THE VARIATION OF THERMIONIC EMISSION WITH TEMPERATURE AND THE CONCENTRATION OF FREE ELECTRONS WITHIN CONDUCTORS*

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Abstract

Equilibrium electron theory of thermionic emission.—The equation for the thermionic saturation current per unit area in the form $I=AT^{\alpha}e^{-b/T}$ is derived according to Richardson's thermodynamical method, assuming (1) the boundary condition that when ψ the free electron evaporation constant is zero, the free electron concentration inside and outside the hot body is the same, and (2) the interior free electron concentration given by the author's equilibrium theory of conduction (Phys. Rev. **22**, 259, 1923). α depends only upon the valence in the electron-forming reaction and always lies between 1/2 and 5/4. β depends upon the valence and the two evaporation constants ϕ_0 and ψ_0, referring respectively to a bound and a free electron. A is found to depend upon the valence, the electronic chemical constant and the concentration of electron-forming particles in the hot body, varying from $4.16(10)^{14}$ for BaO to $8.13(10)^{14}$ for Ni. Values of β calculated from the computed A and experimental data show excellent agreement with β observed for Pt, W, Mo, Ni, Ca, CaO, SrO, and BaO, the verification being more general than by use of Dushman's formula. The experimental data however are not sufficiently accurate to decide between the two formulas. The failure of certain hot bodies to agree with either formula is discussed and possible explanations offered. Assuming the theory correct, the *free electron concentrations in several metals, MoS_2 and CaO are calculated from experimental data.* For metals at 0°C this concentration is of the order of magnitude of 10^{17} per cc, and decreases with rising temperature. A noteworthy consequence of this low concentration is that the contribution of the free electrons to the specific heat of the conductor remains negligible down to very low temperatures.

THE variation of the thermionic saturation current density with temperature is given empirically by an expression of the form

$$I=AT^{\lambda}e^{-b/T} \tag{1}$$

where the exact value of λ matters little in obtaining agreement with experiment, provided it is of the order of magnitude of unity. The well-known theoretical expressions are[1]

$$I=A_1T^{1/2}e^{-\psi/kT} \tag{2}$$

* The main conclusions of this paper were presented before the American Physical Society on Dec. 27, 1923 (Phys. Rev. **23**, 299, 1924)

[1] Richardson, Emission of Electricity from Hot Bodies, p. 36. ψ is used to denote the thermionic work function commonly denoted by ϕ, since in this paper ϕ is reserved for the photo-electric work function.

and $$I = A_2 T^2 e^{-\psi_0/kT} \tag{3}$$

derived respectively from kinetic theory and from thermodynamical considerations. The temperature functions in the two expressions become identical when the thermionic work function ψ is assumed to depend upon temperature according to the equation[2] $\psi = \psi_0 + (3/2)kT$, also derived from thermodynamical reasoning. The same form of equation has been obtained by application of the quantum theory.[3] Although the experimental evidence has thus far not been able to distinguish between Eqs. (2) and (3), Richardson and others have agreed that probably Eq. (3) deserves more confidence from the theoretical standpoint.

The evaluation of the constant A is a matter of interest and importance. Differences in the form of this constant arise chiefly from the different methods by which the concentration of external electrons in equilibrium with the hot body is deduced. Thus we have

$$n_A = n_B e^{-\psi/kT} \tag{4}$$

and

$$n_A = CT^{3/2} e^{-\psi_0/kT} \tag{5}$$

corresponding respectively to Eqs. (2) and (3), where n_A = equilibrium concentration of external electrons, n_B = electron concentration within the hot body, and C involves a constant of integration.

Dushman,[4] by application of the Nernst heat theorem, has recently derived an expression for the thermionic saturation current density of the form of Eq. (3), by evaluating the constant C in Eq. (5), with the interesting result that C, and hence A_2, should be universal constants. However the premises on which this latter derivation is based may possibly be open to question, and furthermore the universality of A_2 does not appear to extend to all possible emitting substances. The author has submitted[5] an expression for the thermionic saturation current density which is also consistent with Eq. (1). The previously omitted details of derivation are presented below, and the work has been extended to include evaluation of the integration constant appearing in the coefficient A (Eq. 1). This makes possible a numerical calculation of the value of A from data independent of thermionics, and thus permits a more substantial examination as to the validity of the formula proposed, as

[2] Richardson, loc. cit.,[1] p. 35
[3] Richardson, loc. cit.[1] p. 41.
[4] Dushman, Phys. Rev. **21**, 623 (1923)
[5] Waterman, Phys. Rev. **22**, 259, 268 (1923)

well as allowing direct comparison with values of A derived by other methods.

Derivation of Expression for Thermionic Saturation Current Density

From the thermodynamic reasoning[6]

$$dn/n_A = \left(\frac{\psi}{kT^2}\right)dT \tag{6}$$

where ψ is the energy required to liberate one free electron from the hot body;[6] k is the gas constant per electron. Hence $\log n_A = \int(\psi/kT^2)dT +$ const. Using the boundary condition that, when $\psi = 0$, the concentration of free electrons inside and outside the hot body is the same, or $n_A = n_B$, we have

$$\log\frac{n_A}{n_B} = \int\frac{\psi}{kT^2}dT\,. \tag{7}$$

Since [2] $\psi = \psi_0 + (3/2)kT$

$$n_A = n_B T^{3/2} e^{-\psi_0/kT}\,. \tag{8}$$

From the writer's equilibrium theory of electrical conduction[7] the internal equilibrium concentration of free electrons n_B is given by

$$n_B = BT^{-3\nu/2(\nu+1)}\, e^{-\nu(\phi_0-\psi_0)/(\nu+1)kT} \tag{9}$$

where ϕ_0 and ψ_0 are respectively the energies (at 0°K) required to liberate a bound and a free electron from the conductor, whence $\phi_0 - \psi_0$ is seen to be the energy (at 0°K) required to change a bound electron into a free electron within the substance;

ν = valence in atomic reaction: Atom $\leftrightarrows$ positive ion $+ \nu$ electrons;

$B = c\,(\nu N)^{1/(\nu+1)}$;

N = concentration of nuclei within conductor (or total concentration of particles in conductor from which electrons may be or have been emitted).

The constant of integration c may be evaluated by noting that the integration constant of Eq. (3) in the writer's article[5] is for the general atomic reaction equal to νi, where i is the chemical constant of the electron, reckoned in absolute units per electron and in terms of concentrations instead of partial pressures.

Then c becomes $e^{\nu i/(\nu+1)}$, whence $B = e^{\nu i/(\nu+1)}(\nu N)^{1/(\nu+1)}$

[6] Richardson, loc. cit.[1] p. 31, Eq. (6)

[7] Waterman, loc. cit.[5] p. 259

Substituting the value of n_B from Eq. (9) in Eq. (8)

$$n_A = e^{\frac{\nu i}{\nu+1}} (\nu N)^{\frac{1}{\nu+1}} T^{\frac{3}{2(\nu+1)}} e^{-\frac{\nu\phi_0+\psi_0}{(\nu+1)kT}}, \tag{10}$$

giving the concentration of external electrons in equilibrium with the hot body. This concentration is seen to depend upon the concentration of nuclei or electron-forming particles within the substance, the valence in the atomic reaction, and the chemical constant of the electron, in addition to the temperature and the evaporation constants.

Following the customary procedure, the thermionic saturation current density now becomes

$$I = A T^{\alpha} e^{-\beta/T} \tag{11}$$

where

$A = \epsilon\sqrt{(k/2\pi m)}\; e^{\nu i/(\nu+1)} (\nu N)^{1/(\nu+1)}$ (ϵ being the electronic charge);

$\alpha = (\nu+4)/2(\nu+1)$;

$\beta = (\nu\phi_0+\psi_0)/(\nu+1)k$.

For different valences $\nu = 1, 2, 3$, the values of α are respectively $\alpha = 1.25$, 1.00, 0.875, and thus the exponent of T for all valences is seen to lie between the usual 1/2 and 2.

It should be observed that the constant β in Eq. (11) as experimentally determined does not necessarily yield directly the energy required to liberate a free electron from the substance (ϕ_0 as usually understood), as is true for b in the ordinary expression for the thermionic saturation current.[5] Instead β involves both the energy required to liberate a free electron and the energy required to liberate a bound electron. It is clear that such must be the case if the external concentration of electrons depends upon the internal concentration of *free* electrons and if the latter in turn is determined by a chemical equilibrium between atoms, positive ions and free electrons. Thus an amount of energy $(\phi_0-\psi_0)$ is required to change a bound electron into an internal free electron, and an amount of energy ψ_0 is then required to liberate this electron from the substance.

Evaluation of Constants and Application to Experimental Data

Using values of constants as follows:

$\epsilon = 4.774\times(10)^{-10}$ e.s.u.; m (electron) $= 8.995\times(10)^{-28}$gm.

$k = 1.372\times(10)^{-16}$ ergs/deg. C; $i = 34.98$;

we have $\log A = -4.129+15.19\ \nu/(\nu+1)+[1/(\nu+1)]\ \log\ \nu N$.

In view of the uncertainty attaching to the theoretical values of the chemical constant of the electron, the value of the chemical constant

used is that selected by Tolman[8] from experimental data, expressed in terms of concentrations instead of partial pressures and in absolute units per electron. N, the concentration of nuclei within the conductor, may be determined by (density/atomic weight)$\times$Avogadro's number.[9] The valence ν is the only arbitrary constant appearing in the expression, and for most substances agreement with experiment is obtained for $\nu=1$ (i.e. a univalent reaction liberating electrons within the conductor). Thus the value of the constant A may be calculated, after which an experimental value for the thermionic saturation current density at any single temperature enables β to be calculated. This computed value of β may then be compared with the value of β obtained directly from the slope of the graph ($\log I=\alpha \log T$) vs. $1/T$. The following table shows the results of this procedure for a number of emitting substances.

TABLE I

Hot body	Observer	Valence	α	A(calc.)	β(calc.)	β(obs.)	Dushman β(calc.)	Dushman β(obs.)	ψ_0
W	Davisson and Germer	1	1.25	7.16(10)^{14}	57,300* 56,800†	53,600* 54,600†	51,950*	52,000*	(volts)
		1.25	1.17	2.98(10)^{14}	54,100*	54,000,*			4.66
	K. K. Smith	1	1.25	7.16(10)^{14}	52,150	53,700	53,900	51,400	
Ta	Deininger	3.3	0.85	4.71(10)^{12}	47,000	47,000	55,000	46,700	
Ca	Horton	2	1.00	3.57(10)^{13}	41,100	41,000	43,800	38,800	3.54
Mo	Stoeckle	1	1.25	7.35(10)^{14}	52,800	52,300	47,850	51,200	4.51
Pt	Schlichter	1	1.25	7.28(10)^{14}	53,100	52,500	49,150	50,000	4.53
	Deininger	1	"	"	51,100	50,000			4.31
Ni	Schlichter	1	1.25	8.13(10)^{14}	51,600	51,500	47,900	49,000	4.44
CaO	Jentsch	1	1.25	5.33(10)^{14}	40,000	39,500	37,000	38,900	1.6
	Deininger	"	"	"	40,750	42,700			($\phi_0=5.3$)
BaO	Jentsch	1	1.25	4.16(10)^{14}	41,000	41,000	38,000	39,700	
SrO	"	1	1.25	4.24(10)^{14}	44,250	44,200	41,100	42,200	

* Worthing and Forsyth temperature scale;
† Langmuir temperature scale.

The value given for β(calc.) in the case of any substance is the mean of separate calculations of β for each temperature at which emission was measured. Naturally, where agreement is close between β(calc.) and β(obs.), these separate values of β(calc.) showed a constancy within the limits of experimental error. Where a discrepancy occurs it is evident that the individual values of β(calc.) showed a progressive variation throughout the temperature range.

Where the accuracy of the experimental data seemed to warrant it, the current density was corrected for the expansion of the emitting surface

[8] Tolman, J. Am. Chem. Soc. **43**, 1592 (1921)
[9] In the case of the oxides the concentration of mole cules was used.

with temperature, since this may cause a difference in β (calc.) of 1 to 2 per cent.

It is seen from the table that a valence $\nu=1$ gives very satisfactory agreement for all hot bodies listed except for W, Ca and Ta. For W exact agreement is secured with $\nu=1.25$, i.e., some of the atoms may ionize doubly, giving a valence between 1 and 2. Ca requires a valence of 2, which appears reasonable, and for Ta ν apparently lies in the neighborhood of 3. The experimental data for Ta given by Deininger are not satisfactory however, in that the graph ($\log T-\alpha \log T$) vs. $1/T$ is not a straight line for any value of α. It may furthermore be noted that the values of A which give excellent agreement between β (calc.) and β (obs.), vary from $8.13\times(10)^{14}$ for Ni to $4.16\times(10)^{14}$ for BaO, even though the valence is the same (unity). However, as far as the effect of this variation in A on the value of β (calc.) is concerned, A might be considered approximately a universal constant for those cases where $\nu=1$, since taking the mean of A (calc.) for such cases would change the calculated value of β by only ± 2 per cent at the most. The obvious reason on this hypothesis for this approximate constancy of A for the same valence lies in the fact that the concentrations of nuclei in different elements and of molecules in compounds are closely of the same order of magnitude. However the use of the valence factor makes it possible to extend agreement to other substances, in which case a large change in A occurs.

Comparison with Other Formulas

For comparison the values of β (calc. and obs.) are included as computed according to Dushman's expression,[4] in which $\alpha=2$, and A is the universal constant $1.80\times(10)^{11}$ in the units employed in this table (e.s.u./cm (deg.)^2).

From the results contained in Table I it appears that the expression here proposed for the thermionic saturation current density compares favorably with that of Dushman, and in fact with any expression where A is taken to be a universal constant. It should be noted that Dushman's value of A for best agreement is based upon the chemical constant of the electron computed from the Sackur-Tetrode expression. The values of A computed in this paper however are based upon Lewis' and Gibson's calculation from the experimental determination of the entropy of helium, following Tolman.[8] The use of the chemical constant derived from Lewis-Gibson-Latimer theory[10] or the one selected by Tolman, when

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

used for calculation of A in Dushman's expression, brings increasing disagreement between β (calc.) and β (obs.). As a matter of fact, the value of A in Dushman's equation which gives the best general agreement for all substances in Table I (omitting Ta) is about $5\times(10)^{11}$ instead of $1.8\times(10)^{11}$. The use of the other two values for the chemical constant results in values of A of $1.53\times(10)^{11}$ and $1.15\times(10)^{11}$ respectively. In the same units the value of A calculated from Richardson's application of the quantum theory is $1.5\times(10)^{10}$.

In justice to Dushman's equation it should be stated that, of the various substances listed, it shows its best agreement for the most reliable data. The expression derived in this paper on the other hand shows substantially the same agreement in these cases, but has a more extensive application.

From the theoretical point of view, aside from the evidence mentioned regarding the choice of chemical constant, the proposed formula for the saturation current seems to rest upon a more satisfactory physical basis, if we leave out of account the particular expression used for the internal electron concentration. On the basic assumption employed in derivation, quantitative results cannot be obtained unless some expression for this internal concentration is assumed. This very fact however may be advantageous in furnishing further evidence concerning the order of magnitude and variation with temperature of the electron concentration in conductors. Whether the expression here used for this internal concentration of free electrons, based upon a chemical equilibrium relation, is justified or not, can only be decided by the success of its application to this and to other electrical phenomena. The measure of its success in explaining the general temperature variation of electrical conductivity for both good and poor conductors has already been discussed.[5]

On the other hand the assumptions underlying Dushman's thermodynamical derivation may be questioned. Thus the hypothesis that thermionic emission is completely analogous to evaporation from a solid or liquid is in all probability merely an approximation. As the electrons are held in the solid only by virtue of the solid atoms, the case would seem to be more strictly analogous to the emission of absorbed gas from a solid or of dissolved gas from a liquid. In the latter case the equilibrium pressure of the external gas is directly proportional to the concentration of gas dissolved in the liquid. This condition is satisfied for the analogous case of electron emission in the present derivation whereas according to Dushman's conclusions the equilibrium pressure of an electron gas should be independent of the electron concentration within the emitting body.

Furthermore, in Dushman's derivation, the specific heat of the internal electrons c_p is assumed to be negligible as compared with that of the external electrons. However, the most probable reason why the internal electrons do not contribute appreciably to the specific heat of a metal, if there is any truth in the application of the kinetic theory to the internal electrons,[11] is that this concentration is small compared with the concentration of atoms. It is not beyond the bounds of possibility that the inclusion of the term involving c_p might produce an appreciable correction to the thermionic current as deduced by Dushman, even though the contribution of c_p to the specific heat of the hot body appears to be negligible. In this way the constant A of the saturation current, Eq. (3), might be found to vary slightly for different substances, and thus agreement be obtained between the two expressions Eqs. (3) and (11).

Values of the Work Functions ϕ_0 and ψ_0

In the last column of Table I are given various values of the energy functions ϕ_0 and ψ_0 which appear in β. As stated above ψ_0 represents the energy required (at 0°K) for emission of one *free* electron from the substance, while ϕ_0 is the energy necessary for emission of one *bound* electron. ϕ_0 has been identified[5] with the photo-electric work function, and ψ_0 with the work function entering into the usual theory of thermionic emission. In the case of metals calculation of ϕ_0 and ψ_0 from β may readily be made, since[5] the conductivity evidence indicates that ϕ_0 and ψ_0 do not differ by more than 1/10 percent. Thus $\beta=(\nu\phi_0+\psi_0)/(\nu+1)k=\psi_0/k$ (or ϕ_0/k) for these substances. But for poor conductors like the oxides ϕ_0 is substantially greater than ψ_0.[5] However, if from data on conduction,

[11] Note added July 19: It has been shown by Davisson and Germer (Phys. Rev. **20**, 329, 1922) and recently emphasized by Richardson (Proc. Roy. Soc. **105**, 387, 1924) that in the accurate work of the former on pure tungsten the values of the thermionic work function ψ (in the present notation) as obtained simultaneously by calorimetric and by thermionic methods agree only when the thermal energy of the internal electrons involved in thermionic emission is negligible. This is naturally accepted as important evidence against the classical free electron theory. It should be pointed out, however, that the argument as presented may fail if the constant A of the thermionic equation is a function of the temperature, which presumably is the case if the concentration of internal free electrons depends upon temperature. In particular, using the function of temperature employed in this paper for the internal free electron concentration the above conclusion is exactly reversed. Thus $\psi=\phi_0=4.66$ v (cf. Table I) for W, whence $\psi=\psi_0+(3/2)kT=4.66+0.29=4.95$ v at 2270°K. On attributing to the internal electrons the classical value for their thermal energy this number should agree with Davisson and Germer's calorimetric value of ψ, without correction, namely 4.91 v. The agreement is seen to be to less than 1 percent on the classical theory, while according to the non-classical point of view, ψ(thermionic) = 4.66 v and ψ(calorimetric) = 4.52 v, a discrepancy of 3 per cent.

$b = \nu(\phi_0 - \psi_0)/(\nu+1)k$ of the expression for specific resistance is found,[12] then the independent values of ϕ_0 and ψ_0 may be computed. For CaO, Horton's data[13] give $b = 21{,}000$ approximately, which taken in conjunction with $\beta = 40{,}000$ results in the values of ϕ_0 and ψ_0 given in the Table.

Discussion of Lack of Agreement for Most Oxides

In the case of oxides other than those listed (i.e. other than those of the alkaline earths) data by Jentsch[14] show lack of agreement in most instances between β(calc.) and β(obs.). In every such case β(obs.) is less than β(calc.), and this statement holds for any of the above-described methods of calculating the constant A. High values of the valence, according to Eq. (11), lessen the discrepancy but do not eliminate it entirely. It is possible that this lack of agreement may not mean a breaking down of the formula, but that it is due to secondary effects. Thus, as Richardson has pointed out,[15] in the variation of ψ with temperature a term involving the specific heat of electricity was neglected which may not be justifiable when dealing with most poor conductors. Furthermore in the case of emission from a poor conductor like an oxide, the latter may find difficulty in replenishing rapidly enough the supply of free electrons near its surface. Thus the condition for current saturation might be hard to fulfill in the case of emission from high resistance material. Difficulty in attaining saturation is common experience in such investigations.

The fact that the discordant oxides have melting points close to the temperature range of measurement, while the alkaline earth oxides for which agreement is excellent have melting points about 1000°C higher than the region of observation, suggests the possibility that the process of vaporization may affect the magnitude of thermionic currents. Since the rate of vaporization follows a law similar to that of thermionic emission, no change in form of the thermionic equation might be expected if this be true, but its constants would be altered. If vaporization should facilitate electron emission this would tend to explain the results observed.

The state of poor conductors like the oxides, particularly as concerns both conductivity and thermionic investigations, is often apparently an extremely sensitive function of temperature, applied potential, and other physical conditions, and it is frequently difficult to distinguish between reversible and irreversible changes which occur. Under these circum-

[12] Waterman, loc. cit.[5] p. 262, Eq. (7)
[13] Horton, Phil. Mag. **11**, 505 (1906)
[14] Jentsch, Ann. der Phys. **27**, 129 (1908)
[15] Richardson, Electron Theory of Matter, p. 452-454

stances it becomes questionable in many cases to expect that any simple theoretical expression may be verified until the nature of such peculiarities is more fully understood.

Calculation of Free Electron Concentrations Within Conductors

To summarize the above, in Eqs. (4), (5), and (10) we have different expressions for the concentration of free electrons in equilibrium with a hot body. Eq. (4) yields a value of A consistent with experiment provided n_B, the concentration of internal free electrons, is of the order of magnitude of the atomic concentration within the substance. Such a magnitude is difficult to reconcile with other phenomena, notably the contribution of the electrons to the specific heat. According to Eq. (5) the concentration of internal electrons does not enter into the problem, the work function only being characteristic of the hot body. For the reasons above stated this appears merely to be an approximation to the truth. It has been shown that Eq. (9) is fully as satisfactory as Eq. (3) in accounting for the thermionic current. Assuming the validity of the hypothesis underlying Eqs. (8) and (9), it is therefore possible to calculate the concentration of free electrons within a conductor from Eq. (7). These free electron concentrations are given in Table II, which includes the variation of the concentration with temperature for Na. The reason that the concentration in metals increases with decreasing temperature lies in the fact that conductivity considerations in the case of metals require that ψ_0 be slightly greater than ϕ_0, the energy of dissociation $(\phi_0-\psi_0)$ of a bound into a free electron being negative.[5] For poor conductors similar considerations require that $\phi_0-\psi_0$ be positive and large.

The valence ν in the atomic reaction liberating electrons is taken to be unity for all substances listed.

Table II

Conductor	N (per cc)	T (°K)	b (°K)	n (per cc)
Na	2.6×10^{22}	273	−26*	$1.0\times(10)^{17}$
		173		$1.5\times(10)^{17}$
		100		$2.6\times(10)^{17}$
		50		$5.6\times(10)^{17}$
		20		$2.4\times(10)^{18}$
		10		$1.5\times(10)^{19}$
Cu	8.5	273	—†	$1.7\times(10)^{17}$
Pt	6.6	273	—†	$1.5\times(10)^{17}$
Ag	5.9	273	—†	$1.4\times(10)^{17}$
Pb	3.3	273	—†	$1.1\times(10)^{17}$
Bi	2.9	273	—†	$1.0\times(10)^{17}$
MoS_2	1.8	273	+3000*	$1.3\times(10)^{12}$
		773	"	$7.4\times(10)^{14}$
CaO	3.3	1273	+21,000*	$2.3\times(10)^{9}$

*from conductivity data; † assumed negligible.

The free electron concentration thus appears lower than most estimates given hitherto. Such an order of magnitude however seems demanded by the study of the specific heats of good conductors. It will be observed that the mean concentration in metals at ordinary temperatures, namely about 10^{17} per cc, gives an entirely negligible electronic contribution to the specific heat of metals, and in the case of Na, which is typical, the specific heat contribution by free electrons remains negligible down to very low temperatures, being 0.0024 at 50°K out of a total of 3.50 cal. per gm atom, the atomic heat of Na at this temperature. Even at 10°K this contribution would only be 0.028. This result appears to be of especial interest and significance, in that these concentrations, which are computed directly from the theoretical expression, remove what has always been a serious obstacle to the progress of a free electron theory.

Concentrations of this order of magnitude necessitate large mean free paths according to the usual simple classical conductivity theory. In the case of Na the electronic mean free path, as calculated from its specific resistance by this method, would be 0.014 cm at 0°C. On the other hand it becomes increasingly probable (cf. results of Ramsauer[16]) that such a mean free path is possible. Bridgman[17] has already concluded that the mean free path in metals is at least 100 or 1000 times as long as the mean distance between atoms. In fact a long mean free path, coupled with the fact pointed out by Eldridge[18] that an electric current is carried by the free electrons whose thermal motions have a component perpendicular to the current flow, may have a share in explaining the abnormally high resistance of thin films.

In conclusion, the hypothesis that in conductors a free electron concentration exists which is determined by chemical equilibrium considerations, yields a value of this concentration as a function of temperature which is competent to explain the observed temperature variation both of electrical conductivity and of thermionic saturation current densities. Furthermore the computed numerical values of these free electron concentrations are not in conflict with a most important requirement of any free electron theory, namely that the equi-partition value for the specific heat of the free electrons be negligible.

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[16] Ramsauer, Ann. der Phys. **66**, 546 (1922)
[17] Bridgman, Nat. Acad. Sci. Proc. **7**, 299 (1921)
[18] Eldridge, Phys. Rev. **21**, 2, 131 (1923)