MAY 1, 1936 PHYSICAL REVIEW VOLUME 49

On the Constant A in Richardson's Equation

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(Received March 16, 1936)

According to Herzfeld, the "chemical constant" of the electron gas is different in the high temperature region, where all actual measurements are carried out, from its value at very low temperatures. Hence the value of the constant A in Richardson's equation must be different at high temperatures from the well-known low temperature value of 120 amp./cm^2 °K^2. The present paper gives a calculation of the high temperature value in terms of thermodynamic quantities and a numerical estimation of these.

1

It is well known that the constant A in Richardson's formula[1] for the thermionic current i

$$i = AT^2e^{-W/RT} \tag{1}$$

(W is the measured work function) should have under ideal conditions the value 120 amp./cm^2 °K^2. Under "ideal conditions" we mean that:

(a) The reflection coefficient r for electrons should be zero, i.e., all electrons striking the surface should be absorbed by the same.

(b) The work function W should be constant. The work function is defined as the energy necessary to remove one electron from the top of the Fermi distribution and bring it to a point near the surface, but still to a distance from it which is large as compared with the lattice constant. The "top of the Fermi distribution" again means the energy of that electron which has the highest energy if all electrons are in the lowest possible state. This is the work function which is measured experimentally by the photoelectric effect if Fowler's method[2] is used for the evaluation.

(c) That the electron gas in free space should behave like an ideal gas.

(d) Finally, the surface must be uniform and thus free from patches and contaminations.

This last condition and its effects have been carefully analyzed by J. A. Becker.[3] It seems that it can account in the case of the most careful experiments, and for low accelerating potentials for small deviations of A from 120 only, and generally only for a lowering of this value. Under the conditions (a)–(d), (1) is a consequence of the principle of detailed balance and general quantum statistical laws.[4]

Condition (c) is fulfilled for not too high temperatures[5] and will be assumed further on. If the reflection coefficient is different from zero, we should only expect an additional coefficient $1-r$ in (1). Since $1-r$ is certainly in the order of magnitude of 1 and smaller than this, the reflection can explain only a deviation of A from 120 by such a factor.[6] In spite of this, the experimental values[7] are in most cases rather far from 120. It must be emphasized, however, that these experimental values are still subject to comparatively large variations and in many cases hardly reproducible. They are most trustworthy if the work function is measured photoelectrically also. It is only too common an experience that a new set of experiments changes the measured values of both A and W considerably, generally both in the same direction, which indicates that not so much the measurement of i, as that of its temperature coefficient, is crucial. In spite of this, it is generally accepted[8]

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[1] For the history of Richardson's discovery cf., e.g., W. Schottky, *Handbuch der Experimentalphysik*, Vol. XIII (Leipzig, 1928), or A. L. Reimann, *Thermionic Emission* (London, 1934).

[2] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

[3] J. A. Becker, Rev. Mod. Phys. **7**, 95 (1935).

[4] Cf. reference 1 and K. F. Herzfeld, Phys. Rev. **35**, 248 (1930), also J. H. Becker and W. H. Brattain, Phys. Rev. **45**, 694 (1934).

[5] Cf. M. v. Laue, *Jahrbuch der Radioaktivität und Elektronik*, Vol. 15, 205, etc. (1918) and W. Schottky, reference 1.

[6] L. Nordheim, Zeits. f. Physik **46**, 833 (1928); Proc. Roy. Soc. **A121**, 626 (1928); R. H. Fowler and L. Nordheim, Proc. Roy. Soc. **A119**, 173 (1928) show that the reflection coefficient is very small in general, around 0.07. See also Langmuir and Jones, Phys. Rev. **31**, 401 (1928).

[7] Cf. A. L. Reimann, reference 1 and A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (New York, 1932). For Cb, H. B. Wahlin and L. O. Sordahl, Phys. Rev. **45**, 886 (1934), for Rh unpublished data of H. B. Wahlin.

[8] I am much indebted to Professor L. A. DuBridge for a discussion on this point. Cf. also his monograph, *Actualités Scientifiques et Industrielles*, No. 268, Paris, 1935.

TABLE I. *Measured values of the constants in Richardson's equation.*

	A	W		A	W
Cs	162	1.81	Ta	60	4.12
Ba	60	2.11	Hf	14.5	3.53
Ni	1,380	5.02	Th	70	3.38
Pd	60	4.98	Re	200	5.1
Pt	17,000	6.27	Cu?	65	4.33
Mo	55	4.15	Ag?	0.76	3.56
W	60	4.53	Au?	40	4.32
Zr	330	4.12	Cb	57	3.96
			Rh	35	4.81

that the deviations of A from 120 are real and must be explained by the breakdown of assumption (b). The present paper will be devoted to a discussion of (b).

2

The consequences of the temperature variation of the work function have often been analyzed,[9] especially by Bridgman and Herzfeld. I shall follow the latter's treatment quite closely. The reason this subject is taken up again, is that our somewhat improved knowledge of the metallic structure allows a somewhat closer analysis which shows that in addition to the effect, analyzed by Herzfeld (which is reproduced), there is another effect which tends to compensate for it in many cases. This is the reason, perhaps, that the measured A's are not all higher than 120, as one may expect from Herzfeld's paper.

It has been emphasized by Becker and Brattain[10] that the quantities measured in case of variable work function (and thus contained in Table I) are W^* and A^*, defined by

$$W^*=RT^2(d/dT)\ \ln i/T^2,$$

$$\begin{aligned}\ln A^*&=\ln i/T^2+T(d/dT)\ \ln i/T^2\\&=\ln i/T^2+W^*/RT,\end{aligned}\tag{2}$$

where i is the thermionic current.

The procedure to obtain theoretical expressions for W^* and A^* is to calculate first i and obtain then W^* and A^* by (2).

3

In order to calculate the current, one may first calculate the vapor pressure P of the electron gas at a point with zero electrostatic potential by thermodynamics. If P is given, the number of electrons striking the surface can be calculated by elementary kinetic theory (m is the electronic mass) to be $P/(2\pi mkT)^{\frac{1}{2}}$. If r is the reflection coefficient, this gives a current i per cm^2 of the metal.

$$i=Pe(1-r)/(2\pi mkT)^{\frac{1}{2}}.\tag{3}$$

The current from the metal is equal to this in equilibrium and is supposed to be equal also under the conditions of thermionic emission. Thus the problem reduces to the calculation of the vapor pressure P.

Both the vapor pressure and the work function[11] depend, in addition to the temperature T, on the (mechanical) pressure p, under which the metal is kept. We shall assume that the metal carries always only an infinitesimally small charge only. If we allow ϵ electrons per mole of metal to escape and keep the volume of the metal constant, the mechanical pressure will increase by $\epsilon p_e(v, T)$. The energy necessary for the removal of ϵ electrons, when the metal is kept at constant volume, is $\epsilon W_v(v, T)$. It seems to be simplest to apply the Clausius Clapeyron cycle by keeping the metal at constant volume. We then have[12]

$$\partial \ln P(v, T)/\partial T=W_v(v, T)/RT^2+5/2T,\tag{4}$$

which gives

$$\begin{gathered}\ln P(v, T)=-\frac{W_v(v, 0)}{RT}+(5/2)\ln T+j\\+\int_0^T[W_v(v, \tau)-W_v(v, {\scriptstyle 0})]\frac{d\tau}{R\tau^2}\\j=(3/2)\ln(2\pi mk/h^2)+\ln 2.\end{gathered}\tag{5}$$

The well-known Sackur-Tetrode value of the chemical constant must be increased by ln 2 because of the spin. In order to determine p_e, we can apply the usual cycle to a piece of metal

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[9] P. W. Bridgman, Phys. Rev. **31**, 90 (1928); K. F. Herzfeld, reference 4.

[10] Reference 4.

[11] For the definition of the work function see the preceding section. The vapor pressure P is a function of the mechanical pressure p for ordinary vaporization also, but this effect is rarely considered.

[12] In this section, temperature T and volume v will be the independent variables. Thus temperature derivatives are always to be taken at constant volume, volume derivatives at constant temperature.

which is deprived of ϵ electrons permole. The pressure is $p+\epsilon p_e$, the energy $E+\epsilon W_v$, so that we have

$$\frac{\partial E}{\partial v}+\epsilon\frac{\partial W_v}{\partial v}+p+\epsilon p_e=T\frac{\partial}{\partial T}(p+\epsilon p_e), \quad (6)$$

which gives in addition to the usual

$$\partial E/\partial v+p=T\partial p/\partial T \quad (7)$$

valid for any substance, the required

$$\partial W_v/\partial v+p_e=T\partial p_e/\partial T \quad (8)$$

since (6) holds for every ϵ. From (8) follows

$$p_e=-\frac{\partial W_v(v,\,0)}{\partial v}+T\int_0^T\left[\frac{\partial W_v(v,\,\tau)}{\partial v}-\frac{\partial W_v(v,\,0)}{\partial v}\right]\frac{d\tau}{\tau^2}. \quad (9)$$

We shall now calculate W^* and A^* by (5), (3) and (2). We have to remember, for this, that when the thermionic current is measured at different temperatures, not the volume, but the mechanical pressure of the metal is kept at constant value, namely zero. The temperature derivatives in (2) are meant to be taken at constant pressure, therefore. Hence, if α is the volume expansion coefficient, v_0 the molal volume, we have

$$W^*=RT^2\left(\frac{\partial}{\partial T}+v_0\alpha\frac{\partial}{\partial v}\right)\ln\frac{i}{T^2}$$

$$=RT^2\left(\frac{\partial}{\partial T}+v_0\alpha\frac{\partial}{\partial v}\right)\ln\frac{P}{T^{5/2}} \quad (10)$$

or

$$W^*=W_v(v,\,T)+v_0\alpha Tp_e \quad (11)$$

as the comparison with (9) shows. For A^*, we have

$$\ln\left(A^*/A(1-r)\right)=-W_v(v,\,0)/RT+W_v(v,\,T)/RT+\int_0^T\left[W_v(v,\,\tau)-W_v(v,\,0)\right](d\tau/R\tau^2)+v_0\alpha p_e/R. \quad (12)$$

Here A is the constant for the ideal case, 120 amp. cm^{-2} °K^{-2}. The last term in (12) is that of Herzfeld, the other ones have been omitted by him, since the work function chiefly depends on the volume. Its contribution to A^* is not negligible, however. In general, p_e is negative, the pressure decreases if an electron is removed.

4

For the evaluation of (12) we shall make assumptions very similar to those of Herzfeld. The total energy of the metal contains two parts. The first, $V(v)$ arises from the motion of the electrons, depending, therefore, on the volume only.[13] The second arises from the motion of the nuclei. The first part is the most important for the actual value of the work function, its change by the removal of electrons from the metal gives practically all of this quantity. For the second part, an expression $RTD(\Theta/T)$ will be used. In this, Θ is a function of the volume and will be changed also by the removal of electrons by the amount $\epsilon\Theta_e$ if ϵ electrons per mole are removed. The total energy of a mole of the metal, out of which ϵ electrons have been removed and brought to a point near the surface but still sufficiently distant from it in order to make the image force negligible, is thus

$$E(v,\,T)+\epsilon W_v(v,\,T)=V(v)+\epsilon W_v(v,\,0)+RTD(\Theta/T)+\epsilon R\Theta_eD'(\Theta/T). \quad (13)$$

These assumptions can be justified on the basis of the usual assumption of fast electronic and slow nuclear motion,[14] but I shall not enlarge upon this subject. From (13) one readily obtains

$$W_v(v,\,T)=W_v(v,\,0)+R\Theta_eD'(\Theta/T), \quad (14)$$

which gives with (12)

$$\ln\frac{A^*}{A(1-r)}=\frac{\Theta_e}{T}D'\left(\frac{\Theta}{T}\right)+\Theta_e\int_0^TD'\left(\frac{\Theta}{\tau}\right)\frac{d\tau}{\tau^2}+\frac{v_0\alpha p_e}{R}$$

$$=(\Theta_e/T)D'(\Theta/T)-(\Theta_e/\Theta)D(\Theta/T)+v_0\alpha p_e/R,$$

$$\ln\left(A^*/A(1-r)\right)=-C_v\Theta_e/R\Theta+v_0\alpha p_e/R$$

$$=-3\Theta_e/\Theta+v_\theta\alpha p_e/R, \quad (15)$$

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[13] We shall neglect the small specific heat of free electrons (cf. A. L. Reimann, reference 1).

[14] Cf., e.g., H. Pelzer and E. Wigner, Zeits. f. physik. Chemie **B15**, 445 (1932); F. London, Zeits. f. Physik **74**, 143 (1932).

where $C_v \approx 3R$ is the specific heat of the metal at constant volume, it has assumed its classical value at the temperatures under consideration.

The thermionic emission can be considered as a generalized dissociation reaction, and calculated, hence, according to the transition state method for calculating reaction rates.[15] The result is identical with the one obtained here, but I preferred this method because it is the more usual one in these problems. As has been remarked by Herzfeld, (15) corresponds to the expression for the chemical constant of the electron gas at high temperatures, while the familiar 120 amp./°K^2 cm^2 is the low temperature expression. This is quite similar to the situation for H_2, e.g.: at low temperatures the chemical constant is $(3/2) \ln (2\pi m k^{5/3}/h^2)$ while at high temperatures there is an additional $\ln 8\pi^2 kJ/h^2$. In contrast to H_2, the change of the "chemical constant" in our case is due to a change in the condensed state. Also the temperature dependence does change in H_2 (from $T^{5/2}$ to $T^{7/2}$) while there is no such change in our case.

5

Next we shall try to estimate the quantities Θ_e and p_e occurring in (15). It must be remarked at the outset that these two quantities are of a rather different nature: Θ_e is a function of the volume only, but p_e depends, according to (9), on the temperature and can be reduced to the more basic quantities, $\partial W_v(v, 0)/\partial v$, Θ_e and $d\Theta_e/dv$ by (14). One obtains thus

$$\ln (A^*/A(1-r)) = -C_v\Theta_e/R\Theta - (v_0\alpha/R)\partial W_v(v, 0)/\partial v - v_0\alpha T(\partial/\partial v)(C_v\Theta_e/R\Theta) \qquad (16)$$

since the integral in (9) is just the v derivative of the expression we have calculated in the previous section.

It would be rather difficult to estimate the last expression in (16) since it contains $d\Theta_e/dv$. If one assumes however, that $v(\partial/\partial v)(C_v\Theta_e/R\Theta)$ is of the order of magnitude of $C_v\Theta_e/R\Theta$ itself—which seems reasonable, the last term can be neglected altogether, because $\alpha T = 10^{-2}$. Since $W_v(v, 0)$ is the energy necessary at the absolute zero, to remove one electron, $\partial W_v(v, 0)/\partial v$ is the negative increase in pressure, due to the removal of one electron. Since the electrons do the binding in the metal, the removal of one will loosen the binding and the actual pressure decrease will not be quite as great as calculated on the free electron hypothesis. For alkalis, one can obtain an estimate of this magnitude from the formulas, derived for the calculation of the work function.[16] Our $W_v(v, 0)$ is in the present approximation what is denoted there by φ. Eq. (7) reference 16 reads in our notation:

$$-W_v(v, 0) = 13.5(E_0 + 5\cdot 2.21/3r_s^2 + 1.18/r_s - 0.58/(r_s+5.1) - 0.19r_s/(r_s+5.1)^2 - eD). \qquad (17)$$

The work function is expressed here in volts, r_s in Bohr's units ($0.528\cdot 10^{-8}$ cm) and is defined by $4\pi r_s^3/3 = v_0/L =$ atomic volume. D is the momentum of the double layer on the surface and will be neglected hereafter. From (17) we obtain

$$v_0\partial W_v/\partial v = (r_s/3)\partial W_v/\partial r_s = -4.5(r_s dE_0/dr_s - 7.4/r_s^2 - 1.18/r_s + 0.58r_s/(r_s+5.1)^2 + 0.38r_s^2/(r_s+5.1)^3). \qquad (18)$$

In order to eliminate dE_0/dr_s, we set the derivative of (8) reference 16 equal to zero. This expresses that the total energy is a minimum for r_s.

$$-r_s dE_0/dr_s + 4.42/r_s^2 + 0.28/r_s - 0.58r_s/(r_s+5.1)^2 = 0. \qquad (19)$$

This gives

$$v_0\partial W_v(v, 0)/\partial v = 4.5(3/r_s^2 + 0.9/r_s - 0.38r_s^2/(r_s+5.1)^3), \qquad (20)$$

which is for $r_s = 4$ about 1.5 volts. The second term in (16) thus becomes with $\alpha = 21.10^{-5}$ about -3.6.

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[15] For the history of this method cf. E. Evans and M. Polanyi, Trans. Faraday Soc. **31**, 875 (1935). The formula

$$i = AT^2e^{-w/RT} \qquad (*)$$

used by J. A. Becker and W. H. Brattain (reference 4) has been derived in the papers to which they take reference only for the case when the work function is independent of temperature. Of course, it is always possible to represent the thermocurrent by a formula (*) with variable w, but this w will not be equal to the work function. It follows furthermore from the third law that w can have no term linear in T at low temperatures (cf. reference 9).

[16] J. Bardeen and E. Wigner, Phys. Rev. **48**, 84 (1935).

The quantity Θ_e/Θ is the percent change of the vibration frequencies for one percent change in the number of electrons. It is, therefore, half the percent change of the restoring force F, if one percent of the electrons is removed.

In order to obtain an estimate for this, we may consider first the whole restoring force if only one ion is displaced. This is the force which acts on the displaced ion and originates from the electron cloud which is itself distorted by the displacement of the ion.

It is difficult, in general, to calculate the distortion of the electron clouds. Naturally, the inner electrons can be considered to be rigidly attached to the ion. We may assume that the valence electrons have an even distribution throughout the lattice and show wriggles in the neighborhood of the ion only. Then, the total charge distribution of the valence electron can be considered to contain two parts: ρ_1, the variations of which are appreciable only in distances comparable with the lattice constant, and ρ_2 which contains the small wriggles only. It seems reasonable to assume that the ion carries the wriggles with itself but as long as only one ion is displaced, the slowly varying part of the charge will not be much affected. If the ion was displaced by x in the X direction, it will be acted upon by a force

$$Fx = xZe\partial E_x/\partial x, \qquad (21)$$

where E is the field due to the slowly varying part ρ_1 of the electronic charge and Ze the ionic charge. We have, by Poisson's equation $\operatorname{div} E = 4\pi\rho_1$ and for a cubic lattice, this gives because of $\partial E_x/\partial x = \partial E_y/\partial y = \partial E_z/\partial z$

$$F = 4\pi\rho_1 Ze/3. \qquad (22)$$

The percent change of this,[17] for a one percent decrease of the number of electrons is simply $-\rho_{1t}/\rho_{1m}$ where ρ_{1t} is the slowly varying part of the density of the highest energy electrons, at the point where the ion is; ρ_{1m} is the mean value of the same quantity for all valence electrons. The first term of (16) is therefore, approximately

$$(3/2)(\rho_{1t}/\rho_{1m}). \qquad (23)$$

This will be comparatively large (~ 1.5), if the last valence electron is an s electron, small otherwise. If the highest energy electron happens to be such an electron in the lattice, for which ρ_{1t} is zero, the whole first term will be negative also, because of the approximations we made.

6

It is hardly necessary to mention that while the considerations of sections 2 and 3 are, (12) inclusive, strictly based on thermodynamics and those of 4 also should be correct within a very small error, the considerations of section 5 are very crude and will not give, in general, more than the sign of the effects and their order of magnitude. What can be claimed safely, is only

(a) that it is purely accidental if the constant A^* in Richardson's equation (defined by (2)) has the value 120 amp./$°\text{K}^2$ cm^2 sec.

(b) that the deviation in the ln of A^* should be of the order of magnitude 1–3, rather negative than positive. It should be negative always when the last valence electron is not essentially an s electron in the lattice.

It should be emphasized once more that rather large deviations in the constant A^* can be caused by a patchy character of the surface, as considered by Becker and Rojansky.[3] These patches can consist in surface contamination or also in the polycrystalline character of the surface, since different crystal planes will have different work functions. It would be desirable, from this point of view, to measure the work function and A^* on definite crystal planes, i.e., to use single crystals for the experiments.[18]

In some cases, zero energy outside of the metal may correspond to a forbidden region inside. This would have as consequence an unusually large reflection coefficient.[19] The effect of a reflection coefficient has also been omitted in this paper.

It is a pleasure to express my gratitude to Professor Herzfeld for his valuable discussion and criticism of this paper.

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[17] One can calculate, from (22), the characteristic temperature of the metal, and it comes out in the right order of magnitude. A more satisfactory calculation of the vibrational frequencies of a metal has been given lately by K. Fuchs, Proc. Roy. Soc. **A153**, 622 (1936).

[18] Professor H. B. Wahlin has pointed out to me that part of the effect of the continued heating and flashing of the samples is perhaps due to recrystallization. Cf. H. B. Wahlin and J. A. Reynolds, Phys. Rev. **48**, 751 (1935).

[19] P. M. Morse, Phys. Rev. **35**, 1310 (1930).