THE UNIVERSAL CONSTANT OF THERMIONIC EMISSION

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Abstract

Theoretical deduction of the formula for thermionic emission.—The constant A of the thermionic emission formula: $I = AT^2 e^{-b_0/T}$ has been shown by Richardson and Dushman by different lines of argument to be a universal constant, and a value for the constant has been deduced by Dushman. The experimental data of Dushman verify this value of A for pure metals, but if the metal is coated there are very wide divergences. In this paper an attempt is made to give a more rigorous deduction of the emission formula, so that it may be plain under what conditions it may be expected that A be universal. Assuming that the entropy of the electron gas is the same as that of an ordinary monatomic gas in the Sackur Tetrode theory, and also assuming that the entropy of a surface charge is zero at 0° Abs. it is shown that an emission formula of the type above necessarily demands that A have the universal value assigned by Dushman, and the necessary and sufficient condition for this is that the difference between the specific heat of the neutral metal and of a charge on its surface vanish ($C_{pm} - C_{p\rho} = 0$). This condition may also be formulated in terms of the surface heat and is equivalent to $\sigma + dP_s/dT - P_s/T = 0$, where P_s is the surface heat and σ the Thomson heat. If σ can be neglected, the emission formula holds with the form given when P_s is proportional to absolute temperature.

Physically it seems probable that (1) if the metal is uncoated the forces on the surface ions are nearly the same as on the neutral atoms, so that the condition $C_{pm} - C_{p\rho} = 0$ is satisfied, but (2) if the surface charge has the properties of a gas, as in an oxygen coated filament, (a) the specific heat may be different from that of the metal, or more probably (b) the entropy of the surface charge may not vanish at 0° Abs.; and (3) if the surface is coated with another more easily ionizable metal there may be electrical forces on the surface ions which modify their specific heat.

Introduction

IN two recent papers Dushman[1] has given a theoretical deduction of the constant A of the formula of thermionic emission

$$I = AT^2 e^{-b_0/T}$$

and has discussed the agreement with experiment in the light of new and more accurate data. The deduction of the value of A involves the Sackur-Tetrode theory of the entropy constant of a monatomic gas (which here is the electron gas in contact with the metal), and the value found by Dushman is $A = 2\pi k^2 m\epsilon/h^3$.

[1] S. Dushman, Phys. Rev. **21**, 623-636 (1923); **25**, 328-360 (1925).

In a note commenting on the first paper of Dushman, Richardson[2] points out that as early as 1915 he had, by a purely thermodynamic argument not involving quantum theory, shown that A is a universal constant, and had even gone further, and by an argument involving quantum theory, had found the factors $k^2 m \epsilon / h^3$ in A, but with a numerical coefficient different from 2π.

Experimentally Dushman found that the formula is entirely satisfactory for tungsten, for which the experimental data are most accurate, and probably is satisfactory for molybdenum and tantalum, for which the data are less accurate, but that if the emitting substance is not a pure metal, but is coated, the values of A range from 5×10^{11} to 3×10^{-3} (1925 paper, page 358). It would appear, therefore, that the arguments of both Dushman and Richardson must neglect some factor which is not important for pure metals, but which may be very important indeed in the more general case to which their arguments apply at least by implication.

Dushman states that his theoretical deduction of A neglects the surface heat, and that the agreement of the formula for tungsten indicates that for this metal the surface heat is small. Dushman, however, does not show at all in detail how the surface heat is concerned in the deduction of the formula, so that although we may be willing to accept his statement that the formula could be obtained by neglecting the surface heat, it is not at all obvious that conversely we may infer that, if the formula holds, the surface heat must be zero. The question of the surface heat was discussed by me at considerable length in the Physical Review[3] several years ago. It is a reversible heat which must be added or subtracted when an electrical charge is applied to or removed from the surface of a conductor isothermally. The possible existence of this surface heat has been neglected in nearly all thermodynamic discussions of this subject.

The original and fundamental thermodynamic discussion of Richardson has been recognized for some time to be lacking in rigor because of his interchangeable use of quantities thermodynamically different. Schottky pointed this out in 1915,[4] and I also discussed the matter at some length[3] (without knowledge of Schottky's work, which was inaccessible because of the war), and gave corrected forms for several of Richardson's formulas. Richardson has recently recognized[5] that

[2] O. W. Richardson, Phys. Rev. **23**, 153-155 (1925).
[3] P. W. Bridgman, Phys. Rev. **14**, 306-347 (1919).
[4] W. Schottky, Verh. D. Phys. Ges. **7**, 109-121 (1915).
[5] O. W. Richardson, Proc. Roy. Soc. **105**, 403 (1924).

he did neglect the difference between two quantities really different, but his present position is that as a matter of experiment the difference is small, and he points to recent experiments on tungsten as justification. He characterizes as "severe" my criticism that "the neglect of the surface heat in Richardson's equation would therefore seem to be indefensible, and until the order of the effect is known we cannot tell whether Richardson's equation is even approximately correct." In view of possible experimental variations from 5×10^{11} to 3×10^{-3} it does not seem to me that this remark is "severe."

It is the purpose of this paper to present a derivation of the thermionic emission equation without the approximations of either Richardson or Dushman, to find under what conditions the formula reduces to the simple form given, and in particular what are the necessary assumptions about the surface heat, and finally to discuss what may be the physical basis for the evident difference between the value of A for coated and uncoated conductors.

Deduction of the Thermionic Emission Formula

It must in the first place be said that it is recognized by everyone that there is an uncertain element in the formula for thermionic emission current in that it is necessary to assume no reflection of electrons on impinging on the metal surface from the gas. Thermodynamically we can find only the density (or pressure) of the electron gas in contact with the metal under equilibrium conditions. To pass from electron density to saturation current involves kinetic theory, assuming Maxwell's distribution of velocity, and also the assumption of no reflection.[6] In the following discussion we consider, instead of the emission current, the electron gas pressure. Under the usual assumptions of kinetic theory Dushman's formula is then equivalent to

$$p = \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} T^{5/2} e^{-b_0/T}$$

where p is the density of the electron gas at points immediately outside the metal, and the significance of the other letters is the conventional one. (I shall assume here as known and accepted the results of

[6] In this discussion no consideration is to be given to the somewhat modified form of the universal constant which would be obtained if the theory of G. N. Lewis of ultimate rational units is accepted. In view of the considerable uncertainty arising from the effect of electron reflections at the surface, I do not believe that any measurements of the saturation current are able at present to distinguish between the two values of the constant.

the long discussion between Schottky and v. Laue as to the justifia-
bility of treating the electron atmosphere as a perfect gas.)

It should also be said that the new ideas about the entropy constant
of a monatomic gas were first applied to the electron vapor by v. Laue,[7]
who obtained a value for p in which the coefficient of the exponential
term is exactly that of Dushman, but which has the exponential
term $e^{-\mu/RT}$. Here μ is the so-called "electron affinity" of the electron
for the metal. v. Laue explicitly recognized and stated that μ may be
a function of temperature. If there are terms in μ proportional to the
temperature the universal constant will obviously be modified, and
in any event the formula does not reduce to that above unless μ is a
constant. Physically, "electron affinity" is a concept most difficult to
interpret in terms of quantities directly measurable, so that the formula
as given by v. Laue actually becomes an equation for finding "electron
affinity" in terms of emission data, and is therefore not adapted to our
purposes, although from the thermodynamic point of view no criticism
can be made of the rigor of the deduction.

Given now a neutral metal at 0° Abs. We raise it, in the neutral condi-
tion, to the temperature T, and at this temperature evaporate from it
reversibly at the equilibrium pressure a certain number of electrons,
leaving behind on the surface of the metal in the form of surface charge
an equal and opposite positive charge. The final system consists of
electron vapor, surface charge, and remaining neutral metal. For the
purposes of this argument we may imagine that all the neutral metal
is evaporated, leaving a final system of only vapor and surface charge.
The entropy of the final system is the sum of the entropy of the gas
and of the surface charge. If we accept the dictum of the third law
that the entropy of the neutral metal is zero at 0° Abs., the entropy
of the final system is also equal to the entropy imparted to the neutral
metal on warming from 0° Abs. to T plus the entropy change during
evaporation. The entropy of the electron gas per electron is

$$s_0 + (5/2)k \log T - k \log p$$

where, according to the Sackur-Tetrode theory s_0 has the value:

$$s_0 = k \left(5/2 + \log \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right)$$

The entropy change of the system during evaporation is η/T, where
η is the latent heat of evaporation per electron, *the system being isolated
so that during the evaporation a compensating surface charge is left on
the metal.* The entropy change of the neutral metal during heating is

[7] M. von Laue, Jahrb. d. Rad. u. Elek. **15**, 257-270 (1918).

$\int_0^T (C_{pm}/T)dT$, where C_{pm} is the specific heat at constant pressure of that number of atoms of the neutral metal which give rise to one electron of vapor. The entropy of the surface charge, assuming that the surface charge acts like a condensed system so that its entropy at 0° Abs. vanishes, is $\int_0^T (C_{pp}/T)dT$, where C_{pp} is the specific heat at constant pressure of the surface charge left when one electron evaporates. Equating these entropies gives

$$\eta/T + \int_0^T (C_{pm}/T)dT = k\left(5/2 + \log\frac{(2\pi m)^{3/2}k^{5/2}}{h^3} + (5/2)\log T - \log p\right) + \int_0^T (C_{pp}/T)dT.$$

This equation may be solved for p, giving

$$p = \frac{(2\pi m)^{3/2}k^{5/2}}{h^3} T^{5/2} e^{5/2 - \eta/kT + (1/k)\int_0^T [(C_{pp}-C_{pm})/T]dT}.$$

In this expression everything except the exponential is of the form deduced by Dushman. Our immediate problem is then to find under what conditions the exponent reduces to $-b_0/T$. We must in the first place use what information we have about η, which is a function of temperature. One relation is immediately obtained from general thermodynamics. We have for the latent heat of any transition

$$\frac{d\eta}{dT} = \frac{\eta}{T} - \frac{\eta}{\Delta v}\left(\frac{\partial \Delta v}{\partial T}\right)_p + \Delta C_p.$$

Here Δv is the change of volume during the transition, and ΔC_p is the difference between the specific heat of the system before and after the transition. Applied to the electron vapor, we may in the first place neglect the volume of the metal and surface charge compared with the volume of the vapor, putting $\Delta v = v = (kT/p)$. ΔC_p, which for usual systems consist of only two terms, here consists of three terms, arising from the gas, the surface charge, and the neutral metal.

$$\Delta C_p = C_{pg} + C_{pp} - C_{pm}.$$

For a monatomic gas $C_{pg} = (5/2)k$. Substituting these values gives

$$\frac{d\eta}{dT} = \Delta C_p = (5/2)k + C_{pp} - C_{pm},$$

which gives on integrating

$$\eta = \eta_0 + (5/2)kT + \int_0^T (C_{pp} - C_{pm})dT.$$

Substituting back in the value for p, we obtain

$$p = \frac{(2\pi m)^{3/2}k^{5/2}}{h^3} T^{5/2} e^{-\eta_0/kT - (1/kT)\int_0^T (C_{pp} - C_{pm})dT + (1/k)\int_0^T (1/T)(C_{pp} - C_{pm})dT} .$$

Now to find under what conditions the exponent has the desired form, we put

$$-\eta_0/kT - (1/kT)\int_0^T (C_{pp} - C_{pm})dT + (1/k)\int_0^T (1/T)(C_{pp} - C_{pm})dT = -b_0/T.$$

Differentiate by T, giving

$$\eta_0/kT^2 + (1/kT^2)\int_0^T (C_{pp} - C_{pm})dT = b_0/T^2.$$

Multiply by T^2 and differentiate again, giving

$$C_{pp} - C_{pm} = 0.$$

Hence we see that the vanishing of $C_{pp} - C_{pm}$ is a necessary and sufficient condition for the formula found by Dushman with his value of the constant. We may go further and inquire under what conditions the formula takes the form $A'T^{5/2}e^{-b_0/T}$ where A' is some constant different from that above. The question is at once answered like that above by putting the exponent equal $-b_0/T + Const.$ Differentiation, as before, again shows that $C_{pp} - C_{pm} = 0$, so that we conclude that if the expression $A'T^{5/2}e^{-b_0/T}$ holds, both $C_{pp} - C_{pm}$ must vanish, and A' must have the universal value above.

The conclusions of the last paragraph have involved the assumption that the surface charge acts like a condensed phase in so far as to have zero entropy at $0°$ Abs. If this condition is not satisfied, there will be a constant in the exponent, so that there results a formula $A'T^{5/2}e^{-b_0/T}$ with a value for A' different from the universal constant above.

That Dushman has essentially neglected the term $C_{pp} - C_{pm}$ may be seen by a detailed examination of his argument, particularly his equation (2) on page 624, and his remarks at the bottom of page 624 and top of page 625.

The conditions under which the general formula with the accepted universal constant is valid have thus far made no mention of the surface heat. The connection may now be shown as follows. Equation (28) of my previous paper,[3] deduced by cyclic operations suggested by Richardson's analysis and entirely different from any used in deducing the previous value of $d\eta/dT$ is equivalent to the equation

$$d\eta/dT = (5/2)k - \epsilon(\sigma + dP_s/dT - P_s/T) .$$

Here P_s is the heat which must be absorbed by the system to maintain it isothermal when one unit of electricity is added to the surface, and σ is the Thomson heat as ordinarily defined. Equating the two values of $d\eta/dT$ gives

$$C_{pm} - C_{pp} = \epsilon(\sigma + dP_s/dT - P_s/T) .$$

Hence the assumption implicitly contained in the argument of Dushman, and also in that of Richardson as far as its application to the present problem is concerned, is equivalent to setting $\sigma + dP_s/dT - P_s/T$ equal to 0. Now it is generally considered that σ is small compared with other terms in problems of this character, so that if we neglect it the condition reduces to $dP_s/dT - P_s/T = 0$, which demands that P_s be proportional to temperature.

It is therefore not necessary that the surface heat vanish in order that the emission formula hold; numerically it may be large or small provided only that it be proportional to temperature.

PHYSICAL SIGNIFICANCE OF THE CONDITIONS

Returning now to the condition expressed in the form $C_{pm} - C_{pp} = 0$, the experimental data obtained by Dushman suggest that the specific heat of the ionized atoms which constitute the surface charge is the same as that of the neutral metal atoms if the metal is pure, but different if the metal is coated. What may we conceive to be the physical reason for this? If the metal is pure the surface charge consists of ionized atoms scattered about in the surface layer of the crystal lattice of the metal, which reaches to the surface without alteration. The analysis of v. Laue has shown that if the electron vapor is to be treated as a perfect gas and the effect of space charge neglected, the electron vapor can occupy a space only a few free paths thick. Under these conditions the distance between the ions in the surface layer is of the same order of magnitude as that between the electrons in the vapor, and since the electrical forces between the electrons in the vapor are negligible under these conditions, it must also be true that in the surface layer the mutual electrical forces between the ions are negligible compared to the forces holding the ions in the crystal lattice. The natural frequency of the surface ions is then approximately the same as that of the surface atoms, and the specific heat is therefore the same.

If, however, the metal is coated, these conditions no longer hold and we may have various sorts of behavior. If the surface coating has approximately the properties of a gas, as in an oxygen coated filament, the surface atoms have the specific heat of a gas atom, which is only

half that of an atom in the solid at high temperatures, but greater at low temperatures. Or, which seems to me much more probable under these conditions, the failure of the formula may be due to the non-vanishing of the entropy of the surface charge at 0° Abs. If on the other hand the coating is another metal, particularly if it is one more easily ionized than the underlying metal, the surface charge will consist of ions of the coating metal. If there is any tendency for the coating atoms to bunch themselves on the surface, the ions to which they give rise will be subject to mutual electrical forces which may modify the specific heat.

One is tempted to try for further information about the precise behavior of $C_{pm} - C_{pp}$ in those substances for which the constant of the emission formula has not the universal value above. This, however, is probably not possible with present experimental data. Our argument above has suggested that $AT^2 e^{-b_0/T}$ cannot be the correct form of the emission formula under these conditions, but that this form is only an approximation. Before we can reason back to the behavior of the specific heats we must know the correct form of the function. It is presumably impossible to do this with sufficient precision until experimental accuracy is very greatly improved, as is suggested by the fact that until very recently it was impossible to decide whether a formula with T^2 or $T^{\frac{1}{2}}$ fitted better the experimental data.

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