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The Effect of High Electrostatic Fields upon the Vaporization and Resistance of Molybdenum Filaments*

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This paper endeavors to show that equations can be obtained to fit Estabrook's observed variation of vaporization rate with electric field strength at wire surface if we consider the vaporization decrease as due to the formation of an adsorbed gas layer on the filament. It is mentioned that electric field strengths of the magnitudes used can be shown to have no appreciable effect upon the motion of the gas particles or metallic atoms in the region between filament and cylinder, and that time lags of the size observed can be approximately accounted for by the times required for formation and removal of the gas layer when the field is applied or withdrawn. The following postulates are proposed: (1) the resistance changes were due to temperature changes resulting from small changes in emissivity; (2) resistance changes in different directions were due to spectral variation in the behavior of the emissivity of a filament when it is coated with gas; (3) Estabrook's vaporization rate was higher than that calculated from an equation given by Jones, Langmuir, and Mackay because the wires used by the latter were more coated with gas; and (4) Jones did not observe any effect of an electric field upon resistance or vaporization because his tube did not contain enough oxygen. These hypotheses remain of course to be proved or disproved by appropriate experiments.

INTRODUCTION

SUPPOSE that we had a fine wire supported along the axis of a metallic cylinder, the whole being in a vacuum. If the wire were heated to incandescence by means of an electric current, its resistance would gradually increase because of vaporization of its atoms. This much is well known. In addition however, Worthing[1] and Estabrook[2] found that the application of a sufficiently high potential difference between filament and the concentric cylinder reduced the rate of increase of resistance of the filament. Their cylinders were made negative with respect to the filaments in order that there would be no emission of electrons. In addition to the change in slope of the resistance *versus* time curve, there was also a change in the actual resistance itself at the instant the field was applied, and a change in the opposite direction when the field was removed. These two effects were found with Pt, W, and Mo filaments, and presumably would exist also with other metals. Estabrook found that for Mo and Pt there was an increase in resistance when the field was applied, and a decrease when it was removed. Worthing found changes in the opposite direction with W. Both observers, however, found a decrease in the rate of resistance change when a radial field was applied. Figure 1 of this article, and Fig. 3 of Estabrook's article illustrate the above. In the graphs it is seen that there is a rounding of the corners indicating that the resistance and vaporization changes do not take place instantaneously.

It seems reasonable to attribute the steady increase in resistance of a wire with time to a gradual vaporization of its atoms. If such is the case, then the applied radial field must decrease the rate of vaporization. The ratio of the rate of vaporization after the field is applied to that

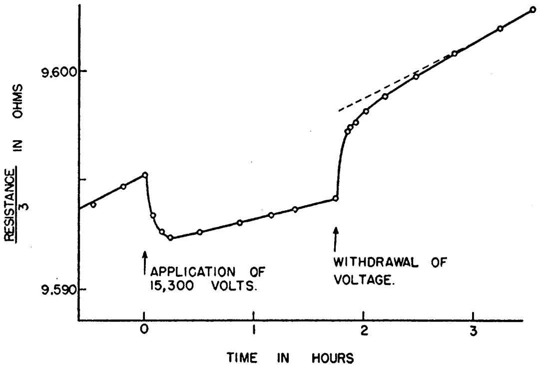

FIG. 1. This curve shows how the resistance of a tungsten wire was affected by the application of a high potential difference between it and a concentric cylinder. The temperature was 2500°K, and the wire radius 0.010 mm. [Taken from A. G. Worthing, Phys. Rev. **17**, 419 (1921).]

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[1] A. G. Worthing, Phys. Rev. **17**, 418 (1921).

[2] See preceding paper.

before is given by the ratio of the two corresponding slopes of the resistance *versus* time curve. Figure 2 shows how this ratio varies with the field at the surface of the filament.

In Fig. 3 we see how the resistance change is affected by the field strength. This figure differs from Estabrook's Fig. 6 only in that the ordinates have been doubled, and a different curve has been chosen. Note that in it, as in Fig. 2, there is no apparent effect for fields of less than 0.5 $\times 10^6$ volts/cm. Both Worthing and Estabrook found the resistance change to go more or less hand in hand with the vaporization change, although the former change has also been found to occur at temperatures where there is no appreciable vaporization at all. Vissat[3] has studied such resistance changes at room temperature and above.

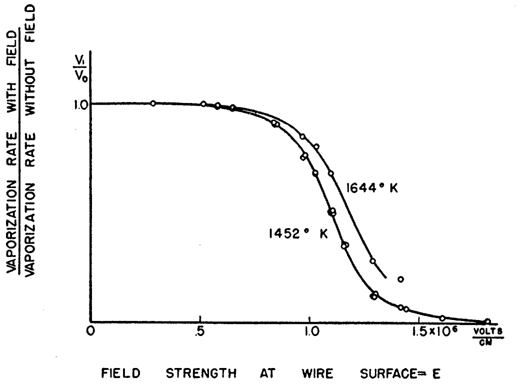

FIG. 2. These curves show the variation in rate of vaporization of molybdenum wires with the electrostatic field at the wire surface. The circles are from Estabrook's data. The solid lines are calculated values.

In this paper we wish to propose a theory to account for the phenomena mentioned. Any such theory should provide an explanation for the following features of the problem as well as those cited above: (1) The vaporization rate observed by Estabrook was much larger than that predicted by the work of Jones, Langmuir, and Mackay,[4] and (2) Lloyd Jones (results unpublished), working with a very good vacuum, did not observe either the resistance or the vaporization change. Before undertaking our treatment, let us consider the dipole theory. This is done because the latter is apparently the explanation which occurs first to a person confronted with the problem.

THE DIPOLE THEORY

The metallic atoms leaving the filament were found to be uncharged, and so it is not easy to see why an electric field should have any effect upon them unless they become dipoles under its influence. If they do become dipoles, then each atom upon evaporation will experience a force tending to return it to the filament. This force arises, of course, from the fact that we have a radial rather than a uniform field. Greibach[5] studied thermodynamically the problem of evaporation of dipoles into an electric field, but was able thereby to account for but one percent of the effect observed.

At first it appears plausible to consider the decrease in vaporization rate as being due to the influence of the electric field upon evaporating metallic dipoles. A closer investigation, however, reveals that an unreasonably large value must be taken for the dipole moment of the metallic atom at the wire surface in order to produce decreases in vaporization of the magnitudes observed. It is also found that many phases of the problem cannot be explained suitably with such a physical picture, as, for example, the fact that quite large fields must be applied before there is any appreciable effect on the vaporization rate. These and other features make the dipole theory untenable.

THE ADSORBED GAS THEORY

It has been quite well established[6] that at least some of the gas particles striking a surface stick to it for a while before leaving again. The process of reflection of gas from a surface consists, therefore, at least in part, of a continual condensation and subsequent reevaporation of the particles. Since some of the molecules linger for a while, it follows that the surface will at all times be partially covered with an adsorbed gas film. The extent to which it is covered will

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[3] P. L. Vissat, Ph.D. Thesis, University of Pittsburgh (1941).

[4] I. Langmuir and G. M. Mackay, Phys. Rev. **4**, 377 (1914). H. A. Jones, I. Langmuir, and G. M. Mackay, Phys. Rev. **30**, 201 (1927).

[5] E. H. Greibach, Phys. Rev. **33**, 844 (1929).

[6] See, for example, L. B. Loeb, *The Kinetic Theory of Gases* (New York, McGraw Hill, 1934), second edition, 338ff.

of course depend upon the conditions. In general gas films are driven off at temperatures much lower than that of 1452°K at which Estabrook worked, but chemisorbed films can adhere quite tenaciously even at temperatures considerably higher. The layer of atomic oxygen on the surface of tungsten filaments has, for example, been studied quite extensively, and is known to persist up to temperatures in the neighborhood of 2000°K. Since Mo is quite similar to W, we can perhaps safely assume that an atomic layer of oxygen could adhere to it too at temperatures such as those used by Estabrook.

Let us get an expression for the fraction of the wire surface covered by gas.[7] We shall do this first for the case where there is no electric field, and on the basis of Langmuir's physical picture. We denote by f_0 the fraction of the total number of adsorbable gas particles striking the filament that stick to it. These molecules upon condensing will dissociate. The separate atoms will remain upon the surface for a while, but will subsequently leave singly, and with a heat of desorption of ϕ_0 per atom. Let ν_0 be the number of adsorbed atoms per unit area; η the number of Mo atoms per unit area; θ_0 the fraction of the surface covered by gas; N_0 the rate at which gas molecules strike per unit area; and N_0' the rate at which molecules of the type being adsorbed strike the surface per unit area. Then $N_0'(1-\theta_0)$ will be the rate per unit area at which the latter strike that portion not covered by gas, and $N_0'f_0(1-\theta_0)$ will be the rate per unit area at which they stick. Since each gas molecule consists of two atoms, it follows that the number of atoms being adsorbed per unit area and per unit time will be given by

$$2N_0'f_0(1-\theta_0). \tag{1}$$

To get the number of atoms leaving[8] per unit area of the surface per unit time, let us first consider the case of a gas escaping through a small opening into a vacuum. Assuming a Maxwellian distribution of velocities for the gas particles, we get as the total number leaving the hole per unit area and per unit time with velocities greater than v_0:

$$[\sigma(\tfrac{1}{2}mv_0^2+kT_0)/(2\pi mkT)^{\frac{1}{2}}] \times\exp(-mv_0^2/2kT_0). \tag{2}$$

If, as in our case, we have gas particles escaping from a surface rather than through an opening in a container, then we can use the above expression for the number leaving provided that we let $\phi_0=\frac{1}{2}mv_0^2$ be the amount of work required to remove a gas particle, and replace σ, the number of molecules per unit volume in the container by something proportional to the surface concentration of gas atoms, or let $\sigma\rightarrow C\nu_0$. This gives

$$[C\nu_0(\phi_0+kT_0')/(2\pi mkT_0')^{\frac{1}{2}}] \times\exp(-\phi_0/kT_0') \tag{3}$$

as the number of gas atoms leaving per unit area and unit time. The prime is used on the T_0 because the effective temperature of the gas departing from the filament may not be the same as that of the surface.

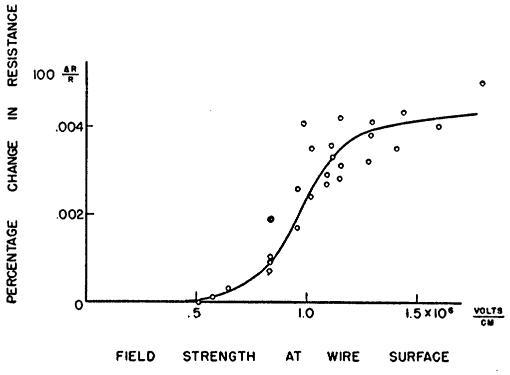

FIG. 3. This graph shows the percentage changes in resistance obtained by Estabrook for the case when the field is removed. The data were obtained with molybdenum wires of radii 0.00229, 0.00243, and 0.00342 cm at 1452°K. Similar changes occur upon application of the field.

It has been found that the number of atoms of oxygen in a complete chemisorbed layer on W is about equal to the number of W atoms on that surface. If the same is true for the gas adsorbed on Mo, then η will be a maximum value for ν_0, and we shall have

$$\theta_0=\nu_0/\eta. \tag{4}$$

Since the rate at which atoms leave must, in the steady state, be the same as the rate at which

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[7] See Neil K. Adam, *The Physics and Chemistry of Surfaces* (Oxford, Clarendon Press, 1938), second edition, p. 264f.

[8] From J. K. Roberts, Trans. Faraday Soc. **31**, part 2, 1710 (1935).

they stick, we set expressions (1) and (3) equal to each other. Upon doing so, and using (4), we get

$$1-\theta_0=\left[1+\frac{2N_0'f_0(2\pi mkT_0')^{\frac{1}{2}}}{C\eta(\phi_0+kT_0')}\times\exp\left(\phi_0/kT_0'\right)\right]^{-1} \tag{5}$$

as the fraction of the surface not covered by gas before the field is applied. The fraction $1-\theta_1$ of the surface not covered after the field is applied is obtained from the last equation by changing the subscripts from 0 to 1 throughout.

If we let V be the rate of vaporization of Mo per unit area of the filament, and assume that it is proportional to the fraction of the surface not covered by gas, we have

$$V_1/V_0=(1-\theta_1)/(1-\theta_0) \tag{6}$$

as the ratio of vaporization after field is applied to that before. Let us apply this equation to Fig. 2. θ_1 is equal to θ_0 when the field E at the filament surface is zero. It seems reasonable to imagine that θ_1 steadily increases as E increases, but yet in Fig. 2 we see that V_1/V_0 remains equal to unity until E is about 0.5×10^6 volts/cm. Hence θ_0 must be essentially equal to zero if Eq. (6) is to apply to Fig. 2, and so Eq. (6) becomes

$$V_1/V_0\doteq1-\theta_1. \tag{7}$$

We next consider the number N_1' of adsorbable molecules striking the filament per unit area and per unit time after the field is applied. Because of the fact that the gas molecules probably become dipoles under the influence of the field, it follows that they would experience forces tending to move them toward the filament. The motion of such dipoles in a radial field was studied mathematically, and led to the result

$$N_1'\doteq N_3'[1+\gamma E^2/2kT_3+\cdots], \tag{8}$$

where N_3' is the number of the molecules striking the cylinder wall per unit area and time after field is applied. γ is the polarizability of a gas molecule. Let us consider it to be about 10^{-24} cm^3, or 1.1×10^{-29} erg cm^2/volt^2. The largest value of E used by Estabrook was about 1.8×10^6 volts/cm. T_3 is the temperature of the cylinder, and was probably just a shade above room temperature, or about 310°K. Using these values, together with the Boltzmann constant k, we obtain

$$(\gamma E^2/2kT_3)_{\text{maximum}}\doteq0.00042. \tag{9}$$

Hence

$$N_1'\doteq N_3'. \tag{10}$$

This means that when the field is on, the number of gas molecules striking the filament per unit area and time is essentially the same as the number striking the cylinder, or that field strengths of the magnitude used have no appreciable effect upon the motion of the gas particles. Since N_3' is known from the kinetic theory of gases, we have

$$N_1'\doteq N_3'=p_3'/(4\pi mkT_3)^{\frac{1}{2}}, \tag{11}$$

where $2m$ is the mass of a gas molecule and p_3' is the partial pressure at the cylinder of whichever gas is being adsorbed.

If we evaluate Eq. (7) by means of Eqs. (5) and (11), we get

$$V_1/V_0\doteq1-\theta_1$$

$$=\left[1+\frac{p_3'f_1(2T_1')^{\frac{1}{2}}\exp\left(\phi_1/kT_1'\right)}{C\eta(T_3)^{\frac{1}{2}}(\phi_1+kT_1')}\right]^{-1}. \tag{12}$$

In order to use this equation, we should know how all of the various terms in it vary with the electric field strength at the wire surface. A study of Fig. 2, however, reveals that the data can most easily be fitted by a linear increase of ϕ_1/kT_1' with the applied electric field. T_1' is known from the experiment to have remained about constant, and so it is a linear increase in ϕ_1 which best fits Eq. (12) to the data. f would probably also increase with E if ϕ_1 increased, but for simplicity let us assume it to be constant.

We shall next put numerical values into Eq. (12). T_1' is the average temperature upon leaving the filament of those gas atoms which have adhered to it for a while, and hence is probably about equal to the temperature of the filament, or 1452°K for the first curve. As before, let us take $T_3\doteq310$°K. η is the number of Mo atoms per unit area of the surface. Assuming that the 110 plane is the one most likely to be along the wire surface, we get $\eta\doteq(14.4)10^{14}$ atoms/cm^2. The constant C, which was originally defined as

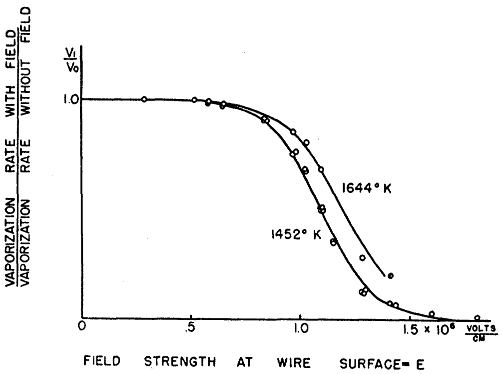

FIG. 4. This graph shows the curves obtained when the heat of desorption of the adsorbed gas is assumed to vary linearly with the field strength at the wire surface. The circles are from Estabrook's data.

the proportionality constant in expression (3), can be found from an equation for the rate of evaporation of adsorbed atoms and molecules given by J. K. Roberts.[8] The constant in his relationship was obtained from some of Langmuir's data on the rate of evaporation of oxygen atoms from a tungsten surface and leads to the value

$$C = (2.56)\times 10^{17} \text{ dynes/calorie.}$$

According to Roberts, this value for C should be the same for all substances. By comparison with experiment, he found his equation to apply accurately to a considerable range of atomic films. Hence we shall use the above value for C. For f we can use the following equation given by Langmuir:[9]

$$\log_{10} f_0 = 1.76 - 5940\text{K}^\circ/T \qquad (13)$$

for $1000^\circ\text{K} < T < 2000^\circ\text{K}$. This expression was obtained for oxygen atoms striking a W wire, but might perhaps hold for our case too. For 1452°K, we get $f_0 = 0.0047 (=f_1)$.

Experiments dealing with the interaction between gas molecules and solid surfaces have led to many conflicting theories and contradictory experimental results. This is due primarily to the fact that the results are quite sensitive to particular conditions existing at the surface, and to the practical impossibility of knowing the nature of the surfaces.[10] Hence the above value for f is quite likely to be in error.

The partial pressure p_3' at the cylinder of whichever gas was coating the wire is not known. We must guess at it, and because of the uncertainty in f_1, let us consider the product $p_3'f_1$ as being unknown, and perhaps within the range covered below:

Case 1. Assume $p_3'f_1 = (10^{-8}\text{ mm Hg})(0.0047)$,
Case 2. Assume $p_3'f_1 = (10^{-7}\text{ mm Hg})(0.0047)$,
Case 3. Assume $p_3'f_1 = (10^{-6}\text{ mm Hg})(0.0047)$.

Upon putting the values above into Eq. (12), and applying the latter to the data at 1452°K in Fig. 2, we find that the equation will fit the data if

$$\phi_1 = \phi_0 + (4.02)10^{-26}E \text{ cal. cm/atom volt,} \qquad (14)$$

where ϕ_0 is about $(18.3)10^{-20}$ cal./atom for Case 1, 17.2 for Case 2, and 16.1 for Case 3. The coefficient of E is approximately the same for the three cases. In curve 1 of Fig. 4, we see the graph of Eq. (12) when the values given above are used for the various quantities in it. The graph turns out to be about the same for each of the three cases and is essentially the same for an even wider range of values chosen for $p_3'f_1$. Thus the coefficient of E in Eq. (14) and the graph of Eq. (12) are not greatly influenced by errors in the choices for constants in Eq. (12). This is the case because the changes in $\phi_1 + kT_1'$ with ϕ_1 are small compared to the changes in $\exp(\phi_1/kT_1')$ in Eq. (12).

When we consider the data at 1644°K, we again find that a linear variation of ϕ_1 with E will give fair agreement between Eq. (12) and the experimental results. The slope of the ϕ_1 *versus* E line turns out to be about the same as at 1452°K, and as before the value for ϕ_0 depends upon our choice of the constants. If we take $p_3' = 10^{-7}$ mm Hg, $T_1' = 1644^\circ$K, f from Eq. (13) as 0.014, and C, η, and T_3 as before, we get

$$\phi_{1\,(\text{at }1644^\circ\text{K})} \doteq [19.0 + (4.02)10^{-6}E \text{ cm/volt}] \times 10^{-20} \text{ cal./atom.}$$

Using this last equation in Eq. (12), we get the second curve in Fig. 4.

From above we see that ϕ_0 appears to be in the neighborhood of 16 to 19×10^{-20} cal. per atom. By way of comparison we find that Roberts[11] gives a mean value of 128 kilogram

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[9] I. Langmuir, J. Am. Chem. Soc. **35**, 105ff (1913).
[10] L. B. Loeb, reference 6, p. 347f.
[11] J. K. Roberts, Proc. Roy. Soc. **A152**, 464 (1935).

calories per gram atom, or 21×10^{-20} cal. per atom for the heat of desorption of oxygen from W filaments. Other values in the literature are of the same magnitude. Our values for ϕ_0 seem, therefore, to be reasonable ones and are of a size which seems to indicate that the adsorbed gas on Estabrook's filaments was oxygen.

AN EXTENSION OF THE ADSORBED GAS THEORY

In Fig. 4 we see that the previous treatment does not give perfect agreement with Estabrook's data. We wish now to show how better correlation can be obtained.

We have assumed that only those Mo atoms which were not covered by the gas layer were capable of evaporating. It is reasonable however to suppose that a Mo atom might be able to leave the surface along with the oxygen atom on top of it. In fact, Langmuir has found that the combination of a W and an oxygen atom does indeed evaporate from the surface of a W filament, and has used this fact to explain the clean-up of oxygen by an incandescent W wire. He showed it to be WO_3 which evaporates, but the molecule is formed by the combination of an impinging O_2 molecule and a WO group from the wire surface. Hence as far as the surface is concerned, it is W plus O which leaves. By analogy, therefore, we shall assume that Mo plus O is capable of leaving the wire surface, perhaps combining with an O_2 molecule to form MoO_3, although it does not matter for our considerations how it leaves.

Let us take the rate at which Mo plus O leaves the wire to be directly proportional to the fraction of the surface covered by gas. Since we have previously assumed that Mo alone leaves at a rate proportional to the fraction of the surface not coated, it follows that the total number of Mo atoms leaving the surface per unit area and time after the field is applied will be given by

$$V_{1T}=A(1-\theta_1)+B\theta_1,$$

and

$$V_{1T}/V_{0T}=[A(1-\theta_1)+B\theta_1]/[A(1-\theta_0)+B\theta_0] \doteq [A(1-\theta_1)+B\theta_1]/A,$$

or

$$V_{1T}/V_{0T}\doteq 1-\theta_1+s\theta_1, \tag{16}$$

where A, B, and s are assumed to be constants depending upon the temperature of the filament, but not upon the electric field applied. Substituting for θ_1 from Eq. (12), we get

$$\frac{V_{1T}}{V_{0T}}=\frac{1+s\dfrac{p_3'f_1(2T_1')^{\frac{1}{2}}\exp(\phi_1/kT_1')}{C\eta(T_3)^{\frac{1}{2}}(\phi_1+kT_1')}}{1+\dfrac{p_3'f_1(2T_1')^{\frac{1}{2}}\exp(\phi_1/kT_1')}{C\eta(T_3)^{\frac{1}{2}}(\phi_1+kT_1')}}. \tag{17}$$

As E gets larger, θ_1 approaches unity, and hence we see by Eq. (16) that V_{1T}/V_{0T} approaches s as a limiting value at high fields. Thus $V_{1T}/V_{0T}=s$ is an asymptote for our curve. If we are to apply Eq. (17) to Estabrook's data, we will have to know s at temperatures of 1452°K and 1644°K. From the data at 1452°K, it seems to be about 0.01. Since the data at 1644°K do not extend to high enough fields, it is difficult to determine a value of s for that temperature. By trial, it was found that a curve which fit the data best would be obtained if s were about 0.12. This seems too large in comparison with the asymptote at 1452°K. The choice of 0.12 was needed because of the last point on the curve. Upon throwing out the latter, it becomes quite impossible to determine an asymptote from Estabrook's data. By developing an approximate expression for s, and substituting into it the best numerical values we could find, we obtained $s\doteq 0.017$ at 1644°K. This seems more reasonable, and so we shall use it.

When we use the above values for s in Eq. (17) and apply the latter to the data, we again find that ϕ_1 must vary approximately linearly with E in order to give agreement. In order to get completely satisfactory correlation between theory and experiment, however, it is found to be desirable to have ϕ_1 increase linearly with the fraction of the surface covered as well as with the electric field. The equation, therefore, is of the general form

$$\phi_1=\phi_0+gE+j\theta_1, \tag{18}$$

and if we substitute for θ_1 from Eq. (16), we get

$$\phi_1=\phi_0+gE+j(V_{1T}/V_{0T}-1)/(s-1). \tag{19}$$

When this relationship is put into Eq. (17), we obtain an expression in terms of V_{1T}/V_{0T} and E

which we shall use as the equation for the curves in Fig. 2. Values for the constants ϕ_0, g, and j can be determined by making the equation fit the data. If we choose $p_3' = 10^{-7}$ mm of Hg, we get for ϕ_0, g, and j, respectively, the values $(17.92)10^{-20}$ cal./atom, $(2.86)10^{-26}$ cal. cm/atom volt, and $(0.90)10^{-20}$ cal./atom at 1452°K, and $(19.42)10^{-20}$ cal./atom, $(3.40)10^{-26}$ cal. cm/atom volt and $(0.70)10^{-20}$ cal./atom at 1644°K. The curves shown in Fig. 2 were obtained by using these values in Eq. (19), and the latter in Eq. (17). They are seen to fit the data quite well except for the last point on the curve at 1644°K, which we decided to ignore, as mentioned before.

The fact that it is necessary to include the term $j\theta_1$ in Eq. (18) is not at all surprising. The heats of desorption of gases are known to change markedly with the fraction of the surface coated. Roberts,[12] for example, found the heat of desorption of H from W wires to decrease from 45 kilocalories per mole for a bare surface to 18 for a surface covered with gas. This change is presumably due to interaction energy between the adsorbed atoms.

The question then is not one of why a variation of ϕ_1 with the fraction of the surface covered was found, but instead—why was the change in our case so small? The answer to this is found in a theoretical treatment by Miller[13] of the problem of adsorption of dipoles. Quoting from his paper, we have ". . . the electrostatic and van der Waals forces give contributions to the variation of the heat of adsorption which are of opposite sign, and almost counterbalance one another, so that the resultant variation in the heat of adsorption is very much less than would be expected from consideration of forces of one type only."

CONSIDERATION OF THE TIME LAGS, RESISTANCE CHANGES, ETC.

As has been mentioned before, the resistance and vaporization changes do not take place instantaneously. This is apparent because of the rounding of the corners in Fig. 1. On the basis of the theory proposed, the explanation for the time lags becomes quite simple. Upon applying an electric field, a gas layer begins to form on the filament. It is not until the fraction of the surface covered reaches a maximum, constant value that the resistance *versus* time curve can have a steady slope. In like manner, we must wait for the gas layer to leave the wire before we can expect the slope of the curve to return to the value that it had before the field was applied.

When we calculate the lags to be expected on the assumption that they are due to the time required for gas layers to form and leave, we find that the magnitudes observed can be accounted for quite easily. It must be assumed, however, that f_1 increases with the electric field if we are to explain the lags with exactly the same numerical values that were used in the treatment of the vaporization change.

By comparing Figs. 2 and 3, we see that the resistance and vaporization changes apparently go hand in hand. Note, for example, that both effects begin at about the same field strength, and that if the curve in Fig. 3 were inverted, it would have the same general appearance as that in Fig. 2. In Worthing's work at 2500°K he also found the two effects to begin at about the same field strength and to increase together. It would seem, therefore, that the theory which has been presented to explain the decrease in vaporization rates should also be able to account for the resistance changes.

Any such explanation must be consistent with the following experimental facts. (a) Worthing and Estabrook found resistance changes in opposite directions. These findings were not contradictory, because different metals were used, and at different temperatures. It means, however, that any theory must be able to account for a change in resistance in either direction depending upon the conditions. (b) Vissat observed resistance changes at room temperature. Thus the changes can occur even when there is no appreciable vaporization. (c) Vissat found that his resistance changes were influenced by vacuum conditions, and were accompanied by a leakage current. (d) Lloyd Jones, working with a very good vacuum, did not observe any resistance or vaporization changes.

Let us attribute the resistance changes to variations in the temperature of the wire resulting from its being coated with gas when a field is applied, and uncoated when field is withdrawn. If the temperature changes are pro-

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[12] J. K. Roberts, Proc. Roy. Soc. **A152**, 445 (1935).

[13] A. R. Miller, Proc. Camb. Phil. Soc. **36**, 69 (1940).

duced by changes in emissivity, and if the emissivity in turn varies linearly with the fraction of the surface covered with gas, then it is not hard to show that the percentage change in resistance would be directly proportional to the change in the fraction of the wire surface covered with gas, or

$$\Delta R/R \doteq (\text{constant})(\theta_1-\theta_0) \doteq (\text{constant})\theta_1. \qquad (22)$$

With this relationship, the curve in Fig. 3 would look the same as the 1452°K curve in Fig. 2 turned upside down. This is seen to be approximately the case.

The fact that Worthing observed a decrease in resistance of his W filament when a field was applied at 2500°K, while Estabrook and Vissat, using Mo and W wires, found increases at lower temperatures can be understood if we imagine that there is a spectral variation in the behavior of the emissivity when a filament is coated with gas. The results are explainable if the presence of a gas layer decreases the long wave-length emissivity below that for a bare wire, but increases the short wave-length emissivity so that at high temperatures there is a resultant increase in the total emissivity, but at lower temperatures a resultant decrease.

Another feature of this work that must be considered is the fact that Estabrook obtained a vaporization rate for Mo at 1452°K which was very much greater than that predicted by an equation set forth by Jones, Langmuir, and Mackay.[4] Estabrook's value was 1.4×10^{-9} g/cm^2 sec., while from J., L., and M., we get 8.0×10^{-15} g/cm^2 sec. Because of this discrepancy, Norris[14] also studied the vaporization of Mo. His work gives 1.9×10^{-13} g/cm^2 sec. as the vaporization rate for Mo at 1452°K, and hence does not agree with either of the above values. Thus the question of what the correct vaporization rate is remains unsettled.

It may be that the variation in values obtained was due to differences in extent to which the filaments were covered with gas. If such is the case, then Estabrook's value should be the best because it is the highest. This is in agreement with our treatment above, in which we found his filament to be essentially uncoated before the field was applied (i.e., $\theta_0\doteq0$). The vaporization rate of Mo as given by Jones, Langmuir, and Mackay would then seem to be in error. As a partial corroboration of this, we note that Wahlen and Whitney[15] were forced to discard the vaporization rates of W as predicted by equations of J., L., and M. In so doing, they say ". . . but their (J., L., and M.) calculations are based on evaporation data obtained at a time when vacuum conditions had not been developed to the present extent; so this value is somewhat questionable."

At the beginning of this paper we mentioned that Lloyd Jones, working with a very good vacuum, had failed to observe either the resistance or the vaporization change. Such a fact would of itself lead one to suspect that the phenomena were in some way due to the gas in the tube. Since we have attributed the effects observed to an adsorbed gas layer, presumably oxygen, on the wire, we can easily account for Jones' failure to find anything by assuming that he had removed too much of the gas from his tube.

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[14] L. A. Norris, M.S. Thesis, University of Pittsburgh (1933).

[15] H. B. Wahlin and L. V. Whitney, Phys. Rev. **50**, 735 (1936).