ denotes the equivalent potential drop which the electrons have to overcome in escaping from the surface of the metal at the temperature T, and F denotes the Faraday constant. It is therefore possible also to calculate S from the observed value of ϕ. These have been determined by Lester[1] for the above metals and are given in the second column of Table I. The values of S calculated on this basis are given in the third column of the table.

Still another check on the value of S may be obtained by means of the fundamental equation (1) combined with Richardson's equation. On this basis,

$$S = \frac{L}{T} = RT \cdot \frac{d \log p}{dT} = RT \cdot \frac{d \log (I/\sqrt{T})}{dT} \, .$$

That is, S can be calculated from the rate of change of the electron emission with temperature. The values of S thus obtained are given in the last column.

TABLE I

	ϕ	S (from ϕ)	S (from I)	S (from slope)
Tungsten.........	4.478	53.6	53.3	54.1
Tantalum.........	4.511	54.0	52.3	51.6
Molybdenum......	4.588	54.9	51.0	51.6

The agreement between the values of the entropy calculated by the different methods leads to the conclusion that the assumptions involved in the application of Eqs. (3) or (13) to electron emission are justifiable. The exact nature of these assumptions has been discussed rather fully by Tolman and also by Laue, so that consideration of this phase of the problem may be omitted in the present connection.

Relation between entropy constant, chemical constant and A in Eq. (8).—It is well in this connection to state briefly the relation between the constant S_1 used by these investigators and the chemical constant i_0

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

introduced in the first part of this paper. This relation is easily derived from the following considerations:

For the evaporation of electrons at the temperature T, it has been shown above that Eq. (2) reduces to $L = L_0 + C_pT$. Therefore,

$$S = L/T = L_0/T + C_p.$$

Substituting for S in Eq. (13) and comparing this with Eq. (5), we obtain the relation

$$i_0 = (S_1 - C_p)/R. \tag{14}$$

By means of this equation combined with Eq. (7) it is therefore possible to calculate the constant A for any given value of S_1.

It is usual in discussions of vapor pressure data to replace the constant i_0 by $C_0 = i_0/2.303$, since this makes it possible to use ordinary logarithms. As this latter constant is the one usually given in most publications on this subject, it has been considered worth while to tabulate for reference the corresponding values of C_0, S_1, and A based on the theories of Sackur and Tetrode on the one hand and of Lewis and his associates on the other. The value of S_1 used by Tolman and the corresponding value of A are also given for comparison.

	S_1	$C_0 = i_0/2.303$	A (amp./cm^2 deg.^{2})
Sackur-Tetrode	25.19	− 1.5877* 4.4178†	60.24
Lewis	24.87	4.354†	51.2
Tolman	24.27		38.4

* Pressure in atm.

† Pressure in bars.

Accuracy of determination of A from electron emission data.—In view of the relation between the value of A and that of S_1 (or C_0) it would appear at first glance as if evidence in favor of one theory or the other might be obtained from electron emission data.

From Eq. (8) it follows that

$$b_0 = \frac{\Delta \log (I/T^2)}{\Delta(1/T)}. \tag{15}$$

Consequently it is possible to derive a value for b_0 independently of any assumed value of A, by plotting log (I/T^2) against $1/T$ and noting the slope of the resulting straight line. From this value of b_0, that of A may then be obtained by direct substitution in Eq. (8).

The difficulty, however, in using this method to determine the value of A, arises from the very form of the above equation, where b_0 and T

both enter into the exponential factor, while A is a coefficient of this factor.[1] Hence, the slightest error in the determination of either b_0 or T leads to a considerably greater error in the resulting value of A.

Thus for the case $T = 2000$, and $b_0 = 50{,}000$, it can be shown that an error of one per cent in b_0 produces an error of 25 per cent in that of A. Hence, to attain a sufficiently high degree of accuracy in the determination of A, for the present purpose, it would be necessary to obtain values of b_0 accurate to at least 0.25 per cent.

The accuracy of temperature determination varies for different metals. In the case of tungsten, for which as a result of the work of Langmuir, and of Worthing and Forsythe, the temperature scale is most accurately known, it is possible to measure temperatures in the range 1500–2500° K with an accuracy of 5 degrees. This is, nevertheless, not exact enough to settle the question as to the most satisfactory value of A.

While the theory advanced by Lewis and his associates must be regarded as much more reasonable than that postulated by Sackur and Tetrode, it has been found in the case of tungsten that with the temperature scale used by Worthing and Forsythe, the observed electron emission data are in somewhat better agreement with the value $A = 60.24$ amp./cm^2 deg.^{2}. It is, however, obvious, as a consequence of the considerations mentioned above, that this result cannot be regarded as a direct confirmation of the Sackur-Tetrode theory. For the present purposes, we must merely regard the value of A given above as one which is in satisfactory agreement with the standard temperature scale for tungsten. It is, therefore, the value which will be adopted in this paper and in subsequent ones on electron emission.

Application of the equation for electron emission to the determination of true temperatures.—The equation for electron emission, as derived on the basis of the considerations stated in the previous section, can be expressed in a form which is much more convenient for calculation as follows:

$$\log_{10} (I/T^2) = 1.7792 - b_0/2.303T, \tag{16}$$

where I = emission in amp./cm^2 at the temperature T.

There is an interesting application of this equation which ought to be pointed out in this connection. It is evident that at any given temperature T, the emissions I' and I'' for two different substances are connected with the corresponding values b_0' and b_0'' by the relation

$$\log_{10} I'' - \log_{10} I' = (b_0' - b_0'')/2.303T. \tag{17}$$

Thus, given any substance for which b_0' is known, it is possible to

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[1] This has also been pointed out bv Richardson, loc. cit., p. 86.

determine b_0'' for the other substance by enclosing the two in a "Hohlraum" ("black body" enclosure) and measuring the relative emissions. For this purpose it is not at all necessary to know the temperature of the enclosure. The value of T in the above equation is determined from the observed value of log I and the corresponding value of b_0. Once b_0' is determined by this method for the second material, it is obviously possible, by going back to Eq. (16), to determine a true temperature scale for this material. That the electron emission may be used to measure temperatures has been pointed out by Richardson and others. However, this method is not so directly applicable if Richardson's equation is adhered to, since this involves also a knowledge of the integration constant A in the latter equation, whereas assuming the validity of Eq. (8), the determination of a true temperature scale for any substance becomes a much simpler matter.

Thermionic work function.—In the derivation of Eq. (8), $b_0 = L_0/R$. This constant is related to the thermionic work function ϕ_0, at the absolute zero, by the relations

$$\phi_0 = L_0/Ne = Rb_0/Ne = kb_0/e = 8.62 \times 10^{-5} b_0 \text{ volts.} \tag{18}$$

Denoting the work function corresponding to b in Richardson's equation by ϕ, it follows that

$$\phi = \phi_0 + \frac{3}{2}\frac{k}{e}T \tag{19}$$

and

$$b = b_0 + \frac{3}{2}T. \tag{20}$$

A number of investigators have attempted to measure ϕ directly by observations on the cooling effect produced by the evaporation of the electrons. In a previous connection, mention has been made of Lester's measurements in the case of several metals. The most recent contribution on this subject is by C. Davisson and L. H. Germer [1] who made some extremely accurate observations in the case of tungsten. It is of interest to point out the relation between the experimental data obtained by such measurements and the values of ϕ_0 as determined from emission data at different temperature.

If we assume that the electrons in the metal do not possess any thermal energy of agitation, and denote the observed cooling effect at the temperature T by P (in volts), it can be deduced from simple considerations that

$$Pe = \phi_0 e + 2kT. \tag{20}$$

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[1] Phys. Rev. **20**, 300 (1922).

That is, the energy absorbed per electron leaving the surface is equal to the work done against electrical forces (see subsequent portion of this paper) plus the kinetic energy of the emitted electrons. As shown by Richardson,[1] the average kinetic energy of the emitted electrons is $2kT$ and not $3/2\, kT$.

Davisson and Germer find that in the case of the electron emission from tungsten, ϕ_0 as derived from calorimetric determinations (*i.e.*, by means of Eq. (20)) is 4.52 volts, whereas direct measurement of the emission as function of temperature leads to the value 4.48 volts. The agreement between the two values may be regarded as very satisfactory, as it is well within the limits of experimental errors.

PART III. EXPERIMENTAL RESULTS

In a series of subsequent papers, experimental data will be given to demonstrate the validity of the equations deduced in this paper, over a large range of temperatures, for several different metals. However, the electron emission data on tungsten recently published by Davisson and Germer[2] serve as a confirmation of the validity of Eq. (10) by independent observers.

These data are given in the first and third columns of Table II. The first column gives the value of T on the basis of the scale used by Worthing and Forsythe, while the fourth column gives the values of $\log_{10} I$, where I denotes the electron emission in amperes per cm^2, as calculated from the values observed for a filament of area 0.1825 cm^2. The observed emissions are given in the third column. From these data the values of b_0 given in the sixth column were calculated by means of Eq. (10). The average of these values is 51,860.

Fig. 1 shows the values of $\log_{10} (I/T^2)$ plotted against $1/T$. As has been pointed out in Part I., a satisfactory test of the validity of Eq. (8) or (10) is obtained when the value of b_0 calculated from the slope $\Delta \log_{10} (I/T^2)/\Delta(1/T)$ is found to be in agreement with the values of b_0 calculated from the emission data at different temperatures. The slope of the straight line drawn through the points in Fig. 1 is actually observed to be identical with the average value of b_0 given in Table II.

Such a test has also been applied to data published by W. Schlichter on the electron emission from platinum and nickel.[3]

Table III. gives the values of b_0 calculated from the emission data for platinum. It will be observed that the greatest deviation from the aver-

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[1] Loc. cit., p. 156.

[2] Loc. cit.

[3] Ann. der Phys. **47**, 573 (1915).

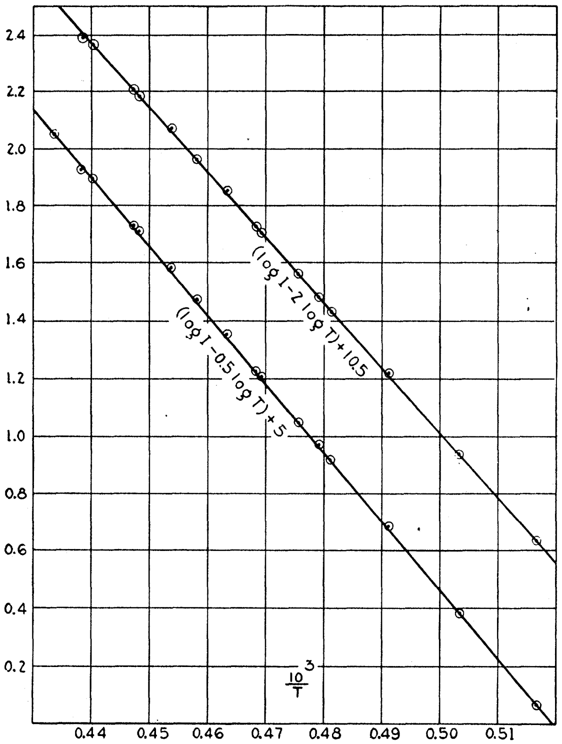

Fig. 1. Plot of emission data for tungsten obtained by Davisson and Germer.

Table II

Electron Emission Data for Tungsten Filament (Area = 0.1825 cm²) Obtained by Davisson and Germer *

T	$\frac{10^3}{T}$	$i \times 10^3$	$\log I + 4$	$\log I - 2 \log T + 10$	b_0	$\log I - 0.5 \log T + 5$
1935.5	0.5167	0.0934	0.7091	0.1355	51,890	0.0658
1986.5	.5034	0.1973	1.0340	0.4378	51,880	0.3850
2036.0	.4912	0.3967	1.3373	0.7197	51,860	0.6829
2077.5	.4813	0.6784	1.5703	0.9351	51,880	0.9116
2086.5	.4793	0.7656	1.6228	0.9838	51,900	0.9631
2102.0	.4758	0.9363	1.7102	1.0650	51,840	1.0489
2131.5	.4692	1.362	1.8729	1.2155	51,840	1.2086
2134.5	.4685	1.419	1.8907	1.2321	51,870	1.2261
2158.0	.4634	1.902	2.0180	1.3500	51,820	1.3510
2182.0	.4583	2.538	2.1433	1.4655	51,810	1.4739
2204.0	.4537	3.269	2.2532	1.5668	51,820	1.5816
2231.0	.4482	4.405	2.3828	1.6858	51,820	1.7086
2235.0	.4474	4.606	2.4022	1.7036	51,870	1.7276
2271.5	.4402	6.875	2.5761	1.8635	51,880	1.8980
2280.0	.4386	7.394	2.6076	1.8918	51,920	1.9287
2306.0	.4337	9.792	2.7297	2.0041	51,900	2.0483
					Avg. 51,860	

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* Ordinary $\log_{10}$ are used in this table.

age value 49,250 is about one half per cent. The same value is obtained from the slope directly. In the case of nickel, the average value of b_0 calculated from the emission data is 47,800, and the value obtained from the slope is 48,000.

TABLE III

Schlichter's Data on Emission from Platinum (Area = 23 cm²)

T	$i \times 10^8$ (amp.)	b_0
1211	0.42	49,300
1243	1.35	49,200
1275	4.17	49,100
1307	9.9	49,300
1339	27.5	49,200
1371	76	49,000
1403	168	49,100
1435	400	49,100
1467	785	49,300
1499	1430	49,500
		Avg. 49,250

While these results and numerous observations by the writer and his associates thus show satisfactory agreement with the deductions based on Eq. (8), it is however only just to point out that all these observations are equally well represented by an empirical equation involving $T^{1/2}$ instead of T^2. Richardson and other observers have in fact noted that within the limits of experimental error it is impossible to show by plotting either $\log_{10}(I/T^2)$ or $\log_{10}(I/\sqrt{T})$ against $1/T$ that either set of data gives a better straight line.

Table II. gives in the last column values of $\log_{10}(I/\sqrt{T})$ calculated from Davisson and Germer's observations. As is evident from Fig. 1, the plot of these data is a straight line, which differs only in the value of the slope ($b_0 = 55{,}410$) from the plot of $\log_{10}(I/T^2)$. The reason for this lack of any difference between the plots is the practical impossibility of measuring emission data over an extremely wide range of temperatures. Thus, in the case of tungsten, over a temperature range from 1000° K to 2500° K, the emission increases in the ratio 10^{15} approximately, while the ratio of values of $T^{1/2}$ is 1.58 and of T^2, 6.25.

The advantages in the equation derived in the present paper lie firstly in the theory underlying its derivation and secondly in the conclusion that the integration constant A is the same for all metals. Consequently it is possible to determine b_0 for any substance by measuring its emission at *only one temperature* instead of at two or more.

The values of b_0 obtained for a number of metals are given in Table

IV.[1] In the case of tungsten and that of thorium (obtained from thoriated tungsten filaments), the values are accurate to about one half per cent, while in the case of molybdenum and that of tantalum the degree of accuracy is probably one per cent. This is largely due to lack of very accurate temperature data for these metals. The emission for uranium, zirconium, yttrium, and cerium was measured on tungsten filaments containing additions of these elements as oxides (in a manner similar to that in which thoria is added to tungsten). It is not certain that in all these cases the maximum emission observed corresponded to that of a surface completely covered with a layer one atom deep of the added element, as the latter are much more volatile than thorium under similar conditions. Hence, the values of b_0 obtained for these elements must be regarded as upper limits.

The value of b_0 for calcium corresponds to the maximum emission observed when evaporating the metal in a vacuum and allowing it to condense on a tungsten surface.

The third column of Table IV. gives the corresponding values of ϕ_0. Schottky[2] and subsequently Langmuir[3] applied the theory of electrical images to calculate the distance x_0 at which the electron leaving the metal ceases to be attracted by the charge induced on the surface. According to this theory, $\phi_0 = e/2x_0$.

Converting to volts

$$x_0 = 7.16 \times 10^{-8}/\phi_0 \text{ cm}. \qquad (22)$$

Now it is reasonable to expect that this distance should be less than the molecular diameter σ, and that the ratio x_0/σ should be greater the more electropositive the element.[3] The value of σ can be calculated from the atomic volume V by the relation

$$\sigma = 1.33 \times 10^{-8} V^{1/3}. \qquad (23)$$

Table IV. gives the values of x_0, σ and x_0/σ calculated by means of these equations for the different elements.

One point that seems to be well established by these results is that the value of b_0 (or ϕ_0) is just as specific a constant for each element as its ordinary latent heat of evaporation. On the basis of some measurements of ϕ obtained by Lester for the elements molybdenum, carbon, tungsten,

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[1] The observations in the case of W, Th, Mo, Ta and Ca were made in conjunction with Mr. H. N. Rowe and Mr. C. A. Kidner, while those on Zr, Yt, Ce and U were made by Mr. D. M. Dennison. The emission data on which the values of b_0 are based will be published in subsequent papers.

[2] Schottky, Phys. Zeits. **15**, 872 (1914).

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

and tantalum, Richardson has suggested that the work functions might be found to be the same for all substances.[1] The data in Table IV. and reliable data on the values of ϕ for different oxides published in Richardson's book, however, show definitely that the above suggestion is quite untenable.

TABLE IV

Values of b_0, ϕ_0, Etc., for Different Metals

Metal	b_0	ϕ_0	$x_0 \times 10^8$	$\sigma \times 10^8$	x_0/σ	N
Calcium.......	26,000	2.24	3.19	3.95	0.81	20
Yttrium.......	37,000	3.19	2.25	3.80	0.59	39
Zirconium.....	38,000	3.28	2.19	3.22	0.68	40
Molybdenum ..	50,000	4.31	1.66	2.93	0.57	42
Cerium........	35,600	3.07	2.33	3.63	0.64	58
Tantalum.....	51,000	4.31	1.66	2.95	0.56	73
Tungsten......	52,600	4.53	1.58	2.81	0.56	74
Thorium......	34,100	2.94	2.44	3.68	0.66	90
Uranium......	38,000	3.28	2.19	3.10	0.70	92

It is, of course, of interest to determine, if possible, the relation between b_0 for any element and other properties of this element. The results obtained so far, however, are insufficient to be more than suggestive. It is evident that b_0 (or ϕ_0) is lower, the greater the atomic volume (or atomic diameter). Also, apparently x_0/σ is a periodic property of the atomic number N with a maximum value which tends to approach 1 for the alkali and alkaline earth elements, while for elements of group VI. (tungsten, molybdenum, and uranium), the value of this ratio is a minimum. Further investigations on the electron emission from other metals must be carried out before any definite theory on this subject can be formulated.

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[1] Loc. cit. p. 189.