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THE SURFACE HEAT OF CHARGING

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Abstract

In recent papers by Bridgman, Langmuir and Tonks, and the author, the deviation of the constant A of *thermionic emission* from the theoretical value has been linked with the surface heat of charging and the *temperature variation of the photoelectric threshold*. In the present paper, at least a part of this effect is explained by the heat expansion of the material together with the dependency of the *work function* on the volume. Numerical calculations both for the deviations of A and for the temperature change of the threshold are made and compared with experiments. Before deciding whether the explanation given here is complete it will be necessary to calculate the space-charge effect of the electrons in the transition layer on the surface of the metal.

I. Introduction

THERE is considerable interest shown in the discussion of the formula for the thermionic emission, to which Richardson gave the form

$$i = BT^2 e^{-b/T}. \tag{1}$$

Equivalent to this, but better suited for our pupose, is the formula for the equilibrium density of the electron gas.

$$c = AT^{3/2} e^{-q/kT}. \tag{2}$$

in which A should be a universal constant[1,2]

$$A = (2\pi mk)^{3/2}/Nh^3. \tag{3}$$

Here the exponent 3/2 of T comes about by putting the specific heat of the electron gas equal to $3R/2$, the specific heat of the electrons in the metal zero.[3]

Independent of this assumption, one can give general formulas connecting vapor pressure and heat of evaporation.[4,5,6] For example Lane[2] and Schottky[7] write in generalization of (2)

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[1] O. W. Richardson, Proc. Cambr. Phil. Soc. **11**, 286 (1901); Phil. Mag. **28**, 633 (1919); Proc. Roy. Soc. **A91**, 530 (1915); Phys. Rev. **23**, 153 (1923).

[2] M. v. Laue, Jahrb. d. Rad. **15**, 205, 257 (1918); S. Dushman, Phys. Rev. **21**, 623 (1923). The same formula had been found by K. F. Herzfeld, Phys. Zeits. **14**, 1119 (1913) but he had made no applications of it.

[3] A. Sommerfeld Zeits. f. Phys. **47**, 1 (1928).

[4] O. W. Richardson, The Electron theory of Matter, Cambridge, 2 ed., 1916 p. 445.

[5] W. Rodebush, Phys. Rev. **23**, 774 (1924); H. A. Wilson, Phys. Rev. **23**, 38 (1924).

[6] C. Davisson and L. H. Germer, Phys. Rev. **20**, 300 (1922); **30**, 634 (1924).

[7] W. Schottky, Handb. d. Experimentalphysik, Vol. XIII, Leipzig 1928, p. 30.

$$c = A T^{3/2} e^{-\mu_s/kT} \tag{4}$$

where μ_s is the chemical potential of the electrons in the metal instead of their potential energy (in other words, the assumptions leading to (2) are equivalent to say $\mu_s = q$) and then proceeds to allow for μ for example a linear variation with T. This procedure is thermodynamically quite correct but leaves the question why μ is a linear function of T unanswered.

As a next step, one can introduce the specific surface heat of charging as the specific heat which enters into the thermodynamical equations.[6,8,9] It has been shown that such an effect might change the apparent value of A, the value of which agrees well experimentally with (3) in many cases but by no means always.

One can on the other hand consider the fact that the mutual potential energy which holds the electrons in the lattice will depend on the lattice distance and if heat expansion occurs will accordingly depend on the temperature.[10] This is closely connected with the temperature variation of the long-wave-length limit of the photoelectric effect. How to treat such a case has been discussed in a short paper[11] but no formulas have been given and some remarks there seem now incorrect.

Bridgman,[12] in a paper that appeared before the one last mentioned has shown quite clearly how the two effects of a variation of the photo-electric stopping potential with temperature and the surface heat of charging are connected and will modify A.

The present paper, while using a different scheme of thermodynamical calculations than Bridgman because it seems simpler, is intended to supplement it by showing just what values the surface heat of charging must have.

We propose first to give the calculations for a somewhat simplified case, in the second part we will discuss a few subtle points to justify our method of procedure.

II. CALCULATIONS FOR A SIMPLIFIED CASE

1. The free energy.

Consider a piece of metal, insulated and surrounded by vacuum. Call the number of electrons the metal contains in excess of the neutral state n, the free electrons in the vacuum n'. Let p be the pressure, V the volume of the metal, V_0 its normal volume when neutral and at zero pressure, $\Delta = (V - V_0)/V_0$.

We then write the formula for the free energy F of the whole system.

$$F = U(V) - nq(V) - \frac{1}{2} en\phi - T\Phi\left(\frac{h\nu}{kT}\right) - Tn\widetilde{\Phi} + n'(\mu_G - kT).$$

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[8] L. Tonks and I. Langmuir, Phys. Rev. **29,** 524 (1926); L. Tonks, Phys. Rev. **32,** 284 (1928).

[9] P. W. Bridgman, Phys, Rev. **27,** 143 (1926).

[10] O. W. Richardson, Phil. Mag. **23,** 594 (1912).

[11] K. F. Herzfeld, Sommerfeld Festschrift, Leipzig, 1928, p. 143.

[12] P. W. Bridgman, Phys. Rev. **31,** 90 (1928).

Here $U(V)$ is simply the (elastic) energy of the neutral metal. On account of deviations from neutrality, there is additional energy, an unelectric part[15] $-nq(V)$ and an electric part $(-1/2)en\phi$. In contradiction to Schottky[13] but in accord with Eckardt[14] we call electric only the part of the field due to excess charges and having accordingly a long range. This part can be changed by connecting the plate with outside sources. Accordingly $\phi=0$ means that there is no field of long range present. The energy then necessary to remove an electron is called the unelectric part $q(V)$. Φ is the integral

$$\Phi\left(\frac{h\nu}{kT}\right)=\int_0^T\frac{dT}{T^2}\int_0^T C_v dT \tag{5}$$

for the specific heat of the metal and will be usually a Debye function Through ν, it will depend on the volume. We assume, (for the discussion of this assumption see under III) that ν does not depend explicitly on the charge.

$n\tilde{\Phi}$ would be the corresponding integral taken over the specific heat of the electrons in the usual sense, as calculated by Sommerfeld.[3] $\partial(n\tilde{\Phi})/\partial n$ corresponds to the part variable with temperature in Sommerfeld's expression of $2kT\ln A$ (which has as physical meaning just the electron part of our $\partial F/\partial n$) and is negligible up to 3000° ($2\cdot 10^{-3}$ compared with 1, although it accounts for Thomson- and thermoelectric effects).

Finally, μ_G is the usual expression for the chemical potential of the electron gas

$$\mu_G=kT\ln c+(3/2)kT\ln T+kT\ln A\,. \tag{6}$$

2. Equilibrium formula.

In equilibrium, F will be a minimum in respect to the possible variations, namely of n(electron emission) and of volume. The first condition will give the equilibrium concentration, the second the equation of state of the charged metal (in making this latter variation, we neglect the fact that an increase of the volume of the metal will decrease the volume of the electron gas).

$$0=-\left(\frac{\partial F}{\partial n}\right)_v=q(V)+\frac{1}{2}e\phi+\frac{1}{2}en\frac{\partial\phi}{\partial n}+T\frac{\partial}{\partial n}(n\tilde{\Phi})+\mu_G \tag{7}$$

$$0=-p=\left(\frac{\partial F}{\partial V}\right)_n=\frac{\partial U}{\partial V}-n\frac{\partial q}{\partial V}-\frac{1}{2}en\frac{\partial\phi}{\partial V}-\frac{h}{k}\Phi'\frac{\partial\nu}{\partial V}-Tn\frac{\partial\tilde{\Phi}}{\partial V}\,\cdot \tag{8}$$

As at least in first approximation $n\partial\phi/\partial n=\phi$ and as we have decided to neglect $\tilde{\Phi}$, we get from (7)

$$-\mu_G=q(V)+e\phi \tag{9}$$

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[13] W. Schottky, Handb. d. Exp. Phys. Vol. XIII, 2 half p. 14 Leipzig 1928.

[14] C. Eckardt, Zeits. f. Physik **47**, 38 (1928).

[15] In this we include the part of the internal electron pressure effect which does not depend on temperature, namely $-W_i$ (Sommerfeld) so that $q=W_a-W_i$.

or

$$c = A T^{3/2} e^{-(q(V)+e\phi)/kT} \tag{10}$$

which for constant volume of the metal, is identical with the usual form (2).

The problem is then to find $q(V)$. Here we use the following approximations: As U refers to the neutral metal, we introduce the common compressibility κ and write, using a familiar development in powers of Δ

$$U(V) = U_0 + V_0 \Delta^2 / 2\kappa. \tag{11}$$

Furthermore, we assume

$$q(V) = q_1 - q_2 \Delta \tag{12}$$

with the expression

$$q_2 = -V_0 \partial q / \partial V.$$

This gives

$$\frac{\Delta}{\kappa} + \frac{nq_2}{V_0} - \frac{1}{2} en \frac{\partial \phi}{\partial V} + \frac{h\nu}{kV_0} \Phi' \gamma = 0 \tag{13}$$

using Gruneisen's result,[15a] that

$$-\gamma = (V_0/\nu) \partial \nu / \partial V \tag{14}$$

is a constant, namely about 1-3 for many metals.

Using the expansion coefficient α for the uncharged metal ($n = 0$), which is according to Gruneisen given by

$$\int_0^T \alpha dT = -\kappa \frac{h\nu}{kV_0} \gamma \Phi' \tag{15}$$

we find

$$\Delta = \int_0^T \alpha dT - nq_2 \frac{\kappa}{V_0} + \frac{1}{2} en\kappa \frac{\partial \phi}{\partial V} \cdot \tag{16}$$

For the approximately neutral metal, $n = 0$, $\phi = 0$, we have

$$c = A T^{3/2} e^{-q_1/kT} \exp\left[\frac{-q_2}{kT} \int_0^T \alpha dT \right]. \tag{17}$$

The last factor is the deviation from the formula (2). It is simply the change in q due to the total expansion of the metal up to T.

Equation (17) can be written for sufficiently high temperature

$$c = A' T^{3/2} e^{-q_1/kT} \tag{18}$$

$$A' = A \exp\left[\frac{q_2}{kT} \int_0^T \alpha dT \right] = A e^{q_2 \alpha / k} \tag{19}$$

[15a] E. Gruneisen. Ann. d. Phvsik **39**, 257 (1912).

3. Calculation of q_2 and numerical value of A'.

It is possible to get an estimate of q_2. We have first to remember that q is a difference between the potential energy of an electron in the metal (Sommerfeld's W_a) and the effect of the internal pressure. (W_i according to Sommerfeld.) Therefore

$$-q_2 = V_0 \frac{\partial W_a}{\partial V} - V_0 \frac{\partial W_i}{\partial V}$$

Bethe[16] attempts a theoretical calculation of W_a; it is composed of a contribution from the positive ions, which is, for a given size of the ions, proportional to their numer per unit volume and which we call therefore

$$W_a^+ V_0/V$$

and a contribution from the electrons, inversely proportional to the distance, or

$$W_a^-(V_0/V)^{1/3}.$$

Finally, W_i is proportional to the 2/3 power of the number of electrons per cm^3.

If we assume that compression does not change the total amount of electrons per atom, we have (W_a^+, W_a^-, W_i^0 constants)

$$q = W_a^+ \frac{V_0}{V} + W_a^- \left(\frac{V_0}{V}\right)^{1/3} - W_i^0 \left(\frac{V_0}{V}\right)^{2/3}. \tag{20}$$

Then

$$q_2 = W_a^+ + \tfrac{1}{3} W_a^- - \tfrac{2}{3} W_i^0. \tag{21}$$

According to Bethe's calculations for nickel, W_a^+ is about 13 volts, W^- 6 volts, W_i^0 15 volts, which would make $q_2 \sim 5$ volts.

If we write $\alpha = \alpha' \times 10^{-5}$, $q_2 = +q_2'$ volt, we have

$$e^{q_2 \alpha / k} = 10^{0.059 q_2' \alpha'} \tag{22}$$

From this it follows: A is always apparently increased $A' > A$. For $q_2'\alpha' < 10$ the factor multiplying the theoretical A is not larger than 3, which is within the limits of the experiment. If the above estimate of q_2 is correct, this means for metals with low expansion coefficient ($\alpha' < 2$), that the theoretical value of A can be made to fit the results.

But we have to expect much higher A's if α' is larger. $\alpha' = 9$ (linear expansion coefficient 3), $q_2' = 5$ means already $A' = A \cdot 10^{2,25} \sim 180 A_i$ $\alpha' = 15$, $q_2' = 6$ means $A' = 30.000\, A$.

While this is in the right order of magnitude, [18,19] we can give no reason why a large A' should always go with a high q_1.

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[16] H. Bethe, Ann. d. Physik **87,** 55 (1928).

[17] The factor $\exp[-(1/k)\ \partial(n\widetilde{\Phi})/\partial n]$ which is responsible for the thermoelectric effects has been neglected.

[18] C. Zwikker, Proc. Amst. Ac. **24,** 1 (1926); A. L. Du Bridge, Phys. Rev. **31,** 236 (1928); **32,** 961 (1928).

[19] A. L. Du Bridge, Proc. Nat. Ac. **14,** 788 (1928); I. Langmuir and K. H. Kingdon, Phys. Rev. **34,** 129 (1929).

4. Temperature change of the heat of evaporation.

We are first going to calculate the heat of evaporation of the electron and show that the deviation can be interpreted as a contribution of the specific surface heat of charging, not to C_v, but to $C_p - C_v$.

The heat of evaporation of an electron at constant volume of the metal would be

$$q(V) + 3RT/2 + e\phi \tag{23}$$

the middle part coming from the specific heat of the electron gas. The contribution of the specific heat of the electrons in the metal has been neglected.

At constant pressure, we have to add to (23)

$$T^2\left(\frac{\partial}{\partial V}\frac{\mu}{T}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{p,n}$$

or take simpler

$$T^2\left(\frac{\partial}{\partial T}\frac{\mu(p,T)}{T}\right)_{p,n} + \frac{3}{2}RT. \tag{24}$$

This is, with

$$\mu(p=0,T) = -q_1 - \frac{h\nu}{k}q_2\frac{\gamma}{V}\kappa\Phi' \tag{25}$$

from (7) for the uncharged plate, $n=0$, leads after a short calculation to the following formula in which the value of Φ has been introduced

$$q_1 - q_2\frac{\gamma}{V_0}\kappa\left(C_vT - \int_0^T C_v dT\right) + \frac{3}{2}RT. \tag{26}$$

Instead of the last $3RT/2$, $2RT$ or $5RT/2$ might have to be introduced, depending on which heat is actually measured.[6]

The interesting point is that for moderate temperatures, $C_vT - \int_0^T C_v dT$ is a constant or, in the presence of zeropoint energy in the vibrations of the solid, even zero. The exponent $-q_1/RT$ in (3) gives therefore at moderate temperatures the real heat of evaporation (apart from the member $3RT/2$, which is due to the electron gas).

In making this statement, we have again neglected the increase with temperature of the kinetic energy of the electrons in the metal as too small to detect. We can expect to find a change of the heat of evaporation with temperature:

(a) at high temperature, where C_v increases

$$C_v = C^0 + C'T$$

$$C_vT - \int_0^T C_v dT = \frac{C'}{2}T^2, \quad \Delta q = -q_2\frac{\gamma}{V_0}\kappa\frac{C'}{2}T^2.$$

This increase will not modify greatly the last factor in (17) because it occurs at high temperatures ($1/T$).

(b) at low temperatures, where quantum effects appear in the specific heat, there will be an increase in the heat of evaporation (apart from $3RT/2$) with decreasing temperature up to the amount

$$q_2 \gamma \kappa N h\nu / V_0 .$$

The value of the specific surface heat of charging at constant pressure follows from (26) to be

$$q_2 \frac{\gamma k}{V_0} T \frac{\partial C_v}{\partial T}$$

(C_v specific heat of the metal at constant volume.) Bridgman[9,12] has shown that if (2) is valid and A' different from A, the specific surface heat of charging must be 0 and there must exist an entropy difference between the charged and the uncharged surface at zero temperature contrary to Nernst's heat theorem. In the case considered here the specific surface heat of charging is zero at zero temperature, takes then positive values and decreases to zero again for high temperatures. Accordingly (2) is valid at very low temperatures with the theoretical A, ceases to be valid afterwards and becomes valid again at high temperatures with $A' > A$. This hump of the specific heat at low temperatures is then responsible for the deviation of A' from A. If one would exterpolate formula (2) with A' different from the theoretical value to zero temperature one would find an entropy difference. A very similar situation is present in a number of chemical reactions. The whole situation is bound up with the fact that the expansion coefficient disappears at zero temperature which fact itself is again connected with Nernst's theorem.

Numerical calculations for the case of potassium give the following result: We use

$\gamma = 1.34$[20] κ[21] $= 35.6 \times 10^{-12}$ $V_0 = 45$ $h\nu/k = 99$[22]

and for $C_v - (1/T)\int_0^T C_v dT$ tables given by Simon.[23]

If we take $q_2 = 5$ volt we find

T	$\beta\nu/T$	$CT - \int CdT$ (cal/Mol)	Δq(millivolts)
495	0.2	0	0
198	0.5	8	1.7
99	1	36	7.8
49	2	92	20
20	5	170	37
10	10	196	43

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[20] E. Grüneisen, Handb. d. Phys. X p. 29, Berlin 1926.

[21] Reference 20, p. 38.

[22] A. Eucken, Handb. d. Exp. VIII, Leipzig 1929, p. 245.

[23] F. Simon, Handb. d. Physik X Berlin, 1926.

5. Photoelectric threshold.

Offhand, one could be doubtful whether the photoelectric threshold is determined by the energy or the free energy of the electrons in the metal. But Bridgman has proved the connections between threshold and contact potentials, and there is no doubt that the contact potentials are determined by the free energy or, more exactly, the chemical potential μ.

The temperature variation of the threshold is then given by

$$q_1+q_2\frac{\gamma}{V_0}\kappa\frac{h\nu}{k}\Phi'=q_1-q_2\frac{\gamma}{V_0}\kappa\int_0^T C_v dT=q_1-q_2\int_0^T \alpha dT.$$

That means, that for an increase of 100°C and $q_2 \sim 5$ volts, the change in the photoelectric threshold is as follows.

K	Al	Mg	Zn	Cu	Ag	Au	Fe	Ni	Pt	Pb	Sb	
125	36	39	43	25	29	21	17	23	15	43	18	millivolts.

Comparing this with experiments, it seems reasonable that such a change could not be detected in the work of Millikan and Winchester[24] who heated Al, Mg, Zn, Cu, Ag, Au, Fe, Ni, Pb, Sb 100° and of Varley and Unwin[25] who varied the temperature of Pt 300°, corresponding to changes of less than 50 millivolts. It is more astonishing that Millikan and Winchester[24] found no change for Al between 50 and 350° (110mv) and Ladenburg[26] for Au, Pt, Ir up to 860° (150mv) and that Dember[27] could not detect any effect on K on heating it to 67°, but it is difficult to estimate how much a change in the long-wave-length limit would affect the current measured by these investigators.

Recently Du Bridge[28] detected a change in current upon heating platinum to 1200° and narrowed down the wave-length shift to a region between 1943-1973A; 30A would correspond to 90 while $q_2 \sim 5\ V$ would lead to 180mv. Measurements of Suhrmann[29] give a few percent shift in Ag, Au, Pt between room temperature and liquid air. Finally Ives[30] has found a shift for K in the same interval of 220mv while $q_2=5$ would give 250 (actually it should be less on account of the smaller coefficient of expansion at low temperatures). It seems therefore that the present theory gives the right order of magnitude.

It should be mentioned in conjunction with the fact that the oxide-coated cathodes have a particularly high A', that Koppius[31] found a very strong variation of their threshold with the temperature.

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[24] R. A. Millikan and G. Winchester, Phil. Mag. **14,** 188 (1907).

[25] W. M. Varley and F. Unwin, Proc. Roy. Soc. Edinburgh **27,** 117 (1907).

[26] R. Ladenburg, Verh. d. D. Phys. Ges. **9,** 165 (1906).

[27] H. Dember, Ann. d. Physik **23,** 957 (1907).

[28] L. A. DuBridge, Phys. Rev. **29,** 451 (1927).

[29] R. Suhrmann, Zeits. f. Physik **33,** 63 (1925); see also A. Becker, Ann. d. Physik **78,** 83 (1924).

[30] H. E. Ives, Journ. Am. Opt. Soc. **8,** 551 (1924); H. E. Ives and A. L. Johnsrud, Journ. Am. Opt. Soc. **11,** 565 (1925).

[31] O. Koppius, Phys. Rev. **18.** 443 (1921).

III. Justification of Method of Procedure

1. We have made our calculations as if the evaporating electron were taken from the interior and have not said anything in particular about the surface. Here we have to distinguish two steps in the equilibrium condition (7) we have put the expression for the thermodynamical potential of an electron deep in the interior of the vessel equal to one in the gas. But as Schottky pointed out, this is justified as the numerical value of μ (not the form of μ) must be the same for an electron in the interior as it is in the surface on account of the internal equilibrium of the electrons. On the other hand, the particular expression for the potential energy (q) in the interior, as calculated by Bethe, might be wrong; this value might be influenced by the surface. But it seems reasonable that this would not change the order of magnitude of q_2, and our calculation does not claim more.

2. We did not include, "electrical contributions," as we defined the Volta potential ϕ as being due to the total charge and we assume this to be zero (compensation for Volta potential in the actual thermionic experiment). The difference between this case and the usual case, for example in the thermodynamics of gases where differentiation at constant pessure (analogous to ϕ) and constant volume (analogous to en) makes a difference even for $n=0$, comes from the fact that

$$pV=nkT$$

and therefore $\partial(pV)/\partial n =kT$ even for $n=0$ while here $ne\phi$ is proportional to n^2 and therefore $[\partial(ne\phi)/\partial n]_{n=0}=0$.

The reason we have deviated from Schottky's[13] definition, which amounts here to saying that the non-electric part in the differences of the (total and free) energy is the one remaining, if the two places to be compared were brought to the same potential, is the following: With this definition all differences in potential energy of the electron would belong to the electrical part. Indeed, the electrical potential of a place is defined only by the work necessary to bring a test charge (electron) there. Accordingly the difference in potential energy q inside and outside of the metal would belong entirely to the electrical part, which does not seem advisable. On the other hand, it is always possible, by measuring at a sufficient distance, to state whether a (large) body is charged. We define as the non-electric part of the (free or total) energy of an electron in respect to a (large) body the part which would be alone present if the body as a whole were uncharged.

In passing, it may be said that this together with the emphasis that in measuring thermionic currents one has always to correct for the Volta potential, that is one always takes care to have $\phi=0$, gives a clear view of the situation in the presence of surface layers.

3. We have assumed that Φ or the specific heat C_v of the metal at constant volume depends upon n only indirectly through the volume. If we now drop this assumption, (8) and (13) remain unchanged, but in (7) we must add

$$-T\left(\frac{\partial}{\partial n}\Phi\right)_{v,T} = -\frac{h}{k}\Phi'\frac{\partial\nu}{\partial n}$$

which then produces finally on the right hand side of (17) another factor

$$\exp\left[\frac{h}{k^2T}\Phi'\frac{\partial\nu}{\partial n}\right].$$

Now we can write, for a plate containing N atoms, at sufficiently high temperature

$$\frac{h}{k^2T}\Phi'\frac{\partial\nu}{\partial n} = -\frac{h}{k^2T}3Nk\frac{kT}{h\nu}\frac{\partial\nu}{\partial n} = -3N\frac{\partial\ln\nu}{\partial n}$$

or better

$$-\partial(\Sigma\ln\nu)/\partial n$$

where the sum is to be extended over all the vibrations which make up the heat movement of the plate. Therefore[32]

$$\exp\left[\frac{1}{R}\left(\frac{\partial\Phi}{\partial n}\right)_{v,T}\right] = \prod_i \exp\left[-\left(\frac{\partial\ln\nu_i}{\partial n}\right)_v\right].$$

If we would assume that the removal of an electron affected only three vibrations (in a primitive picture the vibrations of one atom), we could say safely that the new frequency would lie between half and the double of the original frequency, or

$$\left|\frac{\partial\ln\nu_i}{\partial n}\right| < 1 \quad i = 1,2,3 \quad \frac{\partial\ln\nu_i}{\partial n} = 0 \quad i > 3.$$

Then, the additional factor in (19) woud lie between e^{-3} and $e,^{3}$ 1/20 and 20. If, as will be the case, the change affects all vibrations, it still seems reasonable that

$$\left|\sum\frac{\partial\ln\nu}{\partial n}\right|$$

will be not much larger than 3 and therefore, a direct influence of a removal of electrons on the specific heats at low temperature will probably not influence A' as strongly as the indirect effect through the volume.

4. The most important assumption however that we have made is the omission of a part of q which would be explicitly dependent on temperature. Now the part in the potential energy of an electron which is due to the surrounding charges, as calculated by Bethe,[16] is not dependent directly on temperature (the heat movements of the positive ions will upon averaging have no effect of the first order). But there might be another contribution[32] due to

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[32] W. Schottky, reference 13, p. 96f. See also E. D. Eastman, Jour. Am. Chem. Soc. **48,** 552 (1926), C. Zwikker, Physica, **9,** 321 (1929).

an electric double layer or space charge, which might be formed on the surface of the metal where the electron density drops gradually off. This might depend on T, not in the part farther in, where the electron density is still high, the electron gas degenerate and therefore its μ independent of T, but in the outside layers. How much these contribute, can not be estimated until a calculation has been made.

The only thing to be said is that the part discussed previously gives the right order of magnitude.

IV. Other Applications

The method which we have devloped here can be applied similarly to an ordinary solution, in which the mutual potential energy between the solvent and the dissolved molecules depends on the distance between them and accordingly varies indirectly with the temperature on account of the heat expansion of the solvent.