SYSTEMATIC VARIATIONS OF THE CONSTANT A IN THERMIONIC EMISSION

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Recent measurements[1] on the thermionic emission from a platinum surface during outgassing have brought to the attention of the writer an empirical relation between the thermionic constants for a metallic surface which was discovered by Richardson[2] for tungsten and platinum in 1915, but which has apparently been completely neglected in formulating the various theories of the emission process. This relation may be stated as follows: In the Richardson-Dushman equation,

$$I = A \, T^2 \, e^{-b/T} \tag{1}$$

whenever the work function, b, of a given surface is changed by any method (such as heating, outgassing, coating, etc.) the constant A also changes in such a way that *log A is a linear function of b*.

As is well known, according to Dushman's theory,[3] A should be a universal constant having a numerical value of approximately 60 amp./cm.[2] deg.[2] This conclusion has been confirmed experimentally by Dushman and his co-workers[4] and by Zwikker[5] and Goetz[6] through accurate measurements on a number of clean metals, and has recently received further theoretical justification at the hands of Fowler[7] and Nordheim[8] on the basis of the Sommerfeld electron theory and the wave mechanics. While a number of observers have obtained, under various conditions, values of A differing considerably from the theoretical it has usually been possible to attribute these to the disturbing effects of surface contamination. However, the writer's recent results[1] for platinum (including some still more precise ones as yet unpublished) have shown definitely that it is possible to have a thoroughly cleaned metallic surface exhibiting a value of A 200 times or more greater than 60. Dr. A. Goetz has informed the writer that he has obtained similar results for nickel. The question is therefore raised as to whether some of the observed variations of this "constant" are not of more fundamental nature than had been supposed.

The problem of explaining such variations theoretically has been taken up by a number of writers. Richardson[9] and Wilson[10] were able to explain many results for gas-filled surfaces by assuming the presence of an electric double layer. Bridgman[11] and Langmuir and Tonks[12] related the variations in A to the presence of a surface heat of charging term. However, Davisson and Germer[13] pointed out that such a term should not affect results obtained at constant surface charge and Bridgman[14] later con

cluded that this term in his theory should in fact be zero for all metals. Raschevsky's[15] detailed thermodynamic treatment yields an emission equation which allows for variations in A. Finally, Bridgman,[16] in a very recent paper to be discussed later, shows that all such variations may be simply explained as due to slight variations of b with temperature. None of these theories leads directly to the linear relation between log A and b stated in the first paragraph, which is perhaps not surprising, since this relation, while simple in itself, is the result of very complicated surface phenomena. However, since considerable experimental evidence confirming this relation for many types of surfaces has accumulated in the past


Fig. 1

Fig. 2
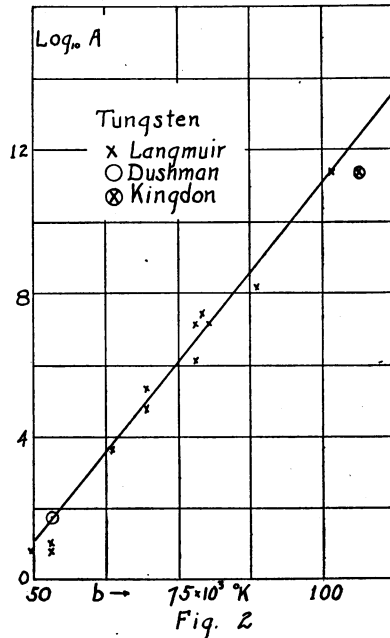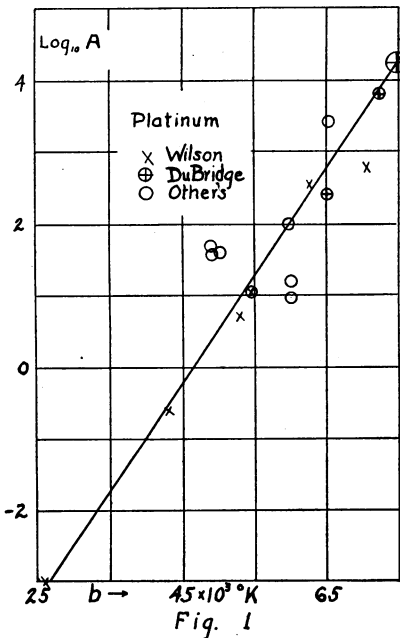
few years, it seemed worthwhile to collect all the published results and suggest their possible significance with particular reference to the results for clean surfaces.

Platinum.—The published data for platinum in various stages of outgassing are plotted in figure 1. This is essentially the same as the curve published originally by Richardson,[2] with the addition of recent data obtained by the writer. The writer's values and those of H. A. Wilson,[10] obtained in each case by observing a single specimen during outgassing, fall remarkably close to the same line. The other points which are more scattered represent individual values obtained by various observers under widely varying conditions. The approximation to the linear relation in

any case is probably within the limits of error. The point representing the value for clean platinum is indicated by the large crossed circle. It will be noted that the extreme values of A plotted differ by a factor of 10^7.

Tungsten.—The curve for tungsten in figure 2 is also similar to one published by Richardson, with the addition of more recent data by Dushman[4] and Kingdon.[17] The older data, obtained chiefly by Langmuir,[18] are for tungsten in the presence of various gases. In spite of the fact that A varies by a factor of 10^{12} the approximation to the linear relation is again very exact.

Thoriated Tungsten.—The data for a thoriated filament in various stages of activation are plotted in figure 3. The curve is taken directly

Fig. 3

Fig. 4
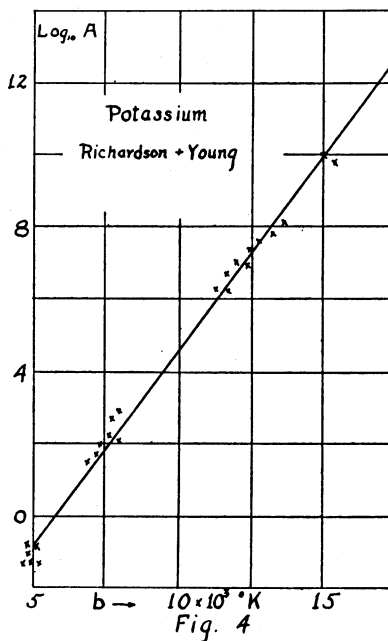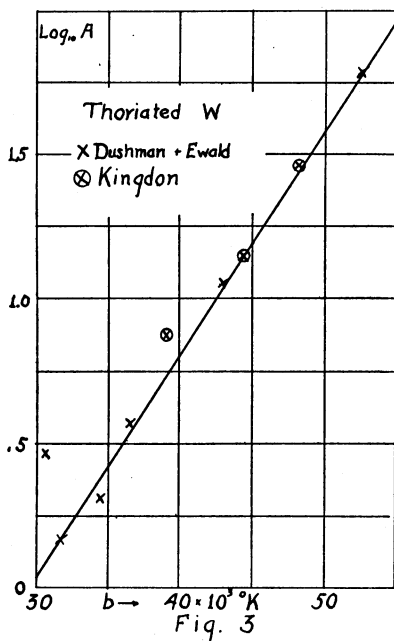
from a paper by Dushman and Ewald,[19] with the addition of some earlier data by Kingdon.[17] Dushman states that his points satisfy the linear relation within the limits of error.

Potassium.—The curve for this metal in figure 4 is taken directly from a paper by Richardson and Young.[20]

Gold, Silver and Copper (Liquid).—Goetz[6] has recently obtained careful measurements of A and b for these metals through the melting points, extending his observations on the liquid surfaces up to the highest possible temperatures. Above the melting point b and A are found to increase rapidly with the temperature, due possibly to the effect of the vapor. His data have been plotted by the writer in figure 5 and it is interesting that

in this case also the linear relation is accurately satisfied. For liquid copper A varies over a factor of approximately 5×10^{13}.

For the sake of comparison all the curves have been plotted to the same scale in figure 6. These represent all the surfaces for which data on the concurrent variations of A and b have been published. In addition Richardson[2] has observed this linear relation for the positive ion emission from platinum. There is thus no known case where the relation fails to hold. In figure 6 the horizontal dotted line represents the value log A = 1.78, A = 60, the theoretical value of Dushman's theory. It will be noted that all the curves, save for K, intersect on or near this line and that the only surfaces showing this value of A are those for which b happens to be about
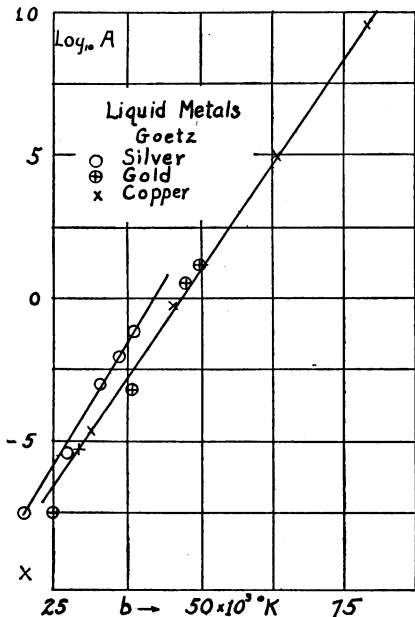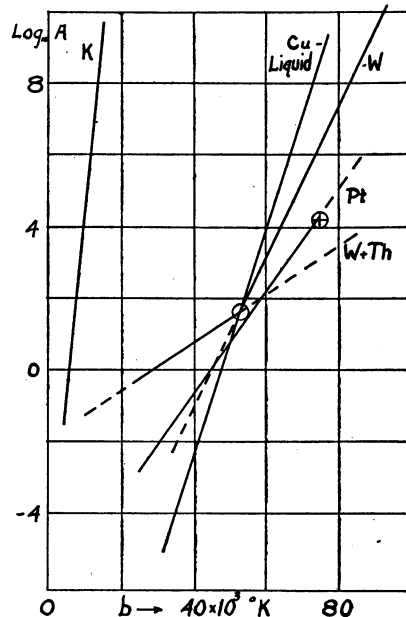

Fig. 5   Fig. 6

52,000°K., corresponding to a work function of 4.5 volts. Surfaces showing a higher or lower value of b—*whether clean or contaminated*—show also correspondingly higher or lower values of A.

Evidently the curves of figure 6 may be represented by the simple empirical equation; (using now natural logarithms)

$$\ln A = \ln A_0 + \beta(b - b_0) \tag{2}$$

where A_0 = 60, β, the slope, is a constant depending on the nature of the surface, and b_0 has the same value for all the more refractory metals. It would be of interest if β could be related directly to other physical properties of the surface, though it is difficult to see how this could be done.

However, for clean metals it is the value of the whole term $\beta(b - b_0)$ which is of interest since this term determines the observed value of A for the surface. Thus for metals for which $A = A_0$ this term must be zero, while for clean platinum it must be positive and for thoriated tungsten negative. If we set

$$\beta(b - b_0) = \alpha \qquad (3)$$

and rewrite (2) in the form,

$$A = A_0 e^{\alpha}. \qquad (4)$$

Then substituting this into (1) we have,

$$I = A_0 T^2 e^{-(b - \alpha T)/T} \qquad (5)$$

Setting,

$$b - \alpha T = b' \qquad (6)$$

we obtain,

$$I = A_0 T^2 e^{-b'/T} \qquad (7)$$

which is of the form of Dushman's equation except that now b' is not independent of temperature. This means simply that the observed variations in A might be ascribed to a small temperature variation of the surface work function.

This is precisely the conclusion recently reached by Bridgman,[16] namely, that in the simple theory of Dushman a term has been neglected which is related to the temperature derivative of the (photoelectric) work function. When this term is included Bridgman obtains an expression for the constant of the emission equation which is identical with equation (4) above, with the constant α interpreted as the negative temperature derivative of the work function. He further shows that α should itself be a function of the nature of the surface, and hence of b. It is of interest to note that if this function be *assumed* to be approximately linear, as in equation (3), then Bridgman's theory leads directly to the empirical relation (2) demanded by the data in figures 1 to 6.

Now α can be obtained from measurements on the shift of the photoelectric threshold with temperature. Such shifts are known to be in general small, but Bridgman points out that they are large enough to account for the very large observed variations in A. Recent work in this laboratory by Dr. Warner, and some previous results of the writer[21] confirm this conclusion. Thus for tungsten Warner has found no appreciable shift in the photoelectric threshold up to 1100 deg. K. This means that $\alpha = 0$ and $A = A_0$, as it should for tungsten. On the other hand for platinum the writer has found $A = 14,000$ approximately, hence, $\alpha = 5.4$, while photoelectric measurements have shown a shift to the red in the threshold between 800° and 1200°C. which may have been as much as 50 A.U. This gives $\alpha = 4.5$ which is of the right sign and right order of magnitude.

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[8] Nordheim, *Zeit. f. Physik*, **46**, 433, 1928.

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[14] Bridgman, *Ibid.*, **31**, 90, 1928.

[15] Raschevsky, *Zeit. f. Physik*, **36**, 628, 1926.

[16] Bridgman, *Phys. Rev.*, **31**, 862, 1928.

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[19] Dushman and Ewald, *Ibid.*, **29**, 867, 1927.

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[21] DuBridge, *Phys. Re .*, **29**, 451, 1927.

THE PHOTOELECTRIC LONG WAVE LIMIT OF POTASSIUM VAPOR

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Introduction.—In the investigation of the alkaline metallic vapors by light, two types of experiment have been performed. In one type[1,2] the vapor was used in equilibrium with the molten metal. In the other,[3,4,5] the vapor from the liquid metallic surface passed through a slightly super-heated tube and then emerged from this tube into a vacuum, the vapor being illuminated and ionized after emergence.

In the first type of experiment, the observed long wave limit agrees within the limits of error with that predicted from the application of quantum ideas to the spectroscopic data, save that in the case of the work of Foote and Mohler with caesium, while a maximum of ionization was found at the proper wave-length, there was a gradual decrease in amount toward the longer wave-lengths. This ionization above the expected limit was accounted for on the basis of a cumulative process involving the energy of the electronic currents necessarily involved in their method.

In the second type of experiment, making use of potassium vapor issuing from a jet, a certain amount of discrepancy has occurred in the work of