

Work Function and Temperature*

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The change in height of the potential energy barrier at the surface of a metal with the expansion of the metal due to heating is investigated. Also, the change of the normal maximum energy of an electron in a metal is calculated as a function of the temperature of the metal. These calculations show that the work function of a metal is a linear function of its temperature. These results, when combined with the thermionic emission equation, show that the thermionic emission constant is a characteristic of the metal, and is no longer the same for all pure metals. The calculated results for the thermionic emission constants for several metals show fair agreement with the experimentally determined values.

SEVERAL suggestions have been offered in an attempt to resolve the difference that is found to exist between the thermionic emission constant, A_0 , predicted by theory and the value which is obtained by experiment. According to modern statistical theory, this constant, which appears in the Dushman equation relating the thermionic emission current density, J_{Th} , with the temperature

$$J_{Th} = A_0 T^2 \epsilon^{-(E_B - E_M)/E_T} = A_0 T^2 \epsilon^{-E_w/E_T} \quad (1)$$

has a value of 120 amperes·cm⁻²·degrees⁻² for all pure metals. Actually, however, a value approximately one-half of this theoretical value has been found to apply for many pure metals, although values which are widely different from 60 amperes·cm⁻²·degree⁻² have been reported for several metals. In this expression E_B denotes the height of the potential barrier at the surface of the metal, E_M is a quantity which is characteristic of the metal (and will be considered in some detail below), E_w (defined as the difference between E_B and E_M) is the work function of the metal, all in electron volts, E_T is the electron volt equivalent of temperature ($=kT/e \cdot 10^7 = T/11,600$; with k = Boltzmann's constant, e = charge of the electron in coulombs), and where T is the temperature in degrees Kelvin.

In order to verify this equation experimentally, a graph based on the logarithm of this equation is plotted. That is, since

$$\log_{10}(J_{Th}/T^2) = \log_{10} A_0 - 0.434(11,600 E_w)/T, \quad (2)$$

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then a plot of $\log_{10} J_{Th}/T^2$ versus $1/T$ should be a straight line having a slope equal to $-0.434(11,600 E_w)$ and an intercept equal to $\log_{10} A_0$. Logarithmic plots of this type yield the low values mentioned.

A careful analysis by Nordheim¹ showed that Eq. (1) should actually have the form

$$J_{Th} = A_0(1 - r)\epsilon^{-E_w/E_T}, \quad (3)$$

where r is a reflection coefficient. This factor expresses the ratio of the number of electrons reflected back into the body of the metal at the surface to the total number of electrons which are moving in the escape direction. However, calculations show that the reflection factor is less than 0.07 for the type of potential variations which exist at the surface of the metal. A physical argument by Becker and Brattain² likewise leads to the conclusion that r must be very small. The presence of the reflection coefficient in Eq. (3) does not, therefore, resolve the difference.

More recently Herzfeld³ and Becker and Brattain² concluded from thermodynamic considerations that the work function, E_w , appearing in Eq. (1) is not a constant, but is a quantity that varies with the temperature. This conclusion has received experimental confirmation.⁴ The magnitude of the variation observed for tungsten is just of the right order to resolve completely the difference between the theoretical value and the

¹ L. Nordheim, Proc. Roy. Soc. **121**, 626 (1928).

² J. A. Becker and W. H. Brattain, Phys. Rev. **45**, 694 (1934).

³ K. F. Herzfeld, Phys. Rev. **35**, 248 (1930).

⁴ A. L. Reimann, Proc. Roy. Soc. **163**, 499 (1937); J. G. Potter, Phys. Rev. **58**, 622 (1940); F. Krüger and G. Stabenow, Ann. d. Physik **22**, 713 (1935).

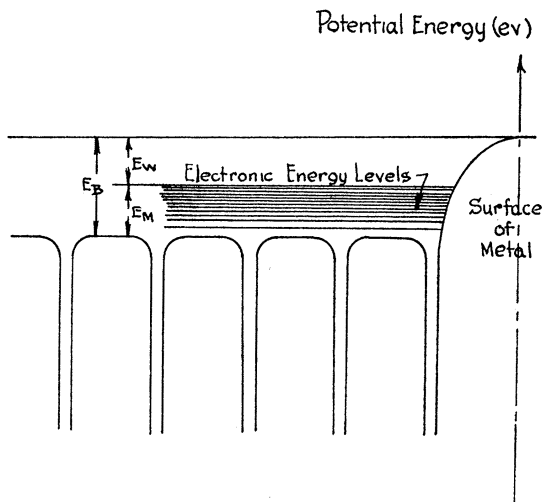


FIG. 1. The potential energy variation along a row of atoms in a metal.

experimental value of the thermionic emission constant.

THE VARIATION OF E_M WITH TEMPERATURE

That E_w cannot be a constant, independent of the temperature, follows from the definition of E_w in terms of E_B and E_M , and the fact that both E_M and E_B can be shown to be temperature dependent functions. According to the electron theory of metals,

$$E_M = E_0 \left[1 - \frac{\pi^2 E_T^2}{12 E_0^2} \right] \text{ (electron volts),} \quad (4)$$

where E_0 may be shown to have the form

$$E_0 = \frac{h^2}{8em10^7} \left(\frac{3N}{\pi} \right)^{\frac{2}{3}} \text{ (electron volts).} \quad (5)$$

The symbols have the following meanings: h is Planck's constant, e is the electronic charge in coulombs, m is the mass of the electron in grams, and N denotes the concentration of free electrons per cc of the metal. By inserting the known values of the constants in this expression, E_0 may be written in the form

$$E_0 = 3.62 \times 10^{-15} N^{\frac{2}{3}} \text{ (electron volts).} \quad (6)$$

As pointed out both by Herzfeld and by Becker and Brattain, the quantity N depends upon the temperature because the density of the material is temperature dependent. By making use of the fact that the linear expansion of most metals can

be written with good approximation by an expression of the form

$$l = l_0(1 + \alpha T), \quad (7)$$

where α is the coefficient of linear expansion, it follows that $N = N_0/(1 + \alpha T)^3$. By combining this expression with (6)

$$E_0 = 3.62 \times 10^{-15} [N_0/(1 + \alpha T)^3]^{\frac{2}{3}}$$

which may be written in the form

$$E_0 = E_{00}/(1 + \alpha T)^2, \quad (8)$$

where the quantity

$$E_{00} = 3.62 \times 10^{-15} N_0^{\frac{2}{3}} \quad (9)$$

is a constant, independent of the temperature.

Equation (4) may then be written in the form

$$E_M = \frac{E_{00}}{(1 + \alpha T)^2} \left[1 - \frac{\pi^2 E_T^2}{12 E_{00}^2} (1 + \alpha T)^4 \right],$$

which reduces to the approximate form

$$E_M = E_{00} \left\{ 1 - 2\alpha T + \left[3\alpha^2 T^2 - \frac{\pi^2 E_T^2}{12 E_{00}^2} \right] \right\}.$$

The third term in this expression is very small compared with the second term over the normal range of temperatures, and so may be neglected. Thus to a good approximation

$$E_M = E_{00}(1 - 2\alpha T). \quad (10)$$

THE VARIATION OF E_B WITH TEMPERATURE

Herzfeld first pointed out that E_B should be temperature dependent. However, his calculations of E_B and dE_B/dT , based upon an approximate method due to Bethe⁵ leads to incorrect results. This calculation predicts a greater variation in the term dE_B/dT than in the term dE_M/dT . The net result is a greater value for the thermionic emission constant than 120 amperes·cm⁻²·degree⁻². This contradicts the facts for all metals.

The explicit dependence of E_B on the temperature may be investigated in two ways. One way makes use of considerations dictated by the modern theory of solids. The other is based on the image law for the force on an electron near the surface of a metal. The results are the same, to the approximation in which we are interested.

⁵ H. Bethe, Ann. d. Physik **87**, 55 (1928).

According to considerations of the theory of solids, the potential energy distribution in a metal has the general form illustrated in Fig. 1. The presence of the potential energy barrier at the surface of the metal results from the lowering of the potential energy in the region within the metal by the contributions of the ions which are tightly bound to fixed points of the crystal lattice, and by the lack of such lowering at the surface of the metal because of the lack of ions in the region outside of the metal. The effective potential energy at any point in the metal will consist of the sum of the contributions to the potential energy of all of the ions in the immediate neighborhood of the point in question. This is so because the potential at any point due to any ion decreases rapidly with the distance from the position of the ion.

In any event, the potential energy at any point in the body of the metal with respect to the exterior will be, if we consider the contributions of all of the ions to this potential energy, of the form

$$U_0 = -e \sum \frac{(Z-S)e}{r},$$

where Z is the atomic number of the atom, S is the atomic screening factor, and r is the distance from the position of each ion to the reference point. The screening factor gives a measure of the effectiveness of the orbital electrons surrounding the nucleus in reducing the nuclear charge. It is, therefore, a function of the distance from the nucleus of the atom. However, as indicated in Fig. 1, the potential energy in the metal is substantially constant throughout the major portion of its volume, except for the rather intense local variations which exist in the immediate neighborhood of the nuclei.

If it is assumed that $(Z-S)$ does not change appreciably when the interionic distances are slightly altered because of the expansion of the metal when its temperature is raised, then

$$U = -e \sum \frac{(Z-S)e}{r(1+\alpha T)}.$$

By expanding the term in the denominator and retaining only the first-order term in the temperature, the result may be written in the form

$$E_B = E_{B_0}(1 - \alpha T), \quad (11)$$

where the term E_B gives the height of the potential energy barrier in electron volts. This expression shows that the height of the potential barrier at the surface of the metal is decreased slightly as a result of the expansion of the metal caused by heating.

According to considerations of the image law of force on an electron at the surface of the metal, the height of the potential barrier is related to the force function by the expression

$$eE_{B_0} \cdot 10^7 = - \int_0^{\infty} f(x) dx, \quad (12)$$

where $f(x)$ is the functional form of the force function, which has the general shape illustrated in Fig. 2. That the image law for the force on the electron is essentially the correct one for thermionic phenomena is shown by the calculations of Schottky⁶ in which the effect of an accelerating field at the surface of a thermionic cathode is successfully explained in terms of this law of force.

Because of the expansion resulting from the heating, it is necessary to calculate the value of

$$eE_B \cdot 10^7 = - \int_0^{\infty} f(x+\Delta) dx, \quad (13)$$

where, from Eq. (7)

$$\Delta = \alpha T x. \quad (14)$$

By expanding the integrand in a Taylor's series, and integrating the series term by term, the result is that given by (11) if we retain only the first-order term in αT .

GENERAL RESULTS

By combining Eqs. (11) and (10) with the definition of E_w ,

$$\begin{aligned} E_w &= E_B - E_M = E_{B_0}(1 - \alpha T) - E_{00}(1 - 2\alpha T) \\ &= (E_{B_0} - E_{00}) - \alpha T(E_{B_0} - 2E_{00}). \end{aligned}$$

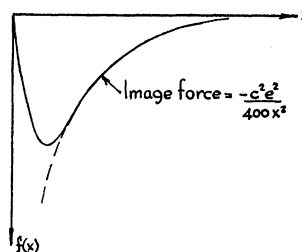


FIG. 2. The image force function at the surface of a metal.

⁶ W. Schottky, Physik. Zeits. 15, 872 (1914).

TABLE I. Comparison of experimental and calculated values of thermionic emission constants.

MATERIAL	MEASURED			CALCULATED		
	A	E_{w0}	$\alpha \times 10^6$ *	E_{00}	C	CA_0
C ⁷	30	4.3	7.9	13.5	0.432	52
Ca ⁸	60	2.2	25	4.7	0.485	58
Mo ⁸	55	4.1	5.5	9.4	0.715	86
Ni ⁸	27	2.8	18.2	11.7	0.153	18
Pt ⁹	32	5.3	11	9.5	0.585	70
W ⁸	60	4.5	7.3	9.1	0.671	80

* From *International Critical Tables*.

It follows from this that

$$E_w = E_{w0} + \alpha(E_{00} - E_{w0})T \text{ (electron volts)} \quad (15)$$

where, by definition $E_{w0} = E_{B0} - E_{00}$. It is observed that this expression predicts a linear dependence of the work function on the temperature. The quantity E_{w0} is independent of the temperature, and may be called the "work function at absolute zero" or the "true work function" of the metal.

For the case of tungsten (based upon the assumption that each tungsten atom supplies 2 free electrons) $E_{00} = 9.1$ ev, and, from experimental measurements, $E_{w0} = 4.5$ ev. These quantities, together with the experimental value of $\alpha = 7.3 \times 10^{-6}$ per degree in Eq. (15) yield

$$E_w = E_{w0} + 3.4 \times 10^{-5} T \text{ (electron volts)}. \quad (16)$$

This result is in fair agreement with the results of Potter,⁴ Reimann⁴ and Krüger and Stabenow who found the values 6.3×10^{-5} , 7.1×10^{-5} and 6×10^{-5} ev/degree, respectively, for the coefficient of T .

By combining Eq. (15) with Eq. (1), the thermionic emission equation may be written in the form

$$J_{Th} = CA_0 T^2 \epsilon^{-E_{w0}/ET}, \quad (17)$$

where the term

$$C = \exp \left[-\frac{\alpha(E_{00} - E_{w0})T}{E_T} \right] \\ = \exp [-\alpha(E_{00} - E_{w0}) \times 11,600] \quad (18)$$

is independent of the temperature, and depends only on the value of E_{00} , E_{w0} , and the coefficient

⁷ A. L. Reimann, Proc. Phys. Soc. London 50, 496 (1938).

⁸ S. Dushman, Rev. Mod. Phys. 2, 381 (1930).

⁹ L. V. Whitney, Phys. Rev. 50, 1154 (1936).

of linear expansion of the metal. Because of this correction coefficient, one no longer expects the thermionic emission constant in Eq. (17) to be the same for all metals.

The values predicted by this expression for CA_0 , and the values obtained experimentally for the thermionic emission constants of several metals are contained in Table I. In columns two, three and four are contained the experimentally determined values of the thermionic emission constants A , the work function, and the coefficient of linear expansion of the material. In columns five, six and seven are contained the calculated values of E_{00} (based on the assumption of 2 electrons/atom), the correction factor C , and the thermionic emission constant CA_0 .

CONCLUSIONS

Based on the foregoing considerations, it appears that the slope of the thermionic emission logarithmic plot should be associated with the true work function of the metal, E_{w0} . This is a quantity which is constant and independent of the temperature. The effect of the temperature on the values of E_M and E_B results in the appearance of a correction term in the thermionic emission equation which lowers the thermionic emission constant below 120 amperes/cm²/degree². Furthermore, the value of the thermionic emission constant will depend upon the metal considered, and will vary from metal to metal. This yields values which are more nearly in agreement with the values determined experimentally.

It must be kept in mind that E_{00} appears in the correction term expressed by Eq. (18). Since the calculation of this quantity requires a knowledge of the number of free electrons per atom of the metal, an unknown error may result from the assumption of two electrons per atom. However, the experiments of Rupp¹⁰ on the diffraction of electrons in passing through matter furnish evidence which, for Mo, Ni and W, removes the uncertainty in this number.

The author wishes to express his thanks to his colleague at the City College, Dr. Jacob Millman, for interesting and helpful discussions of this problem.

¹⁰ H. Rupp (see R. H. Fowler, *Statistical Mechanics*, (Macmillan, 1936), second edition, p. 355).